Statistical Mechanics Lecture Notes

An introduction to Statistical Physics intended for first year graduate students.

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These notes were used for PHYS6327 - Statistical Mechanics
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Errors may exist in these notes, and they are under constant revision. If you find an error, please feel free to email me at gcmorrison -at- uh.edu and I will correct them.

A number of homework problems are listed, many of which are not found in a textbook or online. I am happy to provide solutions to homework problems to *faculty* only. Please email me if you would like the solutions to a particular problem.

Chapter 0

Preface

0.1 About these notes

These course notes cover classical and quantum statistical mechanics, and were written for PHYS6327 at the University of Houston. In principle, all of this material will be fully covered during the one-semester course. In practice, we'll skip a few sections in these notes.

These course notes are under constant development. As such, while I will make every effort to have complete course notes posted to blackboard before class, they may be updated without notice at any time. If you find a typo in the document, please let me know (and apologies if it leads to confusion). I ask that you not post these notes online, since they are still a rough draft.

0.2 What is statistical physics?

Classical physics, quantum mechanics, and general relativity cover a wide range of physical processes and describe the interactions between particles in a huge number of contexts. The beauty of these physical laws is that they are often exactly solvable, and the exact solutions have been shown to agree with experimental results to a remarkable extent. Newtonian mechanics landed rovers on mars, Maxwells equations underly many aspects of modern communication, the prediction of quantum mechanics agrees with experiments to a precision better than 10^{-10}, and general relativity's prediction of gravitational waves has just recently been confirmed. Centuries of co-development of experimental and theoretical techniques has led to a remarkable body of knowledge about how the works on a fundamental level.

Statistical physics deals not with understanding the fundamental dynamics or interactions between particles as the other branches of physics do, but rather tries to understand the behavior of a *large number* of particles. A really large number of particles, on the order of 10^{23}. This is a ridiculously large number, and an exact calculation becomes infeasible in virtually all theories. Even if one were able to solve a many body problem exactly (notoriously difficult for nontrivial interactions) for a more than two particles, would perfect knowledge of the exact properties of 10^{23} particles be useful? How does one organize the information about the state of 10^{23} particles to be able to say something useful about the behavior of the system. Is it feasible to know the initial conditions of 10^{23} particles in such a way that a theoretical prediction is even relevant? In the modern world, it may be tempting to resort to simulations, but a simulation of 10^{23} particles is completely infeasible for existing modern machines.

What is to be done to understand the behavior of a large number of particles then? Fundamentally, the behavior of an individual particle isn't all that interesting when there are a huge number of particles, and we are one will be primarily interested in the global behavior of the system rather than the behavior of each and every particle. Statistical physics is an attempt to extract meaningful properties of the global behavior of huge numbers of particles, even if the specific behavior of each individual particle is unknown. We will attempt to identify *generic* laws for the behavior of a large number of particles using mathematical models that take advantage of the fact that the number of particles $N \gg 1$. Much of our work will focus on developing techniques to understand the behavior of *noninteracting* particles, which lay the foundation for more complex interactions in the future.

0.3 Some Mathematical Reminders

The techniques of statical mechanics often differ from other branches of physics. It's rare (but not forbidden!) to see special functions appearing as is common in electrodynamics and quantum mechanics. The difficulties in this course will primarily be conceptual, and classical statistical mechanics will not require particularly difficult mathematics. It is worth reviewing some mathematical basics in advance, and making sure you're comfortable with all of these before proceeding. Some of these will be quite obvious to you, but if you see something not obvious please be sure to study it carefully to be sure you understand.

0.3.1 Exponentials and Logarithms

There are a few features of exponentials and logarithms that are worth mentioning, since they'll be coming up a lot in the future.

$$e^x e^y = e^{x+y} \qquad \frac{e^x}{e^y} = e^{x-y} \tag{0.1}$$

$$\log(xy) = \log(x) + \log(y) \qquad \log\left(\frac{x}{y}\right) = \log(x) - \log(y) \tag{0.2}$$

$$\left(e^x\right)^a = e^{ax} \qquad e^{x^a}\text{doesn't reduce further} \tag{0.3}$$

$$\log(x^a) = a\log(x) \qquad \frac{\log(x)}{\log(y)}\text{ doesn't reduce further} \tag{0.4}$$

$$e^x + e^y\text{ doesn't reduce further} \qquad \log(x+y)\text{ doesn't reduce further} \tag{0.5}$$

$$e^x + e^{-x} = 2\cosh(x) \qquad e^x - e^{-x} = 2\sinh(x) \tag{0.6}$$

In this course, by log with no specified base, I'm talking about the natural logarithm (sometimes known as ln). Regardless of base, all logarithms share these properties, and any logarithm is related to another via $\log_b(x) = \log(x)/\log(b)$. It's likely you're already aware of these relationships, but be sure to not mix the sum-to-product property of the logarithm with the product-to-sum property of the exponential. Its a common mistake, and you'll always get the wrong answer by making it.

Differentiation of these functions will occur often as well. Using the chain rule, we'll have

$$\frac{\partial}{\partial x}\exp[f(x)] = f'(x)\exp[f(x)] \qquad \frac{\partial}{\partial x}\log[f(x)] = \frac{f'(x)}{f(x)} \tag{0.7}$$

The latter will be extremely important in computing ensemble averages.

0.3.2 Discrete sums

There are a few sums that will constantly reoccur in the course that are worth memorizing:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad \sum_{n=0}^{\infty} \frac{x^n}{n!} = e^x \tag{0.8}$$

Here, we've been sloppy about the convergence of the sums: the former converges only if $|x| < 1$. Generally speaking, when we compute something in statistical mechanics, we must keep that radius of convergence in mind (since the physics of the system you're looking at might change drastically near a divergence...). Note that we can use these to write

$$\sum_{n=0}^{\infty} e^{-\beta\epsilon n} = \frac{1}{1-e^{-\beta\epsilon}} \qquad \sum_{n=0}^{\infty} \frac{e^{-\beta\epsilon n}}{n!} = e^{e^{-\beta\epsilon}} \tag{0.9}$$

if this isn't obvious to you, convince yourself it's true. It will also often be necessary to compute sums that involve exponential and polynomial terms. Often, this is best handled by differentiation under the sum, like so:

$$\sum_{n=0}^{\infty} n e^{-\beta\epsilon n} = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon}\sum_{n=0}^{\infty} e^{-\beta\epsilon n} = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon}\frac{1}{1-e^{-\beta\epsilon}} = \frac{e^{-\beta\epsilon}}{(1-e^{-\beta\epsilon})^2} = \left[2\sinh\left(\frac{\beta\epsilon}{2}\right)\right]^{-2} \tag{0.10}$$

Convince yourself of every step in this, as you'll probably be using this technique on your own in the future. Similar tricks will hold true if the polynomial term has a different order (e.g. n^2 instead of n), they'll just be more tedious to work with.

0.3.3 Integrals

We'll also have lots of integrals of exponentials to deal with, so it's good to recall some of their properties. It's very convenient that $\int dx e^x = e^x + c$, generally making simple exponential integrals easy to deal with. In the same manner as eq. 0.10, we can readily compute

$$\int_0^\infty dx x e^{-kx} = -\frac{\partial}{\partial k}\int_0^\infty dx e^{-kx} = -\frac{\partial}{\partial k}\frac{1}{k} = \frac{1}{k^2} \tag{0.11}$$

In fact, it's possible to show that

$$\int_0^\infty dx x^\alpha e^{-kx} = \frac{\alpha!}{k^{1+\alpha}} = \frac{\Gamma(\alpha+1)}{k^{1+\alpha}} \tag{0.12}$$

which defines the gamma function $\Gamma(\alpha)$. For integer α this is just equal to a factorial: $\Gamma(n) = (n-1)!$. Note that $\Gamma(\alpha+1) = \alpha\Gamma(\alpha)$ in general.

We'll be seeing Gaussian integrals over and over in this class. it's really worth spending a bit of time to be sure you're familiar with evaluating integrals involving e^{-x^2}. To begin, lets remind ourselves of the simplest case:

$$\int_{-\infty}^{\infty} dx\ e^{-x^2} = \sqrt{\pi} \tag{0.13}$$

This one is pretty fundamental and is worth memorizing. If you forget the value, it's pretty easy to recompute if you remember the following trick:

$$\left(\int_{-\infty}^{\infty} dx e^{-x^2}\right)^2 = \int_{-\infty}^{\infty} dx dy e^{-x^2-y^2} = \int_0^{2\pi} d\theta \int_0^{\infty} dr r e^{-r^2} = \pi \int_0^{\infty} e^{-u} = \pi \tag{0.14}$$

where we've converted to polar coordinates to evaluate the integral in the third step. Eq. 0.14 means the square of the integral turns out to be equal to the area of a unit circle, so if you remember that fact you can quickly remember the correct form of eq. 0.13.

There are a couple of tricks useful for computing other Gaussian integrals. First,

$$\int_0^{\infty} dx\ x e^{-kx^2} = -\frac{1}{2k}\int_0^{\infty} dx \frac{\partial}{\partial x} e^{-kx^2} = -\frac{e^{-kx^2}}{2k}\bigg|_0^{\infty} = \frac{1}{2k} \tag{0.15}$$

where we noted the fact that xe^{-kx^2} is proportional to $d(e^{-kx^2})/dx$. Note the bounds on the integral, which run from 0 to ∞, rather than $-\infty$ to ∞ (if it's not obvious, convince yourself that $\int_{-\infty}^{\infty} dx x e^{-kx^2} = 0$). We can also evaluate

$$\int_{-\infty}^{\infty} dx x^2 e^{-kx^2} = -\frac{\partial}{\partial k}\int_{-\infty}^{\infty} e^{-kx^2} = -\frac{\partial}{\partial k}\sqrt{\frac{\pi}{k}} = \frac{\pi^{1/2}}{2k^{3/2}} \tag{0.16}$$

where we've differentiated under the integral in a manner similar to the calculation in eq. 0.10.

Gaussian integrals containing a polynomial term are easy to compute in a different way since we know about the gamma function:

$$\int_0^{\infty} dx x^{2\alpha} e^{-kx^2} = \frac{1}{2}\int_0^{\infty} du u^{\alpha-1/2} e^{-ku} = \frac{\Gamma(\alpha+1/2)}{2k^{\alpha+1/2}} \tag{0.17}$$

If α is a half-integer, $\Gamma(\alpha+1/2)$ is evaluated at an integer and is simple to compute knowing that $\Gamma(n) = (n-1)!$. If α is an integer the gamma function is evaluated at a half-integer, which has a tedious expression of $\Gamma(n+1/2) = (2n)!\sqrt{\pi}/4^n n!$. Don't bother memorizing this, if you need to know it on an exam I'll write it down for you. Note that $\Gamma(1/2) = \sqrt{\pi}$ and $\Gamma(3/2) = \sqrt{\pi/2}$, so that we recover eq. 0.13 and 0.16.

Occasionally we will encounter an error function, defined as

$$\text{erf}(a) = \int_{-a}^{a} dx \frac{e^{-x^2}}{\sqrt{\pi}} \tag{0.18}$$

which is the area of a normal distribution over a finite domain. It is sometimes convenient to note that

$$\int_{-\infty}^{a} dx \frac{e^{-x^2}}{\sqrt{\pi}} = \frac{1}{2}\Big(1+\text{erf}(a)\Big) \tag{0.19}$$

which is the area of a normal distribution up to a fixed point a. This integral is 0 if $a = -\infty$ (so $\mathrm{erf}(-\infty) = -1)$), 1/2 if $a = 0$ (so $\mathrm{erf}(0) = 0$), and is 1 if $a = \infty$ (so $\mathrm{erf}(\infty) = 1$). The error function is often used to represent a sigmoid (a function transitioning between two constant values, in this case -1 and 1).

0.3.4 Delta Functions

A delta function (truly, a functional not a well defined function) is one that satisfies

$$\delta(0) = \infty \qquad \delta(x) = 0 \text{ for } x \neq 0 \qquad \int_{-\infty}^{\infty} dx \delta(x) = 1 \tag{0.20}$$

A functional with these features will satisfy

$$\int dx f(x)\delta(x) = f(0) \tag{0.21}$$

so the delta function will constrain a function to a specific point. When trying to perform an integral with constraints, then, it is often useful to consider δ functions to do so. For example, an integral of a function $f(x, y, z)$ on the surface of a sphere can be written

$$I = \int_{-\infty}^{\infty} dxdydz f(x, y, z)\delta\Big(1 - (x^2 + y^2 + z^2)\Big) \tag{0.22}$$

The integral is over all space, with the constraint imposed using the delta function. This is not always *useful*, but is always possible and we will utilize this approach for representing constraints in the later material. Note also that

$$\delta(x) = \lim_{\epsilon \to 0} \frac{e^{-x^2/2\epsilon}}{\sqrt{2\pi\epsilon}} = \lim_{\epsilon \to 0} \left\{ \begin{array}{cc} \frac{1}{2\epsilon} & |x| \leq \epsilon \\ 0 & |x| > \epsilon \end{array} \right. \tag{0.23}$$

are two ways of writing a delta function (referred to as a 'nascent' δ functions) that can be helpful in explicitly evaluating an integral. The δ function also has the useful property that

$$\int \frac{dk}{2\pi} e^{ikx} = \delta(x) \tag{0.24}$$

0.3.5 Sterling's Approximation

We will often deal with large numbers in this course, and in particular the factorial of a large number. $N!$ grows rapidly as N increases, but it is difficult to manipulate mathematically for large N. Often, we will make use of Sterling's approximation, which states that

$$\log(N!) = \sum_{n=1}^{N} \log(n) \approx \int_0^N dx \, \log(x) = N\log(N) - N + O[\log(N)] \tag{0.25}$$

The proof of this can be found in many textbooks (or Wikipedia), and in this course we will use it without further proof. Note that in addition to reducing the factorial in terms of standard functions, this also allows us to compute derivatives involving factorials:

$$\frac{\partial \log(N!)}{\partial N} \approx \log(N) \tag{0.26}$$

which will be convenient throughout the course.

0.4 Quantum Mechanics, Very Briefly

Classical statistical mechanics is able to describe a wide range of phenomena, including the equilibrium behavior of gasses and chemical reactions, the theory of phase transitions, and fluctuation effects. However, there were a number of truly baffling experimental results that *did not* agree with the classical theory that remained unexplained for decades (we'll talk about them in detail later in the course). Quantum statistical mechanics provided an answer to a host of fundamental problems with classical statistical mechanics. Our goal in this section is not to describe quantum mechanics (you should take a course in it if you haven't already though!), but rather to remind you of some of the fundamental details of single particle quantum mechanics that we'll see throughout the course.

Non-relativistic quantum mechanics is based on the Schrödinger equation, which states that a particle's state can be described by solutions to the

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \hat{H}\Psi(\mathbf{r},t) = \left[\frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r})\right]\Psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r},t) \tag{0.27}$$

for the momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$. Separation of variables readily shows that $\Psi(\mathbf{r},t) = e^{-iEt/\hbar}\psi(\mathbf{r})$ with $\psi(\mathbf{r})$ satisfying the time-independent Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{0.28}$$

$|\psi_{\mathbf{n}}(\mathbf{r})|^2$ is the steady-state probability density of the particle being found within $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$, and must be normalized so that $\int_V d\mathbf{r}|\psi(\mathbf{r})|^2 = 1$. Note that this means one can compute the *quantum average* of the statistics of a particle (eg $\langle\mathbf{r}\rangle_q = \int_V d\mathbf{r}\mathbf{r}|\psi_{\mathbf{n}}(\mathbf{r})|^2$). This quantum average is fundamentally different than the ensemble average of statistical mechanics (which will be discussed extensively throughout the course).

0.4.1 Infinite Square Wells and Plane Waves

For a non-relativistic particle in a three-dimensional cube with sides of length L, the solutions to Schrödinger's equation must satisfy $-\hbar^2/2m\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r})$ along with the boundary conditions that $\psi(\mathbf{r}) = 0$ at any boundary. There are an infinite but countable number of solutions to this problem, which have the form

$$\psi_{\mathbf{n}}(\mathbf{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \tag{0.29}$$

where $\mathbf{n} = \{n_x, n_y, n_z\}$ for integer n_i. If this is not obvious to you, convince yourself it satisfies the differential equation and boundary conditions. Note that this wavefunction is normalized as $\int_{box} |\psi_{\mathbf{n}}(\mathbf{r})|^2 = 1$. Note also that $V = L^3$, and it will often be convenient to replace L with $V^{1/3}$. A particle in a cube has energy $E_{\mathbf{n}} = -\hbar^2/2m\nabla^2\psi_{\mathbf{n}}(\mathbf{r})$, with

$$E_{\mathbf{n}} = \frac{\hbar^2}{2m} \times \frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8mV^{2/3}}(n_x^2 + n_y^2 + n_z^2) \tag{0.30}$$

A particle trapped in the cube can be composed of *any* combination of these eigenfunctions to simultaneously satisfy Schrödinger's equation and the boundary conditions. Note this means there are a quantized set of fundamental eigenfunctions that fully describe any particle in a box.

There are conceptual issues in the case of the free particle, which still must satisfy $-\hbar^2/2m\nabla^2\psi = E\psi$ but has no boundaries (thus no boundary conditions and no possibility of a proper normalization). In this case, there are a continuum of states and an assumed normalization of

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{V^{1/2}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{0.31}$$

with the momentum $\mathbf{p} = \hbar\mathbf{n}/V^{1/3}$ for the wavenumber $\mathbf{n}$. Here we've imposed a volume ion the (unbounded) particle, so this is a useful representation only in the limit of $V \to \infty$. Happily, this limit is precisely the limit relevant for statistical mechanics.

0.4.2 Notation

Particles in a box can be fully described by a complete and orthonormal set of eigenfunctions, from which any property of the particles position can be computed. It is often unwieldy and inconvenient to work with the eigenfunctions directly, though. Often, it's better to refer to eigenstates which symbolically represent the state of the particle without direct reference to position or momentum. The eigenstates are

$$\psi_{\mathbf{n}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{n} \rangle \tag{0.32}$$

where the ket $|\mathbf{n}\rangle$ takes the quantum numbers of the state into account and the bra $\langle \mathbf{r}|$ indicates the state is being evaluated in position space. Alternatively, one could write

$$\psi_{\mathbf{n}}(\mathbf{p}) = \langle \mathbf{p} | \mathbf{n} \rangle \tag{0.33}$$

with the bra $\langle \mathbf{p}|$ indicating the state is being represented in momentum space. This more compact notation allows us to switch between different representations of quantum states, while also

$$\phi(\mathbf{r}) = \sum_{\mathbf{n}} a_{\mathbf{n}} \psi_{\mathbf{n}}(\mathbf{r}) \qquad a_{\mathbf{n}} = \int d\mathbf{r} \psi^*_{\mathbf{n}}(\mathbf{r}) \phi(\mathbf{r}) \tag{0.34}$$

$$|\phi\rangle = \sum_{\mathbf{n}} a_{\mathbf{n}} |\mathbf{n}\rangle \qquad a_{\mathbf{n}} = \langle \mathbf{n}|\phi\rangle \tag{0.35}$$

where $|\mathbf{n}\rangle$ is the n^{th} eigenstate, with the definition $\langle \mathbf{r}|n\rangle = \psi_n(\mathbf{r})$. This notation is very convenient in a lot of cases, but can be confusing if you're unfamiliar. A few identities:

$$\int d^{3N}x \psi^*_n(\mathbf{x}) \psi_m(\mathbf{x}) = \int d^{3N}x \langle n|\mathbf{x}\rangle\langle \mathbf{x}|m\rangle = \langle n|\left(\int d^{3N}x |\mathbf{x}\rangle\langle \mathbf{x}| \right)|m\rangle \equiv \langle n|m\rangle = \delta_{nm}$$

$$|f\rangle = 1 \times |f\rangle \equiv \sum_n |n\rangle\langle n|f\rangle \tag{0.36}$$

$$\hat{O} = \sum_{nm} |n\rangle\langle n|\hat{O}|m\rangle\langle m| \equiv \sum_{nm} O_{nm} |n\rangle\langle m| \tag{0.37}$$

where $|f\rangle$ is an arbitrary state and $\hat{O}$ is an arbitrary operator. This allows us to write orthogonality conditions and basis expansions very compactly.

0.4.3 The quantum harmonic oscillator

The (one dimensional) quantum Hamiltonian is $\mathbf{p}^2/2m + m\omega^2 x^2/2 = \hbar^2/2m\ \partial^2/\partial x^2 + m\omega^2 x^2/2 = \mathbf{a}^\dagger \mathbf{a}$, with $\mathbf{a}_\pm = (\mp \hbar \partial/\partial x/\sqrt{2m} + \omega x \sqrt{m/2})/\sqrt{\hbar\omega}$. We can solve Schrödingers equation directly to determine the eigenfunctions of the system, and would find $\psi_n(x) \propto H_n(x\sqrt{m\omega/\hbar})e^{-m\omega x^2/2\hbar}$ with $H_n(y)$ the n^{th} Hermite polynomial. That's all well and good, but tedious to work with. We can do a lot better by looking at eigenstates rather than eigenfunctions here. The states of a quantum particle in a harmonic potential can be described in terms of eigenstates $|n\rangle$ that satisfy $\hat{H}|n\rangle = E_n|n\rangle$. It is straightforward to show that the combined operator

$$\begin{aligned}
\mathbf{a}_+ \mathbf{a}_- f &= (\mathbf{a}\mathbf{a}^\dagger - \mathbf{a}^\dagger \mathbf{a}) f && (0.38)\\
&= \frac{1}{\hbar\omega}\left(\frac{mw^2 x^2}{2} - \frac{\hbar^2}{2m}\frac{\partial^2 f}{\partial x^2} + \frac{\hbar\omega x}{2}\frac{\partial f}{\partial x} - \frac{\hbar\omega x}{2}\frac{\partial f}{\partial x} - \frac{\hbar\omega}{2} f \right) && (0.39)\\
&= \frac{\hat{H} f}{\hbar\omega} - \frac{f}{2} && (0.40)
\end{aligned}$$

This calculation makes it easy to show that

$$\hat{H} = \frac{\hbar\omega}{2}(2\mathbf{a}_+\mathbf{a}_- + 1) \tag{0.41}$$

$$[\mathbf{a}_+, \mathbf{a}_-] = \mathbf{a}_+\mathbf{a}_- - \mathbf{a}_-\mathbf{a}_+ = -1 \tag{0.42}$$

$$[\hat{H}, \mathbf{a}_\pm] = \pm\hbar\omega a_\pm \tag{0.43}$$

If we suppose there's a state with $\hat{H}|n\rangle = E|n\rangle$ (an eigenstate of the hamiltonian with energy E), then it must be that $\hat{H}\mathbf{a}_\pm|n\rangle = \mathbf{a}_\pm\hat{H} + [\hat{H}, \mathbf{a}_\pm] = \mathbf{a}_\pm E|n\rangle \pm \hbar\omega|n\rangle$. That means that if $\mathbf{a}_\pm|n\rangle$ is also an eigenstate of the hamiltonian, with an energy level that's higher or lower for $+$ or $-$. Thus, the operators $\mathbf{a}_\pm$ act on an eigenstate to move it to another eigenstate with a higher or lower energy level. Since there must be a minimum energy level for the system, there must be a $|0\rangle$ with $\mathbf{a}_-|0\rangle = 0$ (the lowering operator can't go lower). Since $\mathbf{a}_+\mathbf{a}_-|n\rangle = (\hat{H}/\hbar\omega - 1/2)|n\rangle = (E_n/\hbar\omega - 1/2)|n\rangle$, it must be that $E_0 = \hbar\omega/2$ for the lowest energy state (since $\mathbf{a}_-|n\rangle = 0$). Since $\hat{H}\mathbf{a}_-|n\rangle = (E_n - \hbar\omega)|n-1\rangle$, it must be that, for a quantum harmonic oscillator, that

$$E_n = (n + 1/2)\hbar\omega \tag{0.44}$$

In order to actually compute the position of any particle, we need to resort to using the position representation of the states (and thus, the painful Hermite polynomials). However, if we are interested solely in the energy levels of the quantum harmonic oscillator (and often we will be!), we need only use the fact the energies are linear in the quantum number.

0.5 Summary

0.6 Homework Problems

1. The Γ function was defined by $\Gamma(a) = \int_0^\infty dx x^{a-1} e^{-x}$. Show explicitly that $\Gamma(1) = 1$ and $\Gamma(n) = (n-1)\Gamma(n-1)$ for all integers n. Note that this demonstrates by induction that $\Gamma(n) = (n-1)!$.

2. When discussing Sterling's approximation, we ignored higher order terms. The next term in Sterling's approximation is $\log(N!) \approx N\log(N) - N - \frac{1}{2}\log(N)$. For $N = 100$, determine the relative error between this approximation and the one occurring in eq. 0.25. Do the same for $N = 10^{23}$. Is the approximation in eq. 0.25 acceptable for very large numbers?

Chapter 1

A Brief Summary of Thermodynamics

The foundations of modern statistical mechanics rest on the laws of thermodynamics of the early-to-mid nineteenth century, primarily through empirical studies. Through a wide range of experiments (that many of us learned about in high school chemistry), relationships between thermodynamic variables were identified. For example, a variety of experimental observations (Boyle's law, Charles's law, etc) suggested that $PV \propto T$, an empirical statement of the ideal gas law. These relationships lead to a mathematical framework that accurately describe a wide range of experiments and enabled people to design machines leading to the Industrial revolution. Fundamental to this theory is are the laws of thermodynamics.

1.1 The Laws of Thermodynamics

There are many equivalent ways to phrase the laws of thermodynamics, which can be found in a variety of textbooks. In this chapter, we will briefly summarize the laws as:

0. Thermometers exist. This is often phrased in the more precise way: Two systems at equilibrium with a third are at equilibrium with each other.
1. Energy is conserved. This extensively discussed below, but is initially phrased as $dU = đQ - đW$.
2. No engine is perfectly efficient. Equivalently, there is no process whose sole outcome is to extract heat from a reservoir and convert it entirely into work. Equivalently,

any thermodynamic process must increase the total combined entropy of the system and reservoir.

3. There exists an absolute zero of the temperature, at which the entropy is a minimum.

While each is important, we'll be occupied by the first and second in this section. We'll re-discover these laws in more detail using statistical mechanics in later sections.

The statement of the first law is essentially a statement of the conservation of energy. For a system of N particles in contact with a reservoir at temperature T, the change in internal energy dU is

$$dU = \text{đ}Q - \text{đ}W \tag{1.1}$$

where $\text{đ}Q$ and $\text{đ}W$ are the path dependent, inexact differential heat flow (into the system) and work done by the system, respectively. The infinitesimal $\text{đ}W$ infinitesimal work done, with the total work done by the system $W = \int_{path} \text{đ}W$ not path-independent: it depends on the final state of the system as well as how it got there. Increasing pressure then volume produces a greater mechanical work than increasing volume then pressure, as shown in Fig. 1.1 where the mechanical work done in path A is greater than in path B. The heat $\text{đ}Q$ is absorbed by the system *from an external reservoir* if there is a temperature change and no accompanying mechanical work. Note that this requires the existence of some external reservoir held at some temperature T from which energy can be extracted from or pumped into. The first law of thermodynamics is simply a statement that, since energy is conserved, there is a quantity called heat that accounts for the energy difference.

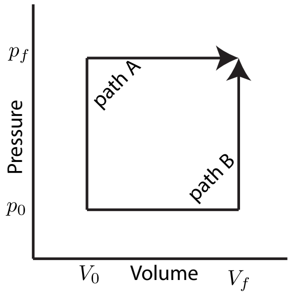


Figure 1.1: Thermodynamic path between an initial and final state. The work along each part of the path is $dW = pdV$, and $\Delta W_A \neq \Delta W_B$. The difference in work along each path is accounted for with a difference in heat absorption.

1.1.1 Exact vs Inexact differentials

Exact differentials

Work and heat are inexact differentials, meaning the change in either in a thermodynamic process depends not only on the initial and final states, but also on the path taken to get there. To understand how this occurs, it is worth examining exact differentials in detail. A one dimensional integral of any function between two points depends only on the boundary. That is, defining $f(x) = dF/dx$, we can compute the integral $\int_o^f dxf(x) = F_f - F_o$. This process is independent of the path between the two points, and depends solely on the initial and final states.

For a function of two variables $F(x, y)$, we can use the chain rule to determine an infinitesimal change:

$$dF = f(x, y)dx + g(x, y)dy \tag{1.2}$$

with $f = \partial F/\partial x|_y$ and $g = \partial F/\partial y|_x$. We now want to integrate this differential from an initial (at $\{x_0, y_0\}$, with value F_o) to final (at $\{x_f, y_f\}$, with value F_f) state. For this exact differential, we can write

$$\int_o^f dF = F_f - F_o = \int_{x_0}^{x_f} dxf[x, y(x)] + \int_{y_0}^{y_f} dyg[x(y), y] \tag{1.3}$$

Note that each of the two integrals at the end of eq. 1.3 *involve* the path taken between $\{x_0, y_0\}$ and $\{x_f, y_f\}$, but the final answer *cannot involve* the path because the final answer depends solely on the endpoints. That is, the specific values of $x(y)$ or $y(x)$ do not affect the value of the integral.

For example, if $F(x, y) = x^2y/2$ over the domain $0 \leq x \leq 1$ and $0 \leq y \leq 1$, we have $\int_o^f dF = F_f - F_o = \frac{1}{2}$. This integral can be performed by integrating

$$\int dF = \int_0^1 dxf\Big(x, y[x]\Big) + \int_0^1 dyf\Big(x[y], y\Big) \tag{1.4}$$

where $f = xy$ and $g = x^2/2$. $y[x]$ (or equivalently $x[y]$) *defines* the path we are taking when we perform the integral, depicted in Fig. **??**. For path A, with $x[y] = y$, $\int_0^1 dxf(x, y[x]) + \int_0^1 dyg(x[y], x) = \frac{1}{3} + \frac{1}{6} = \frac{1}{2}$. For path B, we similarly find $\int_0^1 dxf(x, y[x]) + \int_0^1 dyg(x[y], x) = 0 + \frac{1}{2} = \frac{1}{2}$. Despite the explicit dependence of the path due to the presence of $x[y]$, the integral $\int dF$ is indeed independent of the path.

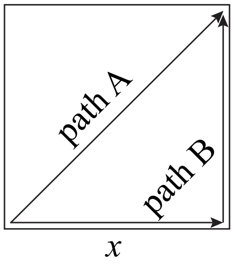


Figure 1.2: Two possible paths between the initial ($(x_o, y_o) = (0,0)$) and final $(x_f, y_f) = (1,1)$ states: a straight line (satisfying $x = y$) or a piecewise constant path (with $y = 0$ for all $x < 1$). For an exact differential, $\int_o^f dF = F(1,1) - F(0,0)$ regardless of the path taken.

Inexact differentials

Of course, we can always write $fdx + gdy$ for some f and g, but it is clearly possible to choose two functions f and g so that they do not satisfy $f = \partial F/\partial x|_y$ and $g = \partial F/\partial y|_x$ for *any* function $F(x,y)$. For example, we could choose $f(x,y) = xy$ and $g(x,y) = 0$. Note that in this example

$$\int f(x,y)dx = \frac{1}{2}x^2 y + c_1(y) \qquad\qquad \int g(x,y) = c_2(x) \tag{1.5}$$

for some unknown functions $c_1(y)$ and $c_2(x)$. It is impossible to equate these two integrals, since one depends on x^2y and the other depends solely on x, which means it's impossible to write this as an exact differential of a single function. In this case, we would have to write the total infinitesimal as inexact: $đF = fdx + gdy$. Note that if we know the path $x(y)$ (or equivalently $y(x)$), we *can* evaluate these integrals. However, the total value of $\int_o^f đF$ does not depend *solely* on the initial or final endpoints, but rather depends on the entire path between the endpoints.

In general, it is tedious to check for exactness by explicitly integrating both functions and determining if two unknown functions $c_1(y)$ and $c_2(x)$ can be chosen to match $\int fdx$ and $\int gdy$. Often, it is simpler to check for exactness by noting that, since $\partial^2 F/\partial x \partial y = \partial^2 F/\partial x/\partial y$, it must be that $\partial f/\partial y = \partial g/\partial x$ for a differential to be exact. This idea will be reused when we discuss Maxwell relations below.

1.2 Entropy and Heat in Reversible Processes

Heat was a poorly understood concept in the nineteenth century. It had units of energy, but could obviously be both created and destroyed. Heat can also flow between two systems, giving rise to the zeroth law of thermodynamics which defines thermal equilibrium as the state with no heat flowing between two connected systems. The fact that heat is not an exact differential (is not path independent) makes eq. 1.1 difficult to use, since one needs to keep track of the entire history of a system in order to determine its energy.

A better understanding of the states a reversible process undergo can be achieved by connecting the mysterious concept of path-dependent heat to the (equally mysterious) concept of path-independent entropy. Here the idea is to recognize that while $đQ$ is inexact and path-dependent, the quantity $dS = đQ/T$ is exact and path independent. This fact is most easily seen by considering an *isothermal* process at equilibrium, for which T is held fixed. This means the internal energy is constant ($dU = 0$), which we will explicitly demonstrate in Ch. 3 and 4 (but was known empirically in the mid 19^{th} century). We will also use the ideal gas law (which we will also show in Ch 3-4 but was known empirically since the early 19^{th} century) is $pV = nRT$. Combining both of these facts, we can thus write

$$đQ = -U + đW = đW = pdV = \frac{nRT}{V}dV \qquad\qquad \frac{dV}{V} \propto \frac{đQ}{T} \tag{1.6}$$

Since dV/V is exact (depending only on the endpoints), it must be that $dS = đQ/T$ is exact as well. This defines the entropy, and allows us to compute the total change in heat for an isothermal path directly, via $\int đQ = \int TdS = TS$.

This derivation depends on the process being isothermal, but it is possible to show that this can be extended to processes in which the temperature varies. This was originally accomplished by Carnot using a hypothetical process that fully separates heat changes from temperature changes, pictured in Fig. 1.3. In the isothermal steps, heat is extracted from the reservoir and converted directly into mechanical work, without any change in temperature or internal energy. Using the ideal gas law, we can show directly that $\Delta Q = \int_o^f pdV = nRT\log(V_f/V_o)$ for either isothermal path. The efficiency of this engine, η, is

$$\eta = \frac{\text{work done}}{\text{max work that could be done}} = \frac{Q_> - Q_<}{Q_>} = \frac{T_> - T_<}{T_>} = 1 - \frac{T_<}{T_>} \tag{1.7}$$

Because the Carnot cycle can be reversed, it is possible to show that all engines *must* have a lower efficiency than a Carnot engine (else they could be coupled to a Carnot refrigerator to produce an efficiency with 100% efficiency, violating the second law).

Since $W = \eta Q_> = (1 - T_</T_>)Q_>$ and $W = Q_> - Q_<$, we find $\frac{Q_>}{T_>} = \frac{Q_<}{T_<}$, or $S = \frac{Q}{T}$ =const. This means

$$\oint_{\text{Carnot cycle}} dS = 0 \tag{1.8}$$

over the Carnot cycle, even if the temperature is varied. Any reversible thermodynamic cycle can be approximated by a sequence of infinitesimal isothermal and adiabatic steps, meaning that

$$\oint_{\text{Reversible cycle}} dS = 0 \tag{1.9}$$

Since we can subdivide any cycle into two paths, it must be that

$$\int_{\text{Reversible path}} dS = S_f - S_o \tag{1.10}$$

is *independent* of the path.

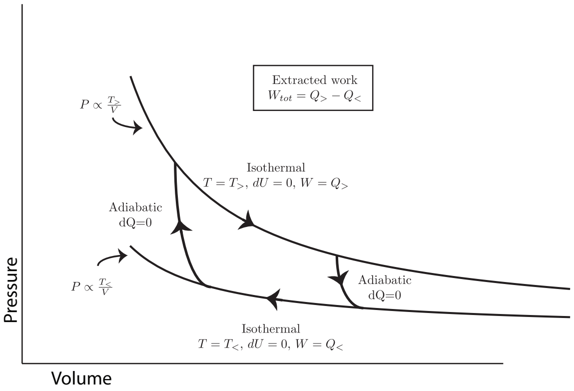


Figure 1.3: The Carnot cycle is a cyclic path, resulting in $\Delta U_{tot} = 0$, under which two steps have constant temperature (isothermal) and two steps have zero heat flow (adiabatic). The isothermal paths are $p \sim T/V$, the adiabatic paths are $p \sim T/V^\gamma$ for the heat capacity ration γ (discussed in the text).

1.2.1 Entropy in the first law

Taken together, the previous section means we can write the first law for any reversible process as

$$dU = TdS - pdV \tag{1.11}$$

Irreversible processes *produce* entropy which can never be spontaneously recovered. Examples include heat loss to the environment, such as a piston with friction, or reversible nonequilibrium processes such as the temperature equilibration of two bodies brought into contact. Thermodynamics is directly applicable only at equilibrium, and entropy estimates based on thermodynamics will always be underestimates out-of-equilibrium. In particular, we will find that $đQ_{irrev} \geq đQ_{rev}$, (since an irreversible process absorbs more heat than a reversible process), so $(đQ)_{irrev} \geq pdV - dU$.

Entropy quickly came to be associated with the notion of disorder for a variety of philosophical reasons, with high entropy states having more disorder and low entropy states having low disorder. Note that the derivation of $dS = dQ/T$ gives absolutely no indication of what entropy *is*. There was no reference to disorder or the arrow of time. A great strength of statistical mechanics is giving insight into the meaning of entropy in terms of accessible states, which we'll be discussing in great detail in later chapters.

1.3 Chemical Potential and varying Particle Number

In the previous sections we discussed solely two contributions to the internal energy: the heat absorbed by the system from the reservoir and the energy converted into mechanical work. An important term not included above is the effect of variation in the number of particles. Thermal equilibrium requires a heat reservoir that defines the temperature of the system, and chemical equilibrium likewise requires a reservoir of particles that can enter and exit the system. The modern representation is

$$dU = TdS - pdV + \sum_i \mu_i dN_i \tag{1.12}$$

where N_i is the number of particles of type i in the system. and μ_i is the chemical potential of that species. μ_i is the energy required to insert a new particle of type i into the system while holding S and V fixed. The chemical potential is essential for *open* systems (say a system immersed in a bath of solvent), where some molecules may move in or out freely.

In the 19^{th} century, prior to the knowledge that physical systems were composed of particles, this would have been described in terms of species concentrations. For an ideal gas (where there is only one species), we expect the equilibrium density in the system to match that of the reservoir ($\rho = \rho_{external}$), something we will show explicitly later. This is similar to the adoption of the same temperature for thermal equilibrium. For this and the next few sections we won't be working with a fixed number of particles, but it's useful to be aware of it from the outset. We'll describe the chemical potential more completely in later sections.

1.4 Other Extensions of the first law

Thermodynamic potentials can be defined for more exotic systems as well, such as charge or angular momentum. For example, if the system has an electrostatic potential ϕ it would take an energy ϕdq to add dq charge to a system at equilibrium with the reservoir. The first law of thermodynamics becomes $dU = TdS - pdV + \phi dq$. Other extensions of the first law include the addition of a dipole moment (with $dU \to dU - BdM$ with B the external field and M the total magnetization of the system), an external tension ($dU \to dU + fdL$ where f is an applied force and L is a stretching length), surface tension ($dU \to dU + \gamma dA$ with γ the surface tension and A the surface area). The first law of thermodynamics will apply to any system of interest so long as it is at thermal equilibrium with a reservoir.

1.5 Legendre Transforms and The Helmholtz Free Energy

Eq. 1.11 is sometimes called the fundamental equation of thermodynamics (for fixed N at any rate), and gives the variation in the energy in terms of variation of entropy and volume. Some terminology is useful for understanding this and other thermodynamic potentials.

- The total internal energy U is a thermodynamic potential
- p and V are called conjugate variables, as are T and S, since they are coupled to each other and not to any other thermodynamic variable.
- The entropy S and volume V are the independent variables or proper variables. These are the quantities that are varied.
- The temperature T and pressure p are dependent variables. Depending on the path, these quantities change with S and V.

While eq. 1.11 is exact in a reversible process, it is actually not useful for many practical reasons. It is difficult to imagine an experiment in which one varies the entropy directly: there is no apparatus with an 'entropy knob' that tunes S directly. While fundamental, Eq. 1.11 lacks the necessary connection to experiments in order to actually make a useful prediction (which is an important aspect of any theoretical undertaking!). However, we all know from experience that varying the temperature T is experimentally possible.

To make the theory more experimentally useful, we must construct new thermodynamic potentials that swap the roles of entropy and temperature. We do this by performing a Legendre transformation, which takes advantage of the fact that

$$d(TS) = T(S,V)dS + S(T,V)dT \tag{1.13}$$

so that

$$d(U - TS) = TdS - (TdS + SdT) - pdV = -SdT - pdV \tag{1.14}$$

This leads to the definition of the Helmholtz free energy $A = U - TS$ (sometimes the letter F is used), whose proper variables (those that are varied) are T and V. This may seem like a trivial exercise: after all, all we did was subtract TS from the energy. The Legendre transform is fundamental and useful because it exchanges one proper variable to another in a mathematically precise and exact way. A variety of thermodynamic potentials have been historically very useful, as discussed in Sec. 1.5.

Often, students come across the Legendre transformation in the context of transforming between the Lagrangian and Hamiltonian systems (with $H = \sum_i p_i \dot{q}_i - L$), and the purpose of the transformation is often not obvious when you first encounter it. In the case of the Legendre transformation in 1.14, the purpose is more clear: we have replaced the energy, whose independent variables *must* be S and V, with a new function whose dependent variables *must* be T and V. Because T and V are easily accessible variables experimentally, the Hemholtz free energy is a far more useful quantity in many experiments.

1.5.1 Free Energy Minimization

The Helmholtz free energy is particularly useful for the fact that it's minimized at equilibrium. This fact arises from the second law of thermodynamics, which can be restated that the entropy change of a system $dS_{system} \geq 0$. This restatement is because the Carnot cycle is as efficient as possible, due to the fact that the total entropy is constant in the process. This implies the entropy change of any system $dS_{system} \geq 0$. If we have a system at thermal equilibrium with a reservoir of temperature T, the total entropy of the combined system is $dS_{tot} = dS_{sys} + dS_{res} \geq 0$. For an isolated system, $dU_{tot} = dU_{sys} + dU_{res} = 0$, and for a reservoir of constant volume $dU_{res} = TdS_{res}$, or $dS_{res} = -dU_{sys}/T$. Then $TdS_{sys} + TdS_{res} = -dU_{sys} + TdS_{sys} \geq 0$. This has two important implications:

- If no work is done ($đW = 0$), $d(U - TS) = dA \leq 0$ for constant volume and temperature. This implies A must be minimized at equilibrium, since it can only decrease. An example of such a minimization is in Sec. 1.5.2.
- The Helmholtz free energy represents the maximum amount of work that can be extracted from a system by the reservoir at constant temperature and volume, since $dU_{sys} - TdS_{sys} = đW_{sys}$.

The former is an important feature of the Helmholtz free energy, because for a system at equilibrium with a bath at constant T and V, the free energy is minimized in terms of all other variables. Note that the internal energy *is not minimized* at equilibrium (energy is minimized for a classical system not coupled to a thermal bath), nor is the system's entropy maximized (the entropy of the universe is always increasing, but small systems can decrease their entropy). A is not minimized with regards to T or V, (the former set by the thermal bath, and the latter fixed unless mechanical work is being done), but is minimized with regards to any other thermodynamic variables.

1.5.2 Example of minimization: Nucleation

An example of how the free energy can be used to determine the equilibrium properties of a system can be found in a simplified model of the nucleation of a droplet in condensing gas. We imagine a gaseous state (red in Fig. 1.4A, having free energy $A_g = N_g\alpha_g$ with α_g the free energy per unit molecule. α takes into account all of the energetic interactions between molecules in the gas phase, the chemical potential, and the entropy (which is difficult to compute). Suppose the gas can also condense into a spherical droplet (diagrammed in Fig. 1.4A), meaning the atoms in the gas can be lost (reducing the free energy of the gas) and added to the droplet (potentially increasing its free energy). We assume the free energy of the droplet has the form

$$A_d = N_d\alpha_d + 4\pi R^2\gamma = \frac{4\pi R^3}{3}\rho_d\alpha_d + 4\pi R^2\gamma \tag{1.15}$$

The first term is the free energy of the droplets in the bulk (in terms of the free energy per molecule in the droplet), and the latter is a surface energy term that resists the formation of an interface. The total free energy of the combined system is

$$\begin{aligned} A(R) &= \frac{4\pi R^3}{3}\rho_d\alpha_d + 4\pi R^2\gamma + \left(N - \frac{4\pi R^3}{3}\rho_d\right)\alpha_g \qquad (1.16)\\ &= \frac{4\pi}{3}R^3\rho_d\Delta\alpha + 4\pi R^2\gamma + const \qquad (1.17)\end{aligned}$$

Equilibrium will occur when A is minimized with respect to R, as required by the second law of thermodynamics. As shown in Fig. 1.4(B), If $\Delta\alpha = \alpha_d - \alpha_g \geq 0$, $A(R)$ is monotonically increasing and the equilibrium droplet size is $R = 0$. This is unsurprising: the droplet phase has a higher free energy than the gas phase, so to minimize the total free energy the system will simply remain in the gas phase. However, if $\Delta\alpha < 0$, the droplet phase has a lower free energy than the gas phase and there is a competition between the bulk phase (where adding atoms decreases the total free energy) and the surface tension (which increases the free energy). The former term scales with R^3 and the latter with R^2, so we know there must be some radius large enough that the reduction in free energy will overcome the surface tension. This occurs where $dA/dR = 0$, or

$$R_0 = 0 \qquad \text{or} \qquad R_{crit} = -\frac{2\gamma}{\rho_d\Delta\alpha} \tag{1.18}$$

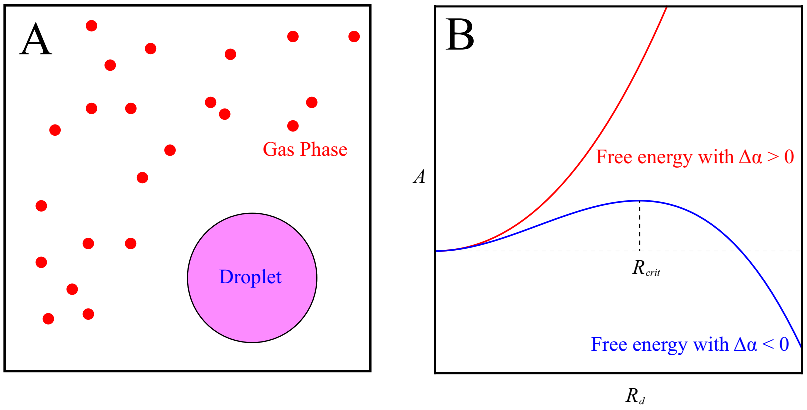


Figure 1.4: default

Beyond R_{crit}, the free energy decreases monotonically (meaning adding more and more atoms to the droplet becomes energetically favorable. Thus, the free energy is minimized when *all* of the molecules are in the droplet. The energy-minimizing radius will satisfy $4\pi R_{eq}^3 \rho_d/3 = N$.

The equilibrium state of any system will be the one that minimizes the energy. Note, though, that it may be difficult for a system to attain equilibrium if it starts in a local energetic minimum. If we prepare a system with $R = 0$ (no droplets), there is a free energy barrier between the local minimum of $R = 0$ and the global minimum of $R = R_{eq}$. This barrier height $F_{barrier} = F(R_{crit}) - F(0) = 16\pi\gamma^3/3\Delta\alpha^2\rho^2$. Since we have not specified these parameters, it is entirely possible for this to be an enormous barrier. If the barrier height is very large, the system will be trapped in the gaseous state until a large droplet is created by chance (a nucleation event). While trapped in the $R \approx 0$ regime, the system is in a metastable state: a state that is thermodynamically stable to small perturbations due to being a local free energy minimum, but is not the global free energy minimum and thus is not the global free energy minimum. Once a droplet has formed of radius $R \geq R_{crit}$, the system will spontaneously condense into the droplet phase, will all gas molecules immediately drawn into the growing droplet.

1.6 Other Thermodynamic Potentials

The Helmholtz free energy is the thermodynamic potential most commonly used by physicists, but others have been particularly useful in other fields (chemistry, biology, etc). Helmholtz holds T and V fixed, Gibbs T and p, and Enthalpy S and p. Each of these potentials are useful in their own domains, depending on what is experimentally accessible and

Table 1.1: Definitions of the various potentials commonly used at constant N.

Potential	Definition	Independent Variables	Dependent Variables
Internal Energy	$U = ST - pV + \mu N$	S, V, N	p, T, μ
Helmholtz Free Energy	$A = U - ST$	T, V, N	p, S, μ
Enthalpy	$H = U + pV$	S, p, N	V, T, μ
Gibbs Free Energy	$G = U - TS + pV$	T, p, N	V, S, μ
Grand potential	$\Phi = U - TS - \mu N$	T, V, μ	p, S, N

measurable. The enthalpy measures the total internal energy of the system independent of the mechanical work (since $\Delta H = \Delta Q$). The Helmholtz free energy measures the *capacity* of the system to do work for an isolated system at constant volume. The Gibbs free energy represents the maximum amount of work extractable from a system at constant pressure, and is minimized at equilibrium if the pressure is held fixed (much like the Helmholtz free energy at constant volume). The use of the grand potential will be seen when we discuss the grand canonical ensemble. The appropriateness of any particular potential depends on the system you're interested in, and what you intend to measure. Generally speaking, physicists tend to work with A, while chemists tend to work with G.

Note that if we have additional terms in our expression for the energy, it is possible to define new thermodynamic potentials. For example, the expression $dU = TdS - pdV + \phi dq$ is not useful if we cannot control the number of charges in the system experimentally, and in some cases it is easier to directly manipulate the potential (by imposing an external field we control precisely for example). A new thermodynamic potential can be defined as $X = U - (TS + \phi q)$, with $dX = -SdT - pdV - qd\phi$. Regardless of your system of interest the ability to switch from an experimentally inaccessible independent variable to one that is experimentally accessible is useful.

1.7 Extensive vs Intensive Variables

A different distinction between thermodynamic variables is *extensive* vs *intensive*, with the former related to variables that *increase* with system size and the latter with variables that are *independent* of system size. If we imagine taking two identical isolated systems and bringing them together, the total system will have the same temperature, the same pressure, and the same chemical potential. However, it will have twice as many particles, twice the volume, and twice the entropy (the latter has not been proven yet, but will be shown to be true in later chapters).

When connected to a heat bath, the distinction between extensive and intensive variables

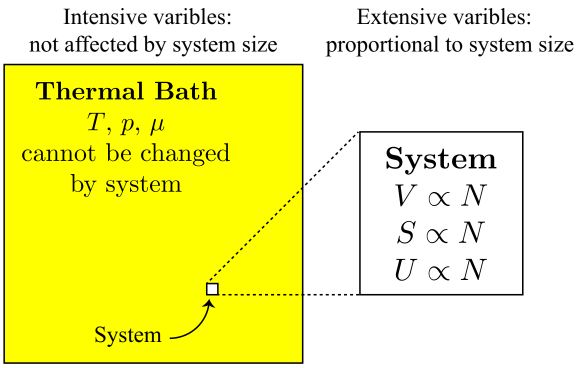


Figure 1.5: Intensive variables associated with the thermal bath, which cannot be affected by the system size, are T, p, and μ. The heat bath is presumed so large that no change to the system can alter their values, and they are intensive variables. Extensive variables S, V, and U are all proportional to N.

are the same, but the argument changes somewhat. For a system connected to a heat bath, the intensive variables summarize the property of the bath. The temperature of the heat bath is independent of the number of particles in the system, as the bath is assumed to be sufficiently large (schematically diagrammed in Fig. 1.5) that heat or energy exchange with the system cannot change the bath's temperature. Likewise, the pressure and chemical potential of the bath is unalterable by the system. Intensive variables are independent of the size of the system.

Extensive variables are those that *are* proportional to the size of the system. For a system at equilibrium with the bath, the density of particles in the volume will be constant (due to the fixed chemical potential of the bath), with $\rho = N/V$ held fixed, so $V \propto N$. Each particle will have an average energy proportional to T, so $U \propto T$. The total entropy of the system is proportional to the number of particles.

1.8 Heat Capacity

The theory in Sec. 1.5 gives a method to link the theory to realistic experimental conditions. To compare the theory to experiment, it's also useful to compute observables that are experimentally accessible. The simplest and most widely used is the heat capacity, which we'll spend a lot of time on throughout this course. The heat capacity determines the change in energy due to a change in temperature, the former of which is easily observed and the latter easily controlled. The heat capacity will depend on the system as well as the experimental protocol, i.e. if pressure or volume is held fixed.

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V \qquad\qquad C_p = \left.\frac{\partial H}{\partial T}\right|_p \tag{1.19}$$

where $H = U + pV$ is the Enthalpy of the system. Note that the specific heat of a system is $c_V = C_V/M_{tot}$, the heat capacity normalized by the mass of the system. Don't get the terms mixed up. In this course we'll generally only be interested in the heat capacity. For an ideal gas of noninteracting particles, it was known that $U = 3nRT/2$ is independent of the volume of the container (we will show this in later sections), and so $dU/dT|_V = 3nR/2$. The specific heat at constant pressure can be computed using by coupling this to the ideal gas law, $pV = nRT$, with

$$C_p = \left.\frac{dH}{dT}\right|_p = \left.\frac{dU}{dT}\right|_p + \left.\frac{d(pV)}{dT}\right|_p = \left.\frac{dU}{dT}\right|_V + \frac{d(nRT)}{dT} = C_V + nR \tag{1.20}$$

Note that we can freely change $dU/dT|_p$ and $dU/dT|_V$ because dU is an exact differential, so the change in U is independent of the path taken.

The fact that the heat capacity is measurable has a variety of benefits beyond providing falsifiability to the theory. We can also physically measure the change in entropy so long as we can measure C_V (assuming a reversible process):

$$\left.\frac{\partial S}{\partial T}\right|_V = \left.\frac{\partial S}{\partial U}\frac{\partial U}{\partial T}\right|_V = \left(\frac{dU}{dS}\right)^{-1}\left.\frac{dU}{dT}\right|_V = \frac{C_V}{T} \qquad\qquad \Delta S = \int_{T_0}^{T_f} dT \frac{C_V(T)}{T} \tag{1.21}$$

This is also a convenient way to represent the variation in energy in some cases, since $TdS = C_V(T)dT$ and therefore $dU = C_V dT - pdV$. Note that this is another way of switching from S as an independent variable to T as an independent variable (in contrast to the Legendre transform used in deriving A).

The heat capacity ratio, γ is used in a number of contexts, and is

$$\gamma = \frac{C_p}{C_V} \tag{1.22}$$

This measures the rate of increase in energy of a system that is able to do mechanical work (through the change in volume) to one that cannot (fixed volume). There are some interesting thermodynamic results that can be derived using the heat capacity ratio at constant volume and pressure for an ideal gas , and in particular for the ideal gas

$$pV^\gamma = const \qquad\qquad TV^{\gamma-1} = const \tag{1.23}$$

This derivation is another homework problem.

1.9 Maxwell Relations

Thermodynamic potentials make it possible to determine a number of relationships between variables that are not obvious. This is due to the fact that they involve exact differentials. For any function $F(A,B)$, if we have

$$dF = a(A,B)dA + b(A,B)dB \tag{1.24}$$

where a and b are the dependent variables and A and B are the independent variables, we can take two derivatives to derive a relationship between a and b. This is due to the fact that

$$\begin{aligned} \frac{\partial}{\partial B}\left(\frac{\partial F}{\partial A}\right) &= \frac{\partial}{\partial A}\left(\frac{\partial F}{\partial B}\right) &(1.25)\\ \frac{\partial a(A,B)}{\partial B} &= \frac{\partial b(A,B)}{\partial A} &(1.26) \end{aligned}$$

Note that the derivatives are taken with all other independent variables held fixed (so B is not varied in a derivative involving $\partial/\partial A$). We've dropped the common notation here. That means, using $dA = -SdT - pdV + \mu dN$, that

$$\left.\frac{\partial S}{\partial V}\right|_{TN} = \left.\frac{\partial p}{\partial T}\right|_{VN} \qquad \left.\frac{\partial S}{\partial N}\right|_{TV} = -\left.\frac{\partial \mu}{\partial T}\right|_{VN} \qquad \left.\frac{\partial p}{\partial N}\right|_{TV} = -\left.\frac{\partial \mu}{\partial V}\right|_{TN} \tag{1.27}$$

Similar relations can be derived using the other thermodynamic potentials. These are generally called Maxwell relations, and are fundamental in relating experimentally measurable variables in some experimental settings (where only specific variables are experimentally accessible).

1.10 Summary

In this chapter, we've talked about predictions of thermodynamics, the variables that are addressed, and the techniques to manipulate those variables. The primary take-away points are

- The predictions of thermodynamics are fundamentally correct. Any theoretical enterprise that does not agree with the laws of thermodynamics is wrong, and we'll need to ensure statistical mechanics actually agrees with thermodynamics before we can believe it is a valid theory.
- Thermodynamics doesn't tell us what entropy is. We can understand its properties mathematically, and can guess it's meaning on philosophical grounds, but there is no formal proof of how entropy relates to any physical property outside of the equally mysterious 'heat.'

- Various relationships exist between thermodynamic potentials (via Legendre transformations) and variables (via Maxwell equations) that can be used in statistical physics. It can still be useful to use this classical theory to identify relationships between variables.
- The internal energy U is useful. The free energy A is useful as well, *for a different reason*. These thermodynamic potentials tell us something different and important about our system.
- Specific heat is one of the fundamentally useful observables in thermodynamics, and will remain so in statistical mechanics. It is measurable, and a great deal of effort has gone into designing the techniques to measure the relationship between temperature and energy.

1.11 Homework Problems

1. An elastic band has the fundamental equation $dU = TdS + fdL$, where f is the externally applied stretching force and L the length of the band. If the elastic band is stretched adiabatically and reversibly (so that $dS = 0$), will the temperature increase or decrease as the length increases?
2. Show that $SdT + Nd\mu = Vdp$.
3. An ideal gas satisfies $U = TS - pV$, $pV = nRT$, and $U = 3nRT/2$, where R is the gas constant and n the moles of gas in the system. For an adiabatic process, with $đQ = 0$, show that an ideal gas satisfies $C_p p dV = -C_V V dp$. Show this implies that $pV^\gamma =$ constant.

   Note: This is a standard result, with a solution easily found on Wikipedia and in most textbooks on thermodynamics. You may use any resources you like, but please recall the academic honesty policy. Directly copying without attribution is cheating.
4. Consider a column of gas divided into a sequence of small volumes $dV = Adh$ at height h, each containing an ideal gas. The temperature at height h is maintained at $T(h)$. The number density is a function of both height and temperature, with $\rho = \rho[h, T(h)]$. In the absence of gravitational forces, the chemical potential is $\mu[\rho]$. In the presence of gravity, each particle has an energy mgh in the volume at height h.
   (a) Show and explain why the gravitational potential energy acts as an effective height-dependent chemical potential in each volume.
   (b) Argue why an infinitesimal change in pressure must satisfy $dp = -mg\rho dh$. Note

that, while not the only possible argument, the discussion in Huang's chapter 2 may be helpful.

(c) For an ideal gas, with $p = \rho k_B T$ with k_B Boltzmann's constant, show that

$$\left.\frac{\partial \rho}{\partial h}\right|_T = -\frac{mg}{k_B T(h)}\rho - \left(\left.\frac{\partial \rho}{\partial T}\right|_h + \frac{\rho}{T}\right)\frac{dT}{dh} \tag{1.28}$$

Hint: One way to approach the problem is to recognize that $d\rho/dh = \partial\rho/\partial h|_T + \partial\rho/\partial T|_h dT/dh$

(d) If the temperature is held constant (a reasonable approximation over short distances), show that eq. 1.28 implies $\rho(h) = \rho_0 e^{-mgh/k_B T}$. Estimate the numerical value of $k_B T/mg$ in km.

(e) For an ideal gas at constant T, the chemical potential is $\mu = k_B T \log[\rho(h)\lambda^3]$ for $\lambda \propto T^{-1/2}$ (we will show this is true in later chapters). Explicitly confirm that chemical equilibrium is satisfied if Eq. 1.28 is satisfied for constant T.

Chapter 2

Kinetic Theory (primarily following Huang ch 3-4)

Thermodynamics gave a remarkably accurate picture of the behavior of a gas, enabling the design of the technology that led to the industrial revolution and internal combustion engines. However, it gave a very little information on the fundamental nature of the gas, with the concept of entropy (1826) useful but totally unclear concept. While physicists were developing Thermodynamics in the early 19th century, a chemist named John Dalton had suggested that chemical reactions could be explained by the existence of atoms, indivisible objects that were identical within chemical species but distinct between chemical species. This concept had gained favor in the chemistry community, but the physics community generally rejected atomistic theories of gasses. Clausius had derived the equipartition theorem (which we'll discuss in later chapters) in 1865, and Maxwell had derived his famous velocity distribution (which we'll discuss later in this chapter) in 1866. At the time, there was no obvious relationship between the idea of an atom and that of entropy, which is where Boltzmann began his work. He used a technique to show that Maxwell's distribution is inevitable for a real gas, suggesting the physical reality of atoms as well as giving a quantifiable sense of entropy as 'disorder.'

2.1 Scattering Processes and Boltzmann's Transport Equation

In a gas of 10^{23} particles, it's essentially useless to know the details of every single particle (as we'll discuss further below). The statistics of the system need to be aggregated on a more coarse grained level in order to be useful. Rather than ask "what is every single particle doing at any given instant in time," it's more useful to understand "what is the probability of any particle having a particular position and momentum at any given time." The former is simply too detailed to be useful, while the latter tells you about the 'typical' behavior of the particles in the system. This single-particle distribution can be understood using the Boltzmann transport equation.

2.1.1 Time-dependent distribution functions

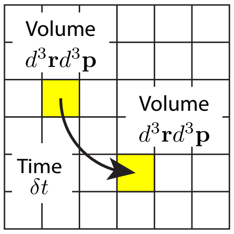


Figure 2.1: Particle density in phase space. Shown are one position and one momentum axes, with the full dimensionality three momentum and three positions. Phase space is divided into bins of volume $d^3\mathbf{r}d^3\mathbf{p}$, with a continuous distribution $f(\mathbf{r}, \mathbf{p}, t)$ assumed since $N \gg 1$. Particles in some position/momentum bin will move to a new bin as time evolves according to Eq. 2.2 or 2.3.

For any system of particles, we can identify the single-particle distribution of position and momentum, $f(\mathbf{r}, \mathbf{p}, t)$, that identifies the fraction of particles at position $\mathbf{r}$ and $\mathbf{r}+\delta\mathbf{r}$ having momentum between $\mathbf{p}$ and $\mathbf{p}$ and $\mathbf{p}+\delta\mathbf{p}$ at time t (see Fig. 2.1). For only a few particles, this will be a very jagged distribution in the 6-dimensional position-momentum space, but for $N = 10^{23}$ particles the distribution will be a smooth function. In this, we will normalize $\int d^3\mathbf{p}d^3\mathbf{r}f(\mathbf{p}, \mathbf{r}, t) = N$ for all t, as it's a distribution function for a single particle (this has no impact on the analysis, but is important to realize when determining system-scale details). If the particles are not interacting, the steady-state dynamics of the system must satisfy

$$f\left(\mathbf{r} + \frac{\mathbf{p}\delta t}{m}, \mathbf{p} + \mathbf{F}\delta t, t + \delta t\right) d^3\mathbf{p}d^3\mathbf{r} = f(\mathbf{r}, \mathbf{p}, t) d^3\mathbf{p}d^3\mathbf{r} \tag{2.1}$$

where $\mathbf{F}$ is the force on each particle (caused by an external field, not by collisions). In the limit as $\delta t \to 0$, we can perform a Taylor expansion and see that

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} + \mathbf{F} \cdot \nabla_{\mathbf{p}}\right) f(\mathbf{r}, \mathbf{p}, t) = 0 \tag{2.2}$$

Here there are no collisions between particles, and if there were no external force applied (if $\mathbf{F} = 0$) there would be no change in the momentum of any particle. Note that there's no well-defined steady-state distribution of the function f in the absence of a force. Any function of the form $f(\mathbf{r}, \mathbf{p}, t) = g(\mathbf{p}t/m - \mathbf{r}, \mathbf{p})$ will satisfy eq. 2.2.

2.1.2 Streaming functions due to collisions

If the particles are interacting and collisions are permitted, Equation 2.2 must be modified to account for interactions between the particles. Without saying anything useful we can write

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} + \mathbf{F} \cdot \nabla_{\mathbf{p}}\right) f(\mathbf{r}, \mathbf{p}, t) = \left(\frac{\partial f}{\partial t}\right)_{coll} \tag{2.3}$$

with $(\partial f/\partial t)_{coll}$ the rate at which the volume element $d^3\mathbf{r}d^3\mathbf{p}$ is populated *due to the collisions*. This equation does not have a prediction for what $(\partial f/\partial t)_{coll}$ is, and simply posits there must be a term accounting for collisions. Eq. 2.3 can be rewritten as

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{stream} + \left(\frac{\partial f}{\partial t}\right)_{coll} \tag{2.4}$$

with $(\frac{\partial f}{/}\partial t)_{stream} = -\frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} - \mathbf{F} \cdot \nabla_{\mathbf{p}}$. This term is often called the 'streaming' term, as particles are streaming into or out of a region without regard to the collisions. Without an estimate of $(\frac{\partial f}{/}\partial t)_{coll}$, we can make no further progress.

We'll soon discuss the BBGKY hierarchy, which will put this term on a more clear theoretical footing. However, at the moment we must derive an approximation for the form of $(\partial f/\partial t)_{coll}$. In particular, we can compute

- $R_{out}(t, \mathbf{r}, \mathbf{p}) dt d^3\mathbf{r} d^3\mathbf{p}$ = # of collisions involving a particle at t *initially* at $\mathbf{r}$ with momentum $\mathbf{p}$ within $dtd^3\mathbf{r}d^3\mathbf{p}$.
- $R_{in}(t, \mathbf{r}, \mathbf{p}) dt d^3\mathbf{r} d^3\mathbf{p}$ = # of collisions involving a particle at t *ending* at $\mathbf{r}$ with momentum $\mathbf{p}$ within $dtd^3\mathbf{r}d^3\mathbf{p}$.

This means we can write

$$\begin{aligned} \left(\frac{\partial f}{\partial t}\right)_{coll} &= \text{\# of particles driven into location and momentum} \\ &\qquad\qquad \mathbf{r} \text{ and } \mathbf{p} \text{ due to a collision at } t \text{ (within } d^3\mathbf{r}d^3\mathbf{p}\text{dt)} \\ &= R_{in} - R_{out} \end{aligned} \tag{2.5}$$

Now we must simply estimate R_{in} and R_{out}.

2.1.3 Estimating the effects of collisions

First, we assume that collisions are binary (i.e. there is never a collision where a third particle has any affect whatsoever). This is the assumption the gas is dilute. That means the collision term can only depend on the properties of two particles at a time: $(\partial f/\partial t)_{coll}$ is a function of t, particle 1's state $\mathbf{r}_1$ and $\mathbf{p}_1$, and particle 2's state $\mathbf{r}_2$ and $\mathbf{p}_2$. If the interaction is extremely short ranged, the particles must occupy *the same* position ($\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$), but can have different momenta. This means we can write

$$\begin{aligned} R_{out}(\mathbf{r},\mathbf{p},t) &= \int d^3\mathbf{p}_1^{init}\mathbf{p}_2^{init}d^3\mathbf{p}_1^{final}d^3\mathbf{p}_2^{final}P_c(\mathbf{p}_1^{final},\mathbf{p}_2^{final}|\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t) \\ &\qquad \times P_0(\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t)\times\delta(\mathbf{p}_1^{init}-\mathbf{p}) \\ R_{in}(\mathbf{r},\mathbf{p},t) &= \int d^3\mathbf{p}_1^{init}\mathbf{p}_2^{init}d^3\mathbf{p}_1^{final}d^3\mathbf{p}_2^{final}P_c(\mathbf{p}_1^{final},\mathbf{p}_2^{final}|\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t) \\ &\qquad \times P_0(\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t)\times\delta(\mathbf{p}_1^{final}-\mathbf{p}) \end{aligned}$$

where $P_c(\mathbf{p}_1^{final},\mathbf{p}_2^{final}|\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t)$ is the conditional probability of finding two particles with momenta $\{\mathbf{p}_1^{final},\mathbf{p}_2^{final}]\}$ given they started with momenta $\{\mathbf{p}_1^{init},\mathbf{p}_2^{init}\}$, and $\mathbf{P}_0(\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t)$ is the joint probability of actually seeing those initial conditions. These equations state that the in- or out-rates can be determined by integrating over the conditional probability of finding a final state given an initial state with a constraint on one initial or final momentum (respectively).

We still haven't done much, since we don't know anything about the conditional or prior probabilities. One final approximation we can make is that the prior probabilities are *uncorrelated*:

$$P_0(\mathbf{p}_1,\mathbf{p}_2;\mathbf{r},t)\propto f(\mathbf{r},\mathbf{p}_1,t)f(\mathbf{r},\mathbf{p}_2,t) \tag{2.6}$$

This means the odds of finding two particles with the given momenta *simultaneously in the same place* is simply the product of the odds of finding one particle there, times the probability of finding the other there without regard for the presence or absence of the first particle. This is referred to as the 'molecular chaos' assumption by Boltzmann (note this term has nothing to do with modern chaos theory), and is essentially a statement that the joint probability is unaffected by the collisions at equilibrium. We still need to account for the conditional probability of taking $\{\mathbf{p}_1^{init},\mathbf{p}_2^{init}\}\to\{\mathbf{p}_1^{final},\mathbf{p}_2^{final}\}$. We cannot know this without specifying the interaction, so we must again make an approximation. We simply state that the total kinetic energy and total momentum must be conserved during the collision, so that

$$P_c(\mathbf{p}_1^{final},\mathbf{p}_2^{final}|\mathbf{p}_1^{init},\mathbf{p}_2^{init};\mathbf{r},t)=\delta(E_{init}-E_{final})\delta(\mathbf{P}_{init}-\mathbf{P}_{final})g(\mathbf{P}_{init},\mathbf{P}_{final}) \tag{2.7}$$

where $\mathbf{P}_{init} = \mathbf{p}_1^{init} + \mathbf{p}_2^{init}$ and $E_{init} = [(\mathbf{p}_1^{init})^2 + (\mathbf{p}_2^{init})^2]/2m$ (and similarly for final). $g(\mathbf{P}, \mathbf{P}')$ is an unknown scattering function that depends on the specific interaction between the particles, and here we simply assume it is a function solely of the initial and final momenta and is reversible, so $g(\mathbf{P}, \mathbf{P}') = g(\mathbf{P}', \mathbf{P})$. The assumption of reversibility is true classically for point particles interacting with a pair potential, and for quantum systems where collisions are specified by a transition matrix between different energy and momentum states (which is reversible). For mesoscopic systems composed of soft, deformable materials, the assumption of reversibility may be violated. Regardless, without specifying the interactions further it is not possible to reduce $g(\mathbf{P}, \mathbf{P}')$, and we will simply assume reversibility is held.

Combining all of these approximations, we have

$$\left(\frac{\partial f}{\partial t}\right)_{coll}\Bigg|_{\mathbf{r},\mathbf{p}_1,t} = \int d^3\mathbf{p}_2 d^3\mathbf{p}_1' d^3\mathbf{p}_2' \delta(E_f - E_i)\delta(\mathbf{P}_f - \mathbf{P}_i) g_{if}(f_1' f_2' - f_1 f_2) \tag{2.8}$$

where the integral is over one initial and two final conditions (note that there is no $\int d^3\mathbf{p}_1$ in eq. 2.8). In eq. 2.8, $f_1 = f(\mathbf{r}, \mathbf{p}_1^{initial}, t)$, $f_2 = f(\mathbf{r}, \mathbf{p}_2^{initial}, t)$, $f_1 = f(\mathbf{r}, \mathbf{p}_1^{final}, t)$, and $f_2 = f(\mathbf{r}, \mathbf{p}_2^{final}, t)$. In order to produce this symmetric form of $f_1' f_2' - f_1 f_2$, we also used the fact that $g(\mathbf{P}, \mathbf{P}') = g(\mathbf{P}', \mathbf{P})$. While the utility of this approach may be somewhat unclear, what we've done is reduce the left-hand and right-hand sides of eq. 2.3 in terms of the distributions $f(\mathbf{r}, \mathbf{p}, t)$.

2.1.4 The Boltzmann Transport Equation at Equilibrium

A remarkable simplification occurs at thermal equilibrium, where the macroscopic details of the system must be time independent. This means the distribution $f(\mathbf{r}, \mathbf{p}, t)$ cannot depend on time, otherwise there would be global density or energy fluctuations. If we also assume there is no external force (just internal collisions), the distributions can further not depend on position, since otherwise there would be global density variations (we assume the volume is large and at equilibrium the system will be homogeneous). Note: you'll address the inclusion of a force in the homework. Inter-particle collisions *only* affect the momentum through the unknown $g(\mathbf{P}, \mathbf{P}')$, so $f(\mathbf{r}, \mathbf{p}, t) \to f_0(\mathbf{p})$ at equilibrium.

These constrains mean the left hand side of eq. 2.3 is necessarily zero. That means the right hand side must vanish, so either $g \equiv 0$ or

$$f_0(\mathbf{p}_1) f_0(\mathbf{p}_2) = f_0(\mathbf{p}_1') f_0(\mathbf{p}_2') \tag{2.9}$$

where the $\mathbf{p}_i$'s and $\mathbf{p}_i'$'s must have non-zero transition probability. This is a conservation law, since

$$\log[f_0(\mathbf{p}_1)] + \log[f_0(\mathbf{p}_2)] = \log[f_0(\mathbf{p}_1')] + \log[f_0(\mathbf{p}_2')] \tag{2.10}$$

for any final states of the system. The conservation law can only depend on the momenta of the system (since no other variables arise), and the only conserved quantities for this system are the energy $\propto p^2$ and the momentum $\propto \mathbf{p}$. Thus, it must be that

$$\log[f(\mathbf{p})] = -A\frac{\mathbf{p}^2}{2m} - \mathbf{B}\cdot\mathbf{p} - C \tag{2.11}$$

for some unknown scalars A and C, and an unknown vector $\mathbf{B}$. If higher order terms were to be included, they would *necessarily* be conserved quantities. Since there's no additional conserved quantities beyond E and $\mathbf{p}$, this is the final form of the equilibrium distribution.

Since we know that

$$\int d^3p\ f(\mathbf{p}) = N \qquad \int d^3p\frac{\mathbf{p}^2}{2m}f(\mathbf{p}) = \epsilon N \qquad \int d^3p\ \mathbf{p}f(\mathbf{p}) = N\langle\mathbf{p}\rangle = 0 \tag{2.12}$$

with ϵ the average kinetic energy per particle and $\langle\mathbf{p}\rangle$ the average momentum per particle. The calculation of A, $\mathbf{B}$ and C is most easily done by computing $\langle\mathbf{p}\rangle$ first, where we can show

$$\begin{aligned}
\int dp_xdp_ydp_z\mathbf{p}e^{-A\mathbf{p}^2/2m-\mathbf{B}\cdot\mathbf{p}-C} &= \int dp_xdp_ydp_z\mathbf{p}e^{-A/2m(\mathbf{p}-m\mathbf{B}/A)^2+m\mathbf{B}^2/2A-C} \\
&= \int dp_xdp_ydp_z\mathbf{p}e^{-A/2m(\mathbf{p}-m\mathbf{B}/A)^2+m\mathbf{B}^2/2A-C} \\
&= e^{m\mathbf{B}^2/2A-C}\int dp_xdp_ydp_z\left(\mathbf{p}+\frac{m\mathbf{B}}{A}\right)e^{-A\mathbf{p}^2/2m} \\
&= (2\pi)^{3/2}\left(\frac{m}{A}\right)^{5/2}e^{m\mathbf{B}^2/2A-C}\mathbf{B}
\end{aligned} \tag{2.13}$$

where the first equality comes from completing the square. This expression looks quite ugly, but we can immediately see that it implies that each component of $\mathbf{B} = 0$. In that case, we can readily evaluate

$$N = \int d^3pe^{-A\mathbf{p}^2/2m-C} = e^{-C}\left(\frac{2\pi m}{A}\right)^{3/2} \tag{2.14}$$

$$N\epsilon = \int d^3p\mathbf{p}^2e^{-A\mathbf{p}^2/2m-C} = e^{-C}\frac{3}{2A^{5/2}}\left(\frac{2\pi m}{A}\right)^{3/2} \tag{2.15}$$

Tedious algebra shows that $A = 3/2\epsilon$ and $e^{-C} = N(3/4\pi m\epsilon)^{3/2}$, yielding

$$f_0(\mathbf{p}) = N\left(\frac{3}{4\pi m\epsilon}\right)^{3/2}\exp\left(-\frac{3\mathbf{p}^2}{4m\epsilon}\right) \tag{2.16}$$

where ϵ is the energy per particle. This result was remarkable at the time, because it reproduced the previously computed Maxwell distribution in the presence of collisions quite naturally. The equipartition theorem (which we'll discuss in detail later) states that $\epsilon = 3k_BT/2$ and was known (but was based on kinetic theory and thus not widely accepted) at the time. This gives what is now called the Maxwell Boltzmann distribution,

$$\begin{aligned} f_0(\mathbf{p}) &= N\left(\frac{1}{2\pi m k_BT}\right)^{3/2} \exp\left(-\frac{\mathbf{p}^2}{2mk_BT}\right) && (2.17) \\ &= N\left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left(-\frac{\beta\mathbf{p}^2}{2m}\right) && (2.18) \end{aligned}$$

for monatomic atoms. This distribution differs for diatomic atoms or more highly structured atoms (where $\epsilon \neq 3k_BT/2$), but the general functional form in eq. 2.16 is predicted regardless of the relationship between temperature and energy.

2.2 Boltzmann's H-Theorem

In the previous section, we showed that a solution to the Boltzmann Transport Equation is the Maxwell Distribution. A critique at the time, and a fair question, is whether it's the only solution. After all, perhaps the Maxwell distribution is one of many solutions, and that at equilibrium another more complicated solution naturally emerges. Is it guaranteed that $f(\mathbf{r},\mathbf{p},t) \to f_0(\mathbf{p})$ as $t \to \infty$? Boltzmann addressed this question in his H-theorem, which defines a clever function

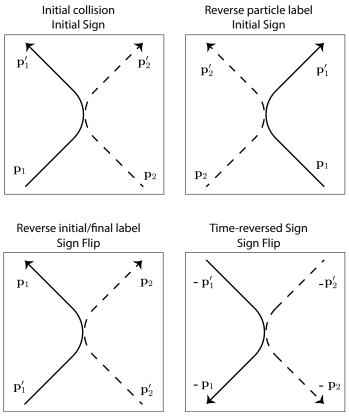
$$H(t) = \int d^3\mathbf{p}\ f(\mathbf{p},t)\log[f(\mathbf{p},t)] \tag{2.19}$$

In this, we are assuming a uniform distribution in position (so $f(\mathbf{r},\mathbf{p},t) = f(\mathbf{p},t)$), but that is not required (Reichl's book has a more complete proof, p. 681). It's straightforward to see that

$$\frac{dH}{dt} = \int d^3\mathbf{p}\frac{\partial f(\mathbf{p},t)}{\partial t}\left(1 + \log[f(\mathbf{p},t)]\right) \tag{2.20}$$

and we know that $\partial f(\mathbf{p},t)/\partial t = (\partial f/\partial t)_{coll}$ in the absence of an external force for a spatially homogeneous distribution. Based on eq. 2.8, we can write

$$\begin{aligned} \frac{\partial f(\mathbf{p},t)}{\partial t} &= \left(\frac{\partial f}{\partial t}\right)_{coll} && (2.21) \\ &= \int d^3\mathbf{p}_2 d^3\mathbf{p}_1' d^3\mathbf{p}_2' \delta(E_f - E_i)\delta(\mathbf{P}_f - \mathbf{P}_i) g_{if}(f_1'f_2' - f_1f_2) && (2.22) \end{aligned}$$



Initial collision
Initial Sign

Reverse particle label
Initial Sign

Reverse initial/final label
Sign Flip

Time-reversed Sign
Sign Flip

Figure 2.2: Permutations that do not alter the statistics of scattering. Each has equal probability of occurring. We can swap the labels of particles 1 and 2 with no change. We can swap the direction of the momenta, flipping the sign of the streaming term. We can swap the 'initial' and 'final' labels, again flipping the sign of the streaming term. Each of these contribute to eq. 2.23-2.26.

It's convenient to write $(\partial f/\partial t)_{coll}$ in four different ways, for reasons we'll see in a moment. These will be the original definition, a permutation of $\mathbf{p}_1$ and $\mathbf{p}_2$, a permutation of $\mathbf{p}_i$ and $\mathbf{p}'_i$, and a time-reversal. These are shown in Fig. 2.2,

$$\frac{\partial H}{\partial t} = \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^3\mathbf{p}'_1 d^3\mathbf{p}'_2 (f'_1 f'_2 - f_1 f_2)(1+\log[f_1])\delta_{E_i E_f}\delta_{\mathbf{P}_i \mathbf{P}_f} g_{if} \tag{2.23}$$

$$\frac{\partial H}{\partial t} = \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^3\mathbf{p}'_1 d^3\mathbf{p}'_2 (f'_1 f'_2 - f_1 f_2)(1+\log[f_2])\delta_{E_i E_f}\delta_{\mathbf{P}_i \mathbf{P}_f} g_{if} \tag{2.24}$$

$$\frac{\partial H}{\partial t} = \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^3\mathbf{p}'_1 d^3\mathbf{p}'_2 (f_1 f_2 - f'_1 f'_2)(1+\log[f'_1])\delta_{E_i E_f}\delta_{\mathbf{P}_i \mathbf{P}_f} g_{if} \tag{2.25}$$

$$\frac{\partial H}{\partial t} = \int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^3\mathbf{p}'_1 d^3\mathbf{p}'_2 (f_2 f_1 - f'_2 f'_1)(1+\log[f'_2])\delta_{E_i E_f}\delta_{\mathbf{P}_i \mathbf{P}_f} g_{if} \tag{2.26}$$

Summing these four terms yields

$$4\frac{\partial H}{\partial t} = \int d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 (f'_1 f'_2 - f_1 f_2)(\log[f_1 f_2] - \log[f'_1 f'_2]) \tag{2.27}$$

There are two immediate observations that one can make:

- $\partial H/\partial t \leq 0$, because $f'_1 f'_2 - f_1 f_2$ has the opposite sign of $\log(f_1 f_2) - \log(f'_1 f'_2)$.
- $\partial H/\partial t = 0$ only when $f_1 f_2 = f'_1 f'_2$. This is the condition we used to derive the Maxwell-Boltzmann distribution.

Thus, convergence to the Maxwell Boltzmann distribution is guaranteed, regardless of the initial conditions of the system. Boltzmann identified $-H(t)$ as a non-equilibrium measure of entropy, because it is monotonically increasing and attains its maximum at equilibrium. The initial value of H will be determined by the initial conditions of the system: what the initial distribution $f(\mathbf{p}, t = 0)$ was. As time evolves, it will eventually settle on the equilibrium distribution $f(\mathbf{p}, t = \infty) = f_0(\mathbf{p})$, at which point the function $-H$ necessarily attains its maximum. The entropy of the system of the system evolves as

$$S(t) = -H(t) = -\int d^3p f(\mathbf{p}, t) \log[f(\mathbf{p}, t)] \tag{2.28}$$

Any system of interacting particles (satisfying molecular chaos) will eventually settle on the Maxwell Boltzmann distribution

$$\begin{aligned} \frac{f(\mathbf{p})}{N} &= \left(\frac{3}{4\pi m\epsilon}\right)^{3/2} e^{-3\mathbf{p}^2/4m\epsilon} && (2.29) \\ &= \left(\frac{1}{2\pi m k_B T}\right)^{3/2} e^{-\mathbf{p}^2/2mk_BT} \qquad \text{for monatomic molecules} && (2.30) \end{aligned}$$

where the last equality comes from the (as yet unproven) equipartition theorem that each particle has energy $\epsilon = 3k_BT/2$.

Note that for $\epsilon \to 0$, Eq. 2.29 becomes a $\delta-$ function, and $H \to +\infty$ (you can confirm this directly in the homework), while for $\epsilon \to \infty$ Eq. 2.29 becomes a uniform distribution and $H \to -\infty$. This continuum representation of the energy thus permits any value of $-\infty < S = -H < +\infty$, unless the total energy is constrained to some finite value. Note that this actually violates the third law of thermodynamics, which states at absolute zero temperature the entropy reaches a finite minimum: in the limit of $T \to 0$ in eq. 2.30 converges on $\epsilon \to 0$, and thus $S \to -\infty$. This was not a critique of the system at the time (as the third law of thermodynamics was first formulated in ~ 1910), but illustrates a fundamental failing in the continuum representation of a statistical system that will only be repaired by incorporating quantum mechanics. Regardless of its failings, the H theorem was the first connection between an atomic theory of gasses and the concept of entropy, and was heavily debated in the scientific community for decades prior to Boltzmann's death.

2.3 Liouville's Theorem

Boltzmann's transport equation and H-theorem were a bridge between thermodynamics and the atomistic theory of gasses, and gives a meaningful, useful interpretation of the entropy of a system in terms of the distribution of particle velocities. These depended on a number of approximations, all of which have an accuracy that is difficult to evaluate. Are all of them reasonable? Can we determine the correct value of $(\partial f/\partial t)_{coll}$ exactly? A method exists called the BBGKY Hierarchy (developed between 1935-1946, over 75 years after Boltzmann's work) allows us to answer those questions. The BBGKY method relies on an older and important result of Liouville's in $\sim$ 1845, which will explore in this section.

The Boltzmann transport equation begins and ends with single particle distribution functions, $f(\mathbf{r}, \mathbf{p}, t)$, with multi-particle correlations completely neglected. This is a reasonable approximation for a dilute gas, but certainly incorrect in general. In order to understand the behavior of real multi-particle systems, we need to begin by considering the behavior of all particles simultaneously (something we actively avoided in the previous sections).

We consider a system of N particles, with the i^{th} particle having generalized momentum p_i and generalized coordinates q_i, interacting with a Hamiltonian H. These particles exist in phase space Γ that encompasses all possible values of $\{p_i, q_i\}$. Within the phase space, there will be a function $\rho(\{p_i, q_i\}, t)$ describing the probability of finding a particle at any $6N + 1$ dimensional point in the system. The density in phase space is evolving in time, but volumes must be conserved: a particle may move from a state $(\{p_i, q_i\}, t)$ to $(\{p_i', q_i'\}, t+\delta t)$, but particles may not appear or disappear. This means $\int d^3\mathbf{r} d^3\mathbf{p} \rho(\mathbf{r}, \mathbf{p}, t) = 1$ is a constant.

The fact that particles cannot disappear implies there must be a *continuity equation* that the system satisfies. The continuity equation can be understood most easily in 1+1 dimension instead of all $6N + 1$ dimensions. Suppose we have $N \gg 1$ particles distributed along the x axis, with time-varying density $\rho(x, t)$. We can define a domain between points a and b, such that at time t the number of particles within the domain is $\int_a^b dx \rho(x, t)$. The number of particles *leaving* the domain is $-\partial/\partial t \int_a^b dx \rho(x, t)$ (the minus sign because they're exiting). Of course, any particles leaving the domain must do so *at the boundary*; the number of particles crossing the boundary at b is $\dot{x}(b, t)\rho(b, t)$ and at a is $-\dot{x}(a, t)\rho(a, t)$, so the total number leaving by crossing the boundary is $\dot{x}(b)\rho(b) - \dot{x}(a)\rho(a) = \int_a^b dx \partial/\partial x(\dot{x}\rho)$.

In higher dimensions, the continuity equation has the same features: the rate of change of the density of particles in the domain must match the flux of particles across the boundary. For an arbitrary set of generalized coordinates, $\mathbf{x} = \{p_i, q_i\}$, we can write

$$-\int_V \frac{\partial \rho}{\partial t} dV = \int_{\partial V} \rho(\dot{\mathbf{x}} \cdot \hat{\mathbf{n}}) ds = \int_V \nabla \cdot (\rho \dot{\mathbf{x}}) dV \tag{2.31}$$

for any domain V. The second equality is Gauss' divergence theorem (the multidimensional version of $f(b) - f(a) = \int_a^b dx f'(x)$). We know that $\int_V dV(\dot{\rho} + \nabla \cdot (\dot{\mathbf{x}}\rho)) = 0$ for any arbitrary domain V, which can only be true if the argument of the integral is itself identically zero.

This leads to the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \dot{\mathbf{x}}) = 0 \tag{2.32}$$

The continuity equation is important in many branches of physics: it underlies much of fluid mechanics and can be derived in any system for which a quantity can evolve in time without being created or destroyed.

Our continuity equation can be reduced further because we have a system of particles that are evolving under a Hamiltonian H, where the coordinates satisfy the equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{2.33}$$

The continuity equation is

$$\begin{aligned} -\frac{\partial \rho}{\partial t} &= \sum_{i=1}^{3N} \left(\frac{\partial(\rho \dot{q}_i)}{\partial q_i} + \frac{\partial(\rho \dot{p}_i)}{\partial p_i} \right) && (2.34) \\ &= \sum_{i=1}^{3N} \left(\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) + \rho \sum_{i=1}^{3N} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) && (2.35) \end{aligned}$$

and using the equations of motion we can cancel the last term, yielding

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) = 0 \tag{2.36}$$

The second term is often referred to as a Poisson bracket

$$[\rho, H] = \sum_i \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \tag{2.37}$$

Note that the Poisson bracket has the same notation as the anticommutator $[\hat{\rho}, \hat{H}] = \hat{\rho}\hat{H} + \hat{H}\hat{\rho}$ in quantum mechanics. We will see later in the course that this overuse of notation is not accidental, and that the total derivative of the density operator $\hat{\rho}$ will satisfy $d\hat{\rho}/dt = \partial\hat{\rho}/\partial t + [\hat{\rho}, \hat{H}]$.

Note that eq. 2.36 is the definition of the total time derivative of the system,

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i} \frac{\partial q_i}{\partial t} + \frac{\partial \rho}{\partial p_i} \frac{\partial p_i}{\partial t} \tag{2.38}$$

implying that any system describable by a classical Hamiltonian conserves density in phase space. Note this doesn't mean it conserves *shape*: a nonlinear Hamiltonian can still produce chaotic dynamics, and nearby volumes of phase space may not be anywhere close to one another in phase space after time has passed. A system evolving from some volume in phase space may eventually reach a highly irregular and stretched shape, but it is necessarily of the same volume (since probability density is preserved) regardless of how different the shape is. That is: a system's distance from nearby points in phase space can be arbitrarily distant as time evolves, but there are constraints on that evolution dictated by the constant density.

2.4 The BBGKY Hierarchy

The Boltzmann Transport equation was derived in a primarily heuristic manner, with a number of approximations whose validity are unclear. It would be beneficial to recover the Boltzmann Transport equation in an 'exact' manner to fully understand the validity of the approximations underlying out work in the previous sections. The BBGKY Hierarchy, named after Bogoliubov-Born-Green-Kirkwood-Yvon, relates the dynamics of the distribution functions of s particles to the distribution functions of $s+1$ particles exactly, by computing averages from Liouville's theorem. This hierarchy allows us to more completely understand the underlying assumptions of the Boltzmann Transport equation.

2.4.1 An exact calculation of multi-particle distributions

As mentioned before, the full distribution in phase space is typically more information than one might care to have: it is rare to need to know the probability of finding 10^{23} individual particles in a very specific state. Typically, one is going to be interested in coarser quantities (e.g. the average energy of the system, or average momentum). By average, we are taking the 'ensemble' average of a large system of particles, with

$$\langle g(\{\mathbf{r}_i, \mathbf{p}_i\}, t)\rangle = \int \prod_i d^3p_i d^3r_i g(\{\mathbf{r}_i, \mathbf{p}\}, t)\rho(\{\mathbf{r}_i, \mathbf{p}\}, t) \tag{2.39}$$

defined as the average of any function g. In the literature, this is sometimes written $\overline{g\{\mathbf{r}_i, \mathbf{p}_i\}, t)}$, but we will not use that notation in these notes. When taking an average, we are weighting the value of g at any point in phase space by its probability of being occupied by a particle at that point, ρ. If the N-particle distribution is sharply peaked somewhere in phase space, the average of g will include contributions mostly from that point in phase space, whereas if the distribution is uniform the average of g will have significant contributions from everywhere in phase space.

We can define a (unnormalized) 1-particle distribution function as

$$f_1(\mathbf{p}, \mathbf{r}, t) = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{p}_i - \mathbf{p}) \right\rangle \tag{2.40}$$

which measures the average number of particles with position $\mathbf{r}$ and momentum $\mathbf{p}$ at time t. Note that we have slightly changed the notation from Sec. 2.1, where we had $f(\mathbf{r}, \mathbf{p}, t) = f_1(\mathbf{r}, \mathbf{p}, t)$; f and f_1 refer to the same quantities. Explicitly writing the average, we find

$$f_1(\mathbf{p}, \mathbf{r}, t) = \sum_{i=1}^{N} \int \prod_j d^3r_j d^3p_j \delta(\mathbf{r}_i - \mathbf{r})\delta(\mathbf{p}_i - \mathbf{p})\rho(\{\mathbf{r}_i, \mathbf{p}\}, t) \tag{2.41}$$

The delta function picks out a specific pair of coordinates $\mathbf{r}_i$ and $\mathbf{p}_i$ and fixes their value, while the rest of the coordinates are integrated over. An important consideration arises if the particles are all identical: their average behavior cannot depend on their index i. That is, the statistics of a particle can't depend on the fact that we labeled it "1", or "2", or any other number. That means that we actually only need to do one integral! We can simply hold the coordinates for particle "1" fixed, and integrate over the rest of the variables. Every term of the sum in eq. 2.41 will be the same, so we need only multiply by N. In this case, we have

$$f_1(\mathbf{p}_1, \mathbf{r}_1, t) = N \int \prod_{i=2}^{N} d^3p_i d^3r_i \rho(\{\mathbf{r}, \mathbf{p}\}, t) \tag{2.42}$$

which is number density of particles with the specific $\mathbf{r} - \mathbf{p}$ point in space, without regard to the index. Single-particle averages can be computed directly from this single-particle distribution function (but one must normalize by N, converting the number density into a probability):

$$\langle g(\mathbf{r}_1, \mathbf{p}_1, t)\rangle = \int \prod_{i=2}^{N} d^3p_i d^3r_i g(\{\mathbf{r}_i, \mathbf{p}\}, t)\rho(\{\mathbf{r}_i, \mathbf{p}\}, t) = \frac{1}{N}\int d^3\mathbf{r} d^3\mathbf{p} g(\mathbf{r}, \mathbf{p}, t) f_1(\mathbf{r}, \mathbf{p}, t) \tag{2.43}$$

Note that the notation in Eq. 2.43 is sometimes used ambiguously in the literature, as $\langle \cdots \rangle$ often refers to an average over *some* of the variables in phase space, rather than all of them. For example, when computing an average only over momentum, we can write $\bar{g}(\mathbf{r}) = \langle g(\mathbf{r}, \mathbf{p})\rangle_{\mathbf{r}} = \langle g(\mathbf{r}', \mathbf{p})\delta(\mathbf{r}' - \mathbf{r})\rangle$, which defines the notation $\langle \cdots \rangle_{\mathbf{r}}$ as the average at the point $\mathbf{r}$. It is often the case that the subscript $\mathbf{r}$ may be left off of the brackets, and the relation written $\bar{g}(\mathbf{r}) = \langle g(\mathbf{r}, \mathbf{p})\rangle$. In these cases, the fact that the left hand side has an explicit $\mathbf{r}$ dependence implies that the average was taken *solely* over momentum, and not over position. Most textbooks will eventually overload their notation in this way (Pathria and Huang both do so when they discuss quantum statistics), and these notes will likely do so as well at points. When discussing averages, it is usually the case that the surrounding text will explain over what the averaging *is* being taken, and the variables on which the expression depends will tell you over what the averaging *is not* being taken.

This symmetry argument regarding index permutability actually holds for all possible distribution functions. Suppose we want to compute the 2−particle distribution function

$$f_2(\mathbf{r},\mathbf{r}',\mathbf{p},\mathbf{p}',t) = \sum_{i=1}^{N}\sum_{j\neq i=1}^{N}\left\langle \delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j-\mathbf{r}')\delta(\mathbf{p}_i-\mathbf{p})\delta(\mathbf{p}_j-\mathbf{p}')\right\rangle \tag{2.44}$$

It once again doesn't matter which particle labels we choose for i and j, they are all equivalent. The sum is composed of exactly $N\times(N-1)$ identical terms, so

$$f_2(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2,t) = N(N-1)\int\prod_{i=3}^{N} d^3p_i d^3r_i \rho(\{\mathbf{r},\mathbf{p}\},t) \tag{2.45}$$

In general, we can compute the s particle correlation function using the exact same arguments

$$f_s(\mathbf{p}_1,\ldots,\mathbf{p}_s,\mathbf{r}_1,\ldots,\mathbf{r}_s,t) = \frac{N!}{(N-k)!}\int\prod_{i=s+1}^{N} d^3p_i d^3q_i \rho(\{\mathbf{p},\mathbf{r}\},t) \tag{2.46}$$

The coefficients come from the number of permutations on each of the variables of integration.

2.4.2 Time evolution of the single particle distribution function

We have determined the unnormalized single particle density $f_1 = N\int\prod_{i=2}^{N} d^3\mathbf{r}_i d^3\mathbf{p}_i\rho$ in terms of the N-particle density ρ, and have determined an exact expression for the time evolution of ρ through Liouville's equation. This suggests we can determine an exact expression for $\partial f_1(\mathbf{r},\mathbf{p},t)/\partial t$, which will lead us to the BBGKY Hierarchy. We can compute

$$\begin{aligned} -\frac{\partial f_1}{\partial t} &= -\frac{\partial}{\partial t} N\int\prod_{l=2}^{N} d^3\mathbf{r}_l d^3\mathbf{p}_l\rho(\{\mathbf{r},\mathbf{p}\},t) && (2.47)\\ &= -N\int\prod_{l=2}^{N} d^3\mathbf{r}_l d^3\mathbf{p}_l\sum_i\left(\frac{\partial\rho}{\partial\mathbf{r}_i}\cdot\frac{\partial H}{\partial\mathbf{p}_i}-\frac{\partial\rho}{\partial\mathbf{p}_i}\cdot\frac{\partial H}{\partial\mathbf{r}_i}\right) && (2.48)\end{aligned}$$

This relationship does not easily reduce to a simpler form without making some assumptions about the form of the Hamiltonian.

2.4.3 Central force interactions and the single particle distribution function

For a simple, central force interaction between particles, we can construct a useful representation of f_s. We take the specific Hamiltonian

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_i U(\mathbf{r}_i) + \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|) \tag{2.49}$$

which includes an external and inter-particle force U and v respectively. Note the sum over interactions is $i < j$, meaning we do not double-count interactions between pairs. This Hamiltonian features an external force applied to each particle $\mathbf{F}_i = -\nabla U(\mathbf{r}_i)$, as well as an interaction force between pairs of particles $\mathbf{k}_{ij} = -\nabla_{\mathbf{r}_i} v(|\mathbf{r}_i - \mathbf{r}_j|)$. Note that this immediately implies $\mathbf{k}_{ji} = -\mathbf{k}_{ij}$.

For this Hamiltonian, Liouville's theorem implies

$$\begin{aligned} -\frac{\partial f_1}{\partial t} &= -N \int \prod_{l=2}^{N} d^3\mathbf{r}_l d^3\mathbf{p}_l \sum_i \Big(\nabla_{\mathbf{r}_i}\rho \cdot \nabla_{\mathbf{p}_i} H - \nabla_{\mathbf{p}_i}\rho \cdot \nabla_{\mathbf{r}_i} H \Big) && (2.50) \\ &= N \int \prod_{l=2}^{N} d^3\mathbf{r}_l d^3 \Big[\sum_i \Big(\frac{\mathbf{p}_i}{m} \cdot \nabla_{\mathbf{r}_i} + \mathbf{F}_i \cdot \nabla_{\mathbf{p}_i} \Big) + \sum_{i\neq j} \mathbf{k}_{ij} \cdot (\nabla_{\mathbf{p}_i} - \nabla_{\mathbf{p}_j}) \Big] \rho && (2.51) \end{aligned}$$

The last term arises from the fact that each term in the sum $\sum_{i<j} v(\mathbf{r}_i - \mathbf{r}_j)$ produces two contributions to the sum $\sum_{ij} \mathbf{F}_i \cdot \nabla_{\mathbf{p}_i}$, a term $\mathbf{k}_{ij} \cdot \nabla_{\mathbf{p}_i}$ and a term $-\mathbf{k}_{ij} \cdot \nabla_{\mathbf{p}_j}$. Note that the first terms in the square brackets in eq. 2.51 are streaming terms for each particle as they appear in the Boltzmann transport equation in Eq. 2.3 (for all particles i). Unlike the Botlzmann transport equation, though, this expression depends on the full particle density ρ, rather than f_1 or the unknown $(\partial f/\partial t)_{coll}$. We will want to reduce this to a single or pair particle distribution $f_1(\mathbf{r}, \mathbf{p}, t)$ or $f_2(\mathbf{r}, \mathbf{r}', \mathbf{p}, \mathbf{p}', t)$. To do so, we'll have to integrate over many all-but-one or all-but-two variables.

2.4.4 Boundary conditions on ρ

Before starting to do those integrals in eq. 2.51, it's useful to realize that integration of a gradient in a multi-dimensional space reduce to an evaluation of the function at a boundary. A simple example is

$$\int_a^b dx \int_a^b dy \frac{\partial}{\partial y} f(x,y) = \int_a^b dx \Big(f(x,b) - f(x,a) \Big) \tag{2.52}$$

so integration over a partial derivative evaluates to a function at a boundary. This is important, because we don't expect any particles to be found precisely at the boundary of our phase space. That is, we don't expect to find particles that have infinite momentum, nor do we expect any particles to be found exactly at the boundary. In a multidimensional space, we expect that

$$\int_\Gamma \prod_i d^3\mathbf{r}_i d^3\mathbf{p}_i \ \nabla_{\mathbf{r}_k}\rho = \int_\Gamma \prod_i d^3\mathbf{r}_i d^3\mathbf{p}_i \ \nabla_{\mathbf{p}_k}\rho = 0 \tag{2.53}$$

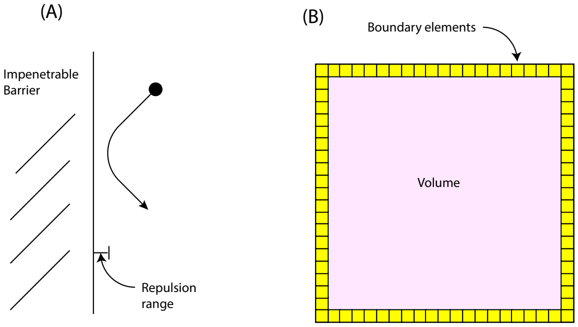


Figure 2.3: (A) Particles can't occupy a boundary due to the repulsive forces between the particle and a boundary. They must interact with hard-core repulsion, and thus cannot occupy the same volume. (B) For a fuzzy boundary, the probability of being found on the edges (yellow) instead of in the volume (cyan) is low if the width of the edges is small.

You may immediately believe that exactly zero particles have infinite momentum, but find it questionable that exactly zero particles are found precisely at the boundary. Physically, one expects there to be a finite distance of closest approach to a barrier (depicted in Fig. 2.3(a)), so that there's a vanishingly small probability of finding a single particle *exactly* at the barrier. However, you'd be correct to recognize that we have not actually specified what our 'boundary' actually is, and thus have therefore not declared what the range of repulsion is. Rather than specifying an interaction range, suppose we have a particle size δr, such that the system can be divided into binds of size δr^3, with the boundary elements occupying only a volume $A\delta r/V$ (where A is the surface area of the region), depicted in Fig. 2.3(B). The probability that a single particle is *not* found in the boundary is $1 - A\delta r/V$, so the probability of all N particles not being found on the boundary is $(1 - A\delta r/V)^N$. With $\rho = N/V$ the density of the gas, the probability of *no* particles being found in a boundary element is

$$\left(1 - \frac{A\delta r}{V}\right)^N = \left(1 - \frac{\rho A\delta r}{N}\right)^N \to e^{-\rho A\delta r} \tag{2.54}$$

in the limit of $N \to \infty$. That is, for a dilute gas ($\rho \to 0$), the probability of seeing no particles near the boundary to be ≈ 1, and the probability of finding a particle within the fuzzy boundary width is $1 - e^{-\rho A\delta r} \approx \rho A\delta r$. However, if the gas is very dense ($\rho \to \infty$) the probability of particles being found in the boundary elements can become non-negligible. In the former limit, it is not necessary to specify the particular interaction between the particles and the walls. In the latter limit, it's more important to understand the interactions between the particles and the boundary. Those interactions between particle and boundary will specify the distance of closest approach between particles and the wall. Regardless of the density, one still expects that an 'impenetrable' wall will have a non-zero distance of closest approach.

2.4.5 Deriving the collision term

Eq. 2.53 implies that if we integrate over the particles $\{s, s+1, \ldots, N-1, N\}$, any term that involves a gradient of ρ with respect to $\mathbf{r}_k$ or $\mathbf{p}_k$ will vanish if $k \geq s$ (because it will evaluate to the particle density at the boundary). Specifically, if we want to compute $f_1(\mathbf{r}_1, \mathbf{p}_1, t)$, we can write

$$-\frac{\partial f_1}{\partial t} = N \int \prod_{l=2}^{N} d^3\mathbf{p}_l d^3\mathbf{r}_l \Bigg[\left(\frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} + \mathbf{F}_1 \cdot \nabla_{\mathbf{p}_1} \right) \rho + \sum_{j=2}^{N} \mathbf{k}_{1j} (\nabla_{\mathbf{p}_1} - \underline{\nabla_{\mathbf{p}_j}}) \rho \tag{2.55}$$

$$+\underline{\sum_{j=2}^{N} \left(\frac{\mathbf{p}_j}{m} \cdot \nabla_{\mathbf{r}_j} + \mathbf{F}_j \cdot \nabla_{\mathbf{p}_j} \right) \rho + \sum_{j,l\geq 2}^{N} \mathbf{k}_{jl} (\nabla_{\mathbf{p}_j} - \nabla_{\mathbf{p}_l}) \rho} \Bigg] \tag{2.56}$$

where the underlined portions include derivatives involving $\mathbf{r}_s$ and $\mathbf{p}_s$ with $s > 1$. Those terms are all identically zero! This allows us to simplify

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} + \mathbf{F} \cdot \nabla_{\mathbf{p}} \right) f(\mathbf{r}, \mathbf{p}, t) = \tag{2.57}$$

$$- \int d^3\mathbf{r}_2 d^3\mathbf{p}_2 \mathbf{k}_{1,2}(\mathbf{r}_1, \mathbf{r}_2) \nabla_{\mathbf{p}_1} f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$$

where the last integral accounts for the integral over $\mathbf{r}_s$ and $\mathbf{p}_s$ for $s > 2$ to result in a term involving $f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$. We can't integrate over both $\mathbf{p}_2$ and $\mathbf{r}_2$, since $\mathbf{k}_{ij}$ depends on $\mathbf{r}_2$, and can thus not reduce this integral further (in terms of pair distribution functions). The left hand side of Eq. 2.57 is identical to Eq. 2.3, meaning the streaming term in the Boltzmann equation is in fact

$$\left(\frac{\partial f}{\partial t} \right)_{coll} = - \int d^3\mathbf{r}_2 d^3\mathbf{p}_2 k_{1,2}(\mathbf{r}_1, \mathbf{r}_2) \nabla_{\mathbf{p}_1} f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) \tag{2.58}$$

where $\mathbf{k}_{12}(\mathbf{r}_1, \mathbf{r}_2) = \nabla_{\mathbf{r}_1} v(|\mathbf{r}_1 - \mathbf{r}_2|)$ is the force by $\mathbf{r}_2$ on $\mathbf{r}_1$. We originally derived $(\partial f / \partial t)_{coll}$ in terms of initial and final momenta (in a very imprecise way). Eq. 2.58 does not reference a final state (since that's dictated entirely by the Hamiltonian), but represents the effect of the collision term *exactly*. The only assumptions made in this analysis is that (a) there's a central force interaction between particles and (b) no particles stick to the walls. Everything else has been exact and without loss of generality.

Eq. 2.57 represents the first term in the BBGKY hierarchy. At this first level, there is an exact relationship between the one-point particle distribution function and an unknown two-particle distribution function. If we knew f_2 exactly, we could compute f_1 exactly. As the name BBGKY 'hierarchy' suggests, there are other levels of the hierarchy. It is tedious (see Huang for details) to show that f_2 can be written exactly in terms of f_3, the three-particle distribution function. In this, we do not go into the details (which can be found in Huang), but the fundamentals of the calculation

$$\left[\frac{\partial}{\partial t} + \sum_{j=1}^{2}\left(\frac{\mathbf{p}_j}{m}\cdot\nabla_{\mathbf{r}_j} + \mathbf{F}_j\cdot\nabla_{\mathbf{p}_j}\right) + \mathbf{k}_{12}\cdot(\nabla_{\mathbf{p}_1} - \nabla_{\mathbf{p}_2})\right] f_2(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2,t)$$

$$= -\int d^3\mathbf{p}_3 d^3\mathbf{r}_3(\mathbf{k}_{13}\cdot\nabla_{\mathbf{p}_1} + \mathbf{k}_{23}\cdot\nabla_{\mathbf{p}_2}) f_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3,t) \quad (2.59)$$

which expresses f_2 in terms of f_3, which we don't know either.

This process can be continued indefinitely, and we can continue the BBGKY Hierarchy to solve for f_3 in terms of f_4, and so on. It's possible to compute any $k-$particle distribution function in terms of an unknown $k+1-$particle distribution. It is tedious to show that the s-particle distribution satisfies

$$\left[\frac{\partial}{\partial t} + \sum_{i=1}^{s}\left(\frac{\mathbf{p}_i}{m}\cdot\nabla_{\mathbf{r}_i} + \mathbf{F}_i\cdot\nabla_{\mathbf{p}_i}\right) + \sum_{i,j=1}^{s}\mathbf{k}_{ij}\cdot(\nabla_{\mathbf{p}_i} - \nabla_{\mathbf{p}_j})\right] f_s \quad (2.60)$$

$$= -\sum_{i=1}^{s}\int d^3p_{s+1} d^3\mathbf{r}_{s+1}\mathbf{k}_{i,s+1}\cdot\nabla_{\mathbf{p}_i} f_{s+1} \quad (2.61)$$

In order to make progress at any level of the hierarchy, we'll need to create a *closure* relationship, such that we can truncate the hierarchy. For example, if we were to have a good approximation for f_n, we would then be able to determine f_{n-1} followed by a chain of solutions down to f_1. There are a variety of possible closure relations that can be used to truncate the hierarchy. There are a variety of closure relations that exist, although they will generally be good approximations for low density gasses (for which higher order correlations are expected to not be important). The BBGKY approximation is exact for central force problems, and allows us to identify exactly where an approximation comes in: through the closure of the hierarchy.

In order to recover the Boltzmann transport equation, we must impose a closure relation to be able to determine f_2. Perhaps the simplest approximation that can be made is that the 3-particle 'collision term' in eq. 2.59 is negligible, with $\int d^3\mathbf{p}_3 d^3\mathbf{r}_3(\mathbf{k}_{13}\cdot\nabla_{\mathbf{p}_1} +$

$\mathbf{k}_{23} \cdot \nabla_{\mathbf{p}_2})f_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, t)] \approx 0$. This first approximation is more precise than the heuristic assumptions we made about the collisions in a dilute gas or that 'molecular chaos' is satisfied. A further approximation is to assume that we are near equilibrium, so that $\partial f_2/\partial t \approx 0$ (in fact, this is a statement that the equilibration of f_2 occurs on a faster timescale than f_1, as argued by Huang). Finally, we simplify the problem by neglecting the external potential $U(\mathbf{r}_i)$ (so that $\mathbf{F}_i = 0$; this is not a necessary approximation). Combined, these imply that $\mathbf{k}_{12}(\mathbf{r}) \cdot (\nabla_{\mathbf{p}_1} - \nabla_{\mathbf{p}_2})f_2 \approx (\mathbf{p}_1 \cdot \nabla_{\mathbf{r}_1} + \mathbf{p}_2 \cdot \nabla_{\mathbf{r}_2})f_2/m = (\mathbf{p}_1 - \mathbf{p}_2)\nabla_{\mathbf{r}} f_2/m$, where we have made the change of variables $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the distance between the pair of particles and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the center of mass of the two particles. A final assumption is that f_2 is independent of the location of the center of mass (that is, the effect of a collision doesn't depend on where it happens, only how far apart the particles are). With this approximation, we have reduced the second BBGKY equation to a separable form, which implies we can write $f_2(\mathbf{r}, \mathbf{p}_1, \mathbf{p}_2) = \phi(\mathbf{r}, \mathbf{p}_1)\phi(\mathbf{r}, \mathbf{p}_2)$. Because we are guaranteed that $\phi \approx f_1$ if the potential is short-ranged (that is: if there were no interactions the particles would be randomly distributed), we have recovered the asumption of molecular chaos: $f_2(\mathbf{r}, \mathbf{p}_1, \mathbf{p}_2) \approx f_1(\mathbf{r}, \mathbf{p}_1)f_1(\mathbf{r}, \mathbf{p}_2)$.

Combining these approximations, the collision term then becomes

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll} = -\int d^3\mathbf{r}_2 d^3\mathbf{p}_2 k_{1,2} \nabla_{\mathbf{p}_1} f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) \tag{2.62}$$

$$= -\int d^3\mathbf{r}_2 d^3\mathbf{p}_2 k_{1,2} (\nabla_{\mathbf{p}_1} - \nabla_{\mathbf{p}_2}) f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) \tag{2.63}$$

$$\approx -\frac{1}{m}\int d^3\mathbf{r}_2 d^3\mathbf{p}_2 (\mathbf{p}_1 - \mathbf{p}_2) \cdot \nabla_{\mathbf{r}} f_1(\mathbf{r}, \mathbf{p}_1) f_1(\mathbf{r}, \mathbf{p}_2) \tag{2.64}$$

Note that the specific form of the direct interaction has been removed here ($k_{12}(\mathbf{r})$) due to the approximations we have made. Huang makes a lengthy calculation that this final expression reduces to the Boltzmann Transport equation.

2.5 Summary

The kinetic theory of Boltzmann (and others before him) was fundamental in the philosophical transition between thermodynamics and an atomistic model for the statistical mechanics of atoms. Gasses are formed by an enormous number of interacting particles (a claim not widely accepted in physics in 1865), and the H-theorem shows that the random collisions between gasses *must* cause an inevitable convergence of the particle momenta distribution on the Maxwell Boltzmann distribution. The sometimes unclear approximations underlying the H theorem are made more precise using the BBGKY hierarchy, which indicate the fundamental assumptions are a dilute gas (with no triplet interactions) whose pair correlations equilibrate rapidly. Importantly, Boltzmann connected the concept of particle momentum distribution to the idea of entropy in his H-theorem, which we will continue to see in the future. Unlike the system energy or pressure, which we will continually find to be proportional to mean particle properties, the entropy is related to the global distribution of the particle properties, and not expressible in terms of the average properties of any individual particle.

2.6 Homework Problems

1. What is the initial entropy of a system with all particles having the same initial momentum, $f_0(\mathbf{p}) = \delta(\mathbf{p} - \mathbf{p}_0)$? Does Boltzmann's H-function satisfy the third law of thermodynamics?

2. A single classical particle in a volume V is at thermal equilibrium with a reservoir at temperature T. Is it possible for this system to have a well defined entropy?

3. In this chapter, we neglected any external force an external force $\mathbf{F} = -\nabla V(\mathbf{r})$ in the derivation of the Maxwell-Boltzmann distribution. We can demonstrate that the equilibrium distribution is $f(\mathbf{p}, \mathbf{r}) = f_0(\mathbf{p})e^{-V(\mathbf{r})/k_BT}$ in the presence of a force by doing the following:

   (a) Show that this form of $f(\mathbf{p}, \mathbf{r})$ still satisfies the requirement that $(\partial f/\partial t)_{coll} = 0$.

   (b) Show that $(\mathbf{p}/m\cdot\nabla_{\mathbf{r}}+\mathbf{F}\cdot\nabla_{\mathbf{p}})f(\mathbf{p}, \mathbf{r}) = 0$ for $f(\mathbf{p}, \mathbf{r}) = \frac{N}{(2\pi m k_B T)^{3/2}} e^{-\mathbf{p}^2/2mk_BT} e^{-V(\mathbf{r})/k_BT}$.

4. Suppose a gas is composed of two types of particles, one with mass m and the other with mass M, with $f_m(\mathbf{r}, \mathbf{p}, t)$ and $f_M(\mathbf{r}, \mathbf{p}, t)$ the distribution of momenta for particles, respectively. There is no external force, and the scattering of the particles depends only on their momentum (is independent of particle type). Show that the Boltzmann transport equation in the limit of a dilute gas yields two coupled equations at equilibrium for the distributions of the momenta:

$$f_m(\mathbf{p}_1')f_m(\mathbf{p}_2') - f_m(\mathbf{p}_1)f_m(\mathbf{p}_2) + f_m(\mathbf{p}_1')f_M(\mathbf{p}_2') - f_m(\mathbf{p}_1)f_M(\mathbf{p}_2) = 0 \tag{2.65}$$

$$f_M(\mathbf{p}_1')f_M(\mathbf{p}_2') - f_M(\mathbf{p}_1)f_M(\mathbf{p}_2) + f_m(\mathbf{p}_1')f_M(\mathbf{p}_2') - f_m(\mathbf{p}_1)f_M(\mathbf{p}_2) = 0 \tag{2.66}$$

   where $\mathbf{p}_1$ and $\mathbf{p}_2$ are initial momenta and $\mathbf{p}_1'$ and $\mathbf{p}_2'$ are final momenta, and $f(\mathbf{r}, \mathbf{p}, t) \rightarrow f(\mathbf{p})$ is independent of position and time.

5. One possible form for the time evolution of momentum distribution is $f(\mathbf{p}, t) = A(t)e^{-(\mathbf{p}-\mathbf{p}_0(t))^2/2m\epsilon(t)}$.

   (a) Normalize the distribution and determine $\langle\mathbf{p}\rangle$ and $\langle\mathbf{p}^2/2m\rangle$ in terms of $\mathbf{p}_0(t)$ and $\epsilon(t)$.

   (b) Determine $S(t) = -H(t)$ explicitly. What are the constraints on $\mathbf{p}_0(t)$ and $\epsilon(t)$ for $S(t)$ to be a strictly increasing function? In particular, does an increasing $S(t)$ require that $\langle \mathbf{p} \rangle \to 0$ as $t \to \infty$?

6. Suppose a system is prepared with the exponential momentum distribution $f(\mathbf{p}, t = 0) = Ae^{-|\mathbf{p}|\sqrt{6/m\epsilon}}$.
   (a) Normalize this distribution and show that $\langle p^2/2m \rangle = \epsilon$.
   (b) Show that the entropy $S(0) = -\int d^3\mathbf{p} f(\mathbf{p}, 0) \log[f(\mathbf{p}, 0)]$ is always less than the entropy for a Gaussian distribution with the same mean particle energy.

7. For a Hamiltonian $H = \sum_i \mathbf{p}_i^2/2m + \sum_i U(\mathbf{r}_i) + \sum_{i>j} v(|\mathbf{r}_i - \mathbf{r}_j|)$,
   (a) Explicitly show that the total number of particles $N = \int d^3\mathbf{p} d^3\mathbf{r} f_1(\mathbf{r}, \mathbf{p}, t)$ is constant in the first level of the BBGKY hierarchy.
   (b) Defining $n(\mathbf{r}, t) = \int d^3\mathbf{p} f_1(\mathbf{r}, \mathbf{p}, t)$, show that

$$\frac{\partial n}{\partial t} + \frac{N}{m} \nabla_{\mathbf{r}} \cdot \langle \mathbf{p} \rangle_{\mathbf{r}} = 0 \tag{2.67}$$

   where $\langle \cdots \rangle_{\mathbf{r}}$ is an average at position $\mathbf{r}$. What does this imply if the momentum distribution is spatially uniform?

Chapter 3

The Microcanonical Ensemble (Pathria Ch 1)

Through the H-Theorem, Boltzmann was able to form a putative connection between the momentum distribution $f(\mathbf{p})$ of the particles in the system and the thermodynamic entropy of the system. Regardless of initial conditions, a gas will necessarily adopt a Maxwell-Boltzmann distribution (so long as it satisfies the assumption of 'molecular chaos' at any rate). This effect was not due to an external temperature, although we made a hand-wavy link to the as-yet unproved equipartition theorem, $\epsilon = 3k_BT/2$, in the previous chapter. Rather, the only constraint implied was that the mean kinetic energy was held at some fixed value, $\langle \mathbf{p}^2/2m \rangle = \epsilon$. One might ask if a similar approach can be used in other contexts, leading to the definition of the microcanonical ensemble.

3.1 The Microcanonical Ensemble

3.1.1 Global Constraints

Suppose we have a constraint on the total energy of a system of particles, with each particle having an average energy $\langle E_i \rangle = \epsilon$ and the total energy $E_{sys} = E = N\epsilon$ for N particles in the system. Here we have no requirement of a thermal reservoir, but rather a *fixed* energy for the system without possibility of work begin done or energy being extracted (a perfectly isolated system). The particles are permitted to be in any combination of states *so long* as their total energy adds up to E. Note that this is different notation than the thermodynamic U used in Ch 1. In this section, we will refer to the total energy as E usually, to clearly denote that the energy is a fixed quantity in the microcanonical ensemble. However, E and U both refer to the total energy of the system.

For a discrete system, we can say n_l particles are in the l^{th} energy level, with energy ϵ_l, while for a continuous system the particle density in state l with energy $\epsilon(l)$ is given by $n(l)$. As an example, the density of particles with energy $\mathbf{p}^2/2m$ was $f(\mathbf{p})$ in the Boltzmann transport equation. In either case, we can immediately write

$$N = \sum_l n_l \qquad E = \sum_l n_l \epsilon_l \qquad \text{discrete} \tag{3.1}$$

$$\tag{3.2}$$

These global constraints still permit a large number of possible states that each particle occupies. For example, the constraints can be satisfied if N particles have the same energy E/N, or alternatively if one particle has energy E and $N-1$ particles have energy 0. This means there will be a total number of states available to a system, $\Omega(E, N)$, which depends solely on the global properties of the system.

3.1.2 Microstates and Equiprobability

In order to determine the statistics of such a system, we now assume that each microstate is equally likely so long as it is consistent with the global constraints. The microcanonical ensemble is the complete set of all microstates that satisfy the global constraints (that is, any state that has N particles whose total energy is E is an element of the microcanonical ensemble). That is, if we know *only* the number of particles and total energy, any possible arrangement of the particles that satisfies those conditions just as likely to have occurred as any other. For example, the *microstates*

1. All particles have energy E/N
2. Particle 1 has energy E, and the rest have energy 0
3. Particle 1 has energy 0, and the rest have energy $E/(N-1)$
4. Particles 1 and 2 have energy $E/2$, and the rest have energy 0
5. Particles 1 and 2 have energy 0, and the rest have energy $E/(N-2)$

This is not a full accounting of all possible microstates that satisfy the constraints, but illustrates their equivalence. In some sense, it may seem counterintuitive that the first and second microsates here are equally likely, since in one case there's a huge energy associated with one particle. However, as we have made no assumptions about the system other than the fact that the total energy is E, there is no reason to treat the first two states as any more or less likely. Each of these states can be grouped into *indistinguishable* microstates, which are identical up to the particle labeling. For example

1. N ways to arrange one particle with energy E, and the rest with energy 0
2. N ways to arrange one particle with energy 0, and the rest with energy $E/(N-1)$
3. $N(N-1)/2$ ways to arrange two particles with energy $E/2$, and the rest with energy 0
4. $N(N-1)/2$ ways to arrange two particles with energy 0, and the rest with energy $E/(N-2)$

In the first two cases, the counting comes from the N possible labels a single particle can have. In the second two cases, the counting comes from the N labels the first particle has, the $N-1$ labels remaining for the second particle, and a division by 2 because we can swap the labels of the first and second particles. The reader will likely (and correctly) recognize this is the number of ways to choose two elements from a list of N, with $\binom{N}{2}$ ways to do so. While each microstate is equally likely, there is variation in the likelihood of equivalent or indistinguishable microstates: the third and fourth microstates are far more likely to occur than the first and second by random chance, since there are $(N-1)/2 \gg 1$ more ways to make those states.

3.1.3 Equilibration of two microcanonical systems

Suppose now we have two systems with energy and number of particles E_i and N_i respectively. Those macroscopic constraints will be satisfied by $\Omega_i(E_i, N_i)$ states for the two systems. This perfectly general, and doesn't depend on the specific interactions of the systems. Suppose the two are brought together in contact such that the are *not* allowed to exchange particles (so N_i is held fixed), but *are* allowed to exchange energy. The energy of the entire system

$$E_{tot} = E_1 + E_2 \tag{3.3}$$

is conserved in this, but now the energies of the individual systems may change. The exchange of energy occurs through heat flow between the two systems, with the heat dQ a thermodynamic concept: we make no assumptions about the mechanism of the energy exchange except that it does not change N_i. Because the system can exchange energy, E_1 and E_2 are allowed to vary, such that at equilibrium the final values of the energy in system i will be $\bar{E}_i$. It is not necessary that the initial and final energy of each system is the same, but it must satisfy the constraint of constant energy $E_{tot} = E_1 + E_2 = \bar{E}_1 + \bar{E}_2$.

Prior to being brought together, there is no interaction between the systems and the arrangement of particles between each system is

$$\Omega_{tot}(E_{tot}) = \Omega_1(E_1)\Omega(E_2). \tag{3.4}$$

Once they are brought into contact, the energy exchanged between the two systems does not alter the number of possible microstates available to system, and they will remain is statistically independent of one another as in eq. 3.4. The equal probability assumption implies that the combined system will *maximize* its accessible states $\Omega_{tot}(E)$, since all states for the combined system are equally likely the system is most likely to be found in a state with the largest number of equivalent states. That is, the final indistinguishable microstate of the combined system will most likely be the one that have the greatest probability of being found by random chance. Assuming this,

$$\begin{aligned}
\frac{\partial \Omega_{tot}}{\partial E_1} &= \frac{\partial[\Omega_1(E_1)\Omega_2(E_2)]}{\partial E_1} && (3.5)\\
&= \frac{\partial[\Omega_1(E_1)\Omega_2(E_{tot}-E_1)]}{\partial E_1} && (3.6)\\
&= \Omega_2(E_2)\frac{\partial \Omega_1}{\partial E_1} - \Omega_1(E_1)\frac{\partial \Omega_2}{\partial E_2} && (3.7)
\end{aligned}$$

At equilibrium, when the total number of accessible states Ω is maximized, we have $\partial\Omega/\partial E_1 = 0$, implying

$$\left.\frac{\partial \log[\Omega_1]}{\partial E_1}\right|_{E_1=\bar{E}_1} = \left.\frac{\partial \log[\Omega_2]}{\partial E_2}\right|_{E_2=\bar{E}_2} \tag{3.8}$$

when evaluated at the equilibrium values of the energy, $\bar{E}_1$ and $\bar{E}_2$.

3.2 Entropy and the number of states

Eq. 3.8 has an interesting form, in that it equates derivatives of a quantity with respect to energy. At equilibrium and for a reversible process, we have

$$TdS = dU + pdV - \mu dN \tag{3.9}$$

where we have continued to use the thermodynamic notation for total energy U. For this system at equilibrium, in the absence of heat flow and with N and V held fixed,

$$dU = TdS \qquad\qquad \frac{1}{T} = \frac{dS}{dU} \tag{3.10}$$

so that if we were to postulate two thermodynamic systems brought into contact, eventual equilibrium between them would imply that

$$\left.\frac{dS_1}{dE}\right|_{\bar{E}_1} = \left.\frac{dS_2}{dE}\right|_{\bar{E}_2} \tag{3.11}$$

This is the definition of thermal equilibrium via the 0^{th} law, which states two systems brought into contact will eventually settle to have the same temperature. Recall that these are isolated systems being brought together, and there is no heat bath at fixed temperature to define T. Rather, the temperature of the system is defined through dS/dE.

Comparing eq. 3.8 and 3.11, we therefore have a possible relationship between the number of microstates and the entropy of the system:

$$S \propto \log(\Omega) \qquad S = k_B \log(\Omega) \tag{3.12}$$

where k_B is Boltzmann's constant. This is at the moment an arbitrary constant, but we'll see soon that it naturally contributes to the ideal gas law, which has been well studied. We've seen that $\partial \log(\Omega)/\partial E$ and $\partial S/\partial E$ are constant at equilibrium. We can also argue the system is extensive by imagining dividing the volume V into many small subunits dv, with $M = V/dv$ small subvolumes that can contain particles. For the first particle, there are M possible bins where the particle can be placed. If the gas is dilute or noninteracting, there are also $\approx M$ bins in which the second particle can be placed, as well as the third, and so on. The number of accessible states is then

$$\Omega = M^N \propto V^N \qquad \log(\Omega) \sim N \tag{3.13}$$

so that the entropy is extensive (at least in this simple case; in general we will still expect the number of states of a system to grow exponentially with the size of the system). We note that our definition of $\Omega(E_{tot})$ was determined by *maximizing* the number of accessible states of the two sub-systems under the global constraint of the total energy. Since we've performed a maximization, we are guaranteed that $\log(\Omega(E_{tot})) \geq \log(\Omega(E_1)) + \log(\Omega(E_2))$. This would imply that $S \geq S_1 + S_2$, consistent with the second law of thermodynamics. Further, if we have a system with exactly one accessible state (so that $\Omega = 1$), $\log(\Omega) = 0$. This implies an absolute minimum of the entropy of a system, consistent with the third law of thermodynamics. $S = k_B \log(\Omega)$ satisfies all laws of thermodynamics regarding entropy, and is thus a plausible definition of entropy.

3.3 Other thermodynamic variables

There's nothing terribly special about a wall permeable only to heat in our example. If we imagine the volume can change (so that $V_{tot} = V_1 + V_2$ is fixed but V_i can vary), we can perform the same analysis:

$$\left.\frac{\partial \log(\Omega_1)}{\partial V}\right|_{\bar{V}_1} = \left.\frac{\partial \log(\Omega_2)}{\partial V}\right|_{\bar{V}_2} \tag{3.14}$$

so $\partial \log(\Omega)/\partial V$ is constant. Likewise, if we let the barrier be permeable to the particles,

$$\left.\frac{\partial \log(\Omega_1)}{\partial N}\right|_{\bar{N}_1} = \left.\frac{\partial \log(\Omega_2)}{\partial N}\right|_{\bar{N}_2} \tag{3.15}$$

so $\partial \log(\Omega)/\partial N$ is constant. The fundamental thermodynamic equation for our system is

$$-dE + pdV - \mu dN = TdS = Td(\log(\Omega)) \tag{3.16}$$

so we can readily identify the meaning of the constants in our statistical variations:

$$\frac{\partial \log(\Omega)}{\partial V} = \frac{p}{k_B T} \qquad \frac{\partial \log(\Omega)}{\partial N} = -\frac{\mu}{k_B T} \tag{3.17}$$

Note that if $\Omega \propto V^N$, then

$$\frac{p}{k_B T} = \frac{\partial \log(\Omega)}{\partial V} = \frac{N}{V} \qquad\qquad pV = Nk_B T \tag{3.18}$$

Again, our identification of $S = \log(\Omega)$ readily reproduces the ideal gas law (sometimes written as $pV = nRT$ with $n = N/N_A$ and $R = k_B N_A$, and $N_A \sim 6 \times 10^{23}$). The constant associated with the ideal gas law has been well studied, and we can copy:

$$k_B = 1.38 \times 10^{-23}\text{J/K} = 8.62 \times 10^{-5}\text{eV/K} \tag{3.19}$$

At room temperature (298K),

$$k_B T = 4.11 \times 10^{-21} J = 4.11\text{pN nm} = 25.7\text{meV} \tag{3.20}$$

These numbers are useful to remember to identify under what conditions you'll need to consider statistical mechanics in a system you're looking at. The behavior of particles that interact with strengths on the order of $k_B T$ may be significantly altered due to thermal fluctuations. This is something we'll talk about more later in the semester, but it is very useful to remember one or more of these numbers depending on your field of research.

3.4 Accessible states for a Classical Ideal Gas

3.4.1 The volume of phase space

We've already seen that we naturally recover the ideal gas law $PV = Nk_B T$ through the connection that $S = k_B \log(\Omega)$ and for $\Omega \propto V^N$. While it's nice we can reproduce this well known result, we can significantly improve on this scaling argument with a more detailed calculation of the number of states to exactly compute the entropy of a system. Classically, we can do this by integrating over all possible configurations that satisfy the constraint of fixed energy and number. In particular, we will have

$$\begin{aligned}
\Omega \propto \int \prod_i d^3\mathbf{r}_i d^3\mathbf{p}_i \; \delta\left(\sum_i \frac{\mathbf{p}_i^2}{2m} - E\right) &= V^N \int_{\sum_{i=1}^N \mathbf{p}_i^2 = 2mE} \prod_i d^3\mathbf{p}_i && (3.21)\\
&= V^N (2mE)^{3N/2} \int_{\sum_{i=1}^N x_i^2 = 1} \prod_i d^3 x_i && (3.22)\\
&= V^N (2mE)^{3N/2} \times \Big(\text{Surface area of } 3N && (3.23)\\
&\qquad\qquad \text{dimensional unit sphere}\Big)
\end{aligned}$$

where the position integrals $\int \prod_i d^3\mathbf{r}_i = (\int d^3\mathbf{r})^N = V^N$, and we wrote each component of the momentum as $p = x\sqrt{2mE}$. All of the dimensionality of the volume of phase space is contained within the leading term, with the integrals (equivalent to the surface area of the unit sphere of 3N dimensions) not dependent on energy or volume, only on N. Note that this has our expected scaling of V^N included already, indicating we will be able to successfully recover the ideal gas law.

In order to determine Ω, we must compute the surface area of a multidimensional sphere. If we imagine we have a sphere of radius R in D dimensions, we know the surface area of the sphere is $A_D = dV_D/dR$ (since the volume can be computed by adding up shells of area A_D, with $V_D = \int dR \frac{dV}{dR} = \int dR A_D(R)$). Dimensionally, we are certain that we can write $V_D = c_D R^D$, with some unknown numerical prefactor c_D depending only on D. We can compute this prefactor a clever trick:

$$\begin{aligned}
\pi^{D/2} &= \left(\int dx e^{-x^2}\right)^D = \int \prod_i dx_i e^{-\sum_i x_i^2} = \int dV_D e^{-R^2} = \int dR \left(Dc_d R^{D-1}\right) e^{-R^2}\\
&= c_D \frac{D}{2}\Gamma\left(\frac{D}{2}\right) = c_D \Gamma\left(\frac{D}{2}+1\right) && (3.24)
\end{aligned}$$

where in the last equation we performed a substitution $u = R^2$ and recalled that $\int_0^\infty dx x^{y-1} e^{-x} = \Gamma(y)$. Then the volume of a d-dimensional sphere is then

$$V_D(R) = \frac{\pi^{D/2}}{(D/2)!} R^D \tag{3.25}$$

with $(D/2)! = \Gamma(d/2+1)$. Thus, $A_D = D\pi^{D/2} R^{D-1}/(D/2)! = 2\pi^{D/2} R^{D-1}/(D/2-1)!$.

Having determined the surface area of the sphere, we can use its value to estimate Ω (which is proportional to the surface area of the unit sphere with $R = 1$). We find

$$\Omega \propto V^N (2mE)^{3N/2} \frac{3N\pi^{3N/2}}{(3N/2)!} \tag{3.26}$$

The constant of proportionality is completely unknown at the moment, but we can recognize that it must have the units required to make Ω nondimensional (since the number of microstates cannot have a dimension). Eq. 3.26 has dimensions of (length×mass$^{1/2}$×energy$^{1/2}$)=(energy×time). We know of one physical constant that has precisely these units: planks constant h. We can then nondimensionalize Ω by writing

$$\Omega = \frac{3N\pi^{3N/2}}{(3N/2)!} \left(\frac{V(2mE)^{3/2}}{h^3} \right)^N \tag{3.27}$$

3.4.2 Justifying the appearance of Plank's constant

An immediate and natural response to the inclusion of Plank's constant is that it's a completely arbitrary choice. *Any* constant could be chosen so long as it has the correct units, e.g. we could just as easily normalize by 1Js. We can make a quantum mechanical argument for why Plank's constant might appear. This treatment is *not* correct, in that the we are ignoring the Pauli exclusion principle, and we will discuss quantum statistical mechanics correctly in a later chapter. However, we can see the emergence of Planks constant by considering a single particle trapped in an impenetrable cube of side L. The eigenfunctions of the Schrödinger equation are

$$\psi_{\mathbf{n}}(\mathbf{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \tag{3.28}$$

whose energy is

$$E_{\mathbf{n}} = \frac{\hbar^2}{2m} \times \frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \tag{3.29}$$

If we imagine N particles that are noninteracting are placed in such a box, so that their states are completely independent of one another (a terrible lie quantum mechanically, but a good approximation at high temperature as we will see), the total energy of the system is

$$E = \sum_{\mathbf{n}} E_{\mathbf{n}} = \frac{h^2}{8mL^2} \sum_{i=1}^{3N} n_i^2 \tag{3.30}$$

Thus, the total number of states at an energy E for N particles in a volume V are the number of integer solutions to the equation $\sum_i n_i^2 = 8mEV^{2/3}/h^2$. Note that Plank's constant has naturally appeared in this calculation, rather than the arbitrary use in Eq. 3.27. We can count the number of states by writing

$$\Omega = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{3N}}^{\infty} \delta\bigg(\frac{h^2}{8mL^2} \sum_i n_i^2 \ , \ E \bigg) \tag{3.31}$$

with $\delta(x,y)$ the Kroniker delta function ($\delta(x,y) = 1$ if $x = y$ and 0 else). This is very difficult to calculate as written, but we can convert this to a continuous representation by writing an effective momentum $p(n) = n \times h/L$. Note that $p(n+1) - p(n) = h/L = dp \ll 1$, with a constant spacing between momentum states that is very small as long as L is large (which is true in the thermodynamic limit of $V \to \infty$). We can then write $\sum_n f(n) = L/h \sum_n h/L f(n) \approx L/h \int_0^\infty dp f(p)$, converting the discrete sum to an integral. Then

$$\begin{aligned}
\Omega &= \frac{L^{3N}}{h^{3N}} \int_0^\infty d^{3N}p\,\delta\bigg(\sum_i \frac{p^2}{8m} - E \bigg) && (3.32)\\
&= V^N \bigg(\frac{2mE}{h^2} \bigg)^{3N/2} 2^N \int_0^\infty d^{3N}x\,\delta\bigg(\sum_i x_i^2 - 1 \bigg) && (3.33)\\
&= V^N \bigg(\frac{2mE}{h^2} \bigg)^{3N/2} \int_{-\infty}^\infty d^{3N}x\,\delta\bigg(\sum_i x_i^2 - 1 \bigg) && (3.34)\\
&= V^N \bigg(\frac{2mE}{h^2} \bigg)^{3N/2} \int_{\sum_i x_i^2 = 1} d^{3N}x && (3.35)\\
&= V^N \bigg(\frac{2mE}{h^2} \bigg)^{3N/2} \times \bigg(\text{Surface area of } 3N\text{-dimensional sphere} \bigg) && (3.36)
\end{aligned}$$

This is identical to eq. 3.23 except for the factor h^{-3N}, which we added based on dimensional arguments in eq. 3.27. While we have still not actually shown that this factor is correct (because this quantum mechanical argument is false: Pauli exclusion is not satisfied), it at least suggests this factor is reasonable. The process we used to reduce a sum to an integral will be repeated in later chapters.

3.5 Entropy, the Gibbs Paradox, and Indistinguishability

Having justified our nondimensionalization with a factor of h^{-3N}, we can write a final expression for the entropy from Eq. 3.27, with

$$S = k_B \log \bigg[\frac{3N\pi^{3N/2}}{(3N/2)!} \bigg(\frac{V(2mE)^{3/2}}{h^3} \bigg)^N \bigg] \tag{3.37}$$

$$\begin{aligned}
&= Nk_B\log\left[V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right] - k_B\log\left[\left(\frac{3N}{2}\right)!\right] + k_B\log(3N) && (3.38)\\
&\approx Nk_B\log\left[V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right] - \frac{3Nk_B}{2}\log\left(\frac{3N}{2}\right) + \frac{3N}{2} + \log(3N) && (3.39)\\
&\approx Nk_B\log\left[V\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right] + \frac{3Nk_B}{2} + O\Big(\log(N)\Big) && (3.40)
\end{aligned}$$

where the first approximation is due to Sterling's approximation and the second is due to neglecting terms of order $\log(N)$. Both are acceptable for $N \to \infty$ (in the latter case, note that $\log(10^{23}) = 23\log(10) \approx 53 \ll 10^{23}$).

We can readily compute the temperature of this system knowing the entropy, with

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3k_BN}{2E} \qquad \Rightarrow \qquad \frac{E}{N} = \frac{3k_BT}{2} \tag{3.41}$$

This is well known as the equipartition of energy that we mentioned in the previous chapter without proof (we'll prove it explicitly in the next chapter). From eq, 3.41, we immediately see that

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{NV} = \frac{3Nk_B}{2} \tag{3.42}$$

which agrees with experimental results on monatomic gasses (but not all gases!). We also see that

$$S = Nk_B\log\left(\frac{V}{\lambda^3}\right) + \frac{3Nk_B}{2} \tag{3.43}$$

where the total system volume is scaled by an effective volume per particle λ^{-3}, with

$$\lambda = \frac{h}{\sqrt{2\pi mk_BT}} \tag{3.44}$$

The emergence of this wavelength λ (having units of 1/distance) is physically relevant, because it is the De Brogle wavelength, with $\lambda \sim h/p$, for a particle with energy $\sim k_BT$. We find for an ideal particle with energy on the order of k_BT

$$k_BT \sim E \sim \frac{p^2}{m} \sim \frac{h^2}{m\lambda^2} \qquad \to \qquad \lambda \sim \frac{h}{\sqrt{mE}} \tag{3.45}$$

where we have neglected dimensionless constants in this argument. λ is thus referred to as the *thermal wavelength* of the gas, and we will find in the future this indicates whether quantum effects are important: if $\lambda \ll 1$ the particles are effectively point-like and classical, and if $\lambda \gg 1$ the statistics of the particles may be altered by quantum mechanics. This sets a more precise meaning on what is dilute: if $V \gg N\lambda^3$, the gas is sufficiently dilute that quantum effects are generally negligible because particles are well separated, but if $V \lesssim N\lambda^3$ we may expect to see the quantum behavior of the particles playing a greater role.

3.5.1 Entropy of Mixing

Generally, we have focused on thermal equilibration between two systems in the previous chapters. In this section, we'll discuss the combining of two systems that begin at the same temperature, but that are permitted to exchange particles. The systems are at thermal equilibrium initially (with $T_1 = T_2$=const), but can exchange particles after they are brought together before they reach chemical equilibrium. Each system has an initial entropy

$$S_i = N_i k_B \log\left(\frac{V_i}{\lambda_i^3}\right) + \frac{3N_i k_B}{2} \tag{3.46}$$

where N_i is the number of particles in system i, V_i its volume, $\lambda_i = h/\sqrt{2\pi m_i k_B T}$ its wavelength, and T its temperature (with no index on i, since the temperatures are the same). After combining the two systems, the total entropy is

$$S_{tot} = (N_1 + N_2)k_B \log(V_1 + V_2) + \frac{3k_B(N_1 + N_2)}{2} - 3N_1 k_B \log(\lambda_1) - 3N_2 k_B \log(\lambda_2)$$

(you should work through the details of that calculation, which is provided as a homework problem), and the entropy due to having combined the two systems is therefore

$$\Delta S = S_{tot} - S_1 - S_2 = k_B\left[N_1 \log\left(\frac{V_1 + V_2}{V_1}\right) + N_2 \log\left(\frac{V_1 + V_2}{V_2}\right)\right] \geq 0 \tag{3.47}$$

This measures the excess entropy produced by combining the two systems. The entropy production during the equilibration is expected to be positive, so thus far nothing has gone wrong.

3.5.2 A paradox: an apparent failure of statistical mechanics

If we assume that our original systems were composed of identical particles (so $m_1 = m_2$) and have the same density (so that $N_1/V_1 = N_2/V_2 = (N_1 + N_2)/(V_1 + V_2)$), we would naturally expect that, at equilibrium, there should be *absolutely no effect* of bringing the two independent systems into contact. Because the particles are identical and the systems have the same density, an equal number of particles should move from system 1 to system 2 as they do from system 2 to system 1. Put another way, the chemical potential of each system should be identical, since they are identical particles at the same density: there's no density difference to balance. There's thus no reason for the entropy to increase, as the systems are identical with or without a hypothetical partition dividing them into two, so we should expect $\Delta S = 0$. Where did we go wrong?

The reason the systems are expected to be identical is that all particles are indistinguishable. If each particle were labeled, there *would* be a difference between the unified and partitioned states, due to the fact that different unique particles can move between the volumes in the unified system. For indistinguishable particles, the system of origin of any particle cannot be identified and we can only look at the number density, which is constant if $N_1/V_1 = N_2/V_2$. That means when we computed the entropy of the combined system, we overcounted the number of states accessible.

We can recover the expected statistics by recognizing that we overcounted the number of states Ω, because we implicitly assumed the particles were identical. When we wrote the integral $\int \prod_i d^3\mathbf{r}_i d^3\mathbf{p}_i \delta(E - \sum_i \epsilon_i)$, we assigned a label to each particle (with ϵ_1 referring to the energy of the first particle, ϵ_2 the energy of the second, and so on). If the particles are indistinguishable we must remove the overcounting due to the equivalent microstates. There are $N!$ was to assign labels to our particles, which lets us normalize the number of states without difficulty. We therefore can write

$$\Omega_{disting} = \int \prod_i \frac{d^3\mathbf{p}_i d^3\mathbf{r}_i}{h^3} \delta\Big(E - \sum_i \epsilon_i\Big) \qquad \Omega_{indisting} = \frac{1}{N!} \int \prod_i \frac{d^3\mathbf{p}_i d^3\mathbf{r}_i}{h^3} \delta\Big(E - \sum_i \epsilon_i\Big) \tag{3.48}$$

to account for the difference between distinguishable and indistinguishable particles. In particular, this means

$$\begin{aligned} S_{indisting} &= S_{disting} - k_B \log(N!) && (3.49) \\ &\approx N k_B \log(V\lambda^{-3}) + \frac{3Nk_B}{2} - k_B\Big(N\log(N) - N\Big) && (3.50) \\ &= -N k_B \log(\rho\lambda^3) + \frac{5Nk_B}{2} && (3.51) \end{aligned}$$

for the fixed density ρ. Note that this quantity is extensive for a constant density: neither ρ nor λ will be proportional to N, so $S \sim N$ explicitly. The division by $N!$ will continue to be necessary in later chapters for indistinguishable particles.

3.6 Summary

In Chapter 2, the kinetics of particles were used to describe the statistics of a dilute gas, partially recovering some of the features expected of thermodynamics by constraining the energy per particle of the system. In this chapter, we have applied this same constraint to an idealized system to show that the entropy is thermodynamically defined to be $\log(\Omega)$ with Ω the number of accessible states. While Ω is difficult to compute in general, we found for an ideal gas (both classically and using the quantum cube well energy levels) that this approach reproduces *all* thermodynamic laws and relationships we saw in Chapter 1 at equilibrium, and in some cases greatly simplifies the calculation of certain quantities. In particular, the equipartition of energy is straightforward to see in the microcanonical ensemble. A surprising feature of the microcanonical ensemble is the distinction between distinguishable and indistinguishable particles, with the latter requiring an additional normalization of $\Omega_{indisting} = \Omega_{disting}/N!$. Despite its usefulness, the microcanonical ensemble lacks an external reservoir (so in this ensemble no heat can be extracted, but only the conversion of internal energy to mechanical work). In the next chapter, we will address the exchange of heat between a system and a thermal bath, referred to as the canonical ensemble.

3.6.1 Homework Problems

1. In the game of Go, black and white stones are sequentially placed at the corners of a n×n grid (forming a grid of $(n-1)$ squares). Without regard for the rules of the game, how many ways total are there to place m black stones and m white stones on the board? (*Hint:* There are 900,900 ways to place them if $n = m = 4$).
   (a) How many ways are there to place m black stones in *only* the top k rows of the board and m white stones in the remaining $n-k$ rows if the squares on the grid are distinguishable (e.g. are numbered)? For $n = m = 19$ (the standard board size with ≈5% of the board filled in) and for $k = 9$, what is the probability of black and white being found on different halves of the board by random chance? You should work out the numerical value of the probability.
   (b) What is the probability if the squares in the grid are indistinguishable (that is, the board can be rotated or flipped)?
2. Suppose the entropy is related to the number of states through an arbitrary function $f(\Omega)$. Show that entropy is additive and the number of states is multiplicative for two systems if and only if $f(\Omega) \propto \log(\Omega)$.
3. (a) Determine the volume of an $d_1 + d_2$ dimensional ellipsoid, which satisfies

$$\sum_{i=1}^{d_1} \left(\frac{x_i}{r_1}\right)^2 + \sum_{i=d_1+1}^{d_1+d_2} \left(\frac{x_i}{r_2}\right)^2 \leq X^2. \tag{3.52}$$

   Using the result of this calculation, determine the entropy, temperature, and heat capacity for the following systems, given the total energy of the systems are constrained to be E.

   (b) Using the results of 3a, determine the entropy and temperature of a system of N distinguishable, three dimensional, classical harmonic oscillators at fixed energy

E, with each particle having energy

$$\epsilon_i = \frac{\mathbf{p}_i^2}{2m} + \frac{m\omega^2}{2}\mathbf{r}_i^2, \tag{3.53}$$

(c) Using the results of 3a, determine the entropy and temperature of a system of N_1 particles with mass m and N_2 with mass M. Assume you can distinguish between particles of mass m and M due to differing masses, but that two particles of mass m are indistinguishable (and likewise for two particles of mass M).

Chapter 4

The Canonical Ensemble (Pathria Ch 3)

In the previous chapter, we developed the microcanonical ensemble, which focused on counting the number of states of a system such that the total energy of the system is precisely constrained, with $\sum_{i=1}^{N} E_i = E$. This was great, in that we were able to link these calculations to thermodynamic variables, which provided insights into the meaning of those variables and guidance into what to attempt to compute using the microcanonical ensemble. The H theorem and the BBGKY hierarchy were derived in the same spirit, with the mean particle energy ϵ the only constraint we imposed. In the microcanonical ensemble, we showed that the temperature of the system $T = \partial S/\partial E|_{V,N}$ satisfied the equipartition theorem, $E = 3Nk_BT/2$, for an ideal gas as well.

There are, however, a few problems with the use of the microcanonical ensemble. First: it's actually pretty hard to compute anything. We can determine the behavior of an ideal gas, but anything more complicated than that (or a harmonic oscillator) is really quite difficult, because we must satisfy a global constraint implying a volume in phase space that can be painful to compute. Second: a fixed energy is an odd thing to expect. It is rare that we hold a system at exactly 1J, we are much more likely to hold the system at exactly 298K via a thermal bath not accounted for in the microcanonical ensemble. Thermodynamics provided a technique in the form of the Legendre transform to control the temperature, and it seems likely some technique will exist to do so in statistical mechanics. This is indeed the case, and is termed the canonical ensemble (in contrast to the microcanonical ensemble, specifying the position and momenta of all particles simultaneously).

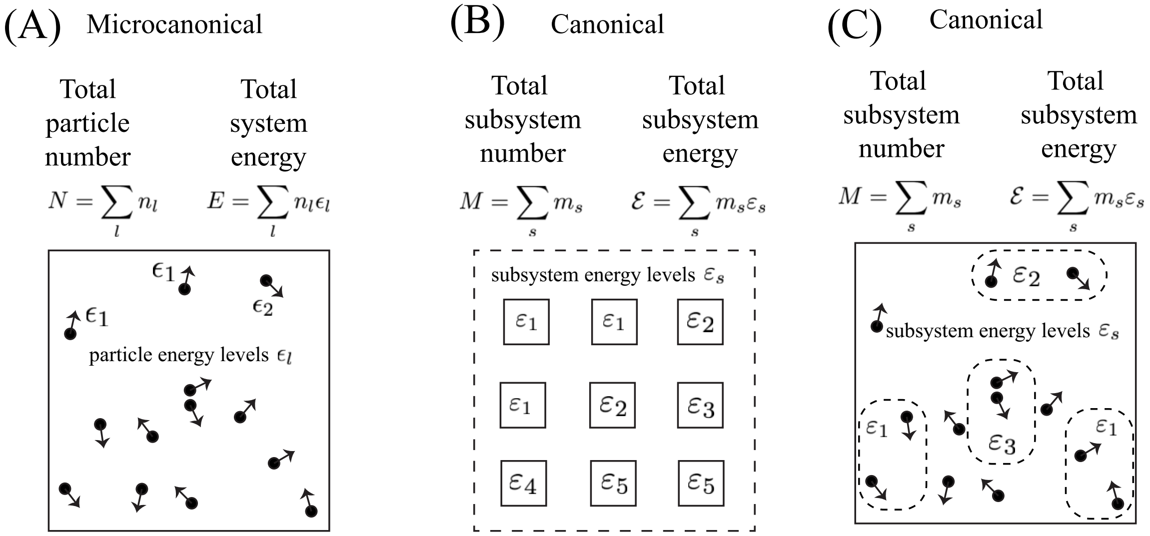


Figure 4.1: Comparison of the microcanonical and canonical ensembles. In the microcanonical ensemble, N particles occupied various energy levels ϵ_l. The canonical ensemble is formed of a variety of subsystems, each of which is composed of particles having some energy ε_s. The total number of subsystems and total energy of the subsystems are constrained, but we no longer fix the energy of any individual subsystem.

4.1 Introducing a heat bath in statistical mechanics

4.1.1 An ensemble of ensembles

The microcanonical ensemble was developed by considering N particles that could be found in different states, and constraining $N = \sum_l n_l$ and $E = \sum_l n_l \epsilon_l$ (depicted in Fig. 4.1(A)). Let us now imagine an ensemble of these ensembles: M systems of composed of a fixed number of N_{sub} particles, with the systems all found with some set of energies ε_s (depicted in Fig. 4.1(B)). The total energy of the ensemble of systems is $\mathcal{E}$, but we do not constrain the energy of any individual subsystem to be some fixed constant. Put another way, we create a large number of microcanonical ensembles of particles, forcing m_s of them to have energy ε_s. Note that we've got a problem of indistinguishability here: we can't determine the microstate of any subsystem, so two subsystems that have exactly the same energy ε_s are totally indistinguishable.

An alternate but equivalent way to understand the construction of the canonical ensemble is to imagine a large system with N_{tot} particles in a volume V_{tot} having a fixed energy E_{tot}, and mentally identifying $N_{sub} \ll N_{tot}$ particles as our first subsystem, having a total energy ε_1 (whatever value it has), depicted in Fig. 4.1(C). This sample is a thermal equilibrium with the entire system, which acts as a 'heat bath'. We can perform this mental exercise an arbitrary number of times, finding ε_s for the s^{th} iteration of a subsystem at equilibrium with the same heat bath. The question then is, what is the probability of a random collection of N particles having an energy ε_s? This is an equivalent definition of a fixed number of simultaneous subsystems.

As was the case in the microcanonical ensemble, we have made no assumptions about the distribution of the energies at this point. Similar to the particle microstates in the previous section, in the canonical ensemble the following states all have equal probability:

1. Subsystem 1 having energy $\mathcal{E}$ and all others having energy 0
2. Subsystem 1 having energy 0 and all others having energy $\mathcal{E}/(M-1)$
3. Subsystem 1 and 2 having energies $\mathcal{E}/2$ and all others having energy 0
4. Subsystem 1 and 2 having energies 0, and all others having energies $\mathcal{E}/(M-2)$

That means, just as in chapter 1, that we expect the most likely distribution of energy among the subsystems will be the distribution that has the greatest probability of occurring by random chance. In the previous chapter, we used this equiprobability argument to determine the effect of energy flowing between two microcanonical systems in order to determine the final temperature of an isolated system. Here, we're envisioning a system immersed in a bath, and that approach will not work. Instead, we will determine the most probable arrangement of $\{\varepsilon_s\}$ that will occur given a total energy budget of $\mathcal{E}$. To do this, we define the statistical weight

$$W[\{n_l\}] = \frac{M!}{\prod_s m_s} \tag{4.1}$$

which is the number of ways we can arrange the M subsystems into n_l indistinguishable bins. Using Sterling's approximation, we find

$$\log(W) \approx M\log(M) - M - \sum_s m_s \log(m_s) + \sum_s m_s = M\log(M) - \sum_s m_s \log(m_s) \tag{4.2}$$

Note that none of this currently refers to an external heat bath yet, this is simply a mathematical statement of the number of configurations.

4.1.2 The most probable distribution

In eq. 4.2, we've done nothing but count the number of ways to seeing a particular arrangement $\{m_s\}$ occur. What we want to do now is *maximize* W, subject to the constraint of a total energy $\sum_s m_s\varepsilon_s = \mathcal{E}$. As a quick reminder, we use Lagrange multipliers when we want to maximize a function $f(x_1, x_2, \ldots)$ subject to the K constraints $g_k(x_1, x_2, \ldots) = 0$ over all of the variables x_l. wen can then write

$$\begin{aligned} \frac{\partial F}{\partial x_i} &= \frac{\partial F}{\partial \lambda_j} = 0 && (4.3) \\ F(x_1, x_2, \ldots) &= f(x_1, x_2, \ldots) + \sum_k \lambda_k g_k(x_1, x_2, \ldots) && (4.4) \end{aligned}$$

because the constraints must be satisfied for a variation on each variable *and* each Lagrange multiplier. Note that in principle we need to ensure that our function is a maximum as opposed to a minimum, which we will not bother with here (although it's very easy to show it's true!). Our two constraints are that $M = \sum_s m_s$ and $\mathcal{E} = \sum_s m_s \varepsilon_s$, so our function to minimize is

$$F(\{m_s\}) = M \log(M) - \sum_s m_s \log(m_s) - \alpha\left(M - \sum_s m_s\right) - \beta\left(\mathcal{E} - \sum_s m_s \varepsilon_s\right) \quad (4.5)$$

which, after differentiation with respect to any m_s leads to

$$\frac{\partial F}{\partial m_s} = 0 = -1 - \log(m_s^*) - \alpha - \beta\varepsilon_s \quad (4.6)$$

so that

$$m_s^* = C \times e^{-\beta\varepsilon_s} \quad (4.7)$$

m_s^* is the most probable number of subsystems in state s, and where $C = e^{-\alpha-1}$ is an unknown constant. We can solve for each m_s since we know that $\sum_s m_s = M$, and so

$$\sum_s m_s = M = C \sum_s e^{-\beta\varepsilon_s} \qquad \Rightarrow \qquad C = \frac{M}{\sum_s e^{-\beta\varepsilon_s}} \quad (4.8)$$

Before moving on, it's worth reminding ourselves of the fundamental assumptions here. We have assumed is that we can define subsystems having potentially different energies, that the energies of those subsystems are fixed in time, and that equal energy systems are indistinguishable. From these (and only these) assumptions, we have determined the most probable arrangement of systems given a total energy $\mathcal{E}$. Note that the most probable fraction of systems with energy ε_s is $m_s^*/M = e^{-\beta\varepsilon_s}/\sum_s e^{-\beta\varepsilon_s}$, which *does not depend* on M or $\mathcal{E}$. This fraction depends solely on the individual energy levels. This fact permits us to use the highly abstract system-of-subsystems that forms the microcanonical ensemble to make useful predictions. Note also that the model *does not* require that the number of particles in our subsystem N_{sub} is large. In fact, we could substitute $N_{sub} = 1$ without changing anything: instead of sampling 'subsystem' energies, we'd specifically be sampling particle energies. Those energies may be degenerate, and the analysis here determines the most probable distribution of particle energies in a system.

This most probable occupancy is not the same thing as the average occupancy, and there are many distributions for which the mean is not identical with the most probable value, $\langle x\rangle \neq x^*$. We make one final approximation: that the distribution of n_s is *sharply peaked* about its mean. If that is the case, the average number $\langle m_s\rangle \approx m_s^*$, with variance scaling with the width of the distribution. Thus, if the distribution is narrow and peaked around its most probable configuration, the final probability of finding a system in state s is

$$P_s = \frac{\langle m_s\rangle}{M} \approx \frac{m_s^*}{M} = \frac{e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}} \tag{4.9}$$

in the context of a system. In the context of individual particles, the same analysis holds and we find

$$P_l = \frac{\langle n_l\rangle}{N_{tot}} \approx \frac{n_l^*}{N_{tot}} = \frac{e^{-\beta\epsilon_l}}{\sum_l e^{-\beta\epsilon_l}} \tag{4.10}$$

where n_l is the number of particles with energy ϵ_l, exactly as we used in the development of the microcanonical ensemble. The mathematics here are the same, but eqs. 4.9 and 4.10 are subtly different: the former talks about the statistics of groups of particles, while the latter talks about the statistics of individual particles. This distinction will be more relevant in the context of the grand canonical ensemble, where the number of particles can vary. The denominator of this probability is referred to as the 'partition function,' $Q_1 = \sum_l e^{-\beta\epsilon_l}$, and we will find this is a useful quantity in a number of cases.

It is worth noting that this calculation was more convenient for determining the statistics of discrete systems, but similar results hold for continuous systems. The construction is similar, where we assume we have M subsystems, with $m(\epsilon)d\epsilon$ having energy between ϵ and $\epsilon + d\epsilon$. Constraints can be developed in a manner similar to before, with $M = \int d\epsilon m(s)$, $\mathcal{E} = \int d\epsilon\epsilon m(\epsilon)$, and $\log(W) = -\int d\epsilon m(\epsilon)\log[m(\epsilon)]$+constant. The derivative $\partial F/\partial m_s$ becomes a functional derivative $\delta F/\delta m(s) = \lim_{\delta\to 0}(F[m(s) + \delta\mu(s)] - F[m(s)])/\epsilon$ for some arbitrary μ. While this is somewhat more difficult to work with, the maximization can be readily shown to reduce to the continuous form of eq. 4.6. That means:

- Analogous to the $P_l =\propto e^{-\beta\epsilon_l}$ in the discrete case, the probability of seeing a particle with energy between ϵ and $\epsilon + d\epsilon$ is $P(\epsilon)d\epsilon \propto e^{-\beta\epsilon}d\epsilon$.
- Analogous to the normalization term $Q_1 = \sum_l e^{-\beta\epsilon_l}$, the normalization in the continuous case is $Q_1 = \int d\epsilon e^{-\beta\epsilon}$

4.2 Thermodynamics and the Canonical Ensemble

4.2.1 Relating the canonical ensemble to the Hemholtz Free Energy

As we did in the microcanonical ensemble, this statistical approach must be connected to thermodynamics in order to be useful. A useful thermodynamic quantity we can compute immediately is the mean energy of a subsystem: $U = \mathcal{E}/M = \sum_s \varepsilon_s e^{-\beta\varepsilon_s} / \sum_s e^{-\beta\varepsilon_s}$. , and we can likewise find

$$U = \frac{\mathcal{E}}{M} = \frac{\sum_s \varepsilon_s e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_r}} = -\frac{\partial}{\partial\beta}\log\left[\sum_s e^{-\beta\varepsilon_s}\right] \tag{4.11}$$

where the last equality is simply a mathematical identity after taking the derivative with respect to β. Note that we've now related the thermodynamic variable U to the derivative of some quantities, which is suggestive. In the microcanonical ensemble, we saw that $\partial\log(\Omega)/\partial E$ was equal between two systems at equilibrium, satisfying the zeroth law of thermodynamics with the identification $S = \log(\Omega)$ (Don't get confused: this was *true in the microcanonical ensemble only!*). Can we identify a similar thermodynamic relationship equating the energy to a partial derivative at constant number and volume?

Indeed we can identify a relationship between our statistical mechanical U and the thermodynamic energy through a relationship with the Helmholtz free energy. Recalling that $A = U - TS$ and $dA = -SdT - pdV + \mu dN$, we readily see that $S = -\partial A/\partial T|_{NV}$. We can then write

$$U = A + TS = A - T\frac{\partial A}{\partial T}\bigg|_{NV} = -T^2\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\bigg|_{NV} = \frac{\partial(A/T)}{\partial(1/T)}\bigg|_{NV} \tag{4.12}$$

where the third and fourth equalities are due differentiation:

$$\frac{\partial(A/T)}{\partial T} = T^{-1}\,\frac{\partial A}{\partial T} - T^{-2}A \tag{4.13}$$

$$\frac{\partial(A/T)}{\partial(1/T)} = -T^2\,\frac{\partial(A/T)}{\partial T} \tag{4.14}$$

This converts the thermodynamic definition of U into a partial derivative at constant N and V, exactly as we needed. Comparing Eqs 4.11 and 4.12 immediately shows that

$$\beta \propto \frac{1}{T} = \frac{1}{k_B T} \qquad \log\left[\sum_s e^{-\beta\varepsilon_s}\right] \propto -\frac{A}{T} = -\frac{A}{k_B T} \tag{4.15}$$

where k_B is (at the moment) an arbitrary constant. Note it must be the same constant between the two terms, since the last equality of eq. 4.11 must be independent of this arbitrary constant. We have thus found a connection between thermodynamics and statistical mechanics. In particular, we have

$$e^{-\beta A} = \sum_s e^{-\beta\varepsilon_s} \equiv Q_N(V,T) \tag{4.16}$$

where $Q = Q_N(V,T)$ is the partition function of the system. This is distinct from the single-particle partition function $Q_1 = \sum_l e^{-\beta\epsilon_l}$, which is a weighted sum over all energy levels for a *single* particle. Q_N sums over all possible energy levels of the *system*, which may depend on interparticle interactions. Sometimes we will write Q for the system's partition function, without explicitly specifying the values of N, V, and T. We will see the partition function plays a significant role in the mathematics of the canonical ensemble, and its physical interpretation will be discussed in the next section.

In later parts of the course, we'll encounter systems that have degenerate energy levels: multiple distinct states the system can occupy that have an identical energy. For example, photons have energy $\epsilon_\nu = h\nu$, but can be polarized in one of two directions. Since $Q = \sum_{states} e^{-\beta\varepsilon_{state}}$, any system whose energy levels have degeneracy g_s will have g_s copies of the term $e^{-\beta\varepsilon_s}$ in the partition function. We then have

$$Q = \sum_{\varepsilon s} g_s e^{-\beta\varepsilon_s} \tag{4.17}$$

where the sum is over unique energies and the coefficient accounts for the degeneracies. We won't deal with this much in the near-term, but it's worth being aware of it at the outset.

4.2.2 Entropy in the canonical ensemble

The mean value of any function f can be determined by

$$\langle f\rangle = \sum_s P_s f(\varepsilon_s) = \frac{\sum_s e^{-\beta\varepsilon_s} f(\varepsilon_s)}{\sum_s e^{-\beta\varepsilon_s}} = Q^{-1}\sum_s e^{-\beta\varepsilon_s} f(\varepsilon_s) \tag{4.18}$$

This provides one important purpose of the partition function: it's the normalization required to compute a probability. Anytime one computes an average in the canonical ensemble, the partition function will be in the denominator. If all states were equally probable, the denominator would simply be the total number of accessible states (with all microstates being equally likely). In the canonical ensemble, some energy levels are more likely than others, so this normalization is weighted.

In Chapter 2, we saw that

$$S_{kinetic} = -\int d^3\mathbf{p} f_0(\mathbf{p}) \log[f_0(\mathbf{p}) \propto \langle\log(f_0)\rangle, \tag{4.19}$$

where $f_0(\mathbf{p})$ was the number density of particles with momentum $\mathbf{p}$, produced a number properties expected of the entropy, $S_{kinetic} = -H(t)$ where $H(t)$ was the H-function *not the Hamiltonian*. S was the mean of the logarithm of the distribution of momenta, and it naturally leads to the calculation

$$\begin{aligned}\langle \log(P) \rangle &= \sum_s P_s \log(P_s) = \sum_s P_s \log\left(\frac{e^{-\beta\varepsilon_s}}{Q}\right) = -\log(Q_N) - \beta U && (4.20)\\ &= \frac{A}{k_B T} - \frac{U}{k_B T} && (4.21)\\ &= -\frac{S}{k_B} && (4.22)\end{aligned}$$

or

$$S = -k_B \sum_s P_s \log(P_s) \qquad (4.23)$$

Once again, we have found that the entropy is related to the global distribution of particle statistics (as it was in Boltzmann's H-theorem). This remarkable result links the statistical theory described here to the classical kinetic theory described in chapter 2 despite radically different approaches and assumptions.

Entropy differs significantly from energy in a fundamental way, in that it depends on the statistics of the entire system, rather than the statistics of single particles. The energy is $U = \sum_s \epsilon_s P_s$, involving a product of a single state and the probability of being found in that state. The entropy $S = -k_B \sum_s \log(P_s) P_s$ involves the distribution in a more fundamental way, since $\log(P_s)$ *does not* depend on a single particle occupying a specific state, but rather is the probability that a particle *could be* found in state s. The entropy cannot be described by discussing the state of a single particle, and is a property of the particle as well as the entire phase space. Eq. 4.23 is an incredibly versatile result, and is used in a wide variety of fields outside of thermal equilibrium to quantify the disorder or unpredictability of systems (with the Shannon entropy perhaps the most common example).

The emergence of the form $S \propto -\langle \log(P) \rangle$ in the kinetic theory and the canonical ensemble begs the question: why we didn't see this relationship in the microcanonical ensemble? Surprisingly, we did, but didn't realize it! In the microcanonical ensemble, the system is constrained to be at a precisely fixed energy, and $S = k_B \log(\Omega)$ is related to the total number of accessible states of that system. Each of those accessible states has a *uniform* probability of occurring, $P_l^{micro} = \Omega^{-1}$. We can therefore write

$$S = k_B \log(\Omega) = -k_B \sum_r \frac{1}{\Omega} \log\left(\frac{1}{\Omega}\right) = -k_B \sum_r P_l^{micro} \log(P_l^{micro}) \qquad (4.24)$$

where the probability of being in the r^{th} state is uniform. Thus, the identification of $S = -\langle \log(P) \rangle$ remains true in the canonical ensemble, but it was not clear that it was *useful* when deriving the microcanonical ensemble.

4.2.3 Entropy Maximization

Because entropy of the form $S \propto -\langle \log(P) \rangle$ comes up in a wide range of fields, it's worth noting that the canonical ensemble can be re-derived in terms of a maximum entropy principle. Suppose we take as given that $S = -\sum_s P_s \log(P_s)$, and wanted to maximize the entropy subject to the constraints that $\sum_s P_s = 1$ and $U = \sum_s P_s \varepsilon_s$. Using the same method of Lagrange multipliers, we can write

$$F(\{P_s\}) = -\sum_s P_s \log(P_s) - \alpha \Big(\sum_s P_s - 1 \Big) - \beta \Big(\sum_s \varepsilon_s P_s - U \Big) \tag{4.25}$$

and find that $\partial F / \partial P_s = 0$ implies

$$P_s \propto e^{-\beta \varepsilon_s} \tag{4.26}$$

Note this has different starting assumptions than how we generated the canonical ensemble (by sampling multiple subsystems at thermal equilibrium with a bath), but still arrives at the same conclusion. If this is coupled with an *assumption* of thermal equilibrium, we'll be able to confirm that $\beta = 1/k_B T$ as before.

The entropy maximization principle is much more flexible than the formal derivation for the canonical ensemble in section 4.1.1, because it applies even when there is no connection to a well defined temperature. Any system with multiple possible states can have an entropy defined as $S \propto -\langle \log(P) \rangle$, and any such function can be maximized. This simple methodology has led to the implementation of statistical mechanics in a wide range of fields, but it is very important to keep in mind that

- For every problem, you are not guaranteed that $S \propto -\langle \log(P) \rangle$ is the 'correct' way to measure disorder or unpredictability. It is a reasonable choice, but you are not guaranteed it's the 'correct' choice. There are generalizations to inextensive forms of entropy
- For every problem, you are not guaranteed that S will always be a maximum. This is particularly an issue for finite size systems! We've had systems of $N = 10^{23}$ particles in mind up to this point, where fluctuations are expected to be small (we'll show this explicitly soon). You can still define $S = -k_B \langle \log(P) \rangle$ for $N = 10$ particles, but in that case fluctuations will be significant and your optimization may not be meaningful.

We'll see that statistical mechanics is powerful and able to make accurate predictions in a wide range of contexts. You may be able to apply these techniques to a novel system, but it's important to carefully consider its appropriateness before doing so!

4.3 The Ideal Gas in the canonical ensemble

4.3.1 Continuum Partition function

The finite energy levels here may seem a bit unwieldy, since we may have a nicely defined Hamiltonian $H(p,q)$ that we want to consider, and we might want to compute statistical observables classically (instead of quantum mechanically, where we are guaranteed discrete eigenvalues for fixed volume). This is straightforward with the identification of $H(\mathbf{p},\mathbf{q}) = E_{subsystem}$, where $\mathbf{p}$ and $\mathbf{q}$ include all N_{sub} particles in the subsystem. We can rewrite the weight factor p_r in terms of the microcanonical variables

$$\rho(\mathbf{p},\mathbf{q}) = e^{-\beta H(\mathbf{p},\mathbf{q})} \Bigg/ \frac{1}{N!h^{3N}} \int d^{3N}p d^{3N}q \; e^{-\beta H(\mathbf{p},\mathbf{q})} \tag{4.27}$$

as the term $e^{-\beta H}$ normalized by its integral over all phase space. This denominator plays the role of $\sum_s e^{-\beta \varepsilon_s} = Q_N$ for the discrete case, and we therefore write

$$Q_N(V,T) = \frac{1}{N!} \int \prod_i \frac{d^3\mathbf{p}_i d^3\mathbf{q}_i}{h^3} \; e^{-\beta H(\{\mathbf{p}_i,\mathbf{q}_i\})} \tag{4.28}$$

as the continuum partition function, where the h^{3N} removes dimensionality (and is assumed to be precisely Plank's constant as before), and $N!$ accounts for the particle indistinguishability. This is *similar* to the integrals we did before over all phase space, except for one fact: we (happily) no longer have a complicated constraint over fixed energy! That is, we are no longer computing a constrained phase space volume in the microcanonical ensemble, with

$$\Omega = \int \frac{d^{3N}p d^{3N}q}{h^{3N}N!} \delta\Big(H(\mathbf{p},\mathbf{q}) - E\Big) \tag{4.29}$$

which was the unpleasant process we worked through in Chapter 3. The partition function simply requires an integration over all possible values of the energy (through the Hamiltonian), weighted by the exponential factor $e^{-\beta H}$. In some sense, the partition function is thus the 'effective volume' of the phase space at constant temperature, rather than a true phase space volume at constant energy represented by Ω.

The meaning of an ensemble average in the continuum is computed in a manner similar to the discrete case, with any function $f(\mathbf{p}, \mathbf{q})$ having an average

$$\langle f\rangle = \frac{\int d^{3N}p d^{3N}q f(\mathbf{p}, \mathbf{q}) e^{-\beta H(\mathbf{p},\mathbf{q})}}{\int d^{3N}p d^{3N}q e^{-\beta H(\mathbf{p},\mathbf{q})}} = \frac{1}{N!}\int \frac{d^{3N}p d^{3N}q}{h^{3N}} \frac{e^{-\beta H(\mathbf{p},\mathbf{q})}}{Q} \times f(\mathbf{p}, \mathbf{q}) \qquad (4.30)$$

Note that this functional form shows that the probability of finding a particle at any $\mathbf{p}-\mathbf{q}$ pair is proportional to $e^{-\beta H(\mathbf{p},\mathbf{q})}$, with a proportionality constant $[N! h^{3N} Q]^{-1}$.

Note again that, as discussed in Ch 2, sometimes the notation $\langle\cdots\rangle$ can be overloaded. We can use the notation $\langle f(\mathbf{r}, \mathbf{p})\rangle_{\mathbf{p}} = \bar{f}(\mathbf{r})$ to denote the average of a function over momentum only (leaving $\mathbf{r}$ fixed). In the literature, you may find the subscript $\langle\cdots\rangle_{\mathbf{p}}$ is dropped. You can identify the variables that are being integrated over by (a) reading the surrounding text (where often the writer will explain s/he is integrating over the momentum degrees of freedom), and (b) identifying the variables that are still present after the averaging (e.g. $\bar{f}(\mathbf{r})$ has an explicit dependence on $\mathbf{r}$, so it cannot have been integrated over).

4.3.2 Statistics of the Ideal Gas

Previously, we computed the thermodynamics of an ideal gas at constant energy, and found $E = 3Nk_BT/2$ as the definition of temperature. In the classical canonical ensemble, we find

$$\begin{aligned} Q &= \int \frac{d^{3N}p d^{3N}q}{h^{3N}N!} e^{-\beta/2m\sum_i \mathbf{p}_i^2} = \frac{V^N}{h^{3N}N!}\left(\int dp e^{-\beta p^2/2m}\right)^{3N} && (4.31)\\ &= \frac{1}{N!}\left(\frac{V}{h^3}\left[\frac{2\pi m}{\beta}\right]^{3/2}\right)^N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N && (4.32)\end{aligned}$$

We can first use this to determine the mean energy

$$U = -\frac{\partial \log(Q_N)}{\partial\beta} = \frac{3N}{2\beta} = \frac{3Nk_BT}{2} \qquad C_V = \left.\frac{\partial U}{\partial T}\right|_{NV} = \frac{3Nk_B}{2} \qquad (4.33)$$

which is the equipartition theorem we previously found. This allows us to identify $k = k_B$ as expected. We also find the Helmholtz free energy

$$A = -k_BT\log(Q_N) \approx -Nk_BT\log\left(\frac{V}{N\lambda^3}\right) - Nk_BT \qquad (4.34)$$

From this, we can readily compute the entropy via

$$S = -\left.\frac{\partial A}{\partial T}\right|_{NV} = \frac{U-A}{T} = k_B\log(Q_N) + \frac{k_B\beta}{Q_N}\frac{\partial Q_N}{\partial\beta} \qquad (4.35)$$

which yields after some algebra

$$S \quad = \quad Nk_B \log\left(\frac{V}{N\lambda^3}\right) + \frac{5Nk_B}{2} \tag{4.36}$$

Perhaps surprisingly, this is *exactly* the same entropy we derived in the microcanonical ensemble, where the energy of the system was held fixed. We will see in a moment that this is because the distribution of the energy is sharply peaked, so a canonical system with $E = 3Nk_BT/2$ for T held fixed and E fluctuating behaves *almost exactly the same* as a system with fixed energy E.

We can also compute

$$p = -\left.\frac{\partial A}{\partial V}\right|_{NT} = \frac{Nk_BT}{V} \tag{4.37}$$

which reproduces the ideal gas law $pV = Nk_BT$. Note that we have differentiated the Helmholtz free energy with respect to V in Eq. 4.37, rather than the internal energy, because in the canonical ensemble the temperature is held fixed (which means it appropriate, as T a proper variable for A). We can compute $p = -\partial U/\partial V|_{NS}$ if we can devise a method to vary the volume while holding the number and entropy fixed. Since $S = Nk_B\log(V/N\lambda^3) + 5Nk_B/2$, the *only* way we can do this is by making the temperature a function of V (that is, cooling our system as we increase the volume so that the entropy stays constant). In particular, we can write

$$\lambda = \left(\frac{V}{N}\right)^{1/3} e^{-S/3Nk_B+5/6} \qquad T = \frac{2\pi m k_B}{h^2}\left(\frac{N}{V}\right)^{2/3} e^{2S/3Nk_B-5/3} \tag{4.38}$$

Given this, we can write

$$p = -\left.\frac{\partial U}{\partial V}\right|_{NS} = -\frac{3Nk_B}{2}\left.\frac{\partial T}{\partial V}\right|_{NS} = \frac{3Nk_B}{2}\frac{2T}{3V} = \frac{Nk_BT}{3} \tag{4.39}$$

where we have used the fact that $T(V) \propto V^{-2/3}$, so $\partial T/\partial V = -2T/3V$.

We can likewise compute the chemical potential as

$$\mu = \left.\frac{\partial A}{\partial N}\right|_{TV} = k_BT\log\left(\frac{V}{N\lambda^3}\right) + \frac{3k_BT}{2} \tag{4.40}$$

Note that the second term here does not depend on any thermodynamic variable except for temperature, and acts as a constant offset for the chemical potential for two thermally equilibrated systems.

4.3.3 Energy Fluctuations

The reason the canonical and microcanonical ensembles (two systems with very different constraints) give an identical expression for the entropy is that the canonical ensemble's energy distribution is sharply peaked about its mean, $3Nk_BT/2$, so behaves *almost* like a system with a fixed total energy. We can show this for a discrete system by manipulating the partition function to compute the mean energy and the energy fluctuations. It is straightforward to see that

$$Q = \sum_l e^{-\beta\epsilon_l} \qquad \Rightarrow \qquad U = \langle E \rangle = -\frac{\partial \log(Q_N)}{\partial \beta} \tag{4.41}$$

which means we can compute energy by simply taking a derivative of the partition function. We can also readily see that

$$\begin{aligned} \frac{\partial^2 \log(Q_N)}{\partial \beta^2} &= -\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}\right] = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} - \left(\frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}\right)^2 \\ &= \langle E^2 \rangle - \langle E \rangle^2 \end{aligned} \tag{4.42}$$

The same calculation works in the continuous case, with $\langle E \rangle = \langle H \rangle$ and $\langle E^2 \rangle = \langle H^2 \rangle$. It's also useful to note that

$$\left\langle (E - \langle E \rangle)^2 \right\rangle = \left\langle E^2 - 2\langle E \rangle E + \langle E \rangle^2 \right\rangle = \langle E^2 \rangle - \langle E \rangle^2 \tag{4.43}$$

so we've computed the fluctuations of the energy about the mean in eq. 4.42. Eq. 4.42 is perhaps surprising, as we can compute fluctuations in the energy by just taking another derivative. This illustrates another use of the partition function: by simply taking derivatives we are able to compute the mean values of a variety of quantities, both directly related to thermodynamics (such as U, A, and S) as well as novel and not easily computed thermodynamically (such as $\langle \Delta E^2 \rangle$).

We therefore have, quite generally that

$$\langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial U}{\partial (k_BT)^{-1}} = k_BT^2 \frac{\partial U}{\partial T} = k_BT^2 C_V \tag{4.44}$$

for the system held at constant volume. This relationship is true *regardless* of the form of the Hamiltonian, even if there are complicated interactions between the particles. Note that for the ideal gas, $C_V = 3Nk_B/2$ and $U = 3Nk_BT/2$, leading to

$$\langle \Delta E^2 \rangle = \frac{3Nk_B^2T^2}{2} \qquad \frac{\langle \Delta E^2 \rangle}{\langle E \rangle^2} = \frac{2}{3N} \tag{4.45}$$

This means that the width of the distribution in energy is large (scaling as N^1). However, the relative fluctuations are vanishingly small for large N, scaling as N^{-1}. The latter can be thought of in terms of a percent fluctuation around the mean, which for a system of 10^{23} ideal particles would be $\sim 6\times10^{-20}\%$, an entirely negligible number. Thus, the distribution in the canonical ensemble can be seen as being sharply peaked about the mean, leading to identical statistics as in the microcanonical ensemble.

4.3.4 Energy fluctuations for noninteracting systems

The relative fluctuations in an ideal gas can be computed in an alternate manner, which can be extended to other uncorrelated systems as well. We can write for the ideal gas that

$$\begin{aligned}
\langle E^2\rangle &= \left\langle\left(\sum_i \frac{\mathbf{p}_i^2}{2m}\right)^2\right\rangle = \frac{1}{4m^2}\sum_{ij}\langle \mathbf{p}_i^2\mathbf{p}_j^2\rangle && (4.46)\\
&= \frac{1}{4m^2}\left(\sum_i\langle\mathbf{p}_i^4\rangle + \sum_{i\neq j}\langle\mathbf{p}_i^2\mathbf{p}_j^2\rangle\right) && (4.47)\\
&= \frac{1}{4m^2}\left(\sum_i\langle\mathbf{p}_i^4\rangle + \sum_{i\neq j}\langle\mathbf{p}_i^2\rangle\langle\mathbf{p}_j^2\rangle\right) && (4.48)\\
&= \frac{1}{4m^2}\left(\sum_i[\langle\mathbf{p}_i^4\rangle - \langle\mathbf{p}_i^2\rangle^2] + \sum_{ij}\langle\mathbf{p}_i^2\rangle\langle\mathbf{p}_j^2\rangle\right) && (4.49)\\
&= \sum_i(\langle\epsilon_i^2\rangle - \langle\epsilon_i\rangle^2) + \langle E\rangle^2 && (4.50)\\
&= N\langle\Delta\epsilon^2\rangle + \langle E\rangle^2 && (4.51)
\end{aligned}$$

where $\Delta\epsilon = \epsilon - \langle\epsilon\rangle$ is the energy fluctuation of a single particle. The important step here is the replacement $\langle\mathbf{p}_i^2\mathbf{p}_j^2\rangle = \langle\mathbf{p}_i^2\rangle\langle\mathbf{p}_j^2\rangle$, which is due to the fact that the particle momenta are independent of one another. Note that eq. 4.51 immediately implies

$$\frac{\langle E^2\rangle - \langle E\rangle^2}{\langle E\rangle^2} = \frac{N\langle\Delta\epsilon^2\rangle}{(N\langle\epsilon\rangle)^2} = \frac{1}{N}\frac{\langle\Delta\epsilon^2\rangle}{\langle\epsilon\rangle^2} \tag{4.52}$$

This means the relative root mean square deviations (RMSD) in energy scale as $N^{-1/2}$, which confirms our assumption that the distribution is sharply peaked: as energy becomes large, deviations from the mean energy become negligible. This scaling is true so long as $\langle\epsilon_i\epsilon_j\rangle = \langle\epsilon_i\rangle\langle\epsilon_j\rangle$: that is that the energies of each particle are statistically independent. Any noninteracting system will have this property.

4.3.5 Separability of the Partition Function

In a continuous system, the partition function is given by

$$Q = \frac{1}{N!}\int \prod_i \frac{d^3p_i d^3r_i}{h^{3n}} e^{-\beta H[\{\mathbf{r}_i,\mathbf{p}_i\}]} \qquad \text{indistinguishable} \tag{4.53}$$

$$Q = \int \prod_i \frac{d^3p_i d^3r_i}{h^{3n}} e^{-\beta H[\{\mathbf{r}_i,\mathbf{p}_i\}]} \qquad \text{distinguishable} \tag{4.54}$$

For *independent systems*, where there is no interaction between any of the particles, $H = \sum_i h(\mathbf{r}_i, \mathbf{p}_i)$ with no coupling between particle i and any other particle j. In this case, we immediately find

$$Q_N = \frac{1}{N!}\left(\int \frac{d^3\mathbf{p}d^3\mathbf{r}}{h^3} e^{-\beta h(\mathbf{r}_i,\mathbf{p}_i)}\right)^N = \frac{Q_1^N}{N!} \tag{4.55}$$

for an indistinguishable system, where Q_N is the partition function for all N particles and Q_1 is the partition for a system of one particle. For distinguishable noninteracting systems, we likewise find $Q_N = Q_1^N$. For separable discrete systems of identical non-interacting particles, we have a similar result if we write $\varepsilon_s = \sum_i \epsilon_i$, with

$$\begin{aligned} Q_N &= \sum_{\text{states } s} e^{-\beta\varepsilon_s} = \frac{1}{N!}\sum_{\text{energies } \epsilon_1} \cdots \sum_{\text{energies } \epsilon_N} e^{-\beta\sum_i \epsilon_i} = \frac{1}{N!}\left(\sum_{\epsilon} e^{-\beta\epsilon}\right)^N \\ &= \frac{Q_1^N}{N!} \end{aligned} \tag{4.56}$$

where the sum over states includes the contribution from each particle and the sum over energies is the the individual contribution from each particle. Note that the sums can be written as a sum over ϵ_{n_i} for N distinct integers n_i; we've written it this way because a sum over indexed integers can be somewhat unclear.

Regardless of the system, if the particles *do not interact*, we only need to do a calculation for one particle. A system of N particles whose energies are separable has a partition function $Q_N = Q_1^N$ for distinguishable particles and $Q_N = Q_1^N/N!$ for indistinguishable particles. Note that this is entirely consistent with eq. 4.32 or **??**, where a single ideal gas particle has a partition function $Q_1 = V/\lambda^3$.

4.4 Equipartition of Energy

4.4.1 Implication of vanishing distribution on the boundary

We've mentioned the equipartition theorem of energy often, every time we see something looking like $E \propto Nk_BT$. The equipartition theorem is an important result in classical statistical mechanics exactly relating the energy to the temperature in a system with a quadratic (sometimes called Gaussian) Hamiltonian. We suppose we have some Hamiltonian $H(\mathbf{p}, \mathbf{q})$ over the generalized coordinates $\mathbf{q}$. We know

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{N! h^{3N} Q} \int \prod_i d^3p_i d^3x_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} \tag{4.57}$$

where x_i and x_j are any of the $6N$ variables $\mathbf{p}_i$ or $\mathbf{q}_i$, and Q is the partition function. A useful result arises if we consider the average of a special family of functions: taking $x_i \neq x_j$ to be any component of any position or momentum variables, we can write the integral over all variables except for x_i and x_j in terms of $d^{6N-2}x$, with

$$\begin{aligned}
\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= \frac{1}{N! h^{3N} Q} \int d^{6N-2}\mathbf{x}' \int dx_i x_i \int dx_j \frac{\partial H}{\partial x_j} e^{-\beta H} && (4.58)\\
&= \frac{1}{N! h^{3N}} \int d^{6N-2}\mathbf{x}' \int dx_i x_i \frac{e^{-\beta H}}{Q} \Bigg|_{x_j^{min}}^{x_j^{max}} && (4.59)\\
&= \frac{1}{N! h^{3N}} \int d^{6N-2}\mathbf{x}' \int dx_i x_i \frac{e^{-\beta H}}{Q} \Bigg|_{x_j^{min}}^{x_j^{max}} && (4.60)\\
&= \frac{1}{N! h^{3N}} \int d^{6N-2}\mathbf{x}' \int dx_i x_i \Bigg(P(\{x\}, x_j = x_j^{max}) - P(\{x\}, x_j = x_j^{min}) \Bigg) && (4.61)\\
&= 0 && (4.62)
\end{aligned}$$

Here, we have used the fact that the probability of being found in a particular configuration is $P(\{\mathbf{r}, \mathbf{p})\}) = Q^{-1} e^{-\beta H(\{\mathbf{r}, \mathbf{p}\})}$, and used the fact that the probability of being found at the boundary of the phase space vanishes. That is, there is vanishing probability of a particle being found with infinite momentum or of sticking to the wall. The arguments here are the same as in Sec. **??** of Ch 2.

This result breaks down if we choose our variables x_i and x_j to be the same. We can compute the average

$$\begin{aligned}
\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle &= \frac{1}{N! h^{3N} Q} \int d^{6N-1}\mathbf{x}' \int dx_i x_i \frac{\partial H}{\partial x_i} e^{-\beta H} && (4.63)\\
&= \frac{1}{N! h^{3N} Q} \int d^{6N-1}\mathbf{x} \Bigg(- \frac{x_i e^{-\beta H}}{\beta} \Bigg|_{x_i^{min}}^{x_i^{max}} + \frac{1}{\beta} \int dx_i e^{-\beta H} \Bigg) && (4.64)
\end{aligned}$$

$$= \frac{1}{\beta N! h^{3N} Q} \int d^{6N-1}\mathbf{x} \int dx_i e^{-\beta H} \tag{4.65}$$

$$= \frac{1}{\beta} \tag{4.66}$$

where we have still assumed that $H \to \infty$ on the boundary (so we can neglect the boundary terms), and have recognized that $\int d^{6N-1}\mathbf{x} \int dx_i e^{-\beta H} = \int d^{3N}\mathbf{p} d^{3N}\mathbf{r} e^{-\beta H} = N! h^{3N} Q$ for any choice of x_i.

We therefore have the general result that for any variable x_i that plays a role in the Hamiltonian that

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T \delta_{x_i, x_j} \tag{4.67}$$

This statement is true for any classical system, regardless of the form of the Hamiltonian. However, it is *very* useful if the Hamiltonian has a special form.

4.4.2 The Equipartition Theorem

If our system is nonrelativistic, the kinetic energy will have the form $\sum_i \mathbf{p}_i^2/2m$, quadratic in each particles momentum. If the Hamiltonian *also* consists of separable, quadratic power law terms, $V(\mathbf{r}) = \sum_i a_i \mathbf{r}_i^2$, then

$$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = \langle x_i \times 2a_i x_i \rangle = 2a_i \langle x_i^2 \rangle = k_B T \tag{4.68}$$

which implies

$$\sum_i \left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = 2\langle H \rangle = fNk_B T \qquad \Rightarrow \qquad U = \frac{fk_B T}{2} \tag{4.69}$$

where f is the number of 'active' degrees of freedom in the system, defined as the number of degrees of freedom that contribute energy to the Hamiltonian. Degrees of freedom that do not have an energetic contribution to the Hamiltonian do not add to the active degrees of freedom, and any terms in the Hamiltonian that are not quadratic will invalidate the equipartition theorem.

For non-relativistic particles, we're guaranteed that at least the momentum terms enter the Hamiltonian quadratically, which immediately implies in three dimensions that

$$\langle K \rangle = \frac{1}{2} \sum_i \langle p_i^2 \rangle = \frac{1}{2} \sum_i \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \frac{3Nk_B T}{2} \tag{4.70}$$

with $f = 3N$ active degrees of freedom (3 momentum per particle), consistent with the energy we found for the ideal gas. Note that this is perfectly general for a classical, nonrelativistic system: regardless of the interactions between particles, the average kinetic energy will *always* be $3Nk_BT/2$. This result will be important in the development of the Virial Theorem, in sec. 4.5

4.5 The Virial Theorem

4.5.1 Mean Energies for interacting particles

In Sec. 4.4.2, we determined the mean kinetic energy for any system of nonrelativistic particles. The kinetic energy is a useful quantity to compute, with $\langle K\rangle = 3Nk_BT/2$ for nonrelativistic particles in three dimensions. A related quantity, termed the Virial $\mathcal{V} = \sum_i \mathbf{r}_i\cdot\partial H/\partial\mathbf{r}_i$ can also be computed in a similar manner. This is most easily performed if there are central force interactions between the particles, having the potential energy $U_{pot} = \sum_{i<j} u(|\mathbf{r}_i - \mathbf{r}_j|)$. This can be simplified significantly by noting that

$$\begin{aligned}
\mathbf{r}_1\cdot\frac{\partial u(\mathbf{r}_1-\mathbf{r}_2)}{\partial\mathbf{r}_1} + \mathbf{r}_2\cdot\frac{\partial u(\mathbf{r}_1-\mathbf{r}_2)}{\partial\mathbf{r}_2} &= \mathbf{r}_1\frac{\partial u(\mathbf{r})}{\partial\mathbf{r}}\bigg|_{\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2} - \mathbf{r}_2\frac{\partial u(\mathbf{r})}{\partial\mathbf{r}}\bigg|_{\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1} && (4.71)\\
&= (\mathbf{r}_1-\mathbf{r}_2)\cdot\frac{\partial u(\mathbf{r})}{\partial\mathbf{r}}\bigg|_{\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2} && (4.72)\\
&= \mathbf{r}_{12}\cdot\frac{\partial u_{12}}{\partial\mathbf{r}_{12}} && (4.73)
\end{aligned}$$

with $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. In this case, we can then write

$$\begin{aligned}
\mathcal{V} &= -3Nk_BT = -2\langle K\rangle && (4.74)\\
&= -\sum_i\left\langle \mathbf{r}_i\frac{\partial H}{\partial\mathbf{r}_i}\right\rangle && (4.75)\\
&= -\left\langle\frac{1}{2}\sum_i \mathbf{r}_i\cdot\frac{\partial}{\partial\mathbf{r}_i}\sum_j u(\mathbf{r}_i-\mathbf{r}_j)\right\rangle && (4.76)\\
&= -\left\langle\frac{1}{2}\sum_{ij}\mathbf{r}_{ij}\cdot\frac{\partial u_{ij}}{\partial\mathbf{r}_{ij}}\right\rangle && (4.77)
\end{aligned}$$

This is an exact expression for any central force problem, but its primary use arises when $u(\mathbf{r}_{ij})$ is a *power law*, with $u(\mathbf{r}) = r^\alpha$ and $\nabla_\mathbf{r}u(\mathbf{r}) = \alpha r^{\alpha-1}\hat{\mathbf{r}}$. In this case, $\mathbf{r}\cdot\nabla_\mathbf{r}u(\mathbf{r}) = \alpha r^\alpha = \alpha u(r)$, so

$$-\mathcal{V} = \left\langle\sum_i \mathbf{r}_i\cdot\frac{\partial H}{\partial\mathbf{r}_i}\right\rangle = \sum_{i<j}\alpha\langle u(\mathbf{r}_{ij})\rangle = \alpha\langle U_{pot}\rangle = 2\langle K\rangle \qquad (4.78)$$

This gives an exact relationship between the mean potential energy and the mean kinetic energy of a system of particles interacting with a power-law central force potential.

For $\alpha = 2$, we have a collection of particles connected by a spring, and we readily find that $\langle U_{pot}\rangle = \langle K\rangle = 3Nk_BT/2$, so that the kinetic and potential energies contribute equally to the total energy of the system. Another interesting choice for the potential is $\alpha = -1$, corresponding to a gravitational attraction between particles. In this case, $\langle U_{pot}\rangle = -2\langle K\rangle$. Deviations from the Virial theorem in the Coma cluster of nebulae was the first evidence that stellar objects were moving too fast to be explained by the observable mass, first observed by Zwicky in 1933. He found that that the cluster velocity determined by redshift gave a mean kinetic energy that was orders of magnitude larger than the total potential energy, determined assuming the nebulae were uniformly distributed in a sphere and luminosity was proportional to mass. The term dark matter was coined in reference to this deviation (but took decades to be widely accepted as the best explanation for the deviation).

4.5.2 Deviation from the ideal gas law

The last term of eq. 4.77 can also be rewritten in a convenient way. The average depends only on the pairwise separation between to particles, so we can compute it directly if we know the probability of finding two particles at any particular locations. Ensemble averages can be computed using the pair correlations, since

$$\langle F(\mathbf{r},\mathbf{r}')\rangle = \int \prod_i d^3\mathbf{p}_i d^3\mathbf{r}_i d^3\mathbf{r}' \rho(\{\mathbf{p},\mathbf{r}\}) F(\mathbf{r}_1,\mathbf{r}_2) \tag{4.79}$$

with ρ the N particle distribution function in phase space. We can simplify this using the two particle distribution in physical space by defining $\rho_2(\mathbf{r}_1,\mathbf{r}_2) = \int \prod_{i=1}^N d^3\mathbf{p}_i \prod_{j=3}^N d^3\mathbf{r}_j \rho_N(\{\mathbf{p},\mathbf{r}\})$. ρ_2 is the joint distribution of the first two particles located at point $\mathbf{r}_1$ and $\mathbf{r}_2$. Because the statistics must be independent of the particle index, it is convenient to define the pair correlation function

$$\rho_0^2 g(\mathbf{r},\mathbf{r}') = N(N-1)\rho_2(\mathbf{r},\mathbf{r}') \qquad \rho_0 = \frac{N}{V} \tag{4.80}$$

which tells us the probability of finding any pair of particles simultaneously at $\mathbf{r}_1$ and $\mathbf{r}_2$. Far from the walls of the container we expect to find $g(\mathbf{r},\mathbf{r}') = g(|\mathbf{r}-\mathbf{r}'|)$, and the probability of finding a pair of particles a distance r from one another is $g(r)/\rho_0^2$.

For any central force interaction between the particles, we can then write

$$-\mathcal{V} = \frac{1}{2}\sum_{ij,i\neq j} \left\langle \mathbf{r}_{ij}\cdot\frac{\partial u_{ij}}{\partial \mathbf{r}_{ij}}\right\rangle \tag{4.81}$$

$$= \frac{1}{2}\sum_{ij,i\neq j}\int d^3\mathbf{r}_i d^3\mathbf{r}_j|\mathbf{r}_{ij}|u'_{ij}\rho(\mathbf{r}_i,\mathbf{r}_j) \tag{4.82}$$

$$= \frac{N(N-1)}{2}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2|\mathbf{r}_1-\mathbf{r}_2|u'(\mathbf{r}_1-\mathbf{r}_2)\frac{\rho_0^2}{N(N-1)}g(\mathbf{r}_1,\mathbf{r}_2) \tag{4.83}$$

$$= \frac{N^2}{2V^2}\int d^3\mathbf{r}d^3\mathbf{R}|\mathbf{r}|u'(\mathbf{r})g(\mathbf{r}) \tag{4.84}$$

$$= \frac{2\pi N^2}{V}\int_0^\infty dr\ r^3u'(r)g(r) \tag{4.85}$$

where $\mathbf{R}$ is the center of mass of the particles and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the displacement vector between them. The virial is thus related to the (generally unknown, as was the case in the BBGKY) pair distribution of the particles. In the next section we will be

4.5.3 Pressure and the Virial Expansion

So far we have only considered the a central force between the particles, but in a volume there's also an interaction with the wall. We neglected this entirely in the pairwise calculation, but we can include it explicitly by writing

$$-\mathcal{V}_{tot} = -\mathcal{V} - \mathcal{V}_{wall} = \sum_{i<j}\left\langle r_{ij}u'(r_{ij})\right\rangle + \sum_i\left\langle \mathbf{r}_i\cdot\mathbf{F}_i^{wall}\right\rangle \tag{4.86}$$

where $\mathbf{F}_{wall}$ is the change in momentum of a particle due to the collision with a wall. This is effectively a δ function interaction (the wall exerts no force on the particle until the particle comes in contact with it, at which point the force is infinite), but we can still compute the Virial from the hard core wall by noting that the total force due to the wall is $-pdA$ (the pressure times the surface element, pointing inwards). So, the contribution to the virial due to the walls is

$$-\mathcal{V}_{wall} = \left\langle\sum_i r_iF_i\right\rangle = \left\langle\int_{\partial V}\mathbf{r}\cdot d\mathbf{F}\right\rangle \tag{4.87}$$

$$= \left\langle\int_{\partial V}\mathbf{r}\cdot d(p\mathbf{A})\right\rangle \tag{4.88}$$

$$= p\int_V\nabla\cdot\mathbf{r}dV = 3p\int dV = 3pV \tag{4.89}$$

where we have used the fact that the average force on a particle is simply defined as the pressure times the area. In the case of an ideal gas, $\mathcal{V}_{tot} = -3Nk_BT = \mathcal{V}_{wall}$ and we have again found that $pV = Nk_BT$ for an ideal gas.

For a real gas, with pairwise interactions, we know that $\mathcal{V}_{tot} = -3Nk_BT$ and $\mathcal{V}_{wall} = 3pV$, and can rewrite the ideal gas law in terms of a correction due to interparticle interactions:

$$pV = Nk_BT + \frac{1}{3}\sum_{i<j}\Big\langle \mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_{ij}} u(\mathbf{r}_{ij})\Big\rangle \tag{4.90}$$

This relation is useful in a number of contexts. First, it can be used to directly compute the instantaneous pressure of a system in a computer simulation at constant volume, by dropping the averages: $p = \rho k_BT - V^{-1}\sum_{i<j}\mathbf{r}_{ij}\cdot\mathbf{F}_{ij}$ with $\mathbf{F}_{ij} = -\partial u_{ij}/\partial\mathbf{r}_{ij}$. This is far more efficient and accurate than trying to compute a pressure from determining the mean force on the boundary due to collisions, a method that would not be possible to accurately compute for each time step of the simulation. Alternatively, in a simulation at constant pressure eq. 4.90 can be used to set a barostat, in which the the volume is dynamically adjusted to maintain the pressure at a set value. This approach to a barostat is similar to some versions of thermostats, which scale the time or velocity in a simulation to keep $T = \sum m_i v_i^2/3Nk_B$ to be a fixed value to hold temperature fixed. One simple computational method for maintaining a constant pressure which holds p fixed in eq. 4.90 is referred to as a Berendsen barostat. Many other barostats exist, some of which more accurately model the dynamics of molecular systems, but the Berendsen algorithms are efficient and simple to understand.

4.5.4 Virial Coefficients

Eq. 4.90 can also be used to define what's called the virial expansion, used in a wide range of contexts. The last term of eq. 4.90 is expected to depend on the density $\rho = N/V$, since it involves averages over intermolecular interactions, and for $\rho \to 0$ the gas will be dilute enough that the interactions become negligible. In that case, we expect we can write

$$\begin{aligned} P &= \rho k_BT\Big(1 + \frac{2\pi\rho}{3}\int_0^\infty dr r^3 u'(r) g(r)\Big) \qquad (4.91)\\ &= \rho k_BT\Big(1 + a_1\rho + a_2\rho^2 + \cdots\Big) \qquad (4.92)\end{aligned}$$

where the a_i are called Virial coefficients. For complex intermolecular interactions, the Virial coefficients often simplify the problem, by breaking the calculation into pieces dependent on the number of particles interacting in a collision. You can see this by imagining the volume is divided into small bins $\delta v = \delta l^3$ with δl an effective interaction range of the particles (assumed short ranged). The total number of bins is $M_{bin} = V/\delta v$, and the probability of a particle being found in a particular bin $p_{bin} = N/M_{bin} \propto \rho$. For a dilute gas without correlations, the probability of two particles being found in the *same* bin, where interactions may matter, is $p_2 \propto \rho^2$, the probability of three particles being found in the same bin $p_3 \propto \rho^3$, and so on. The first term in eq. 4.92 is proportional to ρ, meaning it does not depend on inter-particle interactions, but rather on the particle interactions with the volume (this is correct, since the first term is the ideal gas term). The second term of the Virial expansion is proportional to ρ^2, which means it includes *only* pair interactions between particles. Needing to only consider two particles often makes this coefficient simpler to calculate than later terms that require additional particles. Computing virial coefficients exactly is generally quite difficult, and usually one must resort to simulations to estimate the virial coefficients. Models accurately describing the third virial coefficient for real fluids took decades to develop, and computational approaches to determine the virial coefficients for complex Hamiltonians is still an area of active research in many fields.

4.6 Harmonic Oscillators

4.6.1 Classical Harmonic Oscillators

It's useful to explicitly compute some of the thermodynamics of different systems that are computationally straightforward. The simplest is that of a system of one-dimensional harmonic oscillators, something that we looked at explicitly in the case of the equipartition theorem. We will generally consider harmonic oscillators to be *distinguishable* particles, because each is oscillating around a fixed point which need not be the same. If we imagine these are oscillations in a lattice, for example, each particle is easily distinguishable from the next because they are all pinned to distinct points in the lattice. The Hamiltonian for N one-dimensional oscillators pinned at locations q_i^0 and confined with a line of length $-L$ and L is

$$H = \frac{1}{2m}\sum_i p_i^2 + \frac{m\omega^2}{2}\sum_i (q_i - q_i^0)^2 \tag{4.93}$$

Note that these are generalized coordinates, so q_i could be the angle of a pendulum just as easily as the coordinates of a harmonically bound particle. If all of those points are the same (e.g. we have N particles pinned to the origin), the oscillators are indistinguishable and we require an additional term of $1/N!$.

The partition function for a system of *distinguishable* oscillators is

$$Q_N = \int \frac{d^N p d^N q}{h^N} e^{-\beta H} = Q_1^N \tag{4.94}$$

where

$$Q_1 = \frac{1}{\lambda}\int_{-L}^{L} dq e^{-\beta m\omega^2 (q-q^0)^2} \approx \frac{1}{\lambda}\int_{-\infty}^{\infty} dq e^{-\beta m\omega^2 (q-q^0)^2} = \frac{1}{\lambda}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2} \tag{4.95}$$

where we have assumed that the oscillators are sufficiently tightly bound to their energy-minimizing locations that they rarely interact with the wall (so we can replace the integral from $-L$ to L

$$Q_N = \frac{1}{h^N}\left(\frac{2\pi m}{\beta}\right)^{N/2}\left(\frac{2\pi}{m\omega\beta}\right)^{N/2} = (\beta\hbar\omega)^{-N} \tag{4.96}$$

If they were indistinguishable, of course, we would simply normalize by $N!$. We can immediately compute all of the thermodynamic properties of this system:

$$\begin{aligned}
U &= -\frac{\partial \log(Q_N)}{\partial\beta} = Nk_BT & (4.97)\\
C_V &= \frac{\partial U}{\partial T} = Nk_B & (4.98)\\
A &= -k_BT\log(Q_N) = 3Nk_BT\log\left(\frac{\hbar\omega}{k_BT}\right) & (4.99)\\
p &= -\frac{\partial A}{\partial V} = 0 & (4.100)\\
S &= -\frac{\partial A}{\partial T}\bigg|_{NV} = \frac{U-A}{T} = k_B\log(Q_N) + \frac{k_B\beta}{Q_N}\frac{\partial Q_N}{\partial\beta} = -Nk_B\log\Big(\beta\hbar\omega\Big) + Nk_B
\end{aligned}$$

Note that the equipartition of energy $U_{HO} = Nk_BT$, which satisfies the equipartition theorem of $U = fk_BT/2$ for $f = 2N$ is the number of quadratic terms in the Hamiltonian (for a one-dimensional oscillator).

4.6.2 Quantum Harmonic Oscillators

Quantum mechanically, there are a discrete set of energy levels for a quantum harmonic oscillator given by $\epsilon_n = (n+1/2)\hbar\omega$. This means that for a single harmonic oscillator in one dimension, the partition function is

$$Q_1 = \sum_n e^{-\beta\hbar\omega(n+1/2)} = e^{-\hbar\omega\beta/2}\sum_{n=0}^{\infty}\Big(e^{-\beta\hbar\omega}\Big)^n = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\hbar\omega\beta/2)} \tag{4.101}$$

For N harmonic oscillators in one dimension, the states are completely independent from one another *so long as they are well-separated*, and we can write

$$Q_N = Q_1^N = 2^{-N}\sinh^{-N}(\hbar\omega\beta/2) \tag{4.102}$$

where each particle is associated with three independent quantum numbers. From this, we can compute a number of thermodynamic variables.

$$A = Nk_BT\log[2\sinh(\hbar\omega\beta/2)] \tag{4.103}$$

Note that for $T \to \infty$ ($\beta \to 0$) we can write $2\sinh(\hbar\beta\omega/2) \approx \hbar\beta\omega + O(\beta^3)$, so the free energy scales as $A \sim Nk_BT\log(\hbar\omega\beta)$. This is identical to the free energy we found for the classical oscillator. Thus, at high temperatures we'll see the same behavior we saw for the classical case. This is entirely consistent with the world we see: quantum mechanics begins to look classical as long as the temperature is high enough (which is why the world we live in looks like it behaves classically!). However, for $T \to 0$ ($\beta \to \infty$) we find $2\sinh(\hbar\beta\omega/2) \sim e^{-\beta\hbar\omega/2} + O(e^{-\beta\hbar\omega/2})$, and so in this limit $A \sim Nk_BT\hbar\omega\beta/2 = N\hbar\omega/2$. This is independent of temperature, and is equal to the sum of the ground state energies of each oscillator.

4.6.3 The physical meaning of the low-temperature limit

Is it physically sensible to find $A \to N\hbar\omega/2$ at low temperatures? To understand the physical meaning of this limit, it is useful to compute the energy,

$$U = -\frac{\partial Q_N}{\partial\beta} = \frac{N\hbar\omega}{2}\coth(\hbar\omega\beta/2) \tag{4.104}$$

which at high temperatures satisfies

$$U = \frac{N\hbar\omega}{2}\coth(\hbar\omega\beta/2) \sim \frac{N\hbar\omega}{2} \times \left(\frac{2}{\hbar\omega\beta} + O(\beta^0)\right) = Nk_BT \tag{4.105}$$

which is the classical limit. However, at low temperatures there is a difference between the classical and quantum energies, since $\coth(x) \to 1$ as $x \to \infty$ so

$$U \sim \frac{N\hbar\omega}{2} \not\to 0 \tag{4.106}$$

as is expected classically. This deviation is due to the fact that quantum systems have a ground state, with each particle having energy $\hbar\omega/2$. This means the system doesn't behave like a classical harmonic oscillator at low temperatures, with with $H = \sum_i p_i^2/2m + \sum_i m\omega_i^2 q_i^2/2$, since the classical oscillator has a lower bound on the energy of $E = 0$. This leads to a violation of the equipartition theorem: the particles cannot be represented by a purely quadratic Hamiltonian, so we do not recover the classically expected energy $U = Nk_BT$ at low temperatures. This marks the first time that anything interesting has happened when we considered quantum mechanics! In the low temperature limit, where we expect quantum effects to matter (based on our argument about λ in the ideal gas case), we finally see that the classical prediction is incorrect!

4.6.4 Entropy and the third law

Since $U \to N\hbar\omega/2$ in the limit of $T \to 0$, we expect that all particles are in the lowest energy state. What implication does that have for the entropy of the system? We can compute the entropy directly and find that

$$S = \frac{U - A}{T} = \frac{k_B \beta N \hbar\omega}{2} \coth\left[\frac{\beta\hbar\omega}{2}\right] - k_B N \log\left(2\sinh\left[\frac{\beta\hbar\omega}{2}\right]\right) \tag{4.107}$$

Taking the $T \to 0$ ($\beta \to \infty$) limit here is a bit more tedious, since simply replacing $\coth(\beta\hbar\omega/2)$ with 1 and $\sinh(\beta\hbar\omega/2)$ with $e^{\beta\hbar\omega/2}$ immediately leads to $S = 0$ in the limit of $T \to 0$. This limit provides no insight into how fast the limit is reached. Instead of simply replacing each function by its limit, we can simplify eq. 4.107 b replacing $x = \hbar\omega\beta/2$ and note that $\coth(x) = (1 - e^{-2x})/(1 + e^{-2x})$ and $2\sinh(x) = e^x(1 - e^{-2x})$. We can then Taylor expand S in terms of $y = e^{-2x}$ to find the $T \to 0$ limit, and a bit of algebra shows that

$$S \approx e^{-\beta\hbar\omega}\left(Nk_B\beta\omega - Nk_B\right) \to 0 \tag{4.108}$$

which vanishes exponentially fast. This is physically sensible, because Eq. 4.106 indicates all of the particles are found in the ground state. If all particles are trapped in exactly the same state, there's no disorder at all, and the probability of being found in any particular state is $P_s = \delta_{s,0}$. With all particles being trapped in the same state, the entropy is expected to be low. Of course, this is also expected from the 3^{rd} law of thermodynamics, which says $S = 0$ at $T = 0$. Taken together, we see that TS is negligible in comparison to U, and so $A = U - TS = N\hbar\omega/2$ is reasonable.

4.7 Particles with internal degrees of freedom

An ideal gas of particles with no internal structure has the partition function $Q_N = Q_1^N/N!$, with $Q_1 = V/\lambda^3$ accounting for the three position integrals and three momentum integrals. A gas of structured particles (say a diatomic molecule) will still have the three center of mass coordinates and momenta to integrate over, but will also have internal positions and momenta to integrate over (the vibrational degrees of freedom for a diatomic gas). These variables are *separable*, meaning we can write

$$Q_1 = \frac{V}{\lambda^3} j(T) \tag{4.109}$$

for some internal partition function $j(T) = \sum_\epsilon g_\epsilon e^{-\beta\epsilon}$. The internal partition function itself can be subdivided into $j(T) = \prod_i j_i(T)$ for various types of internal degrees of freedom. The heat capacity is

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{NV} = Nk_B T \frac{\partial}{\partial T} T^2 \frac{\partial}{\partial T} \sum_i \log[j_i(T)] \tag{4.110}$$

For a monotonic gas, rotational and vibrational degrees of freedom do not exist, and the only degrees of freedom are related to internal spin or angular momentum. For a diatomic gas, vibrational and rotational degrees of freedom play a role. Assuming the vibrational states are harmonic, the partition function will be

$$j_{vib}(T) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{e^{-\Theta_v/2T}}{1-e^{-\Theta_v/T}} \tag{4.111}$$

for the activation temperature $\Theta_v = \hbar\omega/k_B$. If $T \ll \Theta_v$, there will be a negligible contribution to the partition function, meaning this degree of freedom is *frozen*: thermal fluctuations are not large enough to excite the ground state. Classically, such a constraint doesn't exist: there's no ground state and so there will always be the possibility of exciting some vibrations. The rotational degrees of freedom can similarly be written in terms of the angular momentum operator $\hat{H}_{rot} = \hat{L}^2/2I$, with $\hat{L}$ the angular momentum operator with eigenvalues $\hbar^2 l(l+1)$ and I the moment of inertia of the molecule. For a pair of identical point masses separated by a distance d, $I = md^2/2$.

$$j_{rot}(T) = \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T} \tag{4.112}$$

with $\Theta_r = \hbar^2/2Ik_B$. The additional factor of $2l+1$ is due to the degeneracy of the l^{th} energy level, with $-l < m < l$ for the azimuthal quantum number. This sum cannot be evaluated in general, but we can still determine the features of the frozen degrees of freedom: If $T \ll \Theta_r$, there will be no rotations for the diatom since the thermal energy is insufficient to excite the first excited state. Once the temperature is well above Θ_r, many energy levels are excited and the rotational degrees of freedom begin to look classical. We find that $\Theta_r \sim$10K and $\Theta_v \sim$ 100K for a variety of diatomic gasses in general (using common values for e.g. H_2 with parameters $d \sim 10^{-10}$m, $m \sim \times 10^{-26}$kg and $\omega \sim$ 34THz).

For a diatomic atom, then, we expect

- For $T < \Theta_r$, only translational degrees of freedom play a role, and $C_V \sim 3Nk_B/2$. These are classical degrees of freedom, and won't be frozen out unless the temperature is low enough for a classical ideal gas to break down.
- For $\Theta_r < T < \Theta_v$ rotational degrees of freedom play a role as well. Classically, one would expect the system to have two additional momentum degrees of freedom from this, giving $C_V = 5Nk_B/2$.
- For $\Theta_v < T$, one expects the vibrations to give an additional two active quadratic degrees of freedom (momentum in the radial direction and the displacement r), yielding $C_V = 7Nk_B/2$.

For particles with a greater degree of structure (triatomic atoms, coupling between atomic energy levels and the rotational degrees of freedom, etc), additional terms will emerge in the partition function. For any independent degree of freedom, though, it will simply add an additional term to the free energy of the particles, accompanied by its own transition temperature

4.8 Other Examples of Canonical Systems

4.8.1 Classical Paramagnetism

A collection of non-interacting magnetic dipoles with magnetic dipole moments $\boldsymbol{\mu}$ will tend to align with an externally applied field $\mathbf{B}$ with energy $E = -\boldsymbol{\mu} \cdot \mathbf{B}$. $|\boldsymbol{\mu}|$ is a property of the particle, proportional to the current in a loop times the area, $\mu = I \times A$ for a classical dipole and proportional to the Bohr magneton μ_b quantum mechanically (we'll discuss the latter in a moment). The direction the moment points is variable, and a strong magnetic field will tend to align the particles with the field's axis. The magnetic moments of the particles won't be interacting if they're sufficiently well separated, and the potential energy can simply be written $U_{pot} = \sum_i \boldsymbol{\mu}_i \cdot \mathbf{B}_i = B\mu_{i,z}$ for a magnetic field aligned with the z axis. A static arrangement of dipoles are all distinguishable from one another (as was the case for the Harmonic oscillator) and can only rotate without translation so the Hamiltonian doesn't depend on the momentum of the particles (unlike the Harmonic oscillator). Classical paramagnetism thus has the Hamiltonian is $H = -B\sum_i \mu_{i,z}$, and the partition function becomes

$$Q_1 = \int \sin(\theta) d\theta d\phi e^{\beta\mu B\cos(\theta)} = \frac{4\pi}{\beta\mu B}\sinh(\beta\mu B) \tag{4.113}$$

where we don't integrate over the magnitude of $\boldsymbol{\mu}$ (which is fixed). For N distinguishable dipoles we again use the fact that $Q_N = Q_1^N$.

The mean magnetic moment of a single particle, $\langle\mu_z\rangle$, is computed as

$$\langle\mu_z\rangle = \mu\langle\cos(\theta)\rangle = \frac{\partial\log(Q_1)}{\partial(\beta B)} = \mu\bigg(\coth(\beta\mu B) - \frac{1}{\beta\mu B}\bigg) \tag{4.114}$$

For low temperatures or strong fields, with $\beta B \to \infty$, the mean magnetization is $\langle\mu_z\rangle \approx \mu$, with the particles fully aligned with the field as expected. For $T \to \infty$ or $B \to 0$, $\langle\boldsymbol{\mu}\rangle \approx 0$, meaning there is no preferred orientation of the dipoles as expected. We can compute all of the statistics of this system just as we did before for the classical harmonic oscillator, with somewhat more complicated expressions:

$$U = -N\langle\mu_z\rangle B = -N\mu B\bigg(\coth(\beta\mu B) - \frac{1}{\beta\mu B}\bigg) \tag{4.115}$$

$$A = Nk_BT\log\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right) \tag{4.116}$$

$$p = 0 \tag{4.117}$$

$$\frac{S}{k_B} = -N\log\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right)+N\mu B\bigg(\coth(\beta\mu B)-\frac{1}{\beta\mu B}\bigg) \tag{4.118}$$

and so on, where we've ignored energy fluctuations and specific heat to avoid too many tedious derivatives.

One new quantity of use to compute in the case of the classical paramagnet is it's susceptibility to the externally applied field, since that's an easily experimentally accessible observation. For historical reasons, the susceptibility is defined as the increase in the total magnetization of the system to a weak magnetic field, where the total magnetization $\mathbf{M} = N\langle\boldsymbol{\mu}\rangle/V = \rho\langle\boldsymbol{\mu}\rangle$ is the total magnetic dipole moment per unit volume. Note that in chapter **??** we will use a definition of magnetization which does not normalize by volume. This simply introduces a constant into the definition, and will not change the physics of the problem. The magnetic susceptibility is defined as the response of the magnetization to a weakly applied external field, with

$$\chi = \lim_{B\to 0}\frac{\partial M}{\partial B} = \lim_{B\to 0}\frac{N}{V}\times\mu\bigg(-\beta\mu\,\mathrm{csch}^2(\beta\mu B)+\frac{1}{\beta\mu B^2}\bigg) \tag{4.119}$$

$$\approx \frac{N\mu}{V}\bigg(-\beta\mu\left[\frac{1}{\beta\mu B}-\frac{\beta\mu B}{6}\right]^2+\frac{1}{\beta\mu B^2}\bigg) \tag{4.120}$$

$$= \frac{N\mu^2}{V3k_BT} \tag{4.121}$$

where we have Taylor expanded $\mathrm{csch}(x)$ in the approximation. This is known as Curie's law, which states that

$$\chi = \frac{c}{T} \tag{4.122}$$

for c the Curie constant. Curie's law was discovered by Pierre Curie (the husband of Marie Curie) for his PhD dissertation at U Paris in 1895, along with the critical temperature associated with ferromagnetism (which we'll talk about later). As a side note, Pierre and Marie curie both received the Nobel prize for their collaborative discovery of radioactivity, and their children both received Nobel prizes for their collaborative work on radioactive elements thirty years later. We'll be examining Curie's law again once we develop quantum statistical mechanics in a few chapters.

4.8.2 Spin-1/2 paramagnetism and two state systems

Quantum paramagnetism arises due to the interaction of an electron or atom's spin and angular momentum with the externally applied field. Rather than a vector, the magnetic moment is a quantum operator with

$$\boldsymbol{\mu} = g\frac{e}{2m}\mathbf{J} \tag{4.123}$$

where $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is the total angular momentum of the particle (incorporating both spin and angular momentum), and the leading coefficient is difficult to compute directly. The factor $g \approx 2$ is known the Lande factor. Ignoring the difficulty in computing these coefficients (which requires quantum electrodynamics), we expect that the $\hat{\boldsymbol{\mu}}$ operator will be quantized, having discrete values

$$\mu_z = g\frac{e\hbar}{2m}m_\mu = g\mu_B m_\mu \tag{4.124}$$

where the Bohr magneton is $e\hbar/2m$ and m_μ is an integer between $-|l-s|$ and $l+s$. For electrons with spin 1/2 and no angular momentum, or for atoms in the ground state with a single electron in the s-orbital (e.g. H, Li, Na, K, Rb, Cs), the magnetic moment can take on only one of two values: parallel with the magnetic field or antiparallel. Pathria has a calculation that includes other energy levels, which is not particularly illustrative, and here we'll focus only on the two-level system.

The energy levels are defined as $E_n = -\epsilon$ or ϵ, where $\epsilon = g\mu_b$ denotes the energy of a particle aligned with the magnetic field. This system is separable, so we can write the partition function as $Q_N = Q_1^N$. The partition function for a single particle is

$$Q_1 = \sum_i e^{-\beta\epsilon_i} = e^{\beta\epsilon} + e^{-\beta\epsilon} = 2\cosh(\beta\epsilon) \tag{4.125}$$

so,

$$Q_N = 2^N \cosh^N(\beta\epsilon) \tag{4.126}$$

The mean energy of the system is

$$U = -\frac{\partial\log(Q_N)}{\partial\beta} = -N\frac{\partial\log(2\cosh[\beta e])}{\partial\beta} = -N\epsilon\frac{\sinh(\beta\epsilon)}{\cosh(\beta\epsilon)} = -N\epsilon\tanh(\beta\epsilon) \tag{4.127}$$

Taking the limits of high or low temperature:

- As $T \to \infty$, $\beta \to 0$ and we find $U = 0$. That's convenient, it implies equal occupancy: half of the particles have energy ϵ and half have energy $-\epsilon$.
- As $T \to 0$, $\beta \to \infty$ and $\tanh(\beta\epsilon) \to 1$ for all $\epsilon > 1$. That means $U \to -N\epsilon$, which is again expected: the lower energy state is fully occupied.

We can compute the number of particles in the higher energy state, denoted n_+, with $N - n_+$ the number of particles in the lower energy state. We know

$$\epsilon\langle n_+\rangle - \epsilon(N - \langle n_+\rangle) = U \tag{4.128}$$

$$\langle n_+\rangle = \frac{N}{2}\bigg(1 - \tanh(\beta\epsilon)\bigg) \tag{4.129}$$

Fluctuations can also be computed here,

$$\langle E^2\rangle - \langle E\rangle^2 = \frac{\partial^2 \log(Q_N)}{\partial\beta^2} = N\epsilon\frac{\partial\tanh(\beta\epsilon)}{\partial\beta} = N\epsilon^2\mathrm{sech}^2(\beta\epsilon) \tag{4.130}$$

where we ended up with expected behavior again:

- As $T \to \infty$ ($\beta \to 0$), $\langle E^2\rangle - \langle E\rangle^2 = N\epsilon^2$, linear in N and proportional to ϵ^2. This means fluctuations are nonzero, have the proper dimensions, and still satisfy our expectations that the relative RMSD fluctuations scale as $N^{-1/2}$.
- As $T \to 0$ ($\beta \to \infty$), the relative fluctuations vanish exponentially fast. This is because the system is frozen into a single state (all in the lower energy state).

The free energy of such a system is

$$A = -k_B T\log Q_N = -Nk_B T\log(2\cosh(\beta\epsilon)) \tag{4.131}$$

from which we can determine

$$S = \frac{U - A}{T} = Nk_B\log[2\cosh(\beta\epsilon)] - k_B N\epsilon\beta\tanh(\beta\epsilon) \tag{4.132}$$

This shows that in the limit of $T \to \infty$ (where $\beta = 0$), $S = Nk_B\log(2)$, a nonzero value that is the maximum entropy possible for this system. Note that this maximum entropy is independent of the energy levels (ϵ). Entropy is maximized when the various energy levels are equally occupied, regardless of the value of energy (since entropy is fundamentally related to distributions as we have seen in many contexts). In the limit of $T \to 0$, we see $2\cosh(\beta\epsilon) \approx e^{+\beta\epsilon}$, so that $S \to 0$ for $T \to 0$. Just as was the case for the harmonic oscillator, we see the entropy vanishes in the limit of $T \to 0$, due to the fact that each particle is in the lowest energy state, with no disorder.

4.8.3 The Zipper Model

The zipper model appears in Kettel's Thermal Physics, and models the unzipping of a zipper from right to left. This is a simple-minded model of DNA melting (which does not describe the process completely). We consider a 1-dimensional chain of sites, with each site in one of two potential states: open or closed. Opening has the energy penalty ϵ, and the closed state has zero energy. Importantly, a site can only be open if the one to the right of it is also open. Thus, the energy of all links closed is 0, the energy with one link open is ϵ (with no degeneracy), the energy with two links open is 2ϵ (with no degeneracy) and so on. Thus, the partition function is

$$Q_N = \sum_{s \text{ open}} e^{-\beta E_s} = \sum_{s=0}^{N-1} e^{-\beta s\epsilon} = \frac{1 - e^{-N\beta\epsilon}}{1 - e^{-\beta\epsilon}} \tag{4.133}$$

We can easily compute the mean energy

$$\begin{aligned} U &= -\frac{\partial \log(Q_N)}{\partial\beta} = \frac{\partial}{\partial\beta}\bigg(\log[1 - e^{\beta\epsilon}] - \log[1 - e^{-N\beta\epsilon}]\bigg) & (4.134) \\ &= \frac{N\epsilon e^{-N\beta\epsilon}}{1 - e^{-N\beta\epsilon}} - \frac{\epsilon e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} & (4.135) \end{aligned}$$

For small T ($\beta \to \infty$) the mean energy is zero. Expected. For large T ($\beta \to 0$), we have to first order in β

$$U \approx \frac{(N-1)\epsilon}{2} \tag{4.136}$$

We note that we could have gotten these two results without going through the effort of actually computing anything. We can actually compute these limits pretty easily though:

$$U = \frac{\sum_s E_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = \frac{\sum_s (\epsilon s) e^{-\beta\epsilon s}}{\sum_s e^{-\beta\epsilon s}} \tag{4.137}$$

For $T \to \infty$ and $\beta \to 0$, the exponential terms are all close to 1 and the energy levels all contribute equally to the sum, so

$$U(\beta = 0) = \epsilon \frac{\sum_{s=0}^{N-1} s}{\sum_{s=0}^{N-1} 1} = \epsilon \frac{N(N-1)/2}{(N-1)} = \frac{(N-1)\epsilon}{2} \tag{4.138}$$

For $T \to 0$ and $\beta \to \infty$, only the $s = 0$ term in each sum will contribute, since all other terms are exponentially smaller. Since the first term in the numerator is multiplied by s, We can then approximate

$$U(\beta = \infty) \approx 0 \tag{4.139}$$

where we have neglected terms scaling as $e^{-\beta\epsilon}$. Note that the mean number of open links can be extracted from the average energy, with $U = \epsilon \times \langle s \rangle$.

4.8.4 The random link model

The zipper model is straightforward, because it is very easy to evaluate. An equally simple model to evaluate is the random link model, where the left-right asymmetry of the zipper model is not required. If we were to imagine a zipper where openings or closings can happen anywhere along the chain, we would have

$$\begin{aligned}
Q_N &= \sum_{s=0}^{N-1} e^{-\beta\epsilon s} \times (\text{number of ways to have } s \text{ open out of } N-1) \qquad (4.140)\\
&= \sum_{s=0}^{N-1} \binom{N-1}{s} e^{-\beta\epsilon s} = (1+e^{-\beta\epsilon})^{N-1} \qquad (4.141)
\end{aligned}$$

from which the mean energy can be easily computed:

$$-(N-1)\frac{\partial}{\partial\beta}\log[1+e^{-\beta\epsilon}] = \frac{(N-1)\epsilon e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} \tag{4.142}$$

For $T \to 0$ ($\beta \to \infty$)the average energy is 0 again (as it was for the zipper model), since there is an energetic cost for the open state. For $T \to \infty$, the mean energy is again $U = (N-1)\epsilon/2$, as it was for the zipper model. These two models give the same limiting behavior at low and high temperatures. Are there any difference between them?

4.8.5 Differences between the zipper and random link models

The differences in the models are not apparent by looking at the mean energy of the system, but can be seen by looking at the fluctuations of the energy. We know that

$$\langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial\langle E\rangle}{\partial\beta} \tag{4.143}$$

which for the zipper model satisfies

$$\begin{aligned}
\frac{\langle\Delta E^2\rangle_{zipper}}{\epsilon^2} &= \frac{\sum_s s^2 e^{-\beta\epsilon s}}{\sum_s e^{-\beta\epsilon}} - \left(\frac{\sum_s s e^{-\beta s}}{\sum_s e^{-\beta s}}\right)^2 \qquad (4.144)\\
&\to \frac{\sum_s s^2}{\sum_s 1} - \left(\frac{\sum_s s}{\sum_s 1}\right)^2 \qquad \beta \to 0 \qquad (4.145)\\
&= \frac{(N-1)(2N-1)}{6} - \frac{(N-1)^2}{4} \sim \frac{N^2}{12} \qquad (4.146)
\end{aligned}$$

Here the fluctuations in energy are on the order of N^2, not N. This means fluctuations in the zipper model will be over the entire length of the zipper, with the zipper fluctuating between nearly-fully-open and nearly-fully-closed states at equilibrium. For the random model, this is not the case:

$$\frac{\langle \Delta E^2 \rangle_{random}}{\epsilon^2} = \frac{\sum_s \binom{N-1}{s} s^2 e^{-\beta\epsilon s}}{\sum_s \binom{N-1}{s} e^{-\beta\epsilon}} - \left(\frac{\sum_s s \binom{N-1}{s} e^{-\beta s}}{\sum_s \binom{N-1}{s} e^{-\beta s}} \right)^2 \tag{4.147}$$

$$\rightarrow \frac{\sum_s s^2 \binom{N-1}{s}}{\sum_s \binom{N-1}{s}} - \left(\frac{\sum_s s \binom{N-1}{s}}{\sum_s \binom{N-1}{s}} \right)^2 \qquad \beta \rightarrow 0 \tag{4.148}$$

$$= \frac{N(N-1)2^{N-3}}{2^{N-1}} - \left(\frac{(N-1)2^{N-2}}{2^{N-1}} \right) \sim \frac{N}{4} \tag{4.149}$$

which does have the fluctuations scaling linearly with N. The fluctuations in the random model behave as we are used to, with the mean number of links open being sharply peaked around $(N-1)/2$, whereas in the zipper model the mean is $(N-1)/2$ but the fluctuations are much larger and the distribution cannot be called 'sharply peaked.'

4.9 Summary

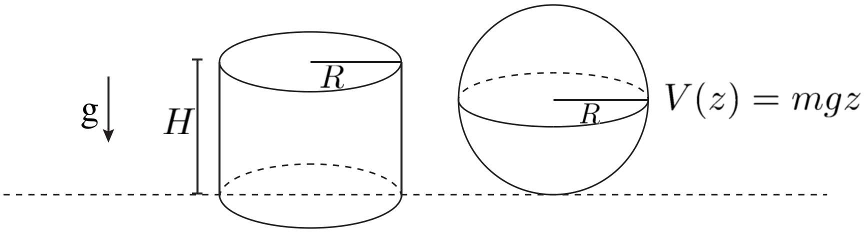
This chapter introduced the partition function for a canonical ensemble, a system at thermal equilibrium with a heat bath. This removes the constraint of fixed energy that was required in the microcanonical ensemble, which was useful only for an isolated system (where no energy can be lost to the environment). The canonical ensemble truly permits heat exchange with a reservoir, and thus is a realistic model for a thermodynamic system at temperature T. We showed that thermodynamic quantities for such a system can be derived by defining a partition function $Q = \sum_\epsilon e^{-\beta\epsilon}$, summing over all accessible energy states normalized by the thermal energy $k_B T$. We put in a good deal of work into developing the tools to extract the ensemble average for quantities of interest (e.g. $U = \langle H \rangle$ or $\langle \mu \rangle$) by manipulating the partition function. We proved a few general theorems, including the Equipartition of energy for quadratic Hamiltonians and the Virial theorem. We found that the quantum mechanical version of these systems behave classically *in the high temperature limit* but do not behave classically in the low temperature limit. The canonical ensemble is fundamental in statistical mechanics, and most of the methods used in this section will be re-used throughout the course.

4.9.1 Homework Problems

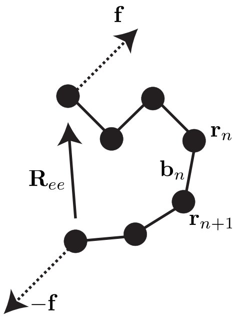
1. Suppose a one-dimensional classical particle has the potential $V(q) = cq^2 - gq^3 - fq^4$, with f and g both small but positive. Show that

$$C_V \approx \frac{3k_B T}{2}\left(\frac{f}{c^2} + \frac{5g^2}{4c^3}\right) \qquad \langle q \rangle \approx \frac{3gk_B T}{4c^2} \tag{4.150}$$

How small must f and g be for these results to be valid?



2. The figure above depicts two different geometries containing N noninteracting indistinguishable classical particles of mass m in a gravitational field: a cylinder with height H and radius R whose axis is aligned with the direction of the gravitational force, and a sphere of radius R. The potential energy for each non-relativistic particle is $V(z_i) = mgz_i$, and both confining volumes are sitting on the ground at $z = 0$ (where $V(z) = 0$). For both geometries, determine the following:
   (a) The partition function Q exactly. Specifically determine Q in the limit of small and large T. Under what conditions do you recover the partition function for an ideal gas?
   (b) The internal energy U for small and large T. Based on this, explain what is happening physically at low and high temperatures.
   (c) The mean height of a particles, $\langle z_i \rangle$, for small and large T. Does the low-T limit agree with your results in 2b? What is the physical meaning of the high-T limit.
3. Consider a Freely Jointed Chain (FJC) in three dimensions under tension: a chain of bonds, each of which has length exactly a, whose directions are randomly chosen.



where $\mathbf{b}_i = |\mathbf{r}_{i+1} - \mathbf{r}_i|$ and with the rigid constraint that $|\mathbf{b}_i| = a$. The end-to-end distance vector is defined as $\mathbf{R}_{ee} = \mathbf{r}_{N+1} - \mathbf{r}_1$, and $Z = \mathbf{R}_{ee} \cdot \hat{\mathbf{f}}$ is the extension along the force axis, with $\hat{\mathbf{f}}$ the unit vector in the direction of the tension. The energy of this system is

$$H = -\sum_{i=1}^{N} \mathbf{f} \cdot \mathbf{b}_i \tag{4.151}$$

(a) Show that the average extension for the FJC is

$$\langle Z \rangle = Na\left[\coth(a\beta f) - \frac{1}{a\beta f}\right] \tag{4.152}$$

Explicitly compute an approximate expression for $\langle Z \rangle$ for small f. *Hint: this looks pretty similar to the expression for the mean magnetic moment in a classical paramagnet. That may be a useful guide.*

(b) Determine the end-to-end fluctuations of the FJC, $\langle Z^2 \rangle - \langle Z \rangle^2$. What does this converge to in the limit of $f \to 0$? From this, infer the value of $\langle \mathbf{R}_{ee}^2 \rangle_{f=0}$ for the FJC.

4. Consider a three dimensional Gaussian chain of bonds under tension, with energy

$$H = \frac{3k_B T}{2a^2} \sum_{i=1}^{N} \mathbf{u}_i^2 - \mathbf{f} \cdot \sum_{i=1}^{N} \mathbf{u}_i \tag{4.153}$$

where $\mathbf{u}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$ is the i^{th} bond vector of the chain and $\mathbf{f}$ is the external tension. The magnitude of $\mathbf{u}_i$ is not constrained in the Gaussian chain (unlike the FJC).

(a) Determine the extension $\langle Z \rangle$ for the Gaussian chain. How does it compare to the $f \to 0$ limit of the FJC?

(b) Compute $\langle \mathbf{R}_{ee}^2 \rangle_{f=0}$ for the Gaussian chain. How does it compare to $\langle \mathbf{R}_{ee}^2 \rangle_{f=0}$ for the FJC from problem 1(b)?

(c) Compute the mean squared fluctuations in the end to end distance, $\langle Z^2 \rangle - \langle Z \rangle^2$. How do the fluctuations depend on f for the Gaussian chain? Do they agree with the FJC?

5. Suppose a diatomic molecule is modeled using the classical Hamiltonian

$$H_2 = \frac{(\mathbf{p}_1^2 + \mathbf{p}_2^2)}{2m} + \frac{\kappa(\mathbf{r}_1 - \mathbf{r}_2)^2}{2} \tag{4.154}$$

representing two particles harmonically bound to one another.

(a) Compute the partition function for N indistinguishable diatomic molecules and determine the mean energy. Does this result agree with the Equipartition and Virial Theorems?

(b) Show that for this model the heat capacity C_V is *not* equal to $7Nk_B/2$, the high-temperature limit of the diatomic molecule described in class. Why is that limit not recovered using this model?

(c) Compute the the root mean square separation $\sqrt{\langle(\mathbf{r}_1 - \mathbf{r}_2)^2\rangle}$ and the mean separation $\langle|\mathbf{r}_1 - \mathbf{r}_2|\rangle$. Are they the same? Do they have the same temperature dependence?

Hint: a change of variables involving the center of mass of the molecule may be helpful in evaluating the position integrals.

6. In contrast to 5 a diatomic molecule is modeled using the classical Hamiltonian

$$H_2 = \frac{(\mathbf{p}_1^2 + \mathbf{p}_2^2)}{2m} + \frac{\kappa(|\mathbf{r}_1 - \mathbf{r}_2| - l)^2}{2} \tag{4.155}$$

with l the rest length of the harmonic bond. Show that for this model the heat capacity C_V *is* equal to $7Nk_B/2$ in the limit of $\kappa \to \infty$. Explain why this model does recover the expected limit. *Note:* you may encounter error functions in this problem.

7. Suppose a triatomic molecule has the classical Hamiltonian

$$H_3 = \frac{(\mathbf{p}_1^2 + \mathbf{p}_2^2 + \mathbf{p}_3^3)}{2m} + \frac{\kappa}{2}\left[(\mathbf{r}_1 - \mathbf{r}_2)^2 + (\mathbf{r}_2 - \mathbf{r}_3)^2 + (\mathbf{r}_1 - \mathbf{r}_3)^2\right] \tag{4.156}$$

representing three particles all bound to one another.

(a) Determine the partition function for N indistinguishable triatomic molecules and the mean energy.

(b) Show that it is generally true that, for any n,

$$\sum_i \langle(\mathbf{r}_i - \mathbf{R})^2\rangle = \frac{1}{n}\sum_{i>j}\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle \tag{4.157}$$

where $\mathbf{R} = n^{-1}\sum_i \mathbf{r}_i$.

(c) Find $\langle(\mathbf{r}_i - \mathbf{R})^2\rangle$, with $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3)/3$ the center of mass of the molecule. Does this mean distance increase or decrease with temperature, and does that make sense physically?

Hint: It may be helpful to know that $\int_{-\infty}^{\infty} dxdy e^{-ax^2-ay^2-bxy} = 2\pi/\sqrt{4a^2 - b^2}$

Chapter 5

The Grand Canonical Ensemble (Pathria Ch 4)

We previously worked out the statistics for a canonical ensemble, a system of N particles in volume V at thermal equilibrium with a heat bath at temperature T. This allowed us to compute the probability of that system at any of its accessible energy values, and we found $p_r \propto e^{-\beta E_r}$. This was useful because we found we could use this to compute the thermodynamics of such systems. However, there is a major limitation of this approach: we've permitted E to fluctuate but N is permanently fixed. To generate the canonical ensemble, we imagined randomly choosing N particles confined to a volume V, which was a artificial but convenient choice. Instead, we now imagine sampling the volume V *without* constraining the number of particles that are found in the volume, and we do so $\mathcal{N}$ times. The total energy will be $\mathcal{E}$ for the $\mathcal{N}$ samples. Sampling without constraining the number of particles in any subsample is a more physically meaningful method of sampling (as it would be very difficult to actually sample holding N and V fixed, but it is very easy to sample a fixed volume without constraint on the number of particles in the volume). This defines the Grand Canonical Ensemble, where the energy and number of particles are allowed to fluctuate when in contact with a reservoir.

5.1 The Grand Canonical Ensemble

5.1.1 The most probable configuration

When we worked out the canonical partition function, we did so by identifying the number of ways to find a given outcome ($W = M!/\prod_s m_s!$ where, m_s were the number of systems with energy level s). Now things are a bit different since the systems can have a different number of particles. The same approach still works, though, we can write

$$W = \frac{M!}{\prod_{rs} n_{rs}!} \approx M\log(M) - \sum_{rs} m_{rs}\log(m_{rs}) \tag{5.1}$$

where n_{rs} is the number of systems *simultaneously* composed of N_r particles with the entire subsystem in energy state s (so we're specifying the total energy, not the individual energies of each particle). This is straightforward to deal with in exactly the same way as before: we maximize W subject to the constraints

$$M = \sum_{rs} m_{rs} \qquad \mathcal{E} = \sum_{rs} \varepsilon_s m_{rs} \qquad \mathcal{N} = \sum_{rs} N_r m_{rs} \tag{5.2}$$

where the first constraint fixes the number of subsystems we're looking at, the second fixes the average energy of all subsystems and the third the average number of particles in the subsystems. Essentially, this means we're choosing the most likely configuration that is consistent with our various constraints on the total behavior of the subsystems. As was the case in the canonical ensemble, we perform this maximization using Lagrange multipliers, finding

$$-\Bigg(\log(m_{rs}) + 1 + \alpha + \beta\varepsilon_s + \delta N_r\Bigg) = 0 \tag{5.3}$$

From this, we find that

$$\frac{m^*_{rs}}{\mathcal{N}} = \frac{e^{-\beta\varepsilon_s - \delta N_r}}{\sum_{rs} e^{-\beta\varepsilon_s-\delta N_r}} \tag{5.4}$$

This is the same thing we computed for the canonical ensemble, except that the probability of finding N_r particles in the system is now exponentially distributed as well. These are the most probable numbers of sates, and we state without proof that $\langle n_{rs}\rangle \approx n^*_{rs}$, just like we did before. Even Pathria doesn't bother to prove this directly, although it has been shown to be the case in the literature.

5.1.2 Connecting to thermodynamics

In order to actually interpret the meaning of β and δ, we now have to link the distribution of states to thermodynamics, as we did before. If we assume that the entropy satisfies the Shannon form, then we immediately find

$$\frac{S}{k_B} = -\sum_{states} p_{state}\log(p_{state}) \quad = \quad \sum_{rs} \frac{e^{-\beta\varepsilon_s-\delta N_r}}{\sum_{r',s'} e^{-\beta E_{r'}-\delta N_{s'}}}\log\left(\frac{e^{-\beta\varepsilon_s-\delta N_r}}{\sum_{r',s'} e^{-\beta E_{r'}-\delta N_{s'}}}\right)]$$

$$= -\frac{1}{\mathcal{Q}}\sum_{rs} e^{-\beta\varepsilon_s-\delta N_r}\Big[-\beta\varepsilon_s-\delta N_r-\log(\mathcal{Q})\Big] \tag{5.5}$$

$$= \beta\langle E\rangle+\delta\langle N\rangle+\log(\mathcal{Q}) \tag{5.6}$$

with $\langle E\rangle$ the average energy of one of our subsystems, $\langle N\rangle$ the average number of particles in one subsystem, and where we have defined the Grand Canonical Partition function

$$\mathcal{Q}=\sum_{rs} e^{-\beta\varepsilon_s-\delta N_r}. \tag{5.7}$$

Rearranging this shows that

$$-\log(\mathcal{Q})=\beta\langle E\rangle-\frac{S}{k_B}+\delta\langle N\rangle \tag{5.8}$$

We recall from chapter 1 that we defined the grand thermodynamic potential as $\Phi = E-TS-\mu N=-pV$ (with independent variables T, μ and V), and a bit of algebra shows that we rewrite this as $-\frac{pV}{k_BT}=\frac{E}{k_BT}-\frac{S}{k_B}-\frac{\mu N}{k_BT}$. From this, we can identify the physical meaning of the grand partition function and the two Lagrange multipliers.

$$-pV=\Phi=-k_BT\log(\mathcal{Q}) \qquad \beta=\frac{1}{k_BT} \qquad \delta=-\frac{\mu}{k_BT} \tag{5.9}$$

There are other methods to show this connection to thermodynamics that do not require the assumption that $S=-\sum p_s\log(p_s)$. Pathria works through this with a different method, but with the same end result. Thus, our Lagrange multipliers turn out to be related to the temperature and chemical potential.

5.1.3 Fugacity

It is generally useful to define the *fugacity*

$$z=e^{\mu/k_BT} \tag{5.10}$$

It's a strange word, and easier to remember by noting it comes from the latin root as 'fugitive,' relating to how particles will leave the system as we'll see in later sections of this chapter. The grand partition function can thus be evaluated as

$$\mathcal{Q}=\sum_r z^{N_r}\sum_s e^{-\beta\varepsilon_s(N_r,V)}=\sum_r z^{N_r}Q_{N_r,V}=\sum_{n=0}^{\infty}z^nQ_n \tag{5.11}$$

relating the grand partition function to the partition function we've already computed. In the last equality, we've assumed that any integer number of particles is possible in a state, which may not always be true for every system (but often is). The grand canonical partition function is in fact a Z-transformation of the canonical partition function. A Z transform is of the form $\tilde{f}(Z) = \sum_{n=0}^{\infty} Z^{-n} f_n$ (note the identity $Z = 1/z$ produces eq. **??**), which is effectively a Laplace transform for a discrete system (where $\tilde{f}(s) = \int_0^{\infty} dx e^{-sx} f(x)$). Much like a Laplace transform, you can easily use a tabulated list of transforms to infer the canonical partition function if you know the grand partition function.

5.1.4 Thermodynamic variables and potentials

We can determine any of our common thermodynamic variables using the grand partition function, similar to what we did before. Specifically, we have

$$\begin{aligned} p &= \frac{k_B T}{V} \log(\mathcal{Q}) && (5.12) \\ N &= k_B T \frac{\partial \log(\mathcal{Q})}{\partial \mu} = z \frac{\partial \log(\mathcal{Q})}{\partial z} && (5.13) \end{aligned}$$

where the average number of particles $N = \langle N \rangle$ can be written in terms of a derivative with respect to μ or with respect to z. We can also compute

$$U = \frac{1}{\mathcal{Q}} \sum_{rs} \varepsilon_s e^{-\beta \varepsilon_s + \beta \mu N_r} = \frac{1}{\mathcal{Q}} \sum_{rs} \varepsilon_s z^{N_r}(\beta) e^{-\beta \varepsilon_s} = -\frac{\partial \log(\mathcal{Q})}{\partial \beta}\bigg|_z \tag{5.14}$$

where the derivative with respect to β now must be performed at constant z when computing quantities involving the energy. Keep this fact in mind when computing the mean energy, as it is easy to accidentally include terms that involve μ if you are not careful. Another thermodynamic quantity is the free energy,

$$\begin{aligned} A = U - TS = -pV + \mu N &= -k_B T \log(\mathcal{Q}) + k_B T \frac{\partial \log(\mathcal{Q})}{\partial \mu} && (5.15) \\ &= \frac{\mu^2}{\beta} \Big(-\frac{1}{\mu^2} \log(\mathcal{Q}) + \frac{1}{\mu} \partial \log(\mathcal{Q}) \Big) && (5.16) \\ &= \frac{\mu^2}{\beta} \frac{\partial}{\partial \mu} \Big(\frac{\log(\mathcal{Q})}{\mu} \Big) && (5.17) \end{aligned}$$

Note that Pathria writes $N\mu = N k_B T \log(z) = k_B T \log(z^N)$, which leads to the expression $A = -k_B T \log(\mathcal{Q}/z^N)$. This is entirely correct, but we will prefer to use eq. 5.17 since the right hand side does not depend on the thermodynamic average N. Note that we can still compute the entropy in the same way as we did in the canonical ensemble, with $S = (U - A)/T$. This expression does not reduce in any meaningful way, and we omit writing it here.

Fluctuations can also be determined with relative ease from the grand partition function, as we saw for the partition function previously. In particular, it's straightforward to see that

$$\langle E^2\rangle - \langle E\rangle^2 = \left.\frac{\partial^2 \log(\mathcal{Q})}{\partial \beta^2}\right|_z \tag{5.18}$$

$$\langle N^2\rangle - \langle N\rangle^2 = (k_BT)^2\frac{\partial^2 \log(\mathcal{Q})}{\partial \mu^2} = z\frac{\partial}{\partial z}z\frac{\partial \log(\mathcal{Q})}{\partial z} \tag{5.19}$$

5.2 The Interpretation of Chemical Potential

5.2.1 Thermodynamic discussion

We discussed the meaning of chemical potential in the context of thermodynamics, but have not revisited the topic since we began discussing statistical mechanics. It is worth restating the discussion from thermodynamics and addressing how chemical potential is to be interpreted in the grand canonical ensemble. In thermodynamics, we found that

$$dA = -SdT - pdV + \mu dN \tag{5.20}$$

so at constant temperature and volume, μ is the free energy required to add a new particle to the system. If $\mu > 0$, you must do work to add a new particle from outside of the system. If $\mu = 0$, there is no energetic cost to adding a particle (for example, adding a photon to a system has a very low chemical potential). If $\mu < 0$, adding a new particle *reduces* the free energy of the system, and it's energetically favorable to add particles.

Thermal equilibrium was discussed extensively in the previous chapters, where two systems were allowed to exchange energy until they equilibrated to be at the same temperature: $T_1 = T_2$ *defines* thermal equilibrium between two systems. This is true of chemical equilibrium as well: at chemical equilibrium two systems that are allowed to exchange particles must settle on having the same chemical potential. This arises from thermodynamics, where the system has the total number of particles $N = N_1 + N_2$ and free energy $A = A_1(N_1) + A_2(N_2)$. At chemical equilibrium,

$$0 = dA = \left.\frac{\partial A}{\partial N_1}dN_1\right|_{TV} + \left.\frac{\partial A}{\partial N_2}\right|_{TV} dN_2 = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_1 - \mu_2)dN_1 \tag{5.21}$$

so $\mu_1 = \mu_2$ at equilibrium.

We can see this directly from the ideal gas in the microcanonical ensemble, where

$$A = U - TS = \frac{3Nk_BT}{2} - T\left[Nk_B\log\left(\frac{V}{N\lambda^3}\right) + \frac{5Nk_B}{2}\right] = -Nk_BT\log\left(\frac{V}{N\lambda^3}\right) - Nk_BT$$

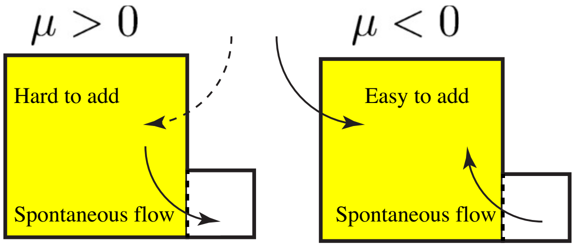


Figure 5.1: Spontaneous motion of particles between the reservoir and subsystem during chemical equilibration. A bath with a large μ will readily add particles to the subsystem and resist the addition of a new particle to the total system of reservoir+subsystem. The opposite is true for negative μ.

$$\mu = \left.\frac{\partial A}{\partial N}\right|_{TV} = -k_B T \log\left(\frac{V}{N\lambda^3}\right) = k_B T \log(\rho\lambda^3) \tag{5.22}$$

Note that we used Helmholtz free energy in this calculation because A is minimized at thermal equilibrium. It's always difficult to add a new particle to an ideal gas, since the particle will collide with the walls increasing the energy (recall that $E \propto N$, so particles increase the energy). However, the addition of a new particle also increases the entropy of the system by adding additional accessible states, and $\mu = \partial U/\partial N|_{SV}$ is the energy associated with adding a particle to the system *at constant entropy*. It is possible for μ to be negative even if particles add energies to the system, due to the change in entropy it brings. We see in particular that $\mu = k_B T \log(\rho\lambda^3) < 0$ for $\rho < \lambda^{-3}$ and $\mu > 0$ for $\rho > \lambda^{-3}$: so for sufficiently dilute gasses the chemical potential is negative and particles can be readily added. Adding new particles increases the chemical potential in the canonical ensemble (since μ increases as $\log(N)$).

5.2.2 Chemical potential in the grand canonical ensemble

In the grand canonical ensemble, we can determine the relationship between the number of particles and the chemical potential for an ideal gas via

$$\mathcal{Q} = \sum_{n=0}^{\infty} \frac{z^n}{n!}\left(\frac{V}{\lambda^3}\right)^n = \exp\left(\frac{zV}{\lambda^3}\right) \tag{5.23}$$

so that the mean number of particles is

$$N = z\frac{\partial \log(\mathcal{Q})}{\partial z} = \frac{zV}{\lambda^3} \tag{5.24}$$

which increases with z (and thus increases with μ for fixed T). That is, if μ is larger (meaning z is larger), the mean number of particles is larger in the grand canonical ensemble. This seems intuitively to violate the thermodynamic definition of chemical potential:

thermodynamically a larger value of μ implies a greater resistance to adding a particle to the system, while in the grand canonical ensemble a larger value of μ implies more particles in the subsystem.

The apparent inconsistency here is due to the fact that the grand canonical ensemble is not isolated, but rather at chemical equilibrium with a bath (diagrammed in Fig. 5.1). The bath has chemical potential μ, and if $\mu > 0$ it is harder to add a new particle to the bath. That means that particles will be more readily removed from the bath and added to the subsystem at high μ, i.e. that particles will spontaneously flow from the bath to the subsystem. Since N is the number of particles found in the subsystem, it is physically meaningful to find N increasing with z, as particles want to leave the reservoir and enter the subsystem spontaneously. At chemical equilibrium, of course, this process will halt when $\mu_{reservoir} = \mu_{subsystem}$. In the opposite limit, if $\mu < 0$ then particles will spontaneously leave the subsystem and enter the bath, since that process is energetically favorable. $\mu < 0$ will reduce the number of particles in the subsystem, consistent with the grand canonical ensemble.

This is completely sensible in the context of chemical equilibrium, but has a number of conceptual implications:

- $\mu = k_B T \log(\rho\lambda^3)$ in the system and reservoir for an ideal gas. Note that this relation depends on the density *in the reservoir* being equal to the density in the subsystem ($\rho_{bath} = \rho_{sys}$), but we are not explicitly defining the reservoir statistics! The volume V_{res} and number $N_{res} = N_{tot} - N$ are not explicitly computed. In the absence of this calculation, the 'correct' value of μ can't be computed explicitly: it depends on the chemical potential of a system we haven't described. Instead of computing μ_{bath}, we simply choose the value of μ to satisfy the observed value of $\langle N \rangle$.
- The internal chemical potential of the entire system of reservoir+subsystem is still $\mu = k_B T \log(\lambda^3\rho)$ (if it's an ideal gas), so increasing N increases the chemical potential. The more particles one adds, the more difficult it is to add particles, as is expected when we refer to internal chemical potential. However, if we *were* to force a particle into the reservoir+subsystem, we would expect to see an increase in $\langle N \rangle$, since we have one more particle in the total system. Thus, as μ (the chemical potential for the entire system) increases, the number of particles in the subsystem increases.

Chemical potential can be a confusing topic in the context of statistical mechanics, because one must consider the reservoir when talking about μ at chemical equilibrium. This is true of temperature too: out of thermal equilibrium the temperature of the cooler system will increase until $T_1 = T_2$. Because we have a more intuitive understanding of temperature from our usual lives, thermal equilibrium often feels relatively natural and obvious.

Chemical potential has properties similar to temperature. In the Grand Canonical Ensemble, the chemical potential is a proper variable we have control over (just like temperature), where μ is controlled physically by adjusting the density of the reservoir (for an ideal gas at least), as in the canonical ensemble we adjust the temperature of the reservoir to change the temperature of the subsystem. However, regardless of the mechanism of control, the chemical potential of the subsystem is most easily chosen such that the value $\langle N \rangle$ matches the experimentally observed value, and is not computed explicitly (since we would need to know the properties of the reservoir).

5.3 Chemical equilibrium between phases

5.3.1 A simple model for ideal gasses and solids

The grand partition function for noninteracting systems is trivial to compute, because we found that $Q_N(V,T) = Q_1(V,T)^N$ for distinguishable and $Q_N(V,T) = Q_1^N(V,T)/N!$ for distinguishable and indistinguishable particles, respectively. For indistinguishable systems this means we can write

$$\mathcal{Q}_{indisting} = \sum_{n=0}^{\infty} z^n \frac{Q_1^n(V,T)}{n!} = e^{zQ_1(V,T)} \tag{5.25}$$

whereas for distinguishable particles, we find

$$\mathcal{Q}_{disting} = \sum_{n=0}^{\infty} z^n Q_1^n(V,T) = \frac{1}{1 - zQ_1(V,T)} \tag{5.26}$$

Note that distinguishable particles have a constraint on the fugacity for the convergence of the grand partition function: $\mathcal{Q}$ converges only if $|zQ_1| < 1$. No such convergence constraint exists for an indistinguishable gas.

For an ideal gas, we determined the partition function was proportional to V, and in this section we define

$$Q_1(V,T) = Vf(T) \qquad \text{ideal gas} \tag{5.27}$$

where we had $f(T) = \lambda^{-3}$ for an ideal gas. Any classical gas whose statistics do not depend on position will have $Q_1 \propto V$ for some constant of proportionality depending on T (which we call $f(T)$). In this case, our thermodynamic variables are easily computed:

$$\begin{aligned} N_{gas} &= z\frac{\partial \log(\mathcal{Q})}{\partial z} = Vzf(T) && (5.28) \\ \langle N_{gas}^2 \rangle - \langle N_{gas} \rangle^2 &= z\frac{\partial N_{gas}}{\partial z} = N_{gas} && (5.29) \end{aligned}$$

Note that the particle fluctuations in the gas phase satisfy $\langle \Delta N_{gas}^2\rangle / \langle N_{gas}^2 \rangle = 1/N_{gas}$, with the relative root mean square fluctuation scaling as $N_{gas}^{-1/2}$. A similar $N_{gas}^{-1/2}$ was found in the root mean square energy fluctuations in the canonical ensemble, and this implies the statistics of the system are sharply peaked around the mean value of N, exactly as we expect from the construction of the grand canonical ensemble.

When we talked about the harmonic oscillator and the paramagnet in Chapter 4, we argued that since they were pinned at distinct locations they were distinguishable. A simple model for a solid phase is a set of particles pinned to a lattice, meaning it is composed of a system of distinguishable particles. Because none of these particles interact with the walls of the container, the canonical partition function for one particle can be written

$$Q_1(V,T) = g(T) \qquad \text{ideal solid} \tag{5.30}$$

with no dependence on the volume. For a 1-dimensional Harmonic oscillator, this was $g(T) = (\beta\hbar\omega)^{-1}$. For these systems, we can take thus $\mathcal{Q}_{disting} = (1 - zg(T))^{-1}$. Thermodynamic variables can again be computed with

$$N_{solid} = \frac{zg}{1-zg}. \tag{5.31}$$

Note that we can solve for z in terms of g and find $z = N_{solid}/[g(T)(N_{solid}+1)]$. This has allowed us to write the fugacity z in terms of the mean number of particles in the solid phase, N. It will often be the case (as discussed below) that we will chose z (or equvialently, μ) to be the value that satisfies $\langle n_r \rangle = N_{solid}$, rather than choosing a specific value of μ and determining N_{solid} from that.

We can also compute the fluctuations in the number of particles

$$\begin{aligned} \langle N_{solid}^2\rangle - \langle N_{solid}\rangle^2 = z_{solid}\frac{\partial\langle N_{solid}\rangle}{\partial z} &= \frac{z_{solid}g}{(1-z_{solid}g)^2} && (5.32)\\ &= N(N+1) && (5.33)\end{aligned}$$

This means $\langle \Delta N\rangle^2/\langle N\rangle^2 \sim N^0$, which imply the fluctuations in the number of distinguishable particles will be enormous: the variance is comparable to the mean, so if we have $N \approx 10^{23}$ particles on average in the solid, there will still be a non-negligible probability of seeing $N = 0$ particles in the system.

Note also that

$$\begin{aligned} U_{indisting} &= -\frac{\partial \log(\mathcal{Q}_{indisting})}{\partial\beta}\bigg|_z = Nk_BT^2\frac{f'(T)}{f(T)} && (5.34)\\ U_{disting} &= -\frac{\partial \log(\mathcal{Q}_{disting})}{\partial\beta}\bigg|_z = Nk_BT^2\frac{g'(T)}{g(T)} && (5.35)\end{aligned}$$

which differ only in the form of the partition function. There is no dependence of the energy in either case on the volume of the system. The pressure can likewise be computed, with

$$\begin{aligned} p_{indisting} &= \frac{k_BT\log(\mathcal{Q}_{indisting})}{V} = zk_BTf(T) && (5.36) \\ p_{disting} &= \frac{k_BT\log(\mathcal{Q}_{indisting})}{V} = -\frac{k_BT}{V}\log(1-zg) && (5.37) \end{aligned}$$

The pressure for the harmonic oscillators vanish for large V, since the particles rarely interact with the walls. It is worth noting that for the ideal gas, $pV = Nk_BT$, and for the ideal solid oscillator $pV = -k_BT\log(1-zg) = k_BT\log(N+1)$. For $N \to \infty$, pV is negligible in comparison to $N\mu$ or U in the solid phase.

5.3.2 Equilibrium between phases

To maintain chemical equilibrium between the phases, it must be that $z_{gas} = z_{solid}$. We note that $\langle N\rangle \propto (1-zg)^{-1}$, so if $z \approx g(T)$ the number of particles found in the solid phase will be large. In this limit, we can write $z_{solid} \approx 1/g(T)$, and combining this with the fact that $z_{gas} = N_{gas}/Vf(T)$ we find that $z_{gas} = z_{solid}$ requires $N_{gas} \approx Vf(T)/g(T) \approx$. Note that this implies $\rho_{gas} = f(T)/g(T)$ is the density of the gas, a function of temperature but not explicitly of the chemical potential.

Importantly, this implies the existence of a critical temperature (see Fig. 5.2) for an equilibrium between solid and gas to exist. If there are N_{tot} particles in the system, equilibrium is impossible if $T > T_c$, where T_c is defined via $f(T_c)/g(T_c) = \rho$ and ρ the density of the gas phase. For $T > T_c$ the ratio $f(T)/g(T) > \rho$ is impossible, since the density of the gas would be larger than the total number N (normalized by the fixed volume V). A solid phase can only form for sufficiently low temperatures, with $T < T_c$, which is determined solely by the ratio of the partition functions of the two phases.

Note that there is a counterintuitive element to this result, since the relative root mean square fluctuations in the gas scale as $\sqrt{\langle N_{gas}^2\rangle/\langle N_{gas}\rangle^2 - 1} \sim N_{gas}^{-1/2}$ but $\sqrt{\langle N_{solid}^2\rangle/\langle N_{solid}\rangle^2 - 1} \sim N_{solid}^0$. One might reasonably wonder how the fluctuations in the number of particles can differ, since one might expect that changes in the particles in the gas phase would be precisely matched by particles in the solid phase. This seeming discrepancy is resolved by noting that *the total number can vary*, since the system is at equilibrium with an external reservoir. In this model, we have not fixed $N_{tot} = N_{solid} + N_{gas}$. We have written a partition function in terms of separable Hamiltonians:

$$\mathcal{Q}_{tot} = \mathcal{Q}_{gas}\mathcal{Q}_{solid} = \sum_n z^n Q_{gas}^n \sum_n z^n Q_{solid}^n = \frac{e^{zQ_{gas}}}{1 - zQ_{solid}} \qquad (5.38)$$

Note that a constraint on the *total* number of particles is not imposed in this. If we wished to have a fixed number of particles, we should instead compute a partition function in the *canonical ensemble* involving coupled Hamiltonians:

$$Q_N^{mixed} = \sum_{n=0}^{N} z^n z^{N-n} Q_{gas}^n Q_{solid}^{N-n} = z^N \sum_{n=0}^{N} Q_{gas}^n Q_{solid}^{N-n} \tag{5.39}$$

where the index n indicates the number of particles in the gas phase, and the number of particles in the gas phase is fixed at $N-n$ for N the total number of particles. Note that if we sum Q_N^{mixed} over all possible values of N, we will find

$$\mathcal{Q}_{tot} = \sum_{N=0}^{\infty} Q_N^{mixed} = \sum_N \sum_n z^n Q_{gas}^n z^{N-n} Q_{solid}^N = \mathcal{Q}_{gas} \mathcal{Q}_{solid} \tag{5.40}$$

which is a trick we will make use of in the next chapter. Variations in the number of particles is irrelevant in the limit of large N_{tot} (since $\langle N_{tot}^2 \rangle - \langle N_{tot} \rangle^2 \propto \langle N_{tot} \rangle$), but as long as there are *many* particles in the system these variations are negligible. Differences in the fluctuations between solid and gas phase must be completely accounted for by excess variation in the total number of particles, but if the variation in the total number is negligible then this difference must also be negligible.

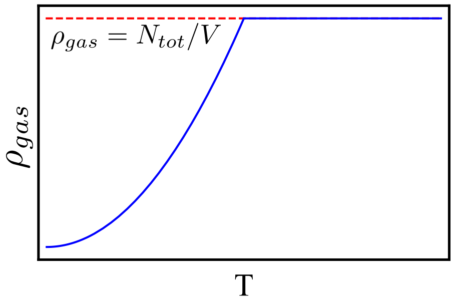


Figure 5.2: Density of the gas phase as a function of temperature for the gas-solid interface for a *fixed* total number of particles in the system. The density of the gas increases with temperature, until reaching T_c at which the density is constant (having value $\rho = N_{tot}/V$) and no particles are in the solid phase. In the grand canonical ensemble, the density of the gas phase is maintained at $\rho_{reservoir}$, with any excess particles being added to the solid phase.

5.4 Summary

In this chapter we've defined the grand canonical ensemble in much the same way as the canonical ensemble. We showed that permitting fluctuations int he number of particles was relatively straightforward in the same manner as fluctuations in energy, and we are able to connect the resulting grand partition function to a number of thermodynamic variables was straightforward. The mechanics of manipulating the grand canonical ensemble is similar to the canonical ensemble, although care is needed in order to remember the differences in how to compute mean properties of these different ensembles (in particular, differentiation with β is risky without accounting for fixed z). The concept of the chemical potential can be easily misinterpreted, because the chemical potential depends on the equilibrium of the system and the reservoir, and the equilibration between these two systems can sometimes feel counterintuitive.

Chapter 6

The Foundations of Quantum Statistics (Pathria Ch 5-6)

Classical statistical mechanics was shown to give physical insight into the meaning of thermodynamics, provided a framework for analyzing many different systems, and made experimentally falsifiable predictions that were later demonstrated to be correct. There's a problem, though: everything we did classically is wrong, and all of the previous chapters rely on fundamentally incorrect assumptions. All particles are truly quantum mechanical, and we did not correctly account for quantum mechanics in the previous chapters. In this chapter, we will more fully consider the meaning of an ensemble and what's meant by the energy in a microstate. We'll find that our treatment of indistinguishability was fundamentally flawed in the previous chapters, correct only at high temperatures, and recover the correct statistics by understanding the underlying quantum mechanics properly. This chapter will give the foundation required for understanding the statistics of particles correctly.

6.1 The Quantum Microcanonical Ensemble

6.1.1 Constant Energy Ensembles

The classical theory of statistical mechanics relied on energy constraints, either through a fixed energy in the microcanonical ensemble or through the Boltzmann weight of a state in the canonical and grand canonical ensembles. The concepts are the same quantum mechanically, but instead of considering a Hamiltonian $H(\{\mathbf{p}_i, \mathbf{r}_i\})$, we need to consider the Hamiltonian operator $\hat{H}$, an operator involving derivatives and not a simple function of momentum or position. Particles in quantum mechanics are represented by the wavefunction ψ, a complex amplitude with $|\psi(\mathbf{x},t)\psi^*(\mathbf{x},t)|$ equal to the probability density of finding the particles within infinitesimal volume elements around positions $\mathbf{x}$ at time t. $\psi(\mathbf{x},t)$ (where $\mathbf{x}$ is a $3N$ dimensional vector, not a 3 dimensional vector of a single particle's position!) will satisfy

$$i\hbar\frac{\partial\psi_i(\mathbf{x},t)}{\partial t} = \hat{H}\psi(\mathbf{x},t) \tag{6.1}$$

The wave functions thus tell us complete statistical information about how the system will evolve in time, in the same way that knowing the positions and momenta of classical particles would.

When we constructed the microcanonical ensemble classically, we treated all arrangements of particles that yielded the fixed total energy E as equally likely to occur. The volume in phase space was given by the number of ways to arrange the particle positions and momenta such that $\sum_i H(\{\mathbf{p},\mathbf{r}\}) = E$. In the quantum world, we cannot simply count the number of ways to arrange the particle positions and momenta, because *the particles don't have well defined positions or momenta.* The entire system is described instead by the wavefunction ψ, which satisfies Schrödingers equation, and we must work instead with energy eigenstates, satisfying $\hat{H}\psi = E\psi$.

6.1.2 Pure states and mixed states

If the energy is not degenerate (e.g. is the ground state of the system), the microcanonical ensemble is remarkably easy to work with in the quantum world: there's only one wavefunction that satisfies the constraint:

$$|\psi\rangle = e^{-iEt/\hbar}|E\rangle \qquad \text{where} \qquad \hat{H}|E\rangle = E|E\rangle \tag{6.2}$$

In principle, we're done in this case: all statistics for our system at energy E is entirely described by $|E\rangle$. This is an important difference between the classical and quantum mechanical case: classically, counting the size of the ensemble of configurations whose energies added up to E was very painful. Quantum mechanically, there's only one solution, and we've solved the problem in one line. It's worth mentioning that there still remains the problem of solving the Schrödinger equation for 10^{23} particles, which is where the painful calculations would enter into the microcanonical ensemble. We'll leave that aside for the moment.

If there is no degeneracy in the energy levels (so $|E\rangle$ is the unique solution to Schrödinger's equation with eigenvalue E), we are guaranteed that the system is found in that state. If we were to imagine having M copies of the same isolated microcanonical system at energy

E, all of them would have to be found in the same non-degenerate state $|E\rangle$. For this reason, such a state is termed a *pure* state.

For a degenerate energy, with $\{|E_d\rangle\}$ the set of degenerate solutions to $\hat{H}|E_d\rangle = E|E_d\rangle$ and $\langle E_d|E_{d'}\rangle = \delta_{dd'}$, the system can be found in some linear combination of any of those states. If we were to have M copies of the same isolated microcanonical system, the k^{th} wavefunction for the system in the energy eigenbasis will be described by

$$|\psi^k\rangle = \sum_d a_d^k(t)|E_d\rangle \tag{6.3}$$

with a_d^k the amplitude of the state $|E_d\rangle$ and $|\langle E_d|\psi^k\rangle|^2 = |a_d^k|^2$ the quantum mechanical probability of being found in the state $|E_d\rangle$. Note that $|a_d^k|^2$ is unrelated to the concept of a thermal probability distribution (we'll get to that soon though).

If we were to imagine sampling the wavefunction of these isolated systems an enormous number of times ($M \to \infty$), we expect that the probabilities of seeing any of the degenerate states must be equal in the microcanonical ensemble: $M^{-1}\sum_k |a_d^k|^2$=const, independent of the index d. This assumption of *equiprobability* (which we used in the classical microcanonical ensemble) asserts that there is an equal probability of being found in any degenerate eigenstate (that is, each $|E_d\rangle$ is just as likely to be observed as any other). This was sensible classically and remains sensible quantum mechanically: if there is only a constraint on energy there is no reason to expect one eigenstate to occur more often than another. We can then compute the probability of being found in a particular energy state in terms of the *ensemble average* of $|a_d^k|^2$ using our equiprobability assumption. We can write

$$Prob(\text{being in state } |E_d\rangle) = \left\langle |\langle E_d|\psi\rangle_q|^2 \right\rangle = \frac{1}{M}\sum_k |a_d^k|^2 = \frac{1}{\Omega} \tag{6.4}$$

where Ω is the number of accessible states that satisfy the energy constraints (the number of $|E_d\rangle$). Eq. 6.4 is a mixture of a quantum mechanical inner product between the measured state and one of the degenerate eigenstates of the energy (a quantum average, denoted $\langle\cdots\rangle_q$), and an ensemble average over all of our M samples. The right hand side of eq. 6.4 is a constraint coming from statistical mechanics: equiprobability of indistinguishable states. All of this mirrors the calculation we made classically: a system state was the collection $\{\mathbf{p}, \mathbf{r}\}$, and the probability of being found in any particular state was uniform. This will provide a useful guide for how to compute thermal averages in the next section.

6.2 The density operator

6.2.1 Density and probability

Statistical mechanics was successful in computing the average of a wide range of classical observables by noting that

$$\langle X\rangle_{classical} = \sum_n X_n p_n \tag{6.5}$$

where p_n was the probability of being found in some state n and X_n the value of the observable in that state. We can use this idea quantum mechanically to determine the thermal average of an operator. This is simplest in the microcanonical ensemble, but we will see the idea works in the canonical and grand canonical ensembles as well.

In the microcanonical ensemble, each of our samples can be written in terms of the degenerate eigenstates $|E_d\rangle$, with $|\psi^k\rangle = \sum_d a_d^k |E_d\rangle$. In that case, we can write the quantum mechanical average

$$\begin{aligned}\langle\hat{O}\rangle_q \langle= \psi^k|\hat{O}|\psi^k\rangle &= \sum_{dd'} \langle\psi|E_d\rangle O_{dd'} \langle E_d'|\psi\rangle &(6.6)\\ &= \sum_{dd'} (a_d^k)^* a_{d'}^k O_{dd'} &(6.7)\end{aligned}$$

where $O_{dd'} = \langle E_d|\hat{O}|E_{d'}\rangle$ is the matrix element of the operator over the basis $\{|E_d\rangle\}$. Note that if the operator $\hat{O}$ commutes with the Hamiltonian, this matrix representation is diagonal in the microcanonical ensemble, with $O_{dd'} = O_d\delta_{dd'}$.

We can determine the statistical average

$$\begin{aligned}\left\langle \langle\psi^k|\hat{O}|\psi^k\rangle \right\rangle &= \frac{1}{M}\sum_k \sum_{dd'} (a_d^k)^* a_{d'}^k O_{dd'} &(6.8)\\ &= \sum_{dd'} O_{dd'}\rho_{d'd} &(6.9)\end{aligned}$$

where we have defined the matrix elements for the density operator

$$\rho_{d'd} = \frac{1}{M}\sum_k (a_d^k)^* a_{d'}^k \tag{6.10}$$

This produces a surprising feature of a statistical average of a quantum mechanical observable: the average is a product of a statistical property (the density matrix, which is independent of the observable in question), and a quantum average (which is independent of the statistics of the system).

In the case of an operator that communtes with the Hamiltonian, we've already noted that the matrix representation of $\hat{O}$ is diagonal. This has a useful interpretation, with

$$\langle\langle\hat{O}\rangle_q\rangle = \sum_d \rho_d O_d \tag{6.11}$$

where $\rho_d = \rho_{dd}$ are the diagonal elements of the density operator. This is suggestive of the role that the density operator plays, since it is very similar to the classical statistical average of $\langle X\rangle = \sum_n p_n X_n$. The classical function X has been replaced by a quantum mechanical average of the operator, and the probability has been replaced by the diagonal density elements ρ_d. We will see that this analogy holds true at equilibrium.

6.2.2 Density in an arbitrary basis

In the microcanonical ensemble, the degenerate basis $\{|E_d\rangle\}$ was a natural choice for the basis of $|\psi^k\rangle$, but any basis could be chosen. If we choose instead to write $|\psi^k\rangle = \sum_n a_n^k|\phi_n\rangle$ for some orthonormal basis $|\phi_n\rangle$. We can compute the density operator in the same way as in the previous section, with

$$\begin{aligned}
\left\langle\langle\psi^k|\hat{O}|\psi^k\rangle\right\rangle &= \frac{1}{M}\sum_k\langle\psi^k|\hat{O}|\psi^k\rangle = \frac{1}{M}\sum_k\sum_{nm}(a_n^k)^* a_m^k\langle\phi_n|\hat{O}|\phi_m\rangle & (6.12)\\
&= \sum_{nm} O_{nm}\frac{1}{M}\sum_k (a_n^k)^* a_m^k & (6.13)\\
&\equiv \sum_{nm} O_{nm}\rho_{mn} & (6.14)
\end{aligned}$$

where we have defined the matrix elements

$$\rho_{mn} = \frac{1}{M}\sum_k (a_n^k)^* a_m^k \tag{6.15}$$

In any basis, we expect that $\rho_{nm}^* = \rho_{mn}$, implying that $\hat{\rho}^\dagger = \hat{\rho}$.

6.2.3 The quantum Liouville's theorem

Let's return to our sampling of the configuration of the system, generating M states $\{|\psi^k\rangle\}$ in any ensemble. First, we note that

$$i\hbar\frac{\partial}{\partial t}|\psi^k\rangle = \hat{H}|\psi^k\rangle = \sum_n a_n^k(t)\hat{H}|n\rangle = \sum_n a_n^k(t)\sum_m |m\rangle\langle m|\hat{H}|n\rangle = \sum_{nm} a_n^k(t) H_{mn}|m\rangle \tag{6.16}$$

where $\{|n\rangle\}$ is the energy eigenbasis. This can be combined with the fact that $|n\rangle$ is independent of time, so $\partial|\psi^k\rangle/\partial t = \sum_m \dot{a}_n^k(t)|n\rangle$, to find

$$\dot{a}_n^k(t) = \frac{1}{i\hbar}\sum_m H_{nm}a_m^k(t) \tag{6.17}$$

Knowing $\dot{a}_n^k(t)$, we can work out the time evolution of the density. This is simplest in the energy eigenbasis (with $\langle n|\hat{H}|m\rangle = E_n\delta_{nm} = H_{nm}$), but any basis will follow the same result:

$$\begin{aligned}
\frac{\partial\rho_{nm}}{\partial t} &= \frac{1}{M}\sum_k \left[(\dot{a}_n^k)^* a_m^k + \dot{a}_m^k (a_n^k)^*\right] && (6.18)\\
&= \frac{1}{M}\sum_{k=1}^{M}\left[\left(\sum_{l=0}^{\infty}\frac{H_{nl}a_l^k}{i\hbar}\right)^* a_m^k - (a_n^k)^*\left(\sum_{l=0}^{\infty}\frac{H_{ml}a_l^k}{i\hbar}\right)\right] && (6.19)\\
&= -\frac{1}{i\hbar}\sum_l \Big(H_{nl}\rho_{lm} - \rho_{nl}H_{ml}\Big) && (6.20)\\
&= \frac{(-\hat{H}\hat{\rho} + \hat{\rho}\hat{H})_{nm}}{i\hbar} && (6.21)
\end{aligned}$$

This result is true for all elements n and m, meaning we finally find

$$\frac{\partial\hat{\rho}}{\partial t} + \frac{[\hat{\rho},\hat{H}]}{i\hbar} = 0 \tag{6.22}$$

which is the quantum mechanical analogue of Liouville's theorem. This can be compared to the classical

$$\frac{\partial\rho}{\partial t} + [\rho, H] = 0 \qquad\qquad [\rho, H] = \sum_i \frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i} \tag{6.23}$$

which says something related (but not identical) to the quantum version in eq. 6.22. The conserved 'volume in phase space' is no longer meaningful, since there is an nonzero probability of being found anywhere in phase space. The mental picture is still useful if you think of the 'volume in phase space' being fuzzy, where regions of high density can 'move' and also become wider or sharper, but it's important to recognize that the volume in phase space is not strictly conserved, because particles don't have precise locations or momenta. However, a very useful aspect of the quantum Liouville equation is that at equilibrium (where $\partial\rho/\partial t = 0$) the density and Hamiltonian operators commute. This means that they can both be simultaneously diagonalized at equilibrium (they share a basis set) and that $\hat{\rho}$ can (at equilibrium) be represented as a function solely in terms of $\hat{H}$ (or other operators that commute with $\hat{H}$.

6.3 The density operator and partition functions in the ensembles

6.3.1 Classical probabilities in the ensembles

At equilibrium, the density operator must commute with the Hamiltonian. That means that we can write the statistical average for *any* statistical ensemble (MCE, CE, or GCE) as

$$\Big\langle \langle\psi^k|\hat{O}|\psi^k\rangle \Big\rangle = \frac{1}{M}\sum_k \langle\psi^k|\hat{O}|\psi^k\rangle = \frac{1}{M}\sum_k\sum_{nm}(a_n^k)^* a_m^k \langle\phi_n|\hat{O}|m\rangle \tag{6.24}$$

$$= \sum_{nm} O_{nm}\rho_n\delta_{nm} \tag{6.25}$$

$$= \sum_n \rho_n \langle n|\hat{O}|n\rangle \tag{6.26}$$

As mentioned previously, this has the precise form of an average if we recognize ρ_n as the *probability of being found in the state* $|n\rangle$.

This is consistent with what we saw in the microcanonical ensemble, where $\rho_n = \Omega^{-1}$ was the probability of being found in a particular state. We can further derive the equilibrium density operator by realizing we have already determined the probability of being found in any state.Classically, we found that the probability of finding the system in a particular state in the canonical and grand canonical ensemble.

$$P_{canon}(\epsilon) = \frac{e^{-\beta\epsilon}}{\sum_\epsilon e^{-\beta\epsilon}} \qquad\qquad P_{grand}(\epsilon) = \frac{z^n e^{-\beta\epsilon}}{\sum_{n,\epsilon} z^n e^{-\beta\epsilon}} \tag{6.27}$$

with the denominators the partition and grand partition functions, respectively.

We can thus write the probability of finding a state with energy E_n at thermal equilibrium in a bath of temperature T in the canonical ensemble:

$$\rho_{nm} = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}\delta_{nm} \tag{6.28}$$

so we can write

$$\hat{\rho} = Q_N^{-1}\sum_n e^{-\beta E_n}|n\rangle\langle n| = \frac{e^{-\beta\hat{H}}}{Q_N}\sum_n |n\rangle\langle n| = \frac{e^{-\beta\hat{H}}}{Tr(e^{-\beta\hat{H}})} \tag{6.29}$$

where

$$Tr(e^{-\beta\hat{H}}) = \sum_n e^{-\beta H_{nn}} = \sum_n \langle n|e^{-\beta\hat{H}}|n\rangle = \sum_n e^{-\beta E_n} = Q_N \tag{6.30}$$

The grand canonical ensemble is derived in exactly the same way, with the addition of a number operator $\hat{n}$ counts the number of particles (of the form $a^\dagger a$) that commutes with the Hamiltonian and counts the number of particles in the system. Repeating these calculations for the grand canonical ensemble shows that

$$\hat{\rho}_{GCE} = \frac{e^{-\beta\hat{H}+\beta\mu\hat{n}}}{Tr(e^{-\beta\hat{H}+\mu\beta\hat{n}})} \tag{6.31}$$

which has all of the properties we've discussed before: diagonal in the energy basis and fundamental for computing the mean values of various observables.

6.3.2 Properties of the trace

If the chosen basis is one that diagonalizes the density operator, $\rho_{nm} = p_n\delta_{nm}$ is the probability of being found in state n. However, if the density is not diagonal in the density, no individual matrix element can be viewed as a probability. The interpretation of a probability is *dependent* on the basis you choose. Despite this issue with the interpretation of the matrix elements, averages computed with the density operator are independent of the basis. We can see this by defining the trace of an operator as the sum of its diagonal elements, $Tr(A) = \sum_n A_{nn} = \sum_n \langle n|A|n\rangle$. We see that the average of any operator is

$$\begin{aligned} \langle\langle\hat{O}\rangle_q\rangle &= \sum_{mn} O_{nm}\rho_{mn} = \sum_{nm}\langle n|\hat{O}|m\rangle\langle m|\hat{\rho}|n\rangle & (6.32)\\ &= \sum_n \langle n|\hat{O}\hat{\rho}|n\rangle = Tr(\hat{O}\hat{\rho}) & (6.33)\end{aligned}$$

Averaging is thus simply computing a trace over the operator multiplied by the density. Again, this is consistent with eq. **??**.

Since the interpretation of the density operator's elements as a probability is dependent on the basis we choose, it is natural to wonder if the average value of $\langle\langle O\rangle_q\rangle$ depends on the chosen basis. We expect it should not (after all, the physical value of an observable is not basis dependent), and can compute

$$\begin{aligned} Tr(A) &= = \sum_n \langle n|A|n\rangle = \sum_{nmm'} \langle n|\phi_m\rangle\langle\phi_m|A|\phi_{m'}\rangle\langle\phi_{m'}|n\rangle & (6.34)\\ &= \sum_{mm'}\langle\phi_m|A|\phi_{m'}\rangle\sum_n\langle n|\phi_m\rangle\langle\phi_{m'}|n\rangle & (6.35)\\ &= \sum_{mm'}\langle\phi_m|A|\phi_{m'}\rangle\langle\phi_{m'}|\phi_m\rangle & (6.36)\\ &= \sum_m\langle\phi_m|A|\phi_m\rangle & (6.37)\end{aligned}$$

were we made use of the fact that $1 = \sum_n |n\rangle\langle n|$ for any complete orthonormal basis. Thus, regardless of our basis-dependent interpretation of the matrix elements of ρ, we can still compute the mean of any operator without concern about the basis. We also might be concerned that ρ operates from the right, but we have not assumed that ρ commutes with $\hat{O}$. Physically, we again expect that the observed mean should be independent of the mathematical details, and find $Tr(\hat{A}\hat{B}) = Tr(\hat{B}\hat{A})$ for all operators:

$$\begin{aligned} Tr(AB) &= \sum_n \langle n|AB|n\rangle = \sum_{nm} \langle n|A|m\rangle\langle m|B|n\rangle && (6.38) \\ Tr(BA) &= \sum_m \langle m|BA|m\rangle = \sum_{nm} \langle m|B|n\rangle\langle n|A|m\rangle && (6.39) \end{aligned}$$

which are the same.

6.4 A single particle in a box

If we imagine having a single particle in a box (*not* a collection of 10^{23} particles yet), we can work out the statistics of the particle in the canonical ensemble. Its possible to compute the mean energy as $\langle\langle \hat{H}\rangle_q\rangle$, with

$$\langle\langle \hat{H}\rangle_q\rangle = \frac{Tr(\hat{H}e^{-\beta\hat{H}})}{Tr(e^{-\beta\hat{H}})} = \frac{\sum_n \langle n|\hat{H}e^{-\beta\hat{H}}|n\rangle}{\sum_n \langle n|e^{-\beta\hat{H}}|n\rangle} = \frac{\hbar^2\pi^2}{2mL^2}\frac{\sum_{\mathbf{n}} \mathbf{n}^2 e^{-\beta\hbar^2\pi^2\mathbf{n}^2/2mL^2}}{\sum_{\mathbf{n}} e^{-\beta\hbar^2\pi^2\mathbf{n}^2/2mL^2}} \tag{6.40}$$

Note that this precisely equivalent to computing $\langle \hat{H}\rangle = -\partial \log(Q_N)/\partial\beta$, as we found classically. We can replace the sum by an integral (assuming $\hbar^2\pi^2/2mL^2 \ll 1$) by writing $\Delta q = 1/L$ and $q = n/L$,

$$\langle \hat{H}\rangle \approx 3 \times \frac{\hbar^2\pi^2}{2m}\frac{\int dqq^2 e^{-\beta\hbar^2\pi^2 q^2/2m}}{\int dxe^{-\beta\hbar^2\pi^2 q^2/2m}} = \frac{3}{2\beta} \tag{6.41}$$

so the quantum statistics for a single free particle still satisfy the equipartition of energy. It's also possible to compute the entropy via $S = -k_B Tr(\hat{\rho}\log(\hat{\rho}))$, the free energy via $A = U - TS$, and all of the other thermodynamic quantities we found classically.

Quantum mechanically, we can compute a few new things as well. Classically, we assumed every particle was point-like, but claimed that the thermal wavelength λ somehow represented its 'size' in quantum mechanics. We can precisely determine the physical particle density in space by recognizing that $\langle \mathbf{r}|\hat{\rho}|\mathbf{r}'\rangle$ represents the average amplitude of the overlap between two positions $\mathbf{r}$ and $\mathbf{r}'$. If $\mathbf{r} = \mathbf{r}'$, this quantity is $\langle \mathbf{r}|\hat{\rho}|\mathbf{r}'\rangle = p(\mathbf{r})$ is the probability density as a function of position in space (the probability of being found at $\mathbf{r}$). These quantities can be computed via

$$\begin{aligned}
\langle \mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle &= \sum_{nm}\langle \mathbf{r}|n\rangle\langle n|e^{-\beta\hat{H}}|m\rangle\langle m|\mathbf{r}'\rangle && (6.42)\\
&= \left(\frac{2}{L}\right)^3\sum_{\mathbf{n}} e^{-\beta E_{\mathbf{n}}}\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right) && (6.43)\\
&\qquad\qquad\times\sin\left(\frac{n_x\pi x'}{L}\right)\sin\left(\frac{n_y\pi y'}{L}\right)\sin\left(\frac{n_z\pi z'}{L}\right)
\end{aligned}$$

which is a terribly unwieldy expression. While we can't perform the sum exactly, in the limit of $L\to\infty$ we can write the sums $\sum_{n=0}^{\infty} f(an/L)\approx L\int_0^\infty du f(au)$. This gives

$$\begin{aligned}
\frac{2}{L}\sum_n e^{-\beta n^2\pi^2\hbar^2/2mL^2}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi x'}{L}\right) &\approx 2\int_0^\infty dq e^{-\beta\pi^2\hbar^2q^2/2m}\sin(x\pi q)\sin(x'\pi q)\\
&= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\left(e^{-m(x-x')^2/2\beta\hbar^2}-e^{-m(x+x')^2/2\beta\hbar^2}\right)\\
&\approx \frac{1}{\lambda}e^{-2m\pi^2(x-x')^2/\beta h^2} && (6.44)\\
&\approx \frac{1}{\lambda}e^{-\pi(x-x')^2/\lambda^2} && (6.45)
\end{aligned}$$

with the approximation due to the fact that the second exponential term is always small far from the walls, and we've used the definition $\lambda^2=h^2/2\pi mk_BT$ for the thermal wavelength. Then

$$\langle \mathbf{r}|e^{-\beta\hat{H}}|\mathbf{r}'\rangle\approx\frac{1}{\lambda^3}e^{-\pi|\mathbf{r}-\mathbf{r}'|^2/\lambda^2} \tag{6.46}$$

The partition function can be evaluated in a number of different ways, but we can do so explicitly by using the position basis

$$Q_1=Tr(e^{-\beta\hat{H}})=\int d^3\mathbf{x}\langle\mathbf{x}|e^{-\beta\hat{H}}|\mathbf{x}\rangle=\frac{V}{\lambda^3} \tag{6.47}$$

which is the partition function for the ideal gas we've already derived. Here the important thing is that one can use $\langle\mathbf{x}|e^{-\beta\hat{H}}|\mathbf{x}'\rangle$ to determine the mean of *any* operator that involves position (e.g. the mean of $|\mathbf{x}|^{-1}$), so that a variety non-trivial averages can be computed.

We also find that

$$\rho(\mathbf{r},\mathbf{r}')=\langle\mathbf{r}|\hat{\rho}|\mathbf{r}'\rangle=\frac{e^{-m(\mathbf{r}-\mathbf{r}')^2/2\beta\hbar^2}}{V}=\frac{e^{-\pi(\mathbf{r}-\mathbf{r}')^2/\lambda^2}}{V} \tag{6.48}$$

which measures the width of the distribution of the location of a particle centered at $\mathbf{x}$ (or $\mathbf{x}'$). It's of course symmetric about the center, and if $\mathbf{x} = \mathbf{x}'$ we find the density is uniform in the container, $\rho(\mathbf{x}, \mathbf{x}) = V^{-1}$. The exponential term decays over a length scale $\hbar^2\beta/m = \lambda^2/(2\pi)$, meaning that the thermal wavelength is indeed (on the same order of) the effective size of a quantum particle at temperature T.

6.5 Indistingishable Quantum Particles

6.5.1 Wavefunction for multiple particles

The previous section applies to a single particles only, and we did not compute the wavefunction for a collection of particles. For a collection of particles, we expect to have the Schrödinger equation

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + V(\mathbf{r}_1, \ldots, \mathbf{r}_N) \qquad \hat{H}\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{6.49}$$

which may be a highly non-trivial problem to solve if V is unfriendly. However, if the particles are non-interacting, life becomes much simpler. In that case, we can write a (possibly non-unique) solution:

$$\hat{H} = \sum_i \left(-\frac{\hbar^2}{2m}\nabla_i^2 + V(\mathbf{r}_i) \right) \tag{6.50}$$

$$\Psi_E(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \prod_i \psi_{\epsilon_i}(\mathbf{r}_i) \tag{6.51}$$

where the $\psi_\epsilon(\mathbf{r}_i)$ is the wavefunction for a single particle under the single particle hamiltonian, $(-\hbar^2\nabla^2/2m + V)\psi_\epsilon = \epsilon\psi_\epsilon$. This immediately implies the product of ψ_ϵ's is an eigenstate of the entire hamiltonian with energy $E = \sum_i \epsilon_i$. If we suppose we order the energies to be $0 < \epsilon_1 < \epsilon_2 < \ldots$, we can specify the state with n_1 particles at energy level ϵ_1, n_2 particles at energy level ϵ_2, and so on, by writing

$$\Psi_E(\{\mathbf{r}_i\}) = \prod_{i=1}^{n_1}\psi_{\epsilon_1}(\mathbf{r}_i) \times \prod_{i=n_1+1}^{n_1+n_2}\psi_{\epsilon_2}(\mathbf{r}_i) \times \cdots \tag{6.52}$$

with the constraints

$$N = \sum_i n_i \qquad E = \sum_i n_i\epsilon_i \tag{6.53}$$

We are starting to recognize elements from the canonical ensemble here! Note that here we've assumed there is no degeneracy in the energy levels; this argument is more tedious if that's not assumed, but it's possible to construct a similar solution.

6.5.2 Indistinguishability and permutations

Indistinguishability of the particles was a major theme when we talked about the canonical ensemble, and it is worth thinking about distinguishability quantum mechanically. It turns out, we'll be able to explicitly compute the Gibbs correction of $N!$ for indistinguishable particles. When we worked out the indistinguishability of particles in the classical case, we made the following argument: if we were to pick up two different particles that had two different energies, we would be able to tell them apart. We used the correction $N!$ in the continuous case (the number of permutations of the indexes of the particles). In the discrete case the appropriate classical correction factor is the number of ways to permute $\{n_i\}$ particles among the energy levels, $N!/\prod_i n_i!$, which we used when generating the classical canonical ensemble.

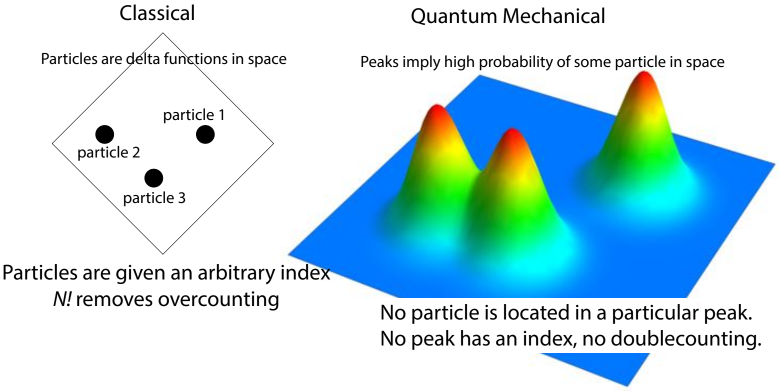


Figure 6.1: A hypothetical distribution of three particles in classical phase space and the corresponding quantum mechanical analog. Classical particles have an index that are arbitrary and lead to double-counting if they are indistinguishable. Quantum wavefunctions have peaks associated with greater density of particles, but no single particle is found anywhere, and no peak (the equivalent of a classical particle) is given an index.

This analysis is incorrect in the quantum case, where the permutation between two particles must still represent exactly the same state. This is diagrammed in Fig. 6.1, which shows a hypothetical wavefunction sampled in the ensemble. Quantum mechanical particles are not δ function distributed, but instead are distributed according to the wavefunctions. This means two things:

- Since high-density locations aren't given an index, we are not going to be overcounting in quantum statistical mechanics. We don't need to include an ad hoc normalization of $1/N!$.

- The wavefunction *must* explicitly account for the fact that all identical particles contribute to the total wavefunction identically, so permutation of particle index *cannot* change the wavefunction.

Similarly, we can consider a hypothetical case of two noninteracting particles with the total system having energy $E = \epsilon_1 + \epsilon_2$. While the wavefunction is composed of two particles with two energy levels ϵ_1 and ϵ_2, *neither particle has that energy.* The state of each particle is entangled, with both particles contributing to the higher energy level and both contributing to the lower energy level. The permutation of particle indices is thus *already built into the wavefunction*, and instead of including a correction factor to account for the fact that the index is arbitrary, we simply need to accurately determine the wavefunction. Specifically, if we have two eigenfunctions of the Hamiltonian,

$$\begin{aligned} \hat{H}\psi_{\epsilon_1}(\mathbf{r}_1)\psi_{\epsilon_2}(\mathbf{r}_2) &= E\psi_{\epsilon_1}(\mathbf{r}_1)\psi_{\epsilon_2}(\mathbf{r}_2) && (6.54) \\ \hat{H}\psi_{\epsilon_1}(\mathbf{r}_2)\psi_{\epsilon_2}(\mathbf{r}_1) &= E\psi_{\epsilon_1}(\mathbf{r}_2)\psi_{\epsilon_2}(\mathbf{r}_1) && (6.55) \end{aligned}$$

then the wavefunction for the entire system must incorporate contributions from both solutions to the Schrödinger equation:

$$\Psi_E^{tot} = \alpha\psi_{\epsilon_1}(\mathbf{r}_1)\psi_{\epsilon_2}(\mathbf{r}_2) + \beta\psi_{\epsilon_1}(\mathbf{r}_2)\psi_{\epsilon_2}(\mathbf{r}_1) \tag{6.56}$$

with the constraint $\alpha^2 + \beta^2 = 1$ (and another constraint coming up soon).

6.5.3 Permutation operators

Regardless of the energy levels, it must be the case that the permutation of the particles has no impact on the state of the entire system. The true wave function of each particle must explicitly incorporate not only the products of single particle wavefunctions, but also all possible permutations. That is, if we define an arbitrary permutation operator $\mathbf{P}$ exchanging the position of some particles, the probability density $|\mathbf{P}\Psi^{tot}|^2 = |\Psi^{tot}|^2$ must be unchanged. This means in general that $\mathbf{P}\Psi^{tot} = e^{i\theta}\Psi^{tot}$, so the permutation of a pair of particles introduces a phase shift in the wave function. Of course, if we undo our permutation by applying the permutation operator twice (since all we've done is swapped the particle indices twice, meaning we recover the same indices as we had originally). Under an even number of permutations, we thus must recover the original wavefunction, so $\mathbf{PP}\Psi^{tot} = e^{2i\theta}\Psi^{tot} = \Psi^{tot}$. This means that not any phase shift is possible, but rather the permutation *must* be either symmetric or asymmetric: $\mathbf{P}\Psi^{tot} = \pm\Psi^{tot}$.

In our two particle case, there are two solutions that satisfies this additional constraint:

$$\Psi_E^{tot} = \frac{1}{\sqrt{2}}\Big(\psi_{\epsilon_1}(\mathbf{r}_1)\psi_{\epsilon_2}(\mathbf{r}_2) \pm \psi_{\epsilon_1}(\mathbf{r}_2)\psi_{\epsilon_2}(\mathbf{r}_1)\Big) \tag{6.57}$$

It's straightforward to show that $|\Psi_E^{tot}(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi_E^{tot}(\mathbf{r}_2, \mathbf{r}_1)|^2$ for this function, which satisfies the permutability constraint.

For an arbitrary number of particles, the wavefunction could be symmetric in all its arguments, so that $\mathbf{P}\Psi^{tot} = \Psi^{tot}$ for all single particle permutations. If the wavefunction is symmetric for one pair permutation, it's easily seen to be symmetric for any number of permutations, since any permutation can be built of individual pair swaps. Thus, a symmetric eigenstate can be constructed knowing the individual particle wavefunctions via

$$\Psi^{symm} = \frac{1}{\sqrt{N!}} \sum_{\mathbf{P}} \mathbf{P}\Psi_E(\{\mathbf{r}_i\}) \tag{6.58}$$

where $\Psi_E(\{\mathbf{r}_i\})$ is any product of single particle wavefunctions consistent with the single particle Hamiltonian, and $\sum_{\mathbf{P}}$ represents a sum over all possible permutations. The factor of $(N!)^{-1/2}$ is required due to the ultimate normalization condition of the total wavefunction, since there are $N!$ possible distinct permutation operators.

We've seen that an antisymmetric solution also exists for the two-particle system, and we would expect an antisymmetric state $\mathbf{P}\Psi = -\Psi$ to be a possible solution to the full Schrödinger equation as well. However, it's not possible for *all* permutations to produce a overall change in sign of the wavefunction. For example, if we apply the same *two particle* permutation matrix twice, $\mathbf{P}_{pair}\mathbf{P}_{pair}\Psi_E = \Psi_E$ for any Ψ, since re-applying the permutation undoes the exchange. Making two pair permutations is an even operation, while making one pair permutation is an odd operation. Generally speaking, Ψ can be an antisymmetric function, which is defined as changing sign if not for any arbitrary permutation, but rather only for those of odd order. This means that

$$\Psi^{asymm} = \frac{1}{\sqrt{N!}} \sum_{\mathbf{P}} (-1)^{o(\mathbf{P})} \mathbf{P}\Psi_E(\{\mathbf{r}_i\}) \tag{6.59}$$

with $o(\mathbf{P})$ the order of the permutation: odd if an odd number of pairs of particles are exchanged and even if an even number of pairs of particles are exchange. Note that any permutation of n particles can be decomposed into individual pairs of particles being permuted, so this is equivalent to the number of single-pair exchanges that compose the total permutation.

6.5.4 Pauli Exclusion principle

The asymmetric state Ψ^{asymm} has an interesting feature if the two particles are located at the same position:

$$\begin{aligned}
\mathbf{P}_{1\leftrightarrow 2}\Psi^{asymm}(\mathbf{r}_1, \mathbf{r}_2, \{\mathbf{r}_k\}) &= -\Psi^{asymm}(\mathbf{r}_2, \mathbf{r}_1, \{\mathbf{r}_k\}) && \text{antisymmetric wavefunction} \\
\mathbf{P}_{1\leftrightarrow 2}\Psi^{asymm}(\mathbf{r}_1, \mathbf{r}_2, \{\mathbf{r}_k\}) &= \Psi^{asymm}(\mathbf{r}_2, \mathbf{r}_1, \{\mathbf{r}_k\}) && \text{if } \mathbf{r}_1 = \mathbf{r}_2
\end{aligned} \tag{6.60}$$

It must therefore be that $\Psi^{asymm} = 0$ if *any* pair of particles occupies the same location $\mathbf{r}$. Such a configuration is absolutely forbidding and has zero probability of occurring. That is, identical particles are forbidden from occupying an identical quantum states. We can equally well see this by noting that the determinant of a matrix has the same structure as the asymmetric functions: exchanging a row flips the sign of the determinant but keeps the magnitude constant. This naturally leads to the construction of the Slater determinant:

$$|\Psi\rangle = \frac{1}{N!}\begin{vmatrix} |\alpha\rangle_1 & |\beta\rangle_1 & \cdots & |\gamma\rangle_1 \\ |\alpha\rangle_2 & |\beta\rangle_2 & \cdots & |\gamma\rangle_2 \\ \vdots & \vdots & \ddots & \vdots \\ |\alpha\rangle_N & |\beta\rangle_N & \cdots & |\gamma\rangle_N \end{vmatrix} \tag{6.61}$$

where $|\alpha\rangle_1$ denotes the first particle being in state α. Note that if two states were identical ($\alpha = \beta$) there would be two columns of the matrix that were the same. This would mean the determinant would be zero, so such a state is disallowed.

This is derived solely through the statistics of the system, without any reference to spin or relativity, but draws a natural connection to the Pauli Exclusion principle. Pauli won the 1945 Nobel Prize by demonstrating in 1925 that the orbital structure of the periodic table could be fully explained if bound electrons are forbidden to occupy identical quantum states (having the same n, l, m, and s). We now know that the exclusion principle only applies to particles with half integer spin, provable only using the Dirac equation that incorporates special relativity into quantum mechanics. Integer spin particles are not constrained by the Pauli exclusion principle, and will therefore have very different statistics. The Pauli exclusion principle is satisfied for antisymmetric states, even though we haven't proved these states are required for spin-1/2 particles. We thus make the connection between fermions and the asymmetric states as well as bosons and the symmetric states in quantum statistical mechanics *without* proof they have anything to do with particle spin at all.

6.6 The Quantum Ideal Gas

6.6.1 Ideal gas of two quantum particles

Surprising quantum effects can come up due to the constraints of symmetrization of the wavefunction. An ideal gas of noninteracting particles, for which $\hat{H} = \sum_i \hbar^2\nabla^2/2m$, can be found in either the symmetric or antisymmetric state (due to them being bosons or fermions), and we'd like to compute the partition function for this system. To do so, we need to determine $Q_N = Tr(e^{-\beta H}) = \int \prod_i d^3\mathbf{r}_i \langle\{\mathbf{r}_i\}|e^{-\beta\hat{H}}|\{\mathbf{r}_i\}\rangle$. The symmetrization arises due to the permutation of particles, so we expect that new quantum effects may arise for two or more particles and for simplicity we'll start with two.

The partition function for two particles can be written

$$Q_2 = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 Q_2(\mathbf{r}_1,\mathbf{r}_2) \qquad\qquad Q_2(\mathbf{r}_1,\mathbf{r}_2) = \langle \mathbf{r}_1\mathbf{r}_2|e^{-\beta H}|\mathbf{r}_1\mathbf{r}_2\rangle \tag{6.62}$$

where $Q_2(\mathbf{r}_1,\mathbf{r}_2)$ is a constrained partition function: the partition function that arises if we fix the positions $\mathbf{r}_1$ and $\mathbf{r}_2$. Classically, this corresponds to pinning the two particles at these positions, while quantum mechanically we are determining the wavefunction at two specific points. Using the energy eigenbasis, we can write

$$Q_2(\mathbf{r}_1,\mathbf{r}_2) = \sum_E e^{-\beta E}|\langle \mathbf{r}_1\mathbf{r}_2|E\rangle|^2 \tag{6.63}$$

where $E = \hbar^2\pi^2/2mL^2(\mathbf{k}_1^2+\mathbf{k}_2^2)$ is the energy of the system. Note that we do *not* begin by summing over the individual particle energies, since the eigenvalues of $|E\rangle$ are the total system energy. We *can* replace the sum over total energies with a sum over particle energies by writing $E = \epsilon_1+\epsilon_2$, but we must recognize that (as we saw classically) the particle indices are irrelevant. We need to include a factor of $1/N! = 1/2$ to account for the indistinguishability of particle index. That means

$$\begin{aligned}
Q_2(\mathbf{r}_1,\mathbf{r}_2) &= \frac{1}{2}\sum_{\epsilon_1,\epsilon_2} e^{-\beta(\epsilon_1+\epsilon_2)}\langle \mathbf{r}_1\mathbf{r}_2|\epsilon_1\epsilon_2\rangle & (6.64)\\
&= \frac{1}{4}\sum_{\epsilon_1\epsilon_2} e^{-\beta(\epsilon_1+\epsilon_2)}|\psi_{\epsilon_1}(\mathbf{r}_1)\psi_{\epsilon_2}(\mathbf{r}_2) \pm \psi_{\epsilon_1}(\mathbf{r}_2)\psi_{\epsilon_2}(\mathbf{r}_1)|^2 & (6.65)\\
&= \frac{1}{4}\sum_{\epsilon_1} e^{-\beta\epsilon_1}|\psi_{\epsilon_1}(\mathbf{r}_1)|^2\sum_{\epsilon_2} e^{-\beta\epsilon_2}|\psi_{\epsilon_2}(\mathbf{r}_2)|^2 & (6.66)\\
&\quad \pm\frac{1}{4}\sum_{\epsilon_1} e^{-\beta\epsilon_1}\psi^*_{\epsilon_1}(\mathbf{r}_1)\psi_{\epsilon_1}(\mathbf{r}_2)\sum_{\epsilon_1} e^{-\beta\epsilon_2}\psi^*_{\epsilon_2}(\mathbf{r}_2)\psi_{\epsilon_2}(\mathbf{r}_1) & (6.67)\\
&\quad \pm\frac{1}{4}\sum_{\epsilon_1} e^{-\beta\epsilon_1}\psi_{\epsilon_1}(\mathbf{r}_1)\psi^*_{\epsilon_1}(\mathbf{r}_2)\sum_{\epsilon_1} e^{-\beta\epsilon_2}\psi_{\epsilon_2}(\mathbf{r}_2)\psi^*_{\epsilon_2}(\mathbf{r}_1) & (6.68)\\
&\quad +\frac{1}{4}\sum_{\epsilon_1} e^{-\beta\epsilon_1}|\psi_{\epsilon_1}(\mathbf{r}_2)|^2\sum_{\epsilon_2} e^{-\beta\epsilon_2}|\psi_{\epsilon_2}(\mathbf{r}_1)|^2 & (6.69)\\
&= f(\mathbf{r}_1,\mathbf{r}_1)f(\mathbf{r}_2,\mathbf{r}_2) \pm |f(\mathbf{r}_1,\mathbf{r}_2)|^2 & (6.70)
\end{aligned}$$

where $f(\mathbf{r},\mathbf{r}') = \sum_\epsilon e^{-\beta\epsilon}\psi^*_\epsilon(\mathbf{r})\psi_\epsilon(\mathbf{r}')$. We evaluated this before for a particle in a box in eq. 6.45, where we found

$$f(\mathbf{r}_1,\mathbf{r}_2) \approx \frac{1}{\lambda^3}e^{-\pi|\mathbf{r}_1-\mathbf{r}_2|^2/\lambda^2} \tag{6.71}$$

from which we find

$$Q_2(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{2\lambda^6}\left(1 \pm e^{-2\pi(\mathbf{r}_1-\mathbf{r}_2)^2/\lambda^2}\right) \tag{6.72}$$

The constrained partition function is readily integrated to determine

$$Q_2 = \frac{V^2}{2!\lambda^6} \pm \frac{V}{2^{5/2}\lambda} \tag{6.73}$$

Recall that the classical ideal gas satisfied $Q_N = V^N/N!\lambda^{3N}$, consistent with the leading order term in this two-particle partition function. This implies there *are* quantum corrections to the ideal gas partition function that are lower order in V/λ^3. If $V \gg \lambda^3$, we find the classical limit (either dilute gasses or high temperatures), but deviations can occur if $V \sim \lambda^3$. We made the argument that quantum effects would become relevant for sufficiently large λ, but were *not* able to determine these corrections before.

We can also compute the density

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \langle \mathbf{r}_1\mathbf{r}_2|\hat{\rho}|\mathbf{r}_1\mathbf{r}_2\rangle = Q_2^{-1}\langle \mathbf{r}_1\mathbf{r}_2|\hat{\rho}|\mathbf{r}_1\mathbf{r}_2\rangle \approx \frac{1}{V^2}\left(1 \pm e^{-2\pi(\mathbf{r}_1-\mathbf{r}_2)^2/\lambda^2}\right) \tag{6.74}$$

In the limit of $\lambda \to 0$, this recovers a uniform particle density, $\rho(\mathbf{r}_1, \mathbf{r}_2) = V^{-2}$. However, a surprising feature of this pair density is that it implies Bosons are found *closer together* than would be expected classically (since there's a positive contribution to the density when $\mathbf{r}_1 \approx \mathbf{r}_2$) and Fermions are found *further apart* than would be expected classically (due to the negative contribution). Note that these are still ideal particles, so there is no direct interaction between them. The differences in the probability destinies are due entirely to the quantum statistics, and could never be recovered classically.

6.6.2 Ideal gas of N particles

The results of the previous subsection hold for N particles as well, although it's more tedious to show. Pathria puts a good deal of work into proving it, but the main result is that we can write

$$\begin{aligned}
\langle\{\mathbf{r}_i\}|e^{-\beta\hat{H}}|\{\mathbf{r}_i\}\rangle &= \frac{1}{N!\lambda^{3N}}\left(1 \pm \sum_{i<j} f(\mathbf{r}_i,\mathbf{r}_j)f(\mathbf{r}_j,\mathbf{r}_i) + \sum_{i<j<k} f(\mathbf{r}_i,\mathbf{r}_j)f(\mathbf{r}_j,\mathbf{r}_k)f(\mathbf{r}_k,\mathbf{r}_i) \pm \cdots\right) \\
&= \frac{1}{N!\lambda^{3N}}\left(1 \pm \sum_{i<j} e^{-2\pi(\mathbf{r}_i-\mathbf{r}_j)^2/\lambda^2} + \sum_{i<j<k} e^{-\pi[(\mathbf{r}_i-\mathbf{r}_j)^2+(\mathbf{r}_j-\mathbf{r}_k)^2+(\mathbf{r}_k-\mathbf{r}_i)^2]/\lambda^2} + \cdots\right)
\end{aligned}$$

which is an expansion in increasing orders of particle permutations. That expansion doesn't necessarily seem useful from the definition of $\Psi = N!^{-1/2}\sum_P(-1)^{o(P)}\prod_i \psi_i$, since the order of the contribution to the wavefunction doesn't appear to depend on the order of the permutation. However, having computed that $f(\mathbf{r}, \mathbf{r}') = \lambda^{-3}e^{-\pi(\mathbf{r}-\mathbf{r}')^2/\lambda^2}$, we can now see that each permutation gives an exponentially small contribution to the sum so long as any particle is separated by a different particle by $|\mathbf{r}_i - \mathbf{r}_j| \approx \lambda$. Thus, if k particles are found close to one another, the k^{th} order permutations may contribute to the k-particle distribution.

6.7 Spin systems and composite particles

In Sec. 6.6.1 we determined the quantum statistics of two noninteracting particles and found quantum mechanical effects can lead to surprising behavior of the pair of particles. This analysis did not include the effects of spin, which must be accounted for in general. The spin states can be written as a linear combination of the four possible arrangements $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $|\downarrow\downarrow\rangle$. For two fermions, we know the total wavefunction must be asymmetric under particle exchange, with

$$\mathbf{P}_{1\leftrightarrow 2}\Psi(\mathbf{r}_1,\mathbf{r}_2) = -\Psi(\mathbf{r}_1,\mathbf{r}_2) \tag{6.75}$$

Under this permutation, any spin associated with the particles would also be swapped, which must be taken into account. Importantly, there are *two distinct* ways to enforce asymmetry in the total wavefunction: an asymmetric position wavefunction and symmetric spin state *or* a symmetric position wavefunction and asymmetric spin state. Defining the symmetric and asymmetric position wavefunctions as

$$\psi_s(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) + \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\Big) \tag{6.76}$$

$$\psi_a(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\Big) \tag{6.77}$$

we can write

$$\Psi_{11}(\mathbf{r}_1,\mathbf{r}_2) = \psi_a(\mathbf{r}_1,\mathbf{r}_2)\,|\uparrow\uparrow\rangle \tag{6.78}$$

$$\Psi_{10}(\mathbf{r}_1,\mathbf{r}_2) = \psi_a(\mathbf{r}_1,\mathbf{r}_2)\times\frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\Big) \tag{6.79}$$

$$\Psi_{1-1}(\mathbf{r}_1,\mathbf{r}_2) = \psi_a(\mathbf{r}_1,\mathbf{r}_2)\,|\downarrow\downarrow\rangle \tag{6.80}$$

$$\Psi_{00}(\mathbf{r}_1,\mathbf{r}_2) = \psi_s(\mathbf{r}_1,\mathbf{r}_2)\times\frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big) \tag{6.81}$$

where Ψ_{00} is the only term with a symmetric position wavefunction, and is referred to as a singlet state. The wavefunctions Ψ_{1M} all involve asymmetric position wavefunctions but symmetric spin states, and are referred to as the triplet states. You might recognize that the coefficients of 1 and $\pm 1/\sqrt{2}$ in eq. 6.78-6.81 are the famous Clebsch-Gordon coefficients (which dictate how to add angular momenta quantum mechanically) for two spin-1/2 particles. The total spin of the system adds up to 1 (so $S = 0$ or 1, and $M = -1, 0, 1$, as indicated by the subscript on $\Psi_{S,M}$. The state $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ is referred to as a singlet state ($S = 0$, only one possible M), while the states $\{|\uparrow\uparrow\rangle, (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}, |\downarrow\downarrow\rangle\}$ are collectively referred to as a triplet state ($S = 1$, three possible values of M).

A surprising feature of a system of 2 fermions is that they collectively behave as a single boson! A pair of bound fermions will have an integral value for the total spin when treated as a composite system, which means the composite particle will be a boson. This surprising behavior is true for any even number of fermions bound together, and will exhibit similarly bosonic behavior (but with a more complex expression for the total wavefunction). This is particularly important for atoms, with protons, neutrons, and electrons all fermions. For a neutral atom, the number of protons and electrons are equal (thus $n_p + n_e$ is an even number), and therefore the total spin of the system is an integer if there are an even number of neutrons and a half integer if there are an odd number of neutrons. Thus, ^{3}He will behave as a fermion (having 1 neutron, and total spin $S = 5/2$) while ^{4}He will behave as a boson (having 2 neutrons and total spin 3). This has been confirmed experimentally for these two isotopes of Helium: ^{4}He exhibits superfluidity (a feature of Bose Einstein condensation we will not discuss extensively) but ^{3}He does not, due to the fact that ^{4}He atoms do not obey the Pauli exclusion principle but ^{3}He atoms do.

6.8 Summary

In this Chapter we've derived a quantum mechanical method for determining the statistics of truly quantum mechanical particles. Averages of operators in quantum statistical mechanics are determined via a density operator: a purely statistical object that describes the probability of being found in any particular state in an ensemble of accessible states. We found indistinguishability of particles was fully accounted for quantum mechanically because of the permutability of the wavefunctions, which led to a natural requirement of purely symmetric and purely antisymmetric states. We refer to these as Fermions and Bosons, despite the fact that we are not able to identify these states as related integer vs half-integer spin states (as is done in field theory). We found that quantum statistics differs from classical predictions at low temperatures (as we already knew before), and were able to derive higher order terms in the partition function (which we had not been able to do before). Despite these successes, dealing with the wavefunctions directly is often tedious and difficult to do exactly for N particles.

Chapter 7

Statistics of Fermions and Bosons (Pathria Ch 6-8)

We've constructed the methods for computing the phase space density of quantum particles in the microcanonical, canonical, and grand canonical ensembles. The density was normalized in terms of $Tr(e^{-\beta\hat{H}})$ or $Tr(e^{-\beta\hat{H}+\beta\mu\hat{n}})$, which we need to compute for the quantum ensembles. Computing the trace requires accounting for the differing statistics of symmetric vs asymmetric quantum states, which can be analytically somewhat painful. Also, while we did derive the density operator in the grand canonical ensemble, accounting for particle permutations with a varying number of particles will increase the complexity of any calculation. Finally, we also did not deal with degenerate energy levels in the previous chapter, which are certainly important for Bosons and Fermions (since we know that the distinction between these types of particles is spin!). In this chapter, we will use entropy maximization to determine the partition function for Bosons and Fermions without having to resort to direct manipulation of the particle wavefunction. From this, we will find remarkable behavior for Bosons and Fermions that would not be predicted classically.

7.1 The Grand Partition Functions

The calculation of the canonical partition function was difficult to compute directly in the case of Bosons and Fermions because of the constraints on the occupancy of each energy level. In position space, that led to complicated expressions involving permutations, but even in the energy eigenbasis computing the partition function can be difficult. Unlike the classical case, where $Q_N = Q_1^N/N!$, there are detailed conditions on the number of accessible states in each energy level that must be satisfied quantum mechanically. We have

$$Q_N = \sum_{\{n_\epsilon\}} \delta\left(N - \sum_\epsilon n_\epsilon\right) \times g(n_\epsilon) e^{-\beta \sum_\epsilon \epsilon n_\epsilon} \tag{7.1}$$

where $g(\{n_\epsilon\})$ is the degeneracy in the energy levels accounting for the particle statistics. Pauli exclusion implies

$$\begin{aligned} g(n_\epsilon) &= 1 && \text{Bosons} && (7.2) \\ g(n_\epsilon) &= \begin{cases} 1 & n_\epsilon \leq 1 \\ 0 & n_\epsilon > 1 \end{cases} && \text{Fermions} && (7.3) \end{aligned}$$

For classical particles we have the total number of ways to arrange the particles was $W = N!/\prod_i n_i!$, and after normalization of $1/N!$ due to the arbitrariness of the particle indices, the statistical weight for classical particles is

$$g(n_\epsilon) = \frac{1}{n_\epsilon!} \qquad \text{Classical Particles} \tag{7.4}$$

that was derived for the canonical partition function in Chapter 4 of these notes. The sum over $\{n_\epsilon\}$ is a sum over all possible arrangements of particles into the various energy levels, and can be written

$$\sum_{\{n_\epsilon\}} = \sum_{n_{\epsilon_0}=0}^{\infty} \sum_{n_{\epsilon_1}=0}^{\infty} \sum_{n_{\epsilon_2}=0}^{\infty} \cdots \tag{7.5}$$

It is not straightforward to perform the required sums because the number of particles in each state must match a global condition (which is imposed by the delta function constraint). Classically, we got around this problem by imposing a Lagrange multiplier and maximizing the entropy, eventually leading to the most probable occupancy $n_\epsilon^* \propto e^{-\beta\epsilon}$. This approach worked fine classically, but will fail for bosons and fermions, since $g(n_\epsilon)$ cannot be easily maximized for $n_\epsilon \to \infty$: $g(n) = 1$ for bosons (so there is no change in the limit of $n \gg 1$) and $g(n) = 1$ for $n < 1$ for fermions (so the limit $n \gg 1$ is meaningless). Computing partition functions is difficult in the canonical ensemble, but surprisingly easy in the grand canonical ensemble. This is because we can write

$$\begin{aligned} \mathcal{Q} &= \sum_N z^N Q_N = \sum_N z^N \sum_{\{n_\epsilon\}} g(n_\epsilon) \delta(N - \sum_\epsilon n_\epsilon) e^{-\beta \sum_\epsilon \epsilon n_\epsilon} && (7.6) \\ &= \sum_{\{n_\epsilon\}} g(n_\epsilon) z^{\sum_\epsilon n_\epsilon} e^{-\beta \sum_\epsilon \epsilon n_\epsilon} && (7.7) \\ &= \sum_{n_{\epsilon_0}} g(n_{\epsilon_0}) \left(z e^{-\beta \epsilon_0}\right)^{n_{\epsilon_0}} \times \sum_{n_{\epsilon_1}} g(n_{\epsilon_1}) \left(z e^{-\beta \epsilon_1}\right)^{n_{\epsilon_1}} \times \cdots && (7.8) \end{aligned}$$

Note that this lacks a constraint on the total number N, and that the occupancy numbers are all now summed over *independently*. That means we can actually evaluate these sums, and actually determine the grand partition function explicitly. We have for Bosons, called Bose-Einstein statistics, that

$$\begin{aligned} \mathcal{Q}_{BE} &= \sum_{n_{\epsilon_0}=0}^{\infty} \left(z e^{-\beta\epsilon_0} \right)^{n_{\epsilon_0}} \times \sum_{n_{\epsilon_1}=0}^{\infty} \left(z e^{-\beta\epsilon_1} \right)^{n_{\epsilon_1}} \times \cdots && (7.9) \\ &= \prod_{\epsilon} \frac{1}{1 - z e^{-\beta\epsilon}} && (7.10) \end{aligned}$$

For Fermions, called Fermi-Dirac statistics, we have the even simpler expression

$$\begin{aligned} \mathcal{Q}_{FD} &= \left(1 + z e^{-\beta\epsilon_0} \right)^{n_{\epsilon_0}} \times \left(1 + z e^{-\beta\epsilon_1} \right)^{n_{\epsilon_1}} \times \cdots && (7.11) \\ &= \prod_{\epsilon} \left(1 + z e^{-\beta\epsilon} \right) && (7.12) \end{aligned}$$

Finally, the classical grand partition function, called Maxwell-Boltzmann statistics, can be written

$$\begin{aligned} \mathcal{Q}_{MB} &= \sum_{n_{\epsilon_0}} \frac{1}{n_{\epsilon_0}!} \left(z e^{-\beta\epsilon_0} \right)^{n_{\epsilon_0}} \times \sum_{n_{\epsilon_1}} \frac{1}{n_{\epsilon_1}!} \left(z e^{-\beta\epsilon_1} \right)^{n_{\epsilon_1}} \times \cdots \\ &= \prod_{\epsilon} \exp(z e^{-\beta\epsilon}) = \exp\left(z \sum_{\epsilon} e^{-\beta\epsilon} \right) = e^{zQ_1} && (7.13) \end{aligned}$$

Note that in the continuous case, without the discrete energy levels assumed here, we found the classical partition function was $\mathcal{Q} = e^{zQ_1} = e^{zV/\lambda^3}$, which we had derived previously using the entropy maximization techniques.

7.2 Statistics for the quantum ideal gasses

7.2.1 Thermodynamic Averages

The pressure in an ideal gas in the grand canonical ensemble is still

$$\beta PV = \log(\mathcal{Q}) \tag{7.14}$$

For the three sets of statistics, the pressure can be written in the very general form

$$\beta PV = \frac{1}{a} \sum_{\epsilon} \log\left(1 + a z e^{-\beta\epsilon} \right) \qquad a = \begin{cases} 1 & \text{Fermi Dirac} \\ -1 & \text{Bose Einstein} \\ 0 & \text{Maxwell Boltzmann} \end{cases} \tag{7.15}$$

with the identification that $1/a \log(1 + aze^{-\beta\epsilon}) \to ze^{-\beta\epsilon} + O(a)$ as $a \to 0$. We can also compute a number of typical quantities in statistical mechanics. The mean number and energy of the system is straightforward to determine, with

$$N = z\frac{\partial \log(\mathcal{Q})}{\partial z} = \frac{1}{a}\sum_{\epsilon} \frac{aze^{-\beta\epsilon}}{1 + aze^{-\beta\epsilon}} = \sum_{\epsilon} \frac{1}{z^{-1}e^{+\beta\epsilon} + a} \tag{7.16}$$

$$U = -\frac{\partial \log(\mathcal{Q})}{\partial \beta}\bigg|_z = \sum_{\epsilon} \frac{\epsilon}{z^{-1}e^{+\beta\epsilon} + a} \tag{7.17}$$

7.2.2 Mean occupancy and quantum statistics

These are global statistics, but it is also straightforward to determine the mean number of particles at any energy level ϵ by computing

$$\langle n_{\epsilon^*}\rangle = -\frac{1}{\beta}\frac{\partial \log(\mathcal{Q})}{\partial \epsilon^*} = \frac{1}{\mathcal{Q}}\sum_{\{n_\epsilon\}} g(n_\epsilon) z^{\sum_\epsilon n_\epsilon} e^{-\beta \sum_\epsilon \epsilon n_\epsilon} \times n_{\epsilon^*} \tag{7.18}$$

$$= \frac{1}{z^{-1}e^{\beta\epsilon} + a} = \frac{1}{e^{\beta(\epsilon-\mu)} + a} \tag{7.19}$$

This is very convenient, because we can compute the average of any quantity given this factor by simply summing over the average number of particles at each energy level:

$$\langle f(\epsilon)\rangle = \frac{1}{N}\sum_{\epsilon} f(\epsilon)\langle n_\epsilon\rangle \tag{7.20}$$

where for example the mean energy of each particle is

$$\langle \epsilon\rangle = \frac{1}{N}\sum_{\epsilon} \epsilon\langle n_\epsilon\rangle \qquad U = N\langle\epsilon\rangle = \sum_{\epsilon} \frac{\epsilon}{z^{-1}e^{-\beta(\epsilon-\mu)} + a} \tag{7.21}$$

in agreement with eq. 7.17

Eq. 7.19 has a number of important properties:

1. For Fermions,
   - $a = +1$
   - $0 < \langle n_\epsilon\rangle < 1$, due to the fact that the maximum occupancy of any energy level is 1.
   - In the limit of $T \to 0$ ($\beta \to \infty$) the occupancy becomes a step function: any states with $\epsilon < \mu$ are occupied, since $\langle n_\epsilon\rangle = (e^{-\beta|\epsilon-\mu|} + 1)^{-1} \to 1$. Likewise, any states with $\epsilon > \mu$ are unoccupied ($\langle n_\epsilon\rangle = 0$. This fact will lead to the definition of the Fermi Energy later in the chapter.

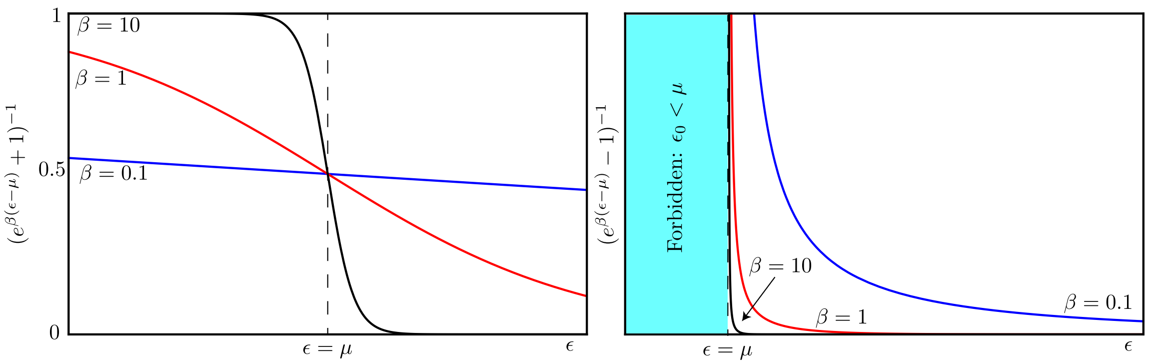


Figure 7.1: Sketches of the features of $(z^{-1}e^{\beta\epsilon}+1)^{-1}$ (left, Fermions) and $(z^{-1}e^{\beta\epsilon}-1)^{-1}$ (right, bosons) for varying energy ϵ at different values of β. For Fermions, $\epsilon = \mu$ is the midpoint of the occupancy ($\langle n_\epsilon\rangle = 1/2$, with a sharper division between occupied and unoccupied states for increasing β. In the limit as $\beta \to \infty$, $\langle n_\epsilon\rangle$ will be a step function: $\langle n_\epsilon\rangle = \Theta(\mu-\epsilon)$. For Bosons, $\langle n_\epsilon\rangle \to \infty$ at $\epsilon = \mu$, and all energy levels are required to satisfy $\epsilon > \mu$. For increasing β, more and more particles are found in the lower energy states.

  - If $\beta(\epsilon-\mu) \ll 1$, $\langle n_\epsilon\rangle \approx e^{-\beta(\epsilon-\mu)}$, proportional to the classical Maxwell-Boltzmann occupancy.

2. For Bosons,
   - $a = -1$
   - $0 < \langle n_\epsilon\rangle < \infty$, since multiple particles can be found at the same energy level.
   - When we computed grand partition function, we performed a sum over all $(ze^{-\beta\epsilon})$, which means it *must* be the case that $\mu < \epsilon_0$ (the ground state) for the sum to have converged. If $\mu = \epsilon_0$, an infinite number of particles are found in the ground state. For low temperatures, higher energy levels will be unoccupied ($\langle n_\epsilon\rangle \to 0$). This fact will lead to the phenomenon of Bose-Einstein condensation below.
   - Maxwell-Boltzmann statistics are found as well when $\beta(\epsilon-\mu) \gg 1$.

Of course, we can still compute our fluctuations as we did classically: by taking a second derivative. It is tedious but straightforward to show that

$$\langle n_\epsilon^2\rangle - \langle n_\epsilon\rangle^2 = -\frac{1}{\beta}\frac{\partial\langle n_\epsilon\rangle}{\partial\epsilon} = \frac{1}{\beta^2}\frac{\log(\mathcal{Q})}{\partial\epsilon^2} = \frac{z^{-1}e^{-\beta\epsilon}}{(z^{-1}e^{-\beta\epsilon}+a)^2} \tag{7.22}$$

which can be simplified to

$$\frac{\langle n_\epsilon^2\rangle - \langle n_\epsilon\rangle^2}{\langle n_\epsilon\rangle^2} = \frac{1}{\langle n_\epsilon\rangle} - a \tag{7.23}$$

which has a variety of properties that are to be expected: the Maxwell-Boltzmann statistics (with $a = 0$) satisfy the typical $1/N$ relative fluctuation rule at every energy level. However, the FD statistics (with $a = +1$) tend to have weaker fluctuations than classically while the BE statistics tend to have greater fluctuations.

7.3 The Density of states

7.3.1 Momentum representation

The spacing between momentum levels or energy levels in quantum statistical mechanics is expected to be small (depending on $\hbar$ to some power). For the ideal gas for which we've derived the partition function, we know the energy is $\epsilon(\mathbf{p}) = \mathbf{p}^2/2m$ with $\mathbf{p} = 2\pi\hbar\mathbf{n}/L = h\mathbf{n}/V^{1/3}$. The small spacing in momentum (due to the smallness of h and the largeness of V) means we can rewrite the pressure in terms of an integral rather than a sum, with

$$\begin{aligned}
\beta PV &= \frac{1}{a}\sum_{\mathbf{n}} \log(1 + aze^{\beta\epsilon(\mathbf{n})}) \times g(\epsilon(\mathbf{n})) && (7.24)\\
&= \sum_{n_1,n_2,n_3} \Delta n^3 f(n_1,n_2,n_3) && (7.25)
\end{aligned}$$

with $f(n_1,n_2,n_3) = V\log(1+aze^{-\beta\epsilon(n_1,n_2,n_3)})g(\epsilon)/ah^3$, $g(\epsilon)$ the degeneracy of energy level ϵ, and $\Delta n = h/L$ is the spacing between points. This is sensible because L can be made arbitrarily large (in the thermodynamic limit). It is tempting to immediately write this sum as an integral, but there is a subtlety that must be addressed to properly perform the limit. The sum only converges to a Riemann-Stijiltes integral so long as $f(\mathbf{n})$ is bounded for all $\mathbf{n}$. For fermions, all terms in the sum are bounded, since $\log(1 + ze^{-\beta\epsilon}) \leq \log(1 + ze^{-\beta\epsilon_0})$, which is always finite for $\epsilon_0 > -\infty$. So (setting $g = 1$)

$$\begin{aligned}
(\beta PV)_{FD} &= \frac{gV}{ah^3}\int d^3p \log(1 + aze^{-\beta\mathbf{p}^2/2m})) && (7.26)\\
&= \frac{4\pi gV}{ah^3}\int_0^\infty dp\; p^2\log(1 + aze^{-\beta p^2/2m}) && (7.27)\\
(N)_{FD} &= \frac{gV}{ah^3}\int d^3p \frac{1}{z^{-1}e^{\beta p^2/2m} + 1} && (7.28)\\
&= \frac{4\pi gV}{ah^3}\int_0^\infty dp\; \frac{p^2}{z^{-1}e^{\beta p^2/2m} + 1} && (7.29)
\end{aligned}$$

$$(E)_{FD} \approx \frac{4\pi g V}{ah^3}\int_0^\infty dp\, \frac{p^2\epsilon(p)}{z^{-1}e^{\beta p^2/2m}+1} \tag{7.30}$$

and similarly for any of the other thermodynamic averages we've computed. Note that we have here computed the thermodynamic variables with the assumption that $g(\epsilon) = g$ is constant for all energy levels (e.g., g=2 for spin 1/2 particles).

We encounter a problem with the sum-to-integral limit for Bosons, where every term in the pressure sum satisfies $\log(1 - ze^{-\beta\epsilon}) \leq \log(1 - ze^{-\beta\epsilon_0})$. Unlike the case of fermions, one of the terms of the sum can diverge: the ground state term. If $z \to e^{\beta\epsilon_0}$, the leading term of the sum becomes arbitrarily large and will not converge in the continuum limit. We must therefore treat that portion of the sum separately, writing (with $g = 1$ for simplicity)

$$\begin{aligned}
(\beta PV)_{BE} &= \log(1 - ze^{-\beta\epsilon_0}) + \frac{V}{ah^3}\int d^3p\log(1 + aze^{-\beta\mathbf{p}^2/2m})) && (7.31)\\
&\approx \log(1-z) + \frac{4\pi V}{ah^3}\int_0^\infty dp\; p^2\log(1 + aze^{-\beta p^2/2m}) && (7.32)\\
(N)_{BE} &= \frac{1}{z^{-1}e^{\beta\epsilon_0}-1} + \frac{V}{ah^3}\int d^3p \frac{1}{z^{-1}e^{\beta p^2/2m}-1} && (7.33)\\
&\approx \frac{z}{1-z} + \frac{4\pi V}{ah^3}\int_0^\infty dp\; \frac{p^2}{z^{-1}e^{\beta p^2/2m}-1} && (7.34)\\
(E)_{BE} &\approx \frac{z\epsilon_0}{1-z} + \frac{4\pi V}{ah^3}\int_0^\infty dp\; \frac{p^2\epsilon(p)}{z^{-1}e^{\beta p^2/2m}-1} && (7.35)
\end{aligned}$$

where we have assumed that $\beta\epsilon_0 \ll 1$ in the latter approximations. Each of the leading order terms are due to the ground state occupancy, which can be large for Bosons. The ground state occupancy is negligible for Fermions, since only 1 one particle can be found in the ground state (or g particles if there is a ground state degeneracy of g). It's therefore useful to think of these thermodynamic variables in terms of the ground and excited contributions: $P_{BE} = P_0 + P_e$, $N_{BE} = N_0 + N_e$, and $E_{BE} = E_0 + E_e$. For Fermions, we will have $P_{FD} = P_e$ since the ground state contribution is negligible (and similarly for the number and energy).

7.3.2 Energy representation and the density of states

Sometimes, we'll want to compute averages in terms of energy rather than momentum. This is straightforward to do because we know that for an ideal gas that $\epsilon = p^2/2m$, so we can make a change of variables and write this as

$$\begin{aligned}
\beta P_e V &= \frac{4\pi V}{ah^3}\int_0^\infty d(\sqrt{2m\epsilon})2m\epsilon\log(1 + aze^{-\beta\epsilon}) && (7.36)\\
&= \frac{2\pi V}{a}\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\infty d\epsilon\sqrt{\epsilon}\log(1 + aze^{-\beta\epsilon}) && (7.37)
\end{aligned}$$

In general, any of our sums over energy states can be immediately replaced by integrals over the energy by replacing $\sum_\epsilon \cdots = \int_0^\infty d\epsilon D(\epsilon)\cdots$, where the density of states is

$$D(\epsilon) = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\epsilon} \tag{7.38}$$

The density of states indicates the number of states between energy ϵ and $\epsilon+d\epsilon$. Note that Pathria uses the label $a(\epsilon)$, which can cause confusion with the already-defined a indicator of BE vs FD statistics. For Bose Einstein statistics, we'll also need to account for the ground state energy term explicitly.

We'll see later in the chapter that many useful quantities can be computed using the continuous form of $\langle n_\epsilon\rangle$ coupled with the density of states, but it's very useful to derive a relationship between pressure and energy that is independent of the statistical model. Noting that $\partial\log(1+aze^{-\beta\epsilon})/\partial\epsilon = -\beta\langle n_\epsilon\rangle$, we can integrate by parts to find

$$\begin{aligned}\beta P_e V &= 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\infty d\epsilon\sqrt{\epsilon}\log(1+aze^{-\beta\epsilon}) &(7.39)\\ &= \frac{2}{3}\times 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\left[\epsilon^{3/2}\log(1+aze^{-\beta\epsilon})\Big|_{\epsilon=0}^{\epsilon=\infty} + \beta\int_0^\infty d\epsilon\epsilon^{3/2}\langle n_\epsilon\rangle\right. &(7.40)\\ &= \frac{2}{3}\beta\int_0^\infty d\epsilon D(\epsilon)\epsilon\langle n_\epsilon\rangle = \frac{2}{3}\beta E_e &(7.41)\end{aligned}$$

Note this is true for Fermi-dirac, Bose Einstein, and Maxwell-Boltzmann statistics. The pressure of an ideal gas due to excited particles always satisfies $PV = 2E/3$.

7.3.3 The density of states in other systems

The density of states $D(\epsilon)$ allows us to convert a sum to an integral, but depends on two features:

1. The dimensionality of the system. When performing the switch between the sum and the momentum integral, we introduced a factor $(V^{1/d}/h)^d$ with $d = 3$, and the factor of p^2 in the final integral is due to the three-dimensional spherical coordinates used. For $d = 2$, we define $A = L^2$ the area of the system and find

$$\begin{aligned}\beta PA &= \frac{1}{a}\sum_{\mathbf{n}}\log(1+aze^{-\beta\epsilon(\mathbf{n})}) &(7.42)\\ &\to \frac{A}{ah^2}\int d^2p\log(1+aze^{-\beta\mathbf{p}^2/2m}) &(7.43)\\ &= \frac{2\pi A}{ah^2}\int_0^\infty dp\; p\log(1+aze^{-\beta p^2/2m}) &(7.44)\end{aligned}$$

$$= \frac{2\pi A m}{a h^2}\int_0^\infty d\epsilon \log(1+aze^{-\beta\epsilon}) \tag{7.45}$$

so that

$$D_{2d} = \frac{2\pi A m}{h^2}\times \epsilon^0 \tag{7.46}$$

which is *independent* of the energy in 2 dimensions!

2. The energy dispersion relation. The density of states depends on the functional form of $\epsilon(\mathbf{p})$ in order to replace a dp with a $d\epsilon$. If we imagine an extreme relativistic gas, with $\epsilon(p) = \sqrt{p^2c^2+m^2c^4} \approx pc$ (instead of the classical $\epsilon = p^2/2m$), we would find

$$\beta P V = \frac{1}{a}\sum_{\mathbf{n}} \log(1+aze^{\beta\epsilon(\mathbf{n})}) \tag{7.47}$$

$$= \frac{4\pi V}{a h^3}\int_0^\infty dp\, p^2 \log(1+aze^{-\beta p c}) \tag{7.48}$$

$$= \frac{4\pi V}{a h^3 c^3}\int_0^\infty d\epsilon\, \epsilon^2 \log(1+aze^{-\beta\epsilon}) \tag{7.49}$$

so that

$$D_{relativistic} = \frac{4\pi V}{(hc)^3}\times \epsilon^2 \tag{7.50}$$

Other dispersion relations are possible (e.g. on a lattice the energy dispersion relation is expected to be periodic in the momentum vector $\mathbf{n}$.).

7.4 The Fermi-Dirac and Bose-Einstein functions

The number of particles in the excited state depends on z and β, but can be simplified by making the change of variables $\epsilon = x k_B T$:

$$N_e = \int_0^\infty d\epsilon \frac{D(\epsilon)}{z^{-1}e^{\beta\epsilon}+a} = \int_0^\infty dx \frac{D(x k_B T)}{z^{-1}e^{x}+a} \tag{7.51}$$

$$= \frac{2}{\sqrt{\pi}}\frac{V}{\lambda^3}\int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^{x}+a} \tag{7.52}$$

This means we can generally write the number of particles in the excited state in terms of the special functions

$$f_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^{x}+1} \qquad g_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^{x}-1} \tag{7.53}$$

where $f_\nu(z)$ is the Fermi Dirac function and $g_\nu(z)$ is the Bose Einstein function. The leading factor of $1/\Gamma(\nu)$ handles the factor of $2/\sqrt{\pi}$ in eq. 7.52. Note that these functions are monotonically increasing in z, since a larger value of z reduces the exponential decay growth of the denominator. A taylor expansion in $z \ll 1$ gives

$$\begin{aligned}
f_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x + a} &= \frac{1}{\Gamma(\nu)}\sum_{n=1}^{\infty} a^{n-1} z^n \int_0^\infty dx\ x^{\nu-1} e^{-nx} && (7.54)\\
&= \frac{1}{\Gamma(\nu)}\sum_{n=1}^{\infty} a^{n-1} \frac{z^n}{n^\nu} \int_0^\infty dy y^{\nu-1} e^{-y} && (7.55)\\
&= \sum_{n=1}^{\infty} a^{n-1} \frac{z^n}{n^\nu} && (7.56)
\end{aligned}$$

so that

$$f_\nu(z) \sim z - \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} - \cdots \qquad g_\nu(z) \sim z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots \tag{7.57}$$

for small z. It's not hard to see from this taylor expansion that

$$z\frac{\partial f_\nu(z)}{\partial z} = f_{\nu-1}(z) \qquad z\frac{\partial g_\nu(z)}{\partial z} = g_{\nu-1}(z) \tag{7.58}$$

These relations are often useful in determining derivatives of thermodynamic variables with respect to β.

Recalling that $P_e V = 2E_e/3$, it is straightforward to show that

$$\begin{aligned}
N_e &= \frac{V}{\lambda^3} \times \begin{cases} f_{3/2}(z) & FD \\ g_{3/2}(z) & BE \end{cases} && (7.59)\\
\beta E_e &= \frac{3}{2}\frac{V}{\lambda^3} \times \begin{cases} f_{5/2}(z) & FD \\ g_{5/2}(z) & BE \end{cases} && (7.60)\\
\beta P_e V = \frac{2}{3}E_e &= \frac{V}{\lambda^3} \times \begin{cases} f_{5/2}(z) & FD \\ g_{5/2}(z) & BE \end{cases} && (7.61)
\end{aligned}$$

While the notation of f and g to distinguish between Fermions and Bosons prevents us from expressing these symmetries in a completely compact manner, it is clear that the mathematical properties of Fermions and Bosons are strikingly similar *except for* the value of $a = +1$ for Fermions and $a = -1$ for Bosons. We will see that this difference causes remarkably different statistics between the two types of particles.

7.4.1 The classical limit

Recall that the number of particles in the classical ideal gas was derived from $\mathcal{Q} = e^{zQ_1} = e^{zV/\lambda^3}$, with the mean number of particles satisfying

$$N_{classical,ideal} = z\frac{\partial \log(\mathcal{Q})}{\partial z} = \frac{Vz}{\lambda^3} \tag{7.62}$$

Recalling that $f_\nu(z) \sim z - z^2/2^\nu + \cdots$ and $g_\nu(z) = z + z^2/2^\nu + \cdots$, it is clear that eq. 7.59 reduces to eq. 7.62 in the limit of $z \to 0$ (where higher order terms can be neglected in $f_\nu(z)$ and $g_\nu(z)$). The limit of $z \to 0$ is thus called the classical limit. Rearranging eq. 7.62 gives a better understanding of the meaning of this limit, with

$$z_{classical} \approx \rho\lambda^3 \propto \rho T^{-3/2} \tag{7.63}$$

The fugacity monotonically increases with density and monotonically decreases with temperature in the classical limit. This is physically sensible: in previous chapters we discussed the expectation that quantum effects would be relevant only when $\rho\lambda^3$ was large. For dilute gasses (with low ρ), the particles are rarely close to one another and 'see' each other as classical point particles. For high temperatures, the thermal wavelength is so small that particles 'see' each other as point particles as well. Both of these possible limits are included in the classical limit of $z \to 0$.

7.5 The Fermi Energy

7.5.1 Low Temperature Statistics

An interesting feature arises from the statistics of the Fermions in the limit of low temperatures. For $T \to 0$,

$$\langle n_\epsilon \rangle = \frac{1}{e^{\beta(\epsilon-\mu_0)}+1} \approx \begin{cases} 1 & \epsilon < \mu_0 \\ 0 & \epsilon > \mu_0 \end{cases} \tag{7.64}$$

where $\mu_0 = \mu(T = 0)$ is the chemical potential at $T = 0$. Recall that the value μ_0 depends on the statistics of the *reservoir* as well as the system, and we do not know it a priori. Fermions must arrange themselves to completely occupy the lowest energy levels available (those below μ_0) with no particle occupying a higher energy level than the Fermi Energy $\epsilon_F = \mu_0$. No particle will be found at an energy level above the Fermi energy at $T = 0$.

In many contexts (particularly spin-1/2 particles), one might care about the degeneracies of each energy level for fermions (e.g. spin, for which two electrons can occupy the same energy level at different spins). We can write the number of particles at any energy level in the presence of degeneracies (with $g(\epsilon)$ the degeneracy of each energy level ϵ) as

$$\langle n_\epsilon \rangle = \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu_0)}+1} \approx \begin{cases} g(\epsilon) & \epsilon < \mu_0 \\ 0 & \epsilon > \mu_0 \end{cases} \tag{7.65}$$

Note that $g(\epsilon)$ is *not* the same as $g_\nu(z)$, and when $g(\epsilon)$ is not specified we are assuming each energy level has no degenerate states. These degeneracies do not affect the Fermi energy $\epsilon_F = \mu_0$ (since the occupancy $\langle n_\epsilon \rangle$ is still a step function), but the presence of degenerate energy levels will increase *the number* of particles in the system since more particles can occupy lower energy levels.

7.5.2 Determining the Fermi energy

The definition of $\epsilon_F = \mu_0$ is not terribly useful, since we don't have a good sense of $\mu(T)$ as $T \to 0$. Surprisingly, we can determine the Fermi energy in terms of the system's physical parameters using our knowledge of the density of states. We know that

$$N = \int_0^\infty d\epsilon D(\epsilon)\langle n_\epsilon \rangle \to \int_0^{\epsilon_F} d\epsilon D(\epsilon) \tag{7.66}$$

with the latter limit assuming $T \to 0$ and $\langle n_\epsilon \rangle$ converging on the step function. Recalling that $D(\epsilon) = 2\pi V(2m/h^2)^{3/2}\sqrt{\epsilon}$ is the density of states of the particles, integration shows that

$$N = \frac{4\pi g V}{3}\left(\frac{2m}{h^2}\right)^{3/2}\epsilon_F^{3/2} \qquad\qquad \epsilon_F = \frac{h^2}{2m}\left(\frac{3N}{4\pi g V}\right)^{2/3} = \mu_0 \tag{7.67}$$

Recall that $N = \langle N \rangle$ is still controlled by the reservoir, so we have not managed to avoid the reservoir altogether. However, given N cold Fermions in our system we are able to determine the maximum energy of each particle. The average energy is easily computed as

$$E = \int_0^{\epsilon_F} d\epsilon D(\epsilon)\epsilon = \frac{3N}{5}\epsilon_F \tag{7.68}$$

which is straightforward to show after integration and fiddling with constants a bit. We can also determine the pressure because we know that

$$PV = \frac{2E}{3} \to \frac{2N\epsilon_F}{5} = \frac{(6\pi^2)^{2/3}\hbar^2 V}{5mg^{2/3}}\left(\frac{N}{V}\right)^{5/3} \tag{7.69}$$

which means $P \sim \rho^{5/3}$ for $T \to 0$. At low temperatures, the pressure of a Fermi gas becomes very large. This is physically intuitive: due to the Pauli exclusion principle, many particles are in excited states well above the thermal energy of the system, and an energetically unfavorable configuration that leads to a high pressure.

Note that we can check

$$\lim_{T\to 0} TS = U + pV - \mu N = \frac{3N\mu_0}{5} + \frac{2N\mu_0}{5} - \mu_0 N = 0 \tag{7.70}$$

The entropy is directly computed via $S = -k_B \sum_\epsilon p_\epsilon \log(p_\epsilon) = \sum_{\epsilon<\epsilon_F} 1\times\log(1) + \sum_{\epsilon>\epsilon_F} 0\times\log(0) = 0$, since all energy levels below ϵ_F are occupied with 100% certainty. The entropy vanishes at $T \to 0$, as is expected from the third law.

7.5.3 The Fermi energy in metals

To determine the importance of the Fermi energy in common systems, it is useful to consider the 'gas' of electrons in a perfect conductor, treated as free to move, and choose the electron density to be

$$\frac{N}{V} \approx \frac{(\#\text{ valence electrons per atom}) \times (\#\text{ atoms per cell})}{\text{volume of a cell}} \tag{7.71}$$

Pathria uses the example of sodium with one valence electron and two atoms per volume $V_{cell} = (0.43\text{nm})^3$, and finds $\epsilon_F = 3.14\text{eV}$. This numerical value for the Fermi energy means the electrons are in the 'cold' limit (with $\epsilon_F \gtrsim k_B T$) for temperatures below

$$T_F = \frac{\epsilon_F}{k_B} \approx 3.64 \times 10^4 K \tag{7.72}$$

The particular value of the Fermi temperature will vary with different atoms or lattice spacings, but we expect this will be a good order-of-magnitude estimate for many metals. In the context of metals and conductance, room temperature is always in the low-temperature limit. The classical limit is *always* wrong for the behavior of electrons in a metal, and the FD statistics must be taken into account in order to determine the properties of the behavior of electrons in atoms. The classical and quantum theories can thus differ significantly.

7.6 Bose-Einstein condensation

7.6.1 Ground state occupancy as $T \to 0$

The low temperature statistics of Fermions was driven by the Pauli exclusion principle, which is not satisfied by Bosons. A large number of Bosons can potentially occupy the same state, and in the limit of $T \to 0$ we naturally expect they may be driven to the ground state. We've seen that the number of particles satisfies

$$N_e = N - N_0 = \frac{V}{\lambda^3} g_{3/2}(z) \qquad N_0 = \frac{z}{1-z} \tag{7.73}$$

We recall that $0 \le z \le 1$ for bosons, because the grand partition function is not a convergent sum otherwise (and an infinite number of particles will be found in the system). $g_{3/2}(1)$ is a finite integral, though, so we are guaranteed that regardless of the temperature that

$$g_{3/2}(z) \le g_{3/2}(1) = \sum_{n=1}^{\infty} n^{-3/2} = \zeta(3/2) \tag{7.74}$$

This means that $N_e \le V/\lambda^3 \zeta(3/2)$ *regardless* of the value of z. We recall that z is a parameter that sets the number of particles in the system and that if $z \to 1$, $N \to \infty$. This immediately implies that for sufficiently low temperatures, we'll find the ground state heavily occupied (unsurprising since $N_0 = z/(1-z)$ and $z \approx 1 - N_0^{-1}$ as $T \to 0$). Since the total number of particles is unbounded ($N \to \infty$ as $z \to 1$), the ground state is unbounded ($N_0 \to \infty$ as $z \to 1$), but total number of particles in all excited states is bounded ($N \to \infty$ as $z \to 1$). This means that at sufficiently low temperatures an infinite number of particles are found in the ground state and a negligible number in any excited state. The probability of finding a particle in any state is $p_\epsilon \to \delta_{\epsilon,\epsilon_0}$, meaning the entropy vanishes again, $S \to 0$ as expected.

The onset of condensation occurs when the ground state begins to become heavily populated, where

$$N > \frac{V g_{3/2}(1)}{\lambda^3} \tag{7.75}$$

due to the fact that $z \to 1$ as $T \to 0$. We could write this in the equivalent ways of a critical density

$$\lambda^3 \rho_c = g_{3/2}(1) = 2.612... \tag{7.76}$$

or critical temperature

$$\begin{aligned} T < T_c &= \frac{h^2}{2\pi m k_B}\left(\frac{N}{V g_{3/2}(1)}\right)^{2/3} && (7.77)\\ &\approx 2 \times 10^{-19} \rho^{2/3} \text{ m}^2\text{K (for } {}^7\text{Li)} && (7.78)\\ &= 0.2 \rho^{2/3} \text{ nm}^2\text{K} && (7.79) \end{aligned}$$

where the numerical values are for Lithium atoms, and indicate that the temperature must be $T \ll 1$K for Bose Einstein condensation to occur for dilute gasses (with the experiments on Lithium performed at $\rho \approx 9\times10^{-8}\text{nm}^{-3}$, having $T_c \approx 4\mu$K and experiments performed at nK temperatures). Above the critical temperature, the majority of particles will be thermally excited and $N_e \gtrsim N_0$, while below the critical temperature the ground state is occupied by the most particles. This feature of Bosons is termed Bose-Einstein condensation: as the temperature is decreased, the particles condense into the same lowest-energy quantum state with virtually no contribution from the excited states. Note that this would not be the case if $N_e \to \infty$ as $z \to 1$: the fact that $\zeta(3/2)$ is finite ensures a finite number of particles are found in the ground state while the total number of particles diverges. If N_e were to diverge (as is possible for systems with $N_e \propto g_\nu(z) \to \infty$ for $\nu \leq 1$), an infinite number of particles would be found in the excited states and condensation to a single state would not occur.

The interpretation of the calculation in eq. 7.75, which takes $N = N_e = V/\lambda^3 g_{3/2}(z)$ is that particles are added *only* to the excited states, with $N_0 = 0$. This is a reasonable approximation for $z \ll 0$, but one might be concerned that as $z \to 1$ there are *some* particles in the ground state, and the number may not be negligible (since $N_0 \to \infty$ if $z = 1$. Note that one could also determine the temperature at which $N_e = N_0$, another proxy for the onset of condensation. In this case, we would have $T_{mid} = T_c + \delta T$, and thus $\lambda_{mid} = \lambda_c(1 - \delta T/2T_c)$. If we assume $\mu(T) \approx \mu_1 \delta T$ (that is, that $\mu = 0$ and thus $z = 1$ precisely at T_c), then we find

$$N_0 = \frac{z}{1-z} \approx \frac{1}{\mu_1 \delta T} - \frac{1}{2} + O(\delta T) \tag{7.80}$$

$$N_e = \frac{V}{\lambda^3} g_{3/2}(z) \approx \frac{V}{\lambda^3}\left(\zeta(3/2) - \sqrt{4\pi\mu_1\delta T}\right) \tag{7.81}$$

$$\approx \frac{V}{\lambda_c^3}\left(1 - \frac{3\delta T}{2T_c}\right)\left(\zeta(3/2) - \sqrt{4\pi\mu_1\delta T}\right) \tag{7.82}$$

The leading order term for $N_0 \approx (\mu_1 \delta T)$, while the leading order term for $N_e \approx V\zeta(3/2)/\lambda_c^3 = N$. When $N_0 = N_e$, $\delta T \approx (N\mu_{)}^{-1} \ll 1$ as expected. Then $T_{mid} = T_c + \frac{1}{N\mu_1}$, with $T_c \propto N^{2/3}$. Clearly, then, the onset of condensation can also be thought of as the crossover from low occupancy of the ground state to high occupancy of the ground state.

7.7 Heat capacities for quantum particles

We showed that

$$U_e = \frac{3Vk_BT}{2\lambda^3}\begin{cases} f_{5/2}(z) & FD \\ g_{5/2}(z) & BE \end{cases} \tag{7.83}$$

If we wish to compute the heat capacity of these quantum systems, we arrive at a problem: since $C_V = \partial U/\partial T|_{NV}$, we must keep N fixed while varying the temperature.

7.7.1 Heat capacity for Fermions

The heat capacity at constant volume for Fermions is

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{NV} \tag{7.84}$$

which leads to a complication: N must be held fixed when performing the temperature variation. In the grand canonical ensemble, we cannot simply take temperature derivatives to compute the heat capacity, we must first ensure that N is constant during the variation. For fermions, we can do this by noting that

$$f_{3/2}(z) = \frac{N\lambda^3}{V} = \rho\lambda^3 \tag{7.85}$$

In the high-temperature limit, $\lambda \propto T^{-1/2} \to 0$, and since $f_{3/2}(z)$ is an increasing function, it therefore must be that $z \to 0$ as $T \to \infty$ as well (the classical limit). If we were to hold μ fixed as T increases, the number of particles would be $N \approx V/\lambda^3 f_{3/2}(1) \propto T^{3/2} \to \infty$ as $T \to \infty$, so N would vary with T. In the classical limit, we can thus write

$$f_{3/2}(z) = z - \frac{z^2}{2^{3/2}} + \cdots \approx z = \rho\lambda^3 \qquad\qquad N \text{ fixed} \tag{7.86}$$

The energy in this limit is therefore

$$U = \frac{3Vk_BT}{2\lambda^3} f_{5/2}(z) = \frac{3Vk_BT}{2\lambda^3}\left(\rho\lambda^3 - \cdots\right) = \frac{3Nk_BT}{2} \tag{7.87}$$

Equipartition is satisfied, and $C_V = 3Nk_B/2$ as is expected classically.

In the low temperature limit, higher order terms in the Taylor expansion contribute and we cannot approximate $z = \rho\lambda^3$. However, we know that $\mu(T \to 0) = \epsilon_F$, which constrains the number of particles (that is, we can set $z = e^{-\beta\epsilon_F}$ to hold N fixed). While a straightforward calculation of the heat capacity is tempting, we find that

$$\begin{aligned}
\left.\frac{\partial U}{\partial T}\right|_{NV} &\approx \frac{3Vk_BT}{2\lambda^3} f_{5/2}(e^{\beta\epsilon_F}) = \frac{15V}{4\lambda^3 k_B} f_{5/2}(e^{\beta\epsilon_F}) - \frac{3V\epsilon_F}{2\lambda^3 T} f_{5/2}(e^{\beta\epsilon_F}) e^{\beta\epsilon_F} \\
&= \frac{15Vk_B}{4\lambda^3} f_{5/2}(e^{\beta\epsilon_F}) - \frac{3V\epsilon_F}{2\lambda^3 T} f_{3/2}(e^{\beta\epsilon_F}) && (7.88) \\
&= \frac{5U}{2T} - \frac{3N\epsilon_F}{2T} && (7.89) \\
&= \frac{5\frac{3N\epsilon_F}{5}}{2T} - \frac{3N\epsilon_F}{2T} = 0 && (7.90)
\end{aligned}$$

That is, we must include higher order terms in our calculation in order to actually determine the heat capacity for small T. To do so, we need an asymptotic form for the low temperature limit of $f_\nu(z)$, which is not easily computed. Pathria shows in Appendix E that

$$f_\nu(z) \approx \frac{\log^\nu(z)}{\nu\Gamma(\nu+1)}\left(1+\nu(\nu-1)\frac{\pi^2}{6\log^2(z)}+\cdots\right) \tag{7.91}$$

which we will use without proof. We then have $U \approx 3N\epsilon_F/5 + 5\pi^2(k_BT)^2/12\epsilon_F^2 + O(T^4)$, so eq. 7.89 becomes

$$C_V \approx \frac{N\pi^2}{2} \quad \frac{k_B^2 T}{\epsilon_F} \sim \frac{T^1 N^{1/3}}{V^{2/3}} \tag{7.92}$$

This differs from the high temperature limit significantly: first $C_V \to 0$ in the limit of $T \to 0$, and second even for finite temperature has a leading order term $\sim k_B/\epsilon_F \sim \rho^{-2/3}$ (so a dense gas has a very low heat capacity even for small T). The heat capacity tells us about the change in energy as temperature increases, and $C_V = 0$ implies there will be no change in U for small T. That's reasonable for a system of Fermions at extremely low temperatures: many particles are *already* in excited states due to the fact that they cannot all simultaneously occupy the same state. Thus, only the highest energy state (the particle with $\epsilon \approx \epsilon_F$) can be excited by a small change in temperature, producing a negligible change in the system's energy. Note that this is *not* the same temperature scaling of the heat capacity for the frozen degrees of freedom, though (which scaled as $e^{-\beta(\epsilon_1-\epsilon_0)}$). Not all particles are trapped in the ground state, and excited energy states are already occupied, contributing to the heat capacity.

7.7.2 Heat capacity for Bosons

The heat capacity for Bosons exhibits strikingly different behavior than for fermions due to the existence of the critical temperature. We still must keep N fixed, but we have a transition at a finite temperature and must account for the behavior of the heat capacity on both sides.

Below the critical temperature ($T < T_c$) we have

$$N \approx N_e = \frac{z}{1-z} \qquad\qquad z \approx 1 - \frac{1}{N} \approx 1 \tag{7.93}$$

which is independent of the temperature and keeps N constant. That is, if z is constant and close to 1, $z/(1-z) = N_0 \approx N$ is constant. The heat capacity below the critical temperature is then

$$C_V = \left.\frac{\partial U}{\partial T}\right|_{NV} = \frac{\partial}{\partial T}\frac{3V}{2\lambda^3}g_{5/2}(1) = \frac{15Vk_B}{4\lambda^3}\zeta(5/2) \qquad\qquad (T < T_c) \tag{7.94}$$

For $T > T_c$ but still small, we can no longer hold z fixed when the temperature is varied. We can directly compute

$$\begin{aligned} C_V &= \frac{3V}{2}\frac{\partial}{\partial T}\frac{k_B T}{\lambda^3} g_{5/2}(z) && (7.95)\\ &= \frac{15Vk_B}{4\lambda^3} g_{5/2}(z) + \frac{3Vk_B T}{2\lambda^3}\frac{\partial g_{5/2}(z)}{\partial T}\bigg|_{NV} && (7.96)\\ &= \frac{15Vk_B}{4\lambda^3} g_{5/2}(z) + \frac{3Vk_B T}{2\lambda^3}\frac{\partial z}{\partial T}\bigg|_{NV} g'_{5/2}(z) && (7.97) \end{aligned}$$

so to constrain constant N we need only compute $\partial z/\partial T|_{NV}$. We do so by noting that since $N = Vg_{3/2}(z)/\lambda^3$ that

$$\frac{\partial N}{\partial T} = 0 = \frac{3V}{2\lambda^3 T} g_{3/2}(z) + \frac{V}{\lambda^3} g'_{3/2}(z)\frac{\partial z}{\partial T} \quad \Rightarrow \quad \frac{\partial z}{\partial T} = -\frac{3g_{3/2}(z)}{2Tg'_{3/2}(z)} = -\frac{3zg_{3/2}(z)}{2Tg_{1/2}(z)} \quad (7.98)$$

Substitution into eq. 7.97 yields

$$\begin{aligned} C_V &= \frac{15Vk_B}{4\lambda^3} g_{5/2}(z) - \frac{9Vk_B}{4\lambda^3}\frac{g_{3/2}(z)}{g_{1/2}(z)} z\frac{\partial g_{5/2}(z)}{\partial z} && (7.99)\\ &= \frac{15Vk_B}{4\lambda^3} g_{5/2}(z) - \frac{9Vk_B}{4\lambda^3}\frac{g^2_{3/2}(z)}{g_{1/2}(z)} && (7.100) \end{aligned}$$

At the critical temperature (where $z \to 1$), we thus see that

$$C_V(z) = \frac{15Vk_B}{4\lambda^3} g_{5/2}(z) \times \left\{ \begin{array}{cc} 1 & T = T_c^- \\ 1 - \frac{3g^2_{3/2}(z)}{5g_{1/2}(z)g_{5/2}(z)} & T = T_c^+ \end{array} \right. = \frac{15Vk_B}{4\lambda^3} g_{5/2}(1) \quad (7.101)$$

We find that

$$\lim_{z\to 1} \frac{3g^2_{3/2}(z)}{5g_{1/2}(z)g_{5/2}(z)} = 0 \quad (7.102)$$

since $g_{1/2}(z) \to \infty$ as $z \to 1$, so we find C_V is a continuous function. We also see that since $N = V/\lambda_c^3 \zeta(3/2)$ that

$$C_V(T_c) = \frac{15\zeta(5/2)}{4\zeta(3/2)} Nk_B \approx 1.926 Nk_B \quad (7.103)$$

Recall, though, that in the limit of high temperature we must recover the classical statistics, with $C_V(T \to \infty) = 3/2Nk_B$. This means that $C_V(T)$ grows as $T^{3/2}$ for $T < T_c$, and at T_c reaches a heat capacity greater than $C_V(\infty)$ and thus begins to decrease. Differentiation of eq. 7.101 is tedious, but we find that while C_V is itself continuous the derivative $\partial C_V/\partial T$ is *discontinuous*: there is a cusp in the heat capacity when $T = T_c$, with C_V an increasing function for lower temperatures and a decreasing function for higher temperatures.

7.8 The virial expansion

Classically we expect $\beta PV/N = 1$, so deviations from this law are driven by the quantum properties of this system. This can be quantified at high temperatures by computing the Virial coefficients, which assume a low density expansion of the equation of state,

$$\frac{\beta PV}{N} = \sum_{l=1}^{\infty} (\pm 1)^{l-1} a_l (\rho\lambda^3)^l \tag{7.104}$$

In order to determine the coefficients a_l, we need to express z in terms of λ, which we can do by writing

$$\rho\lambda^3 = \sum_{n=1}^{\infty} z^n \frac{(\pm 1)^{n-1}}{n^{3/2}} \tag{7.105}$$

with $\rho = N/V$ the number density. We can formally invert this equation to determine z as a function of λ:

$$z = \sum_{n=0}^{\infty} b_n (\rho\lambda^3)^n \tag{7.106}$$

Unfortunately, we do not know the coefficients b_n, and must compute them somehow. We can do that by realizing

$$\rho\lambda^3 \quad = \quad \sum_{n=1}^{\infty} \frac{(\pm 1)^{n-1}}{n^{3/2}} \left[\sum_{m=0}^{\infty} b_m (\rho\lambda^3)^m \right]^n \tag{7.107}$$

All we have to do is solve for the coefficients b_n by matching the coefficients of powers of $(\rho\lambda^3)$. For example, the 0^{th} order terms in $\rho\lambda^3$ are

$$0 = b_0 \pm \frac{b_0^2}{2^{3/2}} + \frac{b_0^3}{3^{3/2}} \pm \cdots \qquad \Rightarrow \qquad b_0 = 0 \tag{7.108}$$

Terms linear in $\rho\lambda^3$ will be

$$\lambda\rho^3 = b_1\rho\lambda^3 \pm b_0 b_1 \rho\lambda^3 \frac{2}{2^{3/2}} + b_0 b_1 \rho\lambda^3 \frac{3}{3^{3/2}} \pm \cdots \qquad \Rightarrow \qquad b_1 = 1 \tag{7.109}$$

It is difficult to determine a general rule for the coefficients, but it is straightforward to determine b_n knowing all $\{b_0, \ldots, b_{n-1}\}$. We find

$$b_0 = 0 \qquad\qquad b_1 = 1 \qquad\qquad b_2 = \frac{\mp 1}{2\sqrt{2}} \qquad\qquad b_3 = \frac{1}{4} - \frac{1}{3\sqrt{3}} \qquad\qquad \cdots \tag{7.110}$$

and can therefore write

$$\frac{\beta P_e V}{N_e} = \begin{cases} \frac{f_{5/2}(z)}{f_{3/2}(z)} & FD \\ \frac{g_{5/2}(z)}{g_{3/2}(z)} & BE \end{cases} \tag{7.111}$$

$$= \frac{\sum_{n=1}^{\infty}[\sum_{m=1}^{\infty} b_m(\rho\lambda^3)^m]^n a^{n-1}/n^{5/2}}{\sum_{n=1}^{\infty}[\sum_{m=1}^{\infty} b_m(\rho\lambda^3)^m]^n a^{n-1}/n^{3/2}} \tag{7.112}$$

with all but the first term arising from determining the linear term in $(b_0 + b_1\rho\lambda^3 + \cdots)^n$. This expression is clearly horrible, but cutting off the sums at a finite value of n and simply taking Taylor expansions isn't all that hard. Grouping the coefficients of $(\lambda^3\rho)$ gives the desired virial coefficients,

$$a_1 = 1 \qquad a_2 = \frac{\mp 1}{4\sqrt{2}} \qquad a_2 = \frac{1}{8} - \frac{2}{9\sqrt{3}} \qquad \cdots \tag{7.113}$$

where the other coefficients have been previously computed. Note that the Virial expansion is generally used to identify the effect of interactions between particles, but in this case these particles are noninteracting! This is a purely quantum effect. All of this work on the virial expansion is only useful so long as $\rho\lambda^3 \ll 1$, which is not a meaningful expansion for low temperatures (with $\lambda \to \infty$).

7.9 Summary

The statistics for Bosons and Fermions exhibits a number of unique and unexpected properties at low temperatures that would never have been predicted classically. In the grand canonical ensemble (which makes the calculation of all thermodynamic variables significantly easier than the microcanonical or canonical ensembles), we found that all thermodynamic variables can be written in terms of Fermi-Dirac or Bose-Einstein functions. Because the occupancy of each energy level approaches a step function for Fermions (due to the Pauli exclusion principle), the low temperature behavior of Fermions is to pack each particle in the lowest energy levels possible up to the Fermi energy ϵ_F. Bosons pack particles in the ground state as the temperature decreases, and exhibit a second order phase transition at a critical temperature T_c at which the chemical potential reaches its minimum and virtually all particles are found in the ground state.

Chapter 8

Bose-Einstein Systems (Pathria Ch 7.2-7.4)

The previous chapter described the statistics of noninteracting quantum particles, and we found a surprising phase transition in the behavior of Bosons: below a critical temperature an infinite number of particles will condense in the ground state but only a finite number in the excited states. This produces a discontinuity in the heat capacity that indicates a phase transition. A remarkable set of experiments was performed in the 1990s to demonstrate this phenomenon does indeed occur, which we will describe in this chapter. Other examples of particles and quasiparticles that are not constrained by the Pauli exclusion principle are photons and phonons, and this chapter will discuss their statistics as well.

8.1 Ultracold gasses and Bose Einstein condensation

8.1.1 Cooling atoms to nanoKelvin temperatures

Bose Einstein condensation occurs

1. For noninteracting bosons. To see this effect in a gas of particles, we must use uncharged (therefore noninteracting) atoms that are composite particles with integral spin. Examples include ^{2}H, ^{7}Li, ^{87}Rb, and a variety of others.
2. When the temperature is low. $T_c = \frac{h^2}{2\pi m k_B \zeta^{2/3}(3/2)}\rho^{2/3}$. Below this temperature, the ground state becomes heavily occupied and effectively all particles will be found in the ground state.

A significant barrier to the creation of a Bose Einstein Condensate (BEC) is that requires a *very* low temperature in practice, on the order of nanokelvins. This is because there is an upper bound on the density of the particles before they begin interacting with each other strongly. Reaching nanokelvin temperatures is hard to imagine in a standard refrigerator, and a number of clever ideas have been designed to reach remarkably low temperatures. Bose Einstein condensation was accomplished via a two-stage cooling process.

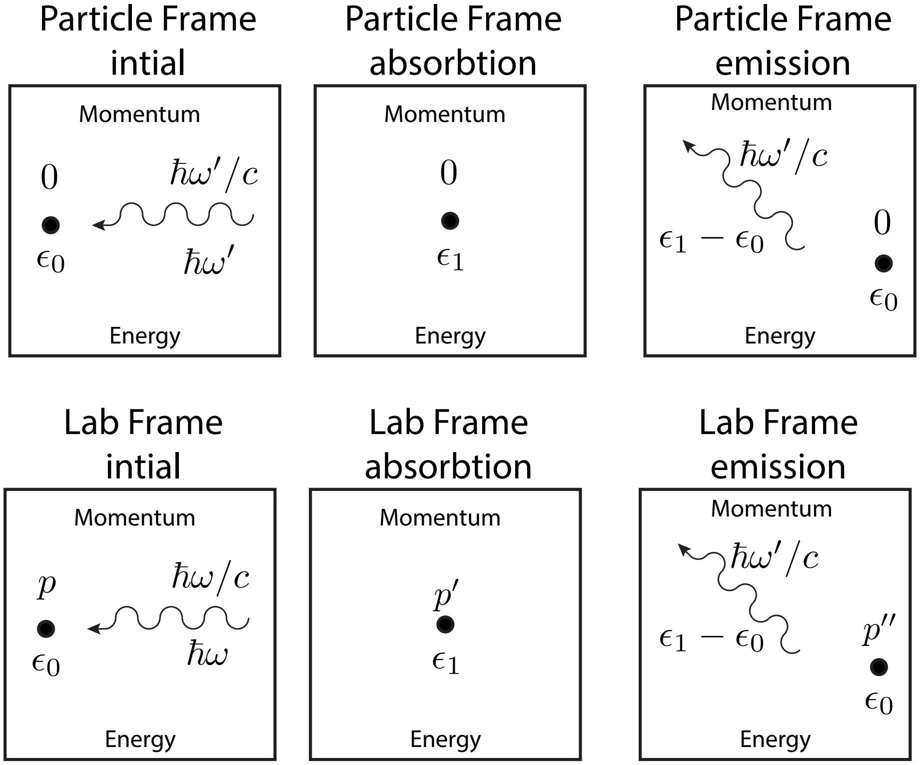


Figure 8.1: Doppler cooling. In the frame of reference of the particle, the photon is doppler shifted to a higher momentum. If the frequency of the laser ω is chosen to match the energy $\epsilon_1 - \epsilon_0$ after that doppler shift, particles will absorb the laser light, and reemit it in a random direction. In the lab frame, photons are absorbed by the particles, then reemitted in a random direction *with a higher energy*, while the momentum of the particle is changed. The momentum of the particle in the original direction of motion is reduced, producing a net slowing of the particle.

1. First, the gas is slowed by a laser (termed laser or doppler cooling, and sometimes called 'optical molasses'). A laser is shone on the gas at a specifically chosen frequency, slightly lower an energy level of the particles. To move between different energy levels, the atom will require a discrete energy quanta to make the transition.

If the frequency of the laser is specifically chosen to be near, but not at, any resonant quanta of energy. Atoms that are moving *toward* the laser beam see a slight doppler shift towards their resonant frequency, and thus are more likely to absorb a photon (as sketched in Fig. 8.1). From the frame of reference of the atom, which is moving in the lab frame,

(a) The atom sees a photon $\hbar\omega' \approx (\epsilon_1 - \epsilon_0) > \hbar\omega$. This photon is at the resonant frequency, so is absorbed. Later, it is reemitted in a random direction, releasing the same amount of energy in the atom's frame: $\hbar\omega'$.

(b) In the lab frame, an atom is moving towards the laser with frequency $\hbar\omega$. It absorbs the photon and slows down due to the absorption of the momentum in the opposite direction. It then later releases a photon of energy $\epsilon_1 - \epsilon_0 > \hbar\omega$. Thus, in the lab frame a photon with higher energy is produced, and thus the atom's energy is reduced.

The slowing of the particles is due to the release of higher energy photons, reducing the kinetic energy of the particles. Some fast moving particles may be lost to the system during this process (those significantly above the optimal doppler shift in the direction of the laser).

While the absorption of a photon is directional (moving towards the laser) the reemission of that energy packet is not directional. That means, by momentum conservation, that atoms moving *towards* the laser source will be slowing down. Atoms at rest or moving away from the laser will not absorb the photons, since the effect of the doppler shift does not bring the photon's energy to match an energy difference between levels. The net result of this is atoms that are stationary relative to some preferred direction. Since this can be applied in all three axes, particles can be localized with a significantly reduced energy.

This approach is limited by the fact that the momentum of a photon is $\hbar\omega/c$, so the momentum of the atom cannot be below $p_{min}^2/2m \sim (h\nu/c)^2/2m \sim k_BT$, or $T_{min} \sim h^2\nu^2/2mc^2k_B$. For ^{87}Rb, the first atom used to exhibit a BEC, this temperature is around 1μK. Seems cold, but not cold enough.

2. Since there is a lower bound on the mean energy, we can't cool below some intrinsic point with laser cooling. Lower temperatures can be obtained by magnetic trapping and evaporative cooling. First, a magnetic trap is generated for the atom with a harmonic profile. Recall that for a noninteracting ideal gas of particles with a dipole moment $\boldsymbol{\mu}$ the energy is $E = -\boldsymbol{\mu} \cdot \mathbf{B}$. An important experimental aspect experimentally is reducing the interactions between atoms, and dipole-dipole coupling is minimized for Alkali metals such as Lithium, Sodium, and Rubidium, for which Bose Einstein condensation has been observed.

Having trapped atoms in an approximately parabolic magnetic trap while avoiding interactions between the atoms, we are still left with μK atoms that are far above the BEC transition temperature. The strength of the magnetic field can be uniformly reduced, meaning that particles with energy approaching the point at which the field is *no longer* locally harmonic are likely to escape from the 'harmonic' well. High energy atoms will be able to escape the trap via barrier crossing while low energy particles will be trapped in the well (pictured in Fig. 8.1(B)). In ^{87}Rb, evaporative cooling reduced the temperature to $\sim$ 20nK, sufficient for Bose Einstein condensation. Arbitrarily low temperatures are obtainable using this approach, but with a loss of the total number of particles in the system.

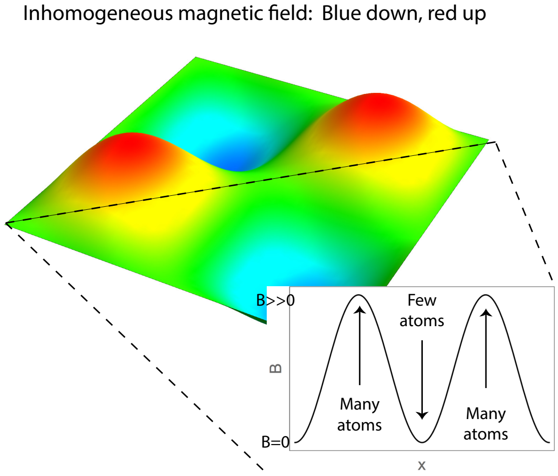


Figure 8.2: Magnetic trapping of particles. Particles in an inhomogeneous field will align their dipole moments with the external field locally (pictured in the main figure). In places with strong fields (either pointing up or down), the particles will be strongly aligned with the field, significantly reducing the lowest energy level. In places with weak external fields, particles will have random dipole orientations with little reduction in the energy. Thus, most particles will be found within some domain of strong magnetic fields with energetic barriers between them associated with weak fields (diagrammed in the inset).

8.1.2 Observation of the condensate

How do we go about 'seeing' the BEC, if one exists? One approach is fluorescence, phase contrast, or other direct imaging techniques. A large number of particles in the same quantum state will scatter light identically, and thus should be detectable. However, the condensate will still be dilute (since the particles need to be effectively noninteracting) so identification of the condensate may not be simple. Alternatively, we can look at the dynamics of the particles after they are released from the trap. If we suddenly turn off the harmonic trapping, all particles suddenly become free particles. All particles in the ground state of the BEC will have the wavefunction

$$\begin{aligned}
\psi(x_\alpha, t) &= \langle x_\alpha | e^{-i\hat{H}_{free}t/\hbar} |0\rangle_{HO} && (8.1)\\
&= \sum_n e^{-(\hbar n^2\pi^2/2mL^2)it/\hbar} e^{-i\pi n x_\alpha/L} \langle n|_{free}|0\rangle_{HO} && (8.2)\\
&= \sum_n e^{-(\hbar n^2\pi^2/2mL^2)it/\hbar} e^{-i\pi n x_\alpha/L} \int dx' e^{-i\pi n x'/L} \left(\frac{m\omega_\alpha}{\pi\hbar}\right)^{1/4} e^{-m\omega (x')^2/2\hbar}
\end{aligned}$$

which mixes the harmonic oscillator states with the free particle hamiltonian (recall that the trap strength does not need to be identical in all cartesian coordinates). From this it is possible (and is a homework problem) to show that

$$\begin{aligned}
|\psi(x_\alpha, t)|^2 &= \frac{1}{\tau_\alpha}\left(\frac{2m}{h\omega_\alpha}\right)^{1/2} \exp\left(-\frac{2\pi m x^2}{h\omega_\alpha \tau_\alpha^2}\right) \qquad \tau_\alpha(t) = \omega_\alpha^{-2} + t^2 && (8.3)\\
&\to \frac{1}{\tau_\alpha}\left(\frac{2m}{h\omega_\alpha}\right)^{1/2} \exp\left(-\frac{2\pi m x^2}{h\omega_\alpha t^2}\right) && (8.4)
\end{aligned}$$

which in the limit of $t \to 0$ approaches a delta function (with $\sigma_\alpha(t) \to \infty$) and approaches a uniform distribution at $t \to \infty$. Importantly, $\tau_\alpha \to t$ for $t \to \infty$. This means the particle is expected to eventually become delocalized, but the rate at which it does so is dependent on the confinement frequency ω_α, which can be tuned to differ across each axis.

We can likewise determine the distribution of particle locations for the excited states as

$$\psi_e(\mathbf{r}, t) = \frac{1}{N_e} \langle \mathbf{r}| e^{-i\hat{H}t/\hbar} \sum_{k=1}^{\infty} \langle n_k\rangle |k\rangle_{HO} \qquad (8.5)$$

which incorporates all contributions from the excited states. This requires us to compute the overlap of the free particle wavefunctions with all excited harmonic oscillator states, which is highly non-trivial. Beale has a very incomplete and unclear argument that the eventual expression for the number density of atoms is

$$\begin{aligned}
|\psi_e(\mathbf{r}, t)|^2 &= \frac{1}{N_e\lambda} \sum_{j=1}^{\infty} \frac{e^{\beta\mu j}}{j^{3/2}} \prod_\alpha \frac{1}{\sqrt{1+\omega_\alpha^2 t^2}} \exp\left(-j\frac{\beta m \omega_\alpha^2 r_\alpha^2}{2(1+\omega_\alpha^2 t^2)}\right) && (8.6)\\
&\to \frac{1}{N_e\lambda} \sum_{j=1}^{\infty} \frac{e^{\beta\mu j}}{t^3\omega_1\omega_2\omega_3 j^{3/2}} \exp\left(-j\frac{\beta \mathbf{r}^2}{2t^2}\right) && (8.7)
\end{aligned}$$

Accepting this equation without actually calculating it, the significant factor is the fact that, as $t \to \infty$, the exponential term becomes *isotropic*, and does not depend on the axes.

This means that the distribution of the particle positions in the ground state will not be homogeneous after the trap is removed, but the positions of the particles in the excited states will be. Inhomogeneities in the position distribution were found in the velocity distribution function after the magnetic trap was turned off, showing that the

The evolution of the momentum of the higher energy states is more spatially symmetric than that of the single ground state. This difference provides the ability to observe the BEC. By creating an inhomogeneous harmonic oscillator, atoms are trapped and a BEC is created (specifically, with $\omega_x = \omega_y \ll \omega_z$). Once the trap is turned off, the particle density will evolve such that the excited states depart symmetrically, but the BEC departs much more slowly in the x and y directions. All of this was observed experimentally with Rubidium, and later with Lithium, Sodium, Potassium, etc.

8.2 Blackbody Radiation

Blackbody radiation is one of the most fundamental applications of quantum statistics, and one of its earliest successes. A blackbody is typically described as a cavity with a small hole through which photons can be emitted, but these details aren't important thermodynamically. We imagine some object with volume V maintained at a temperature T. Atoms in the blackbody will be thermally excited, and will spontaneously emit photons due to the excitation. The particular insight from quantum mechanics was that $\epsilon_s = \hbar\omega_s$ for a photon with frequency ω_s. Photons emitted with frequency ω_s will have energy $\hbar\omega_s$. The energy will be Boltzmann distributed (since we're specifying the body is at temperature T), but since photons are being spontaneously created we don't have a restriction on the total number of particles. Thus, if we define n_s as the number of photons with frequency ω_s, we will have

$$\begin{aligned}
\langle n_s \rangle &= \sum_s n_s p_s && (8.8)\\
&= \frac{\sum_{\epsilon_s} n_s e^{-\beta\epsilon_s}}{\sum_{\epsilon_s} e^{-\beta\epsilon_s}} = \frac{\sum_{n_s=0}^{\infty} n_s e^{-\beta n_s \hbar\omega_s}}{\sum_{n_s=0}^{\infty} e^{-\beta n_s \hbar\omega_s}} && (8.9)\\
&= -\frac{1}{\hbar\beta}\frac{\partial}{\partial\omega_s}\log\left(\sum_{n_s} e^{-\beta n_s \omega_s \hbar}\right) && (8.10)\\
&= \frac{1}{e^{+\beta\hbar\omega_s} - 1} && (8.11)
\end{aligned}$$

This is equivalent to a system of bosons with $z = 1$ (no restriction on the number of particles). You may immediately think: 'what's the scam here? $z = 1$ is forbidden for bosons! They're all in the ground state!' You would be correct, but here, the ground state is a *non-existent* photon (one with zero energy, and thus un-emitted). The 'ground state' in this case is defined by the absence of radiation, so having an infinite number of particles in the ground state does not correspond to 'condensation'. Thus, $z = 1$ is fine here: the excited states N_e are finite (as we showed in the previous sections), N_0 refers to the ground state of our blackbody (meaning zero-energy photons), and thus the total energy of the system is finite.

We now know $\langle n_s \rangle$, but in order to compute averages easily we need to determine the density of states $D(\epsilon)$, or equivalently $D(\omega)$ recognizing that $\epsilon = \hbar\omega = pc$ since a photon carries momentum $p = \hbar\omega/c$. The standard calculation of

$$\sum_n f(n) \to \frac{V}{h^3}\int d^3p f(p) = \frac{4\pi V}{h^3}\int_0^\infty dp p^2 f(p) = \int_0^\infty d\omega D(\omega) f(\omega) \tag{8.12}$$

yields

$$D(\omega) = \frac{4\pi V \hbar^3 \omega^2}{h^3 c^3} = \frac{V\omega^2}{2\pi^2 c^3} \tag{8.13}$$

In this calculation, we have neglected a factor of 2 due to the fact that photons can be polarized in two directions (relative to their axis of propagation), so in fact the density of states must be increased by a factor of 2. This factor is important for a precise calculation, but we can simply accept the fact that that $D(\epsilon) = gD_{g=0}(\epsilon)$ with a degeneracy g, and photons have a degeneracy $g = 2$.

In particular, we can determine the energy density (energy per unit volume)

$$u(\omega) \quad = \quad \epsilon(\omega) D(\epsilon)\langle n_\epsilon \rangle = \hbar\omega D(\omega)\langle n_\omega \rangle = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega\beta} - 1} \tag{8.14}$$

which is the energy density between ω and $\omega + d\omega$ (that is, we can compute the mean energy by integrating $E/V = \int u(\omega) d\omega$). This is a major success of quantum mechanics (which prescribes an energy $\hbar\omega$ to a photon) because of the absurd limit as $\hbar \to 0$ that was obtained classically:

$$u(\omega) = \frac{\omega^3}{\pi^2 c^3}\frac{\hbar}{e^{\beta\hbar\omega} - 1} \approx \frac{k_B T \omega^2}{\pi^2 c^3} \tag{8.15}$$

which permits an infinite energy $\int u(\omega) d\omega = \infty$. This was known as the ultraviolet catastrophe, and prior to QM there was no clear resolution to the problem. Both Plank and Einstein worked on the development of quantum blackbody radiation, and energy quantization was assumed by Plank specifically to resolve the ultraviolet catastrophe. Classically, electromagnetism was a continuous spectrum, and this was the first time that it was proposed that light came in discrete packets (quanta) called photons.

There are a few features that are worth noting:

$$U = V\int d\omega u(\omega) = \frac{\hbar V}{\pi^2 c^3}\int d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} = \frac{(k_B T)^4}{\pi^2 \hbar^3 c^3}\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{6(k_B T)^4}{\pi^2 \hbar^3 c^3} g_4(1) \tag{8.16}$$

where we've already sorted out the Bose Einstein function of $g_4(1) = \sum_n n^{-4} = \zeta(4)$, and Mathematica will tell us that $\zeta(4) = \pi^4/90$. We thus find that

$$U = \frac{\pi^2 (k_B T)^4 V}{15 \hbar^3 c^3} \tag{8.17}$$

which, importantly, is not infinite (as predicted classically). This is wholly dependent on the concept of Boson statistics (although it predates it by decades): there are a finite number of bosons that can occupy excited states, and in our case particles refer to photons with nonzero frequencies.

8.3 Normal Modes and Phonons

We can imagine a system of N sites located at $\bar{x}_i$. Particles are bound to these sites with a potential $\Phi(x_1, \ldots, x_N)$, where $\partial\Phi/\partial x_i|_{\bar{x}_i} = 0$, so the energetic minimum occurs when each particle is located at the site $\bar{x}_i$. We can then write

$$\begin{aligned} \Phi(x_1 \cdots x_N) &\approx \Phi(\bar{x}_1, \cdots, \bar{x}_M) + \frac{1}{2}\sum_{ij} \left.\frac{\partial^2 \Phi}{\partial x_i \partial x_j}\right|_{\{\bar{x}_i\}} (x_i - \bar{x}_i)(x_j - \bar{x}_j) && (8.18) \\ &= \Phi_0 + \frac{1}{2}\sum_{ij} \alpha_{ij} y_i y_j && (8.19) \end{aligned}$$

with $y_i = x_i - \bar{x}_i$. This is simply a multidimensional Taylor expansion, neglecting cubic and other higher order terms. The Hamiltonian is then

$$H = \Phi_0 + \sum_i \frac{p_i^2}{2m} + \sum_{ij} \frac{\alpha_{ij} y_i y_j}{2} \tag{8.20}$$

These are coupled harmonic oscillators, which are difficult to deal with since all of the variables are coupled to one another. However, we do know we can make a change of variables to find a harmonic oscillator (we've done this in a number of homework problems). The normal modes are simply determined by the eigenvectors of the matrix $\mathbf{A}_{ij} = \alpha_{ij}$, and the characteristic frequencies are given by the eigenvalues of the matrix (over m). Writing $\mathbf{A} = \mathbf{P}^T \mathbf{\Lambda} \mathbf{P}$, we can see that $U_{pot} = \mathbf{y}^T \mathbf{A} \mathbf{y} = \mathbf{y}^T \mathbf{P}^T \mathbf{\Lambda} \mathbf{P} \mathbf{y} = \mathbf{q}^T \Lambda \mathbf{q}$ with $\mathbf{q} = \mathbf{P}\mathbf{y}$ a linear combination of the original $y_i's$, and where $\mathbf{P}^{-1} = \mathbf{P}^T$ since $\mathbf{A}$ is real and symmetric. Importantly, the potential energy is now $U_{pot} = \sum_i \lambda_i q_i^2$ is diagonal in this normal basis, and the kinetic energy is as well: $K = \frac{m}{2}\dot{\mathbf{y}}^T \dot{\mathbf{y}} = \frac{m}{2}\dot{\mathbf{q}}\mathbf{P}\mathbf{P}^{-1}\dot{\mathbf{q}} = \frac{m}{2}\dot{\mathbf{q}}^T \dot{\mathbf{q}}$. Thus we can rewrite,

$$H = \Phi_0 + \frac{m}{2}\sum_i \left(p_i^2 + \omega_i q_i^2\right) \tag{8.21}$$

where the $\omega_i = 2\lambda_i/m$'s are the characteristic frequencies. We also saw that this trick worked quantum mechanically as well: we used the same change of variables to write

$$-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_{ij}\alpha_{ij}y_i y_j = \frac{1}{2m}\sum_i\left(\hat{p}_i^2 + m^2\omega_i^2 q_i^2\right) \tag{8.22}$$

So, we've successfully replaced our N interacting particles with a set of N non-interacting *phonons*: quasiparticles that represent the physics of the system (assumed quadratic) as a set of noninteracting harmonic oscillators. Phonons are not particles, but rather normal modes of motion in the original system. In particular, the energy of the system is going to be the same if we treat it on the level of particles (which is hard, since they're interacting through the matrix $\mathbf{A}$) or phonons (which is very easy because they are non-interacting). The energy of a one-dimensional system will be $\Phi_0 + \sum_s \hbar\omega_s(n_s + 1/2) = (\Phi_0 + \hbar/2\sum_s \omega_s) + \hbar\sum_s n_s\omega_s$, with each oscillator having quantum numbers $\{n_i\}$. Note that unlike blackbody radiation, there are precisely N oscillators (rather than an arbitrary number of photons).

The probability of a particular oscillator being at energy level n_s is determined from the Boltzmann distribution $p(n_s) \propto e^{-\beta\hbar\omega_s(n_s+1/2)}$, which is normalized noting that $\sum_n e^{-\beta\hbar\omega(n+1/2)} = e^{\beta\hbar\omega/2}/(e^{\beta\hbar\omega} - 1) = Q_1(\omega)$, the partition function for a single phonon. We can then determine the mean energy

$$U = \Phi_0 + \sum_{i=1}^{N}\sum_{n_i=0}^{\infty}\frac{\hbar\omega_i(n_i+\frac{1}{2})e^{-\beta\hbar\omega_i(n_i+1/2)}}{Q_1(\omega_i)} \tag{8.23}$$

$$= \left(\Phi_0 + \frac{\hbar}{2}\sum_i \omega_i\right) + \sum_i \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} \tag{8.24}$$

where the sum can be easily evaluated by computing $-\beta^{-1}\partial\log(Q_1(\omega))/\partial\beta$. The first terms are temperature-independent and refer to the intrinsic energy of the lattice. The temperature dependent second portion is the only term that contributes to the statistics at nonzero temperatures, and is *exactly* the same as the energy we found for photons in a blackbody, with

$$\langle\epsilon_s\rangle = \frac{\hbar\omega_s}{e^{+\beta\hbar\omega_s} - 1} = \epsilon_s\langle n_{\epsilon_s}\rangle \tag{8.25}$$

where we have identified the mean occupancy $\langle n_\epsilon\rangle = 1/(z^{-1}e^{\beta\epsilon} - 1)$ for $z = 1$. There are some differences between the physical systems, though: the blackbody had a variable number of particles (photons), but our solid has a specific set of N characteristic frequencies (phonons).

A problem with this analysis is that we have no idea what the frequencies ω_i are. Computing ω_i for an arbitrary system is complicated, because we've got to diagonalize an $N \times N$ matrix (which is painful analytically and computationally problematic if N is large). It's easier to simply write down a model for the ω_i. By far the simplest approximation is that all ω_i are equal, and originally used by Einstein. However, we can compute the average energy quite easily: $U = U_{lattice} + N\hbar\omega/(e^{\beta\hbar\omega} - 1)$. The heat capacity is

$$C_V = \frac{\partial U}{\partial T} = k_B N \frac{e^{\beta\hbar\omega}(\beta\hbar\omega)^2}{(e^{\beta\hbar\omega} - 1)^2} \quad = \quad N k_B E(\beta\hbar\omega) \tag{8.26}$$

with $E(x) = x^2 e^x/(e^x - 1)^2)$. This means $C_V \to 0$ as $T \to 0$ exponentially fast as the vibrational degrees of freedom become frozen. This assumes the vibrations are in one dimension, but since the phonons are noninteracting we can write $C_V = 3Nk_B E(\beta\hbar\omega)$ in three dimensions.

Assuming ω_i is a constant is a really strong assumption, and it's better to assume that there are some distribution of frequencies. Initially, we might expect that there is a maximum vibrational frequency available to the solid, so the number density of the normal mode frequencies $D(\omega)$ will satisfy

$$\int_0^{\omega_d} D(\omega) d\omega = 3N \tag{8.27}$$

with the factor of three coming from the assumption that this is a three dimensional solid. We've seen an expression like this before: the Fermi energy was defined as $\int_0^{\epsilon_F} d\epsilon D(\epsilon) = N$, which allowed us to determine the unknown maximum energy ϵ_F in terms of N. Don't get confused, though: eq. 8.27 does not require fermion statistics, but rather solely relies on a distribution of frequencies that is capped. In order to use the same trick here as we did for computing the Fermi energy, we need to determine a reasonable estimate of the density of states. We found previously that in the case of blackbody radiation that in the classical limit (with $\hbar \to 0$) that

$$D_{blackbody}(\omega) = \frac{V\omega^2}{2\pi^2 c^3} \tag{8.28}$$

which we also derived in eq. 8.13 as well with $\epsilon = \hbar\omega$. Here we'll reuse this result, with an additional assumption that the 'speed of light' in a material system is (a) not actually c, but is a speed determined by the inter-particle interactions, and (b) may differ for transverse and longitudinal wave propagation. Assuming the frequency distribution is uniform, we then can write

$$\int_0^{\omega_D} d\omega \frac{\omega^2 V}{2\pi^2} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) = 3N \tag{8.29}$$

and after integration we find the Debye frequency ω_D:

$$\omega_D^3 = \frac{18\pi^2 N}{V} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right)^{-1} \tag{8.30}$$

which means the density of states can be written in the simpler form

$$D(\omega) = \frac{9N\omega^2}{\omega_D^3} \tag{8.31}$$

This is a fine enough approximation, although to see the definition of a 'bad fit', see Pathria Fig 7.15 (7.9 2nd ed) comparing the Debye estimate for the density of states to an experimentally determined distribution. We can use the density of frequencies to compute the heat capacity as

$$\begin{aligned} C_V &= -k_B\beta^2\frac{\partial}{\partial\beta}\int_0^{\omega_D} D(\omega)\frac{\hbar\omega}{e^{\hbar\omega\beta}-1} = k_b\int_0^{\omega_D} d\omega D(\omega)\frac{e^{\beta\hbar\omega}(\hbar\omega\beta)^2}{(e^{\beta\hbar\omega}-1)^2} &(8.32)\\ &= \frac{9Nk_B}{(\beta\hbar\omega_D)^3}\int_0^{\beta\hbar\omega_D}\frac{x^4e^x}{(e^x-1)} &(8.33)\\ &= 9Nk_B\Big(\frac{(\beta\hbar\omega_D)}{e^{\beta\hbar\omega_D}-1}+\frac{4}{(\beta\hbar\omega_D)^3}\int_0^{\beta\hbar\omega_D}\frac{x^3}{e^x-1}dx\Big) &(8.34)\end{aligned}$$

where the last relation comes from integration by parts (with $du = dxe^x/(e^x-1)^2$). In the limit of $T \to 0$ ($\beta \to \infty$) the first term vanishes exponentially fast and the second term looks like

$$C_V \approx \frac{36Nk_B}{(\beta\hbar\omega_D)^3}\int_0^{\infty} dx\frac{x^3}{e^x-1} = \frac{216Nk_B}{(\beta\hbar\omega_D)^3}g_4(1) \tag{8.35}$$

The heat capacity of a solid thus vanishes as T^3. This differs from the heat capacity we found with simple harmonic oscillators, with

$$C_V^{HO} = \frac{x^2e^x}{(e^x-1)^2} \tag{8.36}$$

which vanishes exponentially fast. The T^3 law is in fact observed in experiments, so it is therefore important to account for the distribution of frequencies in a solid (even if the approximation is a very poor fit to the actual distribution).

8.4 Summary

Photons and the quasiparticle phonons are well described by noninteracting particles, and are Bosons since they are not constrained to be in different quantum states. That is, a photon can have frequency ω without forbidding another photon to be emitted with the same frequency, and likewise for phonons. In this chapter, we saw that the statistics of these systems are well described by Bose Einstein statistics given the density of states $D(\epsilon)$, with an important exception: the ‘ground states’ could never be meaningfully occupied by an infinite number of particles. The phenomenon of Bose Einstein condensation was indeed observed experimentally on ultracold Rubidium-87 atoms in a remarkable series of experiments, demonstrating the correctness and utility of Bose Einstein systems.

Chapter 9

Fermi-Dirac Systems (Pathria Ch 8.2-8.3)

Bosons provided a rich set of interesting physics in the previous chapter, with the condensation transition occurring when the temperature reached a critical point. Each of these Bose-Einstein systems were integral spin, meaning that the statistics of individual electrons (either free or those that cannot be treated as part of a composite) cannot be described using any of the previous chapter. In this chapter, we'll explore the implications of Fermi-Dirac statistics on the behavior of particles in a magnetic field, and the thermoionic emission of electrons.

9.1 Paramagnetism

9.1.1 The Fermi Energy in a magnetic field

A first example is that of a gas in a magnetic field, with $\epsilon = p^2/2m - \boldsymbol{\mu} \cdot \mathbf{B}$ with $\boldsymbol{\mu}$ the intrinsic magnetic moment of the particles. For the moment, let us consider only spin 1/2 particles, so $\boldsymbol{\mu}$ points parallel or antiparallel to the magnetic field, with no change in magnitude. The notation of $\boldsymbol{\mu}$ as a dipole moment and μ a chemical potential here is quite obnoxious but necessary for historical reasons. In this chapter, I will simply replace occurrences of the chemical potential with $\beta^{-1}\log(z) = \mu$, and the notation $\epsilon_B = \boldsymbol{\mu} \cdot \mathbf{B}$ as the energy associated with the magnetic field.

The average number of particles at each energy level is computable straight from our results in Sec. 7.2.2,

$$\langle n_p^+ \rangle = \frac{1}{z^{-1} e^{\beta(p^2/2m - \epsilon_B)} + 1} \qquad \langle n_p^- \rangle = \frac{1}{z^{-1} e^{\beta(p^2/2m + \epsilon_B)} + 1} \tag{9.1}$$

where $\langle n_p^\pm \rangle$ is the average number of particles with momentum p and parallel (or antiparallel) to the field. In the limit as $T \to 0$, these distributions will both become step functions, but *not* the same step function, due to the differing sign of B. Antiparallel particles are constrained to have a lower momentum than parallel particles. We can find in particular that

$$N^\pm = \int_0^\infty \frac{D(\epsilon)}{z^{-1} e^{+\beta\epsilon \mp \beta\epsilon_B} + 1} \approx \int_0^{\log(z)/\beta \pm \epsilon_B} D(\epsilon) = \frac{4\pi V}{3} \left(\frac{2m}{h^2} \right)^{3/2} \left[\frac{\log(z_0)}{\beta} \pm \epsilon_B \right]^{3/2} \tag{9.2}$$

To determine ϵ_F, we would need to solve

$$N = N^+ + N^- = \frac{4\pi V}{3} \left(\frac{2m}{h^2} \right)^{3/2} \left[\left(\epsilon_F + \mu B \right)^{3/2} + \left(\epsilon_F - \mu B \right)^{3/2} \right] \tag{9.3}$$

Determining ϵ_F in terms of N in this equation is no easy task (try solving it using Mathematica...). However, it is possible to consider the magnetization in the limit of $B \to 0$. In that case,

$$N \approx \frac{8\pi V}{3} \left(\frac{2m}{h^2} \right)^{3/2} \epsilon_F^{3/2} + O(B^2) \tag{9.4}$$

which gives the leading order Fermi energy in the presence of a weak field. This is the same as what we found in the absence of a magnetic field in chapter 7. Note that the factor of 8 is twice the original factor of 4 for the fermi energy we derived previously, because the particle can either be spin up or down, and without an external field this is simply a degeneracy of $g = 2$. This leads to a Fermi energy of $\epsilon_F \approx h^2/8m(3N/2\pi V)^{2/3} + O(B^2)$.

9.1.2 Paramagnetic effects

The total magnetic moment is the net magnetic dipole moment of the entire system, $M = \mu(N^+ - N^-)$. We computed the magnetic susceptibility for a classical gas, with

$$\chi_0 = \lim_{B \to 0} \frac{1}{V} \frac{\partial M}{\partial B} \approx \frac{N\mu^2}{3k_B T} \qquad \text{(classical)} \tag{9.5}$$

For fermions with a magnetic dipole moment, we find

$$\begin{aligned} M = \mu(N^+ - N^-) \quad &\approx \quad \mu \frac{4\pi V}{3} \left(\frac{2m}{h^2} \right)^{3/2} \times 3\epsilon_F^{1/2} \mu B + O(B^2) & (9.6) \\ &= \quad \frac{4\pi \mu V}{3} \left(\frac{2m}{h^2} \right)^{3/2} \epsilon_F^{3/2} \left[\left(1 + \frac{\mu B}{\epsilon_F} \right)^{3/2} - \left(1 - \frac{\mu B}{\epsilon_F} \right)^{3/2} \right] & (9.7) \end{aligned}$$

so that

$$\chi_0 = \frac{4\pi\mu^2(2m)^{3/2}}{h^3}\sqrt{\epsilon_F} = \frac{2m(12\pi^2)^{1/3}}{h^2}\mu^2\left(\frac{N}{V}\right)^{1/3} \qquad (fermions) \tag{9.8}$$

where we have used the fact that $\epsilon_F = (3N/8\pi V)^{2/3}h^2/2m$ derived when we first worked out the fermi energy. Note that this is *independent* of the temperature as $T \to 0$, meaning the classically derived curie's law will not hold for fermions. It will, however, hold for bosons (for which no fermi energy exists). These results show that Fermions with an intrinsic dipole moment:

- Will align with an externally applied magnetic field, as their magnetic susceptibility is positive
- Will have a finite response for low temperature, unlike the classically predicted $\chi_0 \sim T^{-1}$. For $T \to 0$, classical particles have a large response because all particles are in the ground state, and aligning with the magnetic field produces a huge decrease in the total system energy. Since all particles can occupy the same quantum state, there is no problem with this arrangement. Quantum mechanically, the energy associated with aligning with the field is relatively modest in comparison to the Fermi energy for low fields, so the response of the system to a weak field will be smaller.
- Will not retain their magnetization after the field is removed, since $M \to 0$ as $B \to 0$ (unlike ferromagnets). We'll be talking about spontaneous magnetization again soon.

This effect is called paramagnetism, and this low temperature limit twas not explainable using classical mechanics as the magnetic dipole moment arises from the particle's spin.

9.2 Diamagnetism

9.2.1 Quantization due to a vector potential

There is another quantum effect in a magnetic field that becomes important in the absence of an intrinsic magnetic moment. The Hamiltonian for a charged particle in a magnetic field is

$$\hat{H} = \frac{1}{2m}\left(\hat{p} - e\mathbf{A}\right)^2 \tag{9.9}$$

with $\mathbf{A}$ the vector potential and $\mathbf{B} = \nabla \times \mathbf{A}$. We can choose $A_x = -By$, $A_y = A_z = 0$ for a field pointed in the z direction (this chooses a gauge, and other choices are possible) which produces a magnetic field in the z direction. The Hamiltonian is then

$$H = \frac{1}{2m}\left[(\hat{p}_x - eBy)^2 + \hat{p}_y^2 + \hat{p}_z^2\right] \tag{9.10}$$

which couples the momentum in the x direction with the position in the y direction. In the z direction the Hamiltonian decouples nicely, so we assume that we can use separation of variables to find $\psi(x, y, z) = \psi_2(x, y)Z(z)$ from which we readily find that $Z(z) \propto e^{ip_z z/\hbar} = e^{ik_z z}$. The separation in x and y is less clear, because the Hamiltonian couples $\hat{p}_x$ with y. These operators commute, though, and we'll find we can still use separation of variables. Taking $\psi = XYZ$, we find

$$\frac{\hat{H}\psi}{\psi} = -\frac{\hbar^2}{2m}\left(\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z}\right) + \frac{i\hbar eBy}{m}\frac{X'}{X} + \frac{(eBy)^2}{2m} = E \tag{9.11}$$

If we take the anzatz that $X(x) \propto e^{ip_x x/\hbar}$, we can readily see that

$$-\frac{\hbar^2}{2m}\frac{Y''}{Y} + \frac{eBp_x y}{m} + \frac{(eBy)^2}{2m} = E - \frac{\hbar^2(p_x^2 + p_z^2)}{2m} \tag{9.12}$$

$$\tag{9.13}$$

or after completing the square

$$-\frac{\hbar^2}{2m}\frac{Y''}{Y} + \frac{(eB)^2}{2m}\left(y + \frac{\hbar p_x}{eB}\right)^2 - \frac{\hbar^2 p_x^2}{2m} = E - \frac{\hbar^2(p_x^2 + p_z^2)}{2m} \tag{9.14}$$

$$\tag{9.15}$$

finally leading to

$$-\frac{\hbar^2}{2m}\frac{Y''}{Y} + \frac{m\omega^2\tilde{y}^2}{2} = E - \frac{\hbar^2 p_z^2}{2m} \tag{9.16}$$

$$\tag{9.17}$$

with $\tilde{y} = y - k_x/eB$ and $\omega = eB/m$. This final equation is simply a harmonic oscillator, leading to a total energy of the system

$$\epsilon = \frac{p_z^2}{2m} + m\omega(n_y + \frac{1}{2}) \tag{9.18}$$

Note that p_x does not appear in this expression, as it has been merged into the harmonic oscillator term. The momentum in the x direction thus acts solely as a degeneracy: regardless of the particle's x momentum the total energy is the same. There is a constraint on the momentum though: y is still confined within a box and the offset on position ($k_x/eB = 2\pi n_x/eBL$ for n_x the integer energy level) should not shift the particle outside of the box. Then we expect $n_x \lesssim hL^2/eB$, giving a degeneracy (number of equivalent energy states) of $g = hL^2/eB$ due to the x momentum.

9.2.2 Statistics of diamagnetism

The partition function for the particle can now be computed:

$$\log(\mathcal{Q}) = \frac{hL^2}{eB} \int \frac{Ldp_z}{h} \sum_j \log\left(1 + ze^{-\beta p_z^2/2m - \beta\hbar\omega(j+1/2)}\right) \tag{9.19}$$

with the multiplying factor accounting for the degeneracy in the x direction. The $T \to 0$ limit is complicated to analyze, but it is often the case that particles can be found in magnetic fields for finite T. For sufficiently large T we expect the system will be Botltzmannian, and will thus satisfy

$$\begin{aligned} \log(\mathcal{Q}) &= \frac{eBL^2}{h} \int \frac{Ldp_z}{h} \sum_j ze^{-\beta p_z^2/2m - \beta\hbar\omega(j+1/2)} && (9.20) \\ &= \frac{zVeB}{h^2}\left(\frac{2\pi m}{\beta}\right)^{1/2} \frac{1}{2\sinh(\beta\hbar\omega/2)} && (9.21) \\ & && (9.22) \end{aligned}$$

from which we can derive the mean magnetization $M = \langle \partial H/\partial B \rangle = \beta^{-1}\partial\log(\mathcal{Q})/\partial B = (m/e\beta)\partial\log(\mathcal{Q})/\partial\omega$, yielding

$$\chi = \frac{zV}{\lambda^3}\frac{e\hbar}{2m}\left(\frac{1}{\sinh(x)} - x\frac{\cosh(x)}{\sinh^2(x)}\right) \tag{9.23}$$

with $x = \beta e\hbar B/2m$. However, we also can compute the average number of particles in the system,

$$z\frac{\partial \log \mathcal{Q}}{\partial z} = \frac{zVeB}{h^2}\left(\frac{2\pi m}{\beta}\right)^{1/2} \frac{1}{2\sinh(\beta\hbar\omega/2)} \tag{9.24}$$

and some algebra shows that

$$M = -\frac{\hbar Ne}{2m}\left(\coth(x) - \frac{1}{x}\right) \approx -\frac{(\hbar e)^2 B}{6m^2 k_B T}N \tag{9.25}$$

The important aspect of this is that the sign of the mean magnetiszation is negative, not positive. These particles will become *antiparallel* to the field, not parallel. This is a purely quanttum mechanical effect (is zero in the limit of $\hbar \to 0$), and was observed and unexplained prior to the introduction of QM. Note that this contribution would also exist in the case of particles with a dipole moment (like the paramagnet above). However, the diamagnetic effect will be small so long as the magnetic dipole moment μ is not very small ($\propto \hbar^2$)

9.3 Thermoionic emission and the photoelectric effect

9.3.1 Current density over a work function

In order to accurately predict the behavior of current and electron statistics in a metal, we'll make a simple approximation: electrons must overcome some fixed barrier height in order to transition from bound to unbound. This assumes the details of the potential are unimportant, and ignores any details of the band structure of the system. In order for the electron to move in a particular direction, we assume it must be unbound by having a momentum $p_z \geq \sqrt{2mW}$ where W is the barrier height. Note that this transition is directional, as opposed to isotropic, providing the general feature of a lattice of atoms (so that a 'free' electron can move up or down if its momentum in the z direction is high enough, but not left or right).

We then expect that the current due to a single electron in a particular direction will be

$$I = e\left\langle \frac{p_z}{m}\Theta\left[\frac{p_z^2}{2m} - W\right]\right\rangle = \int \frac{Vd^3p}{h^3}\frac{p_z\langle n_\epsilon\rangle}{m}\Theta\left[\frac{p_z^2}{2m} - W\right] \tag{9.26}$$

which is the velocity of an electron, times its charge, subject to the constraint it must be unbound. The current density (electrons per unit area crossing a surface) is

$$\begin{aligned}
J &= \frac{e}{h^3}\int_{\sqrt{2mW}}^{\infty} dp_z \int_{-\infty}^{\infty} dp_x dp_y \frac{2p_z/m}{e^{\beta(\epsilon-\mu)} - 1} && (9.27)\\
&= \frac{2e}{mh^3}\int_{\sqrt{2mW}}^{\infty} dp_z \int_{-\infty}^{\infty} dp_x dp_y \frac{p_z}{z^{-1}e^{\beta((p_x^2+p_y^2)/2m+p_z^2/2m)} + 1} && (9.28)\\
&= \frac{4\pi e}{mh^3\beta}\int_{\sqrt{2mW}}^{\infty} dp_z \int_0^{\infty} ds \ \frac{p_z s}{z^{-1}e^{\beta(s^2/2m+p_z^2/2m)} + 1} && (9.29)\\
&= \frac{4\pi e}{h^3\beta}\int_{\sqrt{2mW}}^{\infty} dp_z \log\left(1 + ze^{-\beta p_z^2/2m}\right) && (9.30)\\
&= \frac{4\pi me}{h^3\beta^2}\int_W^{\infty} dx \log\left(1 + ze^{-x}\right) && (9.31)
\end{aligned}$$

Note that we did not need to make reference to $D(\epsilon)$ here, since we never converted this away from the momentum (which are linear in the quantum numbers for the free particles, and thus do not require a density of states approximation). The leading factor of two accounts for spin degeneracy in the second equation, we switched to polar coords in the third equation, and we recognized an easy antiderivative in the fourth equation. We can write this final integral as

$$J = \frac{4\pi me}{\beta^2h^3}\int_0^L dx \log(1 + ze^{-x+W}) = \frac{4\pi me}{\beta^2h^3}\int_0^L dx \frac{x}{e^{x-W} + 1} = \frac{4\pi me}{\beta^2h^3} f_2(ze^{-\beta W}) \tag{9.32}$$

In the limit of low temperature, the quantity $(W-\mu)/k_BT \to \infty$, consistent with the idea of having to tunnel over some barrier tunneling over a barrier, so we approximate

$$J \approx \frac{4\pi e}{h^3\beta}\int_{\sqrt{2mW}}^{\infty} e^{\beta(p_z^2/2m-\mu)}p_z dp_z = \frac{4\pi me}{\beta^2h^3}e^{-\beta(\mu-W)} \tag{9.33}$$

Classically, $N = V/\lambda^3 e^{\beta\mu}$, with $\lambda \sim T^{-1/2}$, so there is a temperature dependence of the classical chemical potential down to zero. We'd expect then

$$J = \frac{N}{V}\sqrt{\frac{e^2k_B}{2\pi m}}\,T^{1/2}e^{-\beta W} \qquad (classical) \tag{9.34}$$

Quantum mechanically, we found ourselves in the regime of fixed chemical potential, with $\mu \approx \epsilon_F$. Note there are higher order corrections, but this is the general behavior for $T \to 0$. That means that

$$J = \frac{4\pi mek_B^2}{h^3}\,T^2e^{-\beta(\epsilon_F-W)} \qquad (quantum) \tag{9.35}$$

The existence of the Fermi energy acts as a factor to lower the barrier from $W \to W-\epsilon_F$, so quantum mechanically we expect to see a much greater thermoionic current than would be expected classically at low temperatures. $W-\epsilon_F$ is referred to as the work function: the effective barrier felt by the highest energy electron in the limit as $T \to 0$. Classically, each electron can have arbitrarily low energy, so all of them would have to tunnel across the full barrier W. Quantum mechanically, electrons on the Fermi surface have a much easier time escaping.

9.3.2 The photoelectric effect

Explaining the photoelecctric effect is what won Einstein the nobel prize, but strangely Pathria doesn't mention him in this section. The idea here is strongly related to the contribution made in the context of blackbody radiation: each photon carries a discrete quanta of energy $\epsilon_\omega = \hbar\omega$, a quantum mechanical postulate that Einstein fully embraced. The work we did understanding the thermoionic transmission of electrons suggests that by adding energy in the form of photons would increase the flow of electrons as well. A photon incident on a metal would thus change

$$J \;=\; \frac{4\pi e}{\beta^2h^3}f_2(ze^{\beta\hbar\omega-\beta W}) \tag{9.36}$$

For $\omega \to 0$ there is little change in the behavior of the system, with $\epsilon_F' \approx \epsilon_F+\hbar\omega$. However, for high frequency photons the imparted energy is significant and causes a significant change in the current, since it becomes possible for $\beta(\hbar\omega + \epsilon_F - W) \to \infty$ even though T is small. In that limit, we use the scaling of $f_2(e^\delta) \approx \delta^2/2$ as $\delta \to \infty$, and thus find

$$J \approx \frac{2\pi me}{h^3}(\hbar\omega + \epsilon_F - W)^2 \qquad (\textit{photoelectric dominated}) \tag{9.37}$$

A similar effect can also be found by applying a constant field in the z direction, lowering the work function required for barrier crossing. Pathria mentions this briefly and in a somewhat unclear manner, and we won't work out his solution. It should be clear, though, that by applying a potential we'll induce electron motion by lowering the energetic barrier.

9.4 Summary

The statistics of electrons at low temperatures is dominated by the constraints imposed by the Pauli exclusion principle: each particle wants to be found in the lowest energy level, but only one (or $g(0)$ for a degenerate ground state) can actually attain this lowest energy state. The Pauli exclusion principle that Fermions must satisfy lead to significant differences between the classical and quantum mechanical predictions, particularly in the susceptibility for both paramagnets (finite at $T \to 0$) and diamagnets (negative). The photoelectric effect is also driven by the difference between the Fermi energy and a work function, which are fundamentally quantum mechanical properties with no classical analogue. Fermi statistics have important effects in a wide range of material systems.

Chapter 10

The Ising Model (Ch 12-13)

We've spent a huge amount of time trying to determine the statistics for a set of N non-interacting particles, and have seen that some very surprising behavior can be found. In particular, we saw that there was a phase transition in the Bose Einstein statistics for some critical temperature, and classically for a solid/gas interface for some critial density. However, we have yet to see a phase transition in any other context, and in particular we have never seen any evidence of spontaneous magnetization: a system with a positive magnetization in the absence of an externally applied field. We have seen positive magnetization in the case of a paramagnet, with $H = p^2/2m - \boldsymbol{\mu} \cdot \mathbf{B}$, and in the classical dipole approximation, with $H = -\boldsymbol{\mu} \cdot \mathbf{B}$, but the magnetization $M(B, T) \propto \langle \mu \rangle$ vanishes for $B = 0$. In this chapter, we'll explore the Ising model, which predicts spontaneous magnetization for simple systems driven by the interactions between particles.

10.1 The Heisenberg Hamiltonian

Paramagnetism was observed for a very simple system, whose spins could align either up or down with an applied magnetic field. None of those spins interacted with one another, so it was impossible for the system to support magnetization without an applied field. A simple generalization of this model would include an interaction between the particles themselves. That is, we're actually going to try to work out the statistics of a system of interacting particles, rather than ideal gasses!

Suppose two quantum particles interact with each other with a potential $V(\mathbf{r}_1, \mathbf{r}_2)$ acting as a perturbation. We recall these two particles must be in symmetric or asymmetric states, with

$$\psi_{\pm} = \frac{1}{\sqrt{2}}\Big(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\Big) \tag{10.1}$$

The first order term for the interaction energy between the particles will be

$$\begin{aligned} \langle\Psi|V(\mathbf{r}_1,\mathbf{r}_2)|\Psi\rangle &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \Big(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\Big)^* V(\mathbf{r}_1,\mathbf{r}_2) \qquad (10.2) \\ &\qquad \times\Big(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\Big) \\ &= 2(K \pm J) \qquad (10.3) \end{aligned}$$

where

$$\begin{aligned} K &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 |\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 V(\mathbf{r}_1,\mathbf{r}_2) \qquad (10.4) \\ J &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \psi_1^*(\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2) V(\mathbf{r}_1,\mathbf{r}_2) \qquad (10.5) \end{aligned}$$

K is the mean energy of the particles given the specific states ψ_1 and ψ_2, the mean we would compute if there were no symmetry requirement on the wavefunction. J is an integral involving the overlap between wavefunctions (called an exchange energy) due solely to the symmetry requirement. Note that if $\psi_1(\mathbf{r}_1)$ does not significantly overlap with $\psi_2(\mathbf{r}_1)$ at the same point, the integral will vanish. For an electrostatic interaction between atoms, $V \propto |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ and so J is always positive, which has an important implication: a pair of particles that are in the symmetric position state have a *higher* interaction energy than those in an asymmetric position state. For Fermions with spin 1/2, this means the singlet state $|\Psi\rangle = |\psi\rangle_+|00\rangle$ is energetically less favorable than the triplet state $|\Psi\rangle = |\psi\rangle_-|1s\rangle$.

The exchange integral J is complicated to work with for free particles, where the wavefunctions $\psi_k(\mathbf{r}) \propto e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$, and contributions from $|\mathbf{r}_1 - \mathbf{r}_2| \to 0$ may lead to important higher-order effects. Instead, we consider a pair of localized particles, pinned to be a fixed distance a from one another. The wavefunction of each particle will thus be decaying over some length scale d, and the value of the exchange integral can be tuned by adjusting a relative to d: If $a \ll d$ then J is large but finite, while if $a \gg d$ then J vanishes. The ground state energy of the pair of particles is thus $E_0 = K + J$ for the singlet state and $K - J$ for the triplet states. This can be conveniently rewritten in terms of what is called the Heisenberg Exchange Hamiltonian,

$$\hat{H}_H = K + \frac{1}{2}J + 2J\hat{S}_1 \cdot \hat{S}_2 \tag{10.6}$$

$$\hat{H}_H|00\rangle = (K+J)|00\rangle \qquad \hat{H}_H|1m\rangle = (K-J)|1m\rangle \tag{10.7}$$

The later equalities arise because $2\hat{S}_1 \cdot \hat{S}_2 = \hat{S}_{tot}^2 - \hat{S}_1^2 - \hat{S}_2^2$. Fundamentally, this means that interacting fermions on a lattice will have an effective Hamiltonian that depends solely on their spin state.

10.2 The Ising model

10.2.1 The Ising Hamiltonian

The Heisenberg Hamiltonian is defined in terms of quantum spin operators, and for spin 1/2 Fermions takes on one of two values. While this is physically correct (in some limit at any rate), it's worthwhile to consider an even simpler model: a two state system where each particle can take on one of two values (up or down), and whose energy depends only on the product of those values. That is,

$$\begin{aligned} E_{pair} &= -Js_1s_2 \qquad\qquad s_1 = \pm 1 \qquad s_2 = \pm 1 && (10.8)\\ E_{pair} &= -J \qquad\qquad s_1 = s_2 && (10.9)\\ E_{pair} &= J \qquad\qquad s_1 = -s_2 && (10.10)\end{aligned}$$

which has the same features of the original problem: the energy of a state is $\pm J$ (ignoring an unimportant constant) depending on some property of the neighboring particles on the lattice. Spins that are aligned are energetically favorable (representing the triplet state), spins that are misaligned are energetically disfavored (representing the singlet state). This is no longer a quantum mechanical system, but is expected to reflect the essential physics of a pair of particles separated by a fixed distance. The system is thus reduced to “spins” that are integers (positive or negative, sometimes called up and down), rather than a quantum mechanical eigenstates with a Hamiltonian involving quantum operators. This is convenient for a number of reasons, but is a classical approximation: these “spins” are an analogy with the quantum mechanical case, with the triplet states incorporating the aligned cases ($|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$) and the singlet state composed solely of the antiparallel states.

For this classical approximation we can ignore the details of the quantum mechanical effects and consider a lattice of N particles with *only* nearest neighbor interactions (that is, completely neglecting all interactions between particles beyond the length scale a). This system was originally studied by Ising, with

$$H_{Ising} = -J\sum_{\langle ij\rangle} s_is_j = -J\sum_{nn} s_is_j \tag{10.11}$$

The (modern) notation $\langle ij\rangle$ and the (older) notation nn are equivalent, and refer to a sum over i and j that are nearest neighbors. The notations s_i and σ_i are both common for the

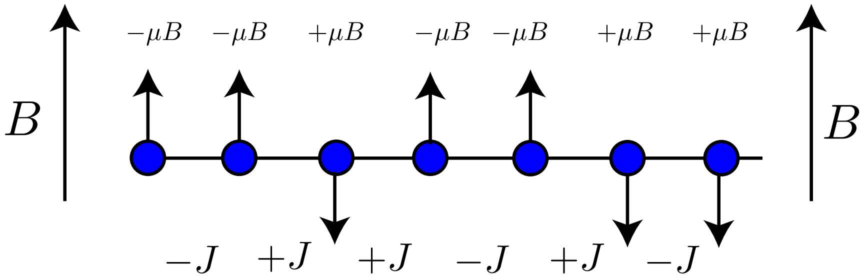


Figure 10.1: Schematic diagram of the Ising model in a uniform field, with the energetic contributions of the site spins (top) and interactions (bottom) indicated. Agreement with the external field gives an energetic reduction $-\mu B$, while disagreement increases the energy by μB. Likewise, agreement between nearest neighbors decreases the energy by $-J$ while disagreement causes an increase J.

state of each site having an interaction strength J, with all other interactions having zero interaction strength. H is minimized if all of the spins are aligned, and maximized if they are all of alternating sign. Continuing the analogy of the "spin" of a particle corresponding to the quantum mechanical state, introducing a magnetic field simply adds an energy $-B\mu s_i$ for each site i, where μ is the magnetic dipole moment at the site. For a uniform magnetic field applied to each site, we then have

$$H = -J \sum_{\langle ij \rangle} s_i s_j - \mu B \sum_i s_i \tag{10.12}$$

with the first term a sum over *pairs* spin-spin interactions and the second term a sum over spins. J is taken to be constant for all pairs, which is consistent with particles on a lattice. This Hamiltonian is often written with $\mu = 1.$ since it does not strictly correspond to the quantum mechanical Bohr magneton. So long as $J > 0$, the lowest energy state will have all connected spins aligned with one another, and the pair alignment will match an applied magnetic field in the energy minimizing state.

Because the Ising model is drawn from analogy rather than fundamental physical principles, there are many possible generalizations of the Ising model. Common generalizations include

1. Long range interactions: Next-nearest neighbor or longer range interactions will change the statistics of the model. The interaction between distant points will sometimes have a lower energetic contribution (e.g. $J_{nearest} > J_{next-nearest}$), but this is not required and is not always used.
2. Multiple states at sites: Instead of taking on two values (± 1), the state of the sites can take on multiple values. The energy associated with a pair of particles in state n

and m are J_{nm}, some undetermined (and usually not physically defined) function of the energy associated with two differing states. If the number of states is finite, the model is called a 'Potts' model, and a common choice is $J_{nm} = \cos(2\pi(n-m)/M)$ where M is the number of possible states, but this is not required. For an infinite number of states ($M \to \infty$), the model becomes $J(\theta_1\theta_2) = \cos(\theta_1 - \theta_2)$ and is referred to as an X-Y model.

3. Inhomogeneous energy interactions: The interactions between nearest neighbors may differ between pairs, with $J_{ij} \neq$constant, in which case there are an *ensemble* of Ising models, with each realization of interactions $\{J_{ij}\}$ an element of the ensemble. To compute the statistics of the system, one averages over all states in a realization of the ensemble *and* all realizations in the ensemble. that is, the partition function is computed by summing over all possible states $\{s_i\}$ as well as all possible pair interactions J_{ij}. These models are called spin-glass models: spin for the ising-like characteristic and glass because of the disordered interactions between the sites (similar to the molecular disorder in a pane of glass).

These models can be used to qualitatively describe a huge range of systems of physical, biological and sociological interest. There is an art in choosing a 'good' model for any particular system, but the underlying idea of having sites that have an 'interaction' based on their 'states' is generic enough to be broadly applicable.

10.2.2 Statistical Mechanics for the Ising Model

Knowing a Hamiltonian, we can compute the statistics of the Ising model at thermal equilibrium. The Ising model treats particles on a lattice, which means we can't freely add particles as we can in the grand canonical ensemble. We also aren't terribly interested in the fixed energy state of a microcanonical ensemble. Instead, we will focus on the statistics of Ising spins in thermal equilibrium with a reservoir at temperature T. In this case, we begin (as one always does):

$$Q_N = \sum_{states} e^{-\beta H} = \sum_{\{s_i=\pm 1\}} e^{-\beta H(\{s_i\})} = \sum_{\{s_i=\pm 1\}} \exp\left(\beta J \sum_{nn} s_i s_j + \beta\mu B \sum_i s_i\right) \tag{10.13}$$

Note that the sign of the exponent is positive due to the fact that energetic contributions are negative in Eq. 10.12. The compact notation of eq. 10.13 incorporates a sum over all possible states, which hides some of the complexity of the result. For example,

$$\begin{aligned} Q_3 &= \sum_{s_1=\pm 1}\sum_{s_2=\pm 1}\sum_{s_3=\pm 1} e^{\beta J(s_1 s_2 + s_2 s_3) + \beta\mu B(s_1+s_2+s_3)} \qquad (10.14) \\ &= e^{2\beta J + 3\beta\mu B} + e^{2\beta J - 3\beta\mu B} + e^{-2\beta J + \beta\mu B} + e^{-2\beta J - \beta\mu B} + 2e^{\beta\mu B} + 2e^{-\beta\mu B} \end{aligned}$$

which is certainly not easily generalized to N particles for $J \geq 0$. However, in the absence of interactions we have already computed

$$Q_N^{J=0} = \left(\sum_{s_1=\pm 1} e^{\beta\mu B s_1} \right) \times \cdots \times \left(\sum_{s_N=\pm 1} e^{\beta\mu B s_N} \right) = 2^N \cosh^N(\beta\mu B) \tag{10.15}$$

as we saw in eq. 4.126. The calculation is significantly more complicated if $J \neq 0$, since we have interactions between neighbors and can't yet perform the sum. Regardless of our ability to actually compute the partition function, we still know that we can determine thermodynamic quantities, such as

$$U = -\frac{1}{\beta}\frac{\partial \log(Q_N)}{\partial \beta} \qquad \beta A = -\log(Q_N) \qquad S = \frac{U-A}{T} \tag{10.16}$$

and so on. These quantities will be identical to what we saw in the canonical ensemble. A less commonly used identity (but one discussed in the context of paramagnetism in Sec. 4.8.2 is the total magnetization, given by the total magnetic moment of all of the particles:

$$\langle M(B,T)\rangle = \mu \left\langle \sum_i s_i \right\rangle = \frac{1}{\beta}\frac{\partial \log(Q_N)}{\partial B} \tag{10.17}$$

$$\sum_{\langle ij\rangle} s_i s_j = \frac{1}{\beta}\frac{\partial \log(Q_N)}{\partial J} \tag{10.18}$$

The magnetization at $B = 0$ is referred to the *spontaneous* magnetization, and we have previously found $M(B = 0, J = 0)$ classically and quantum mechanically for every noninteracting system we have considered.

10.2.3 Counting spin states

On a perfectly homogeneous lattice, each site will have a fixed number of nearest neighbors called the coordination number q, which depends on the dimensionality as well as the lattice geometry. For one dimension, $q = 2$. For 2 dimensions $q = 3$ for a hexagonal lattice, 4 on a square lattice, or 6 on a triangular lattice. For three dimensions $q = 6$ for a simple cubic lattice, but other geometries will produce a different q. First, note is *not* unique to the dimensionality, but rather depends on the details of the lattice. Also, note that the coordination number refers to the bulk properties of the system (far from the boundaries of the system), since the number of nearest neighbors at the boundary will be different (since sites at a boundary have fewer neighbors in total). The number of nearest neighbor pairs is $Nq/2$, with the factor of 2 avoiding double counting.

Assuming a homogeneous lattice, we can rewrite the Hamiltonian (which depends on the individual spin states) in terms of global properties of the system:

- N_+ and N_-, the number of particles parallel or antiparallel with the field
- N_{++}, N_{+-}, and N_{--}, the number of *pairs* both aligned with the field, one aligned and one misaligned, and both misaligned with the field.

The first of these accounts for site statistics and the second for pair statistics. The energy can be re-expressed in terms of these global quantities

$$H = -J(N_{++} + N_{--} - N_{+-}) - \mu B(N_+ - N_-) \tag{10.19}$$

Since the site and pair statistics must be related to one another, we can simplify these parameters by noting that we have a fixed number of particles N and a fixed number of neighbor pairs $N_{edges} = Nq/2$. Specifically, we can rewrite

$$N_+ + N_- = N \qquad \Rightarrow \qquad N_- = N - N_+ \tag{10.20}$$

$$qN_+ = 2N_{++} + N_{+-} \qquad \Rightarrow \qquad N_{+-} = qN_+ - 2N_{++} \tag{10.21}$$

$$qN_- = 2N_{--} + N_{+-} \qquad \Rightarrow \qquad N_{--} = q(N - N_+) - (qN_+ - 2N_{++}) \tag{10.22}$$

which allows us to reduce our Hamiltonian to

$$H = -J\left(4N_{++} - 2qN_+ + \frac{Nq}{2}\right) - \mu B(2N_+ - N) \tag{10.23}$$

The partition function will become

$$Q_N \approx \sum_{N_+=0}^{N} \sum_{N_{++}=0}^{qN/2} g(N_+, N_{++}) e^{-\beta H(N_+, N_{++})} \tag{10.24}$$

where $g(N_+, N_+ +)$ is the statistical weight associated with the particular configuration of simultaneously N_+ up spins and N_{++} up-up pairs. Note that there are many configurations that are not physically realizable (e.g. if $N_+ = 0$, then N_{++} must also be zero, so $g(0, x) = 0$ for $x > 0$), so this is a nontrivial task. This approach ignores boundary effects due to the $N_{edges} \approx Nq/2$ approximation.

10.3 The Mean Field approach to the Ising Model (Pathria 12.5)

10.3.1 The Bragg-Williams approximation

Computing $g(N_+, N_{++})$ is actually quite difficult and it is worth considering a different approach to determining the thermodynamics of the Ising model. Rather than attempting to exactly evaluate the partition function, we will make a *mean field* approximation for the state of each site. In quantum statistics, we ignored the canonical partition function and moved to the grand canonical partition function that was easier to compute. That's no longer possible here, and we need to use a new approach.

The reason this system is complicated is because of the interactions between atoms (as we know we can solve it if $J = 0$). A simple approximation is to replace the specific interactions between atoms by typical interactions between particles, a so-called mean-field approximation. We can define the long range order parameter

$$m = \frac{1}{N}\sum_i s_i = \frac{N_+ - N_-}{N} \tag{10.25}$$

The average magnetization is $M = \mu\langle\sum_i s_i\rangle = \mu N\langle m\rangle$, so m represents an average spin per particle *for a specific realization.* Pathria uses the notation $L = N^{-1}\sum_i s_i$ to indicate the long-range ordering of the system. In the Bragg Williams approximation, we replace the sum

$$\sum_{\langle ij\rangle} s_i s_j \approx \frac{1}{2}\left(\sum_{\langle ij\rangle}\langle m\rangle s_i + \sum_{\langle ij\rangle}\langle m\rangle s_j\right) = \frac{Nq\langle m\rangle}{2}m \tag{10.26}$$

so that the interactions between pairs of spins are replaced by an interaction between a spin and *the average spin* of every other particle in the system. This is not an unreasonable approximation: we simply assume that the interactions between all particles are in some sense typical, with each particle interacting with the average spin in the system. This is still an approximation, and ignores possible correlations in the statistics of the system. This leads to a mean field approximation for the energy,

$$\begin{aligned} E &= -J\sum_{\langle ij\rangle} s_i s_j - \mu B\sum_i s_i && (10.27) \\ &= -\frac{1}{2}NqJ\langle m\rangle m - \mu BNm && (10.28) \end{aligned}$$

This energy is a function of the (unknown) mean magnetization $\langle m\rangle$, which we must determine somehow. We can determine the mean magnetization $\langle m\rangle$ of the system by flipping one (and only one) site's value, with all other sites presumed to have the mean magnetization. For example, if we imagine $s_i = -1$ and we flip the state to $s_i = +1$, there will be a change in the energy of

$$\Delta\epsilon = E_{final} - E_{initial} = -2Jq\langle m\rangle - 2\mu B \tag{10.29}$$

This comes from the fact that if you flip a spin, exactly q interaction edges are changed, contributing a factor $2s$ additional energy (with no need to remove doublecounting). If

$\Delta\epsilon < 0$, flipping a spin from a $-$ to a $+$ is energetically favorable, and we expect the system to be more likely to be found in the spin-up state instead of the spin down state. If we assume the spin statistics are Boltzmann distributed, we would expect to find

$$\frac{N_+}{N_-} \approx \frac{1+\langle m\rangle}{1-\langle m\rangle} \quad = \quad e^{-\beta\Delta\epsilon} = e^{2\beta Jq\langle m\rangle + 2\beta\mu B} \tag{10.30}$$

It turns out that that $\log[(1+\langle m\rangle)/(1-\langle m\rangle)]/2 = \tanh^{-1}(\langle m\rangle)$, we finally find from eq. 10.30 that

$$\langle m\rangle = \tanh[\beta(Jq\langle m\rangle + \mu B)] \tag{10.31}$$

which provides a *self consistent* equation for the mean magnetization.

Note that we could have derived the self consistent equation by flipping spins from $+$ to $-$ as well. We would find the energy change is $E_{final} - E_{initial} = -\Delta\epsilon$, and we would make the same argument that the $+$ state is preferable if the final energy is increased (i.e. if $\Delta\epsilon$ is positive). We would then write $N_+/N_- = e^{-\beta\Delta\epsilon}$ to ensure the number of up-spins increases with decreasing $\Delta\epsilon$, just as before.

10.3.2 Weiss mean field theory

The Bragg-Willaims approximation is one way of approaching the problem (and what is used in Pathria), but the Mean Field approach does not produce a unique Hamiltonian. An alternate method for treating spins on the mean field level is the Weiss approach. We write

$$\begin{aligned}
\sum_{\langle ij\rangle} s_i s_j &= \sum_{\langle ij\rangle}(s_i - \langle m\rangle + \langle m\rangle)(s_j - \langle m\rangle + \langle m\rangle) && (10.32)\\
&= \sum_{\langle ij\rangle}(\delta s_i + \langle m\rangle)(\delta s_j + \langle m\rangle) && (10.33)\\
&= \sum_{\langle ij\rangle}\left(\delta s_i \delta s_j + \langle m\rangle\delta s_i + \delta s_j\langle m\rangle + \langle m\rangle^2\right) && \\
&\approx \sum_{\langle ij\rangle}\left(\langle m\rangle\delta s_i + \langle m\rangle\delta s_j + \langle m\rangle^2\right) && (10.34)\\
&= \langle m\rangle\sum_{\langle ij\rangle}(s_i + s_j - \langle m\rangle) && (10.35)
\end{aligned}$$

where s is the mean spin. In the fourth line, we neglected the term involving $\delta s_i \delta s_j$. This has a specific and non-perturbative meaning. This approximation does not mean that

$s_i - \langle m \rangle$ is small (since $s = \pm 1$ so a flip in sign will be large), but rather an assumption that flipped spins are uncorrelated: it may be that some spins are flipped but it is rare that neighboring spins are flipped simultaneously. That means that while δs_i is potentially large, it is rare that *both* δs_i and δs_j are simultaneously large for nearest neighbors.

The Weiss approximation leads to the Hamiltonian

$$H \approx \frac{1}{2}\langle m \rangle^2 NJq - \langle m \rangle Jq \sum_i s_i - \mu B \sum_i s_i \tag{10.36}$$

This expression is useful because instead of having a difficult-to-handle interaction term, we simply have an effective magnetic field $\mu B_{eff} = \mu B + Jqs$. The partition function for this system can be quickly evaluated:

$$\begin{aligned} Q_N &= \sum_{\{s_i = \pm 1\}} e^{-\beta H} = 2^N \cosh^N[\beta(\mu B + Jq\langle m \rangle)] e^{-JNq\langle m \rangle^2/2} && (10.37) \\ M &= \frac{1}{\beta}\frac{\partial \log(Q)}{\partial B} = N\mu \tanh[\beta(\mu B + Jq\langle m \rangle)] \equiv \langle m \rangle N\mu && (10.38) \end{aligned}$$

Here, we have the same result as in the Bragg-Williams case, but were able to compute the mean field properties of the system using the techniques we've already worked out. We can easily compute expressions for the energy and entropy using this approach as well. Either approach leads to the same self consistent equation for $\langle m \rangle$.

10.3.3 Critical Exponents on the Mean Field level (Pathria 12.5 & 12.7)

In both cases, the mean magnetization can be determined from the self consistent equation, with $\langle m \rangle$ depending on T and B. If $B = 0$, we have the somewhat simple condition

$$\langle m \rangle = \tanh\left(\frac{Jq}{k_B T}\langle m \rangle\right) = \tanh\left(\frac{T_c}{T}\langle m \rangle\right) \tag{10.39}$$

with $T_c = Jq/k_B$. This is a transcendental equation that we can't solve it exactly except for when $\langle m \rangle = 0$. We can, however, solve it graphically, and nonzero solutions exist if $Jq/k_B T = T_c/T > 1$ (that is, $T < T_c$). The mean field approach predicts that the Ising model *can* produce spontaneous magnetization: a non-zero mean magnetization even when $B = 0$. This is the first time we've seen magnetization in the limit of $B \to 0$, which suggests that permanent magnetization depends on dipole-dipole interactions.

There are a total of three solutions, $\langle m \rangle = 0$ and $\langle m \rangle = \pm s_0$, with s_0 the nonzero solution to the transcendental equation for $T < T_c$. In the absence of a magnetic field there is no bias in the positive or negative direction and all three solutions exist as a local extremum.

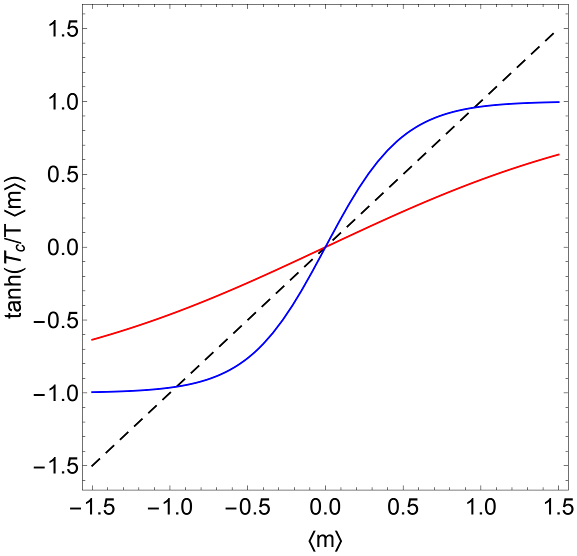


Figure 10.2: Intersection of x with $\tanh(T_c/T\ x)$ for $T > T_c$ (Red) and $T < T_c$ (blue). Above T_c there is exactly one solution, below T_c there are three solutions (two of which are nonzero).

In the limit as $T \to T_c = Jq/k_B$ from below, the mean magnetization $\mu N\langle m\rangle \ll 1$ and we can write

$$\tanh\left(\frac{T_c}{T}\ \langle m\rangle\right) \approx \left(\frac{T_c}{T}\ \langle m\rangle\right) - \frac{1}{3}\left(\frac{T_c}{T}\ \langle m\rangle\right)^3 \tag{10.40}$$

Solving the equation $\langle m\rangle = \tanh(T_c/T\langle m\rangle)$ in this limit yields

$$\langle m\rangle = 0, \quad \pm\sqrt{3}\frac{T}{T_c}\frac{\sqrt{T_c - T}}{\sqrt{T_c}} \tag{10.41}$$

with three zeros. The first is at $\langle m\rangle = 0$ indicating the mean magnetization is zero at $B = 0$ as we've seen previously. There are also two at non-zero roots (which are real only when $T < T_c$) that occur for $B = 0$, meaning that spontaneous magnetization *can* for the Ising model in this mean field approximation. It is convenient to write $t = (T - T_c)/T_c$ as a nondimensional temperature, and we find

$$\langle m\rangle \approx \sqrt{3}\frac{T}{T_c}\frac{\sqrt{T_c - T}}{\sqrt{T_c}} = \sqrt{3}(t+1)\sqrt{-t} \sim |t|^{1/2} \tag{10.42}$$

for $t \to 0$ (or $T \to T_c$). This means $\langle m\rangle \sim |t|^\beta$ with $\beta = 1/2$ a *critical exponent.* These exponents are an important feature in the theory of phase transitions, and indicate the behavior of a system near a critical point.

The energy of the Ising model near the critical point using the mean field approximation is

$$U(B=0) = -\frac{1}{2}qNJ\langle m\rangle^2 \approx \begin{cases} \frac{3NqJ}{2}t & t<0 \\ 0 & t>0 \end{cases} \tag{10.43}$$

The heat capacity can be computed exactly using the mean field approach, with

$$\frac{\partial U}{\partial T} = -NqJ\langle m\rangle\frac{\partial\langle m\rangle}{\partial T} \tag{10.44}$$

where we can use the fact that $\langle m\rangle = \tanh(T_c\langle m\rangle/T)$ to write

$$\begin{aligned} \frac{\partial\langle m\rangle}{\partial T} &= \frac{\partial}{\partial T}\tanh\left(\frac{T_c}{T}\,\langle m\rangle\right) && (10.45)\\ &= \operatorname{sech}^2\left(\frac{T_c}{T}\,\langle m\rangle\right)\left(\frac{T_c}{T}\frac{\partial\langle m\rangle}{\partial T} - \frac{T_c}{T^2}\langle m\rangle\right) && (10.46)\\ &= \left(1-\langle m\rangle^2\right)\left(\frac{T_c}{T}\frac{\partial\langle m\rangle}{\partial T} - \frac{T_c}{T^2}\langle m\rangle\right) && (10.47) \end{aligned}$$

Here we have used the fact that $\partial\tanh(x)/\partial x = \operatorname{sech}^2(x) = 1-\tanh^2(x)$ to simplify the expressions. Thus, we find that

$$C_V = -NqJ\langle m\rangle^2\left(\frac{1}{T} + \frac{1}{(1-\langle m\rangle)^2T_c - T}\right) = -Nk_B\frac{\langle m\rangle^2(1-\langle m\rangle^2)}{(1+t)(\langle m\rangle^2+t)} \tag{10.48}$$

If $\langle m\rangle = 0$, $C_V = 0$ identically since $\langle m\rangle = 0$. However, if $\langle m\rangle \neq 0$ at $t = 0^-$, a nonzero heat capacity will be found. Substituting $\langle m\rangle^2 \approx 3t$ into the heat capacity gives $C_V \approx 3Nk_B/4$ for $t<0$. The energy is thus continuous at the critical temperature but has a discontinuous derivative. This means the Ising model is predicted to have a second order phase transition on the mean field level, just as the Bose Einstein particles did during condensation.

In the presence of a field ($B \neq 0$), we can determine the magnetization as a function of the $\langle m\rangle \ll 1$. Note that this is not the same limit as in eq. 10.41, since $\langle m\rangle$ will depend on B and be nonzero for $B \neq 0$. We can write

$$\langle m\rangle = \tanh[\beta(qJ\langle m\rangle + \mu B)] \tag{10.49}$$

from which we can compute the magnetic susceptibility

$$\chi = \lim_{B\to 0}\frac{\partial M}{\partial B} = N\mu\lim_{B\to 0}\frac{\partial\langle m\rangle}{\partial B} \tag{10.50}$$

Much like in the computation of C_V, we can determine

$$\frac{\partial\langle m\rangle}{\partial B} = \operatorname{csch}^2\left(\frac{T_c}{T}\langle m\rangle + \frac{\mu B}{k_BT}\right)\left(\frac{T_c}{T}\frac{\partial\langle m\rangle}{\partial B} + \frac{\mu}{k_BT}\right) \tag{10.51}$$

so that

$$\frac{\partial\langle m\rangle}{\partial B}=\frac{\mu}{k_B}\frac{1-m^2}{T-(1-m^2)T_c} \tag{10.52}$$

For $T > T_c$ and as $B \to 0$, we have $\langle m\rangle = 0$, whereas for $T < T_c$ and $B \to 0$ we have $\langle m\rangle = \sqrt{3}T/T_c\sqrt{1-T/T_c}$. While $\langle m\rangle = 0$ precisely at $T = T_c$, the different limiting behaviors have an effect on the susceptibility. In particular, we find

$$\chi=\frac{N\mu^2}{k_b|T-T_c|}\begin{cases}\frac{1}{2} & T<T_c\\ 1 & T>T_c\end{cases} \tag{10.53}$$

This relation is a modification of Curie's law, where $\chi_{Curie} \propto T^{-1}$ without any critical temperature. Recall that we computed Curie's law for a noninteracting collection of paramagnets, with $J = 0$, meaning that Curie's law is identical to the Ising model with a critical temperature $T_c = 0$. That is, if $J = 0$ there is no finite critical temperature (as expected), but interactions shift the divergence in the susceptibility to a finite T_c if we include interactions.

Another quantity of interest is the magnetization as a function of the field.

$$\begin{aligned}\beta\mu B &= \tanh^{-1}(\langle m\rangle)-\beta qJ\langle m\rangle \approx \langle m\rangle+\frac{\langle m\rangle^3}{3}-\beta qJ\langle m\rangle && (10.54)\\ \mu B &\approx k_B(T-T_c)\langle m\rangle+\frac{k_BT\langle m\rangle^3}{3} && (10.55)\end{aligned}$$

where $T_c = qJ/k_B$ as before. Note that the term linear in $\langle m\rangle$ is multiplied by $T - T_c$, meaning that if $T = T_c$ only the cubic term contributes. This implies that $M(T = T_c) \sim B^{1/3}$ for weak fields, with the magnetization $M = N\mu\langle m\rangle$. For $t > 0$ the magnetization will be nonzero for $B \neq 0$, since even if $\langle m\rangle$ is small the spins will still partially align with the external field.

These critical exponents can be gathered together to define the critical behavior of the system for small t. The exponents have standardized variable symbols, with

$$\begin{aligned}C_V &\sim \begin{cases}|t|^{-\alpha} & T=T_c^+\\ |t|^{-\alpha'} & T=T_c^-\end{cases} && (10.56)\\ m &\sim t^{\beta} && (10.57)\\ \chi &\sim \begin{cases}|t|^{-\gamma} & T=T_c^+\\ |t|^{-\gamma'} & T=T_c^-\end{cases} && (10.58)\\ m &\sim B^{1/\delta} && (10.59)\end{aligned}$$

with $\alpha = \alpha' = 0$, $\beta = 1/2$, $\gamma = \gamma' = 1$, and $\delta = 3$. These critical exponents give information about how the system approaches a phase transition. They can be calculated for any details of the Ising model, and models that have the same critical exponents respond to temperature or external fields in *identical* ways. Note that there are two additional critical exponents not discussed here (one will be described below), and that the critical exponents are inter-related via the Ginzburg criterion (which we will not discussed).

10.3.4 Universality Classes (Pathria 12.2) - Being skipped

An example of another system in the Ising Universality class is the Van der Waals (VdW) gas, a simple model of a gas that incorporates excluded volume and intermolecular attraction, with

$$p = \frac{Nk_BT}{V - Nb} + \frac{N^2a}{V^2} \tag{10.60}$$

where b is the volume of a single particle and a is an interaction energy. We'll briefly sketch the derivation of the critical exponents for the VdW gas, but it is worth emphasizing that this system bears no obvious resemblance to the Ising model:

- The particles in the VdW gas are mobile, unlike the fixed Ising sites
- The interactions in the VdW gas are all-to-all, not nearest neighbors
- The particles are not constrained to be in one of two states in the gas.
- There is no applied magnetic field in the VdW gas, but rather an external pressure (note that this means we're in the Gibbs Ensemble with pressure an independent variable and V the dependent variable.

Despite the fact that the physics differs significantly, the fact that the free energy has qualitative features in common is sufficient to produce the same scaling laws. The VdW gas has been well studied, and It has been show that we can non-dimensionalize the VdW equation of state by defining the nondimensional pressure, volume, and temperature

$$\bar{p} = \frac{27b^2p}{a} - 1 \qquad \bar{v} = \frac{3bV}{N} - 1 \qquad t = \frac{27Bk_BT}{8a} - 1 \tag{10.61}$$

After some tedious algebra, we can write the equation of state as can be rewritten

$$3\bar{v}^3 + 8(\bar{p} - t)\bar{v}^2 + (7\bar{p} - 16t)\bar{v} + 2(\bar{p} - 4t) = 0 \tag{10.62}$$

For $\bar{v} \ll 1$ near the critical point, it must be that $\bar{p} \approx 4t$ near the critical point (else the term independent of $\bar{v}$ would not vanish). Then near the critical point we can evaluate the equation of state at this point yields three possible roots for the nondimensional volume: $\bar{=}0$ or $\bar{v} = \pm 2\sqrt{-t}$ (remember that $\beta = 1/2$ in the Ising model). The latter roots are valid only when we have $t < 0$, same as with the Ising model. The equivalent of the susceptibility is $\partial\bar{v}/\partial\bar{p}$, which we can extract by implicit differentiation of the equation of state, with $\partial\bar{v}/\partial\bar{p} \approx 2/(7\bar{p}+9\bar{v}^2-16t)$. In the limit of $T \to T_c$ we have $\bar{p} \propto t$ and $\bar{v}^2 \propto t$, so the susceptibility is $\partial\bar{v}/\partial\bar{p} \propto t^{-1}$. Finally, if $t=0$ and $\bar{p} \ll 1$ we find the leading order behavior of $\bar{p} \approx -3\bar{v}^3/2$ from the equation of state in eq. 10.62. That means

$$\bar{v} \sim t^{\beta} \qquad \beta = \frac{1}{2} \tag{10.63}$$

$$\frac{\partial\bar{v}}{\partial\bar{p}} \sim |t|^{\gamma} \qquad \gamma = -1 \tag{10.64}$$

$$\bar{v} \sim \bar{p}^{1/\delta} \qquad \delta = 3 \tag{10.65}$$

all of which are identical to the Ising critical exponents (we didn't compute C_V, which is more tedious). The Lattice gas (particles randomly assigned to points on a lattice) are also in the same universality class as the Ising model.

10.4 Transfer Matrices and exact solutions (Pathria 13.2)

We've determined the predicted mean field behavior, which indicates that below a critical temperature $T = T_c = Jq/k_B$ spontaneous magnetization will occur. But it's important to remember that the mean field approach was an approximation, and not exact. So, is it correct? It turns out that the Ising model in 1 and 2 dimensions are exactly solvable, so we can check!

To do so, it's convenient to define what's called a transfer matrix, which we can see easily by considering a 4 spin 1 dimensional Ising model. We define the pairwise energy

$$E(s_i, s_{i+1}) = -Js_is_{i+1} - \frac{1}{2}\mu B(s_i + s_{i+1}) \tag{10.66}$$

$$H = -\frac{1}{2}\mu B(s_1 + s_N) + \sum_i E(s_i, s_{i+1}) \tag{10.67}$$

This specific form is due to the fact that the nearest neighbor interactions are between s_i and s_{i+1}, and won't work in two dimensions as written. It turns out that the simple pair interaction $E(s_i, s_{i+1})$, which takes on only four values, leads to a very simple expression for the partition function. To gain insight into why, recall that we were previously able to write the partition function

$$Z = Tr(e^{-\beta H}) \tag{10.68}$$

in quantum statistical mechanics. That was convenient because the density operator was diagonal in the energy eigenbasis. The Ising model does not have a particularly obvious basis that we can use to perform the trace, so it's not obvious how to use this. However, we can see that the constrained partition function $Z(s_1, s_N)$ (whose spins at the endpoint are s_1 and s_N and are not summed over) can be written

$$\begin{aligned}
Z(s_1, s_N) &= e^{\beta\mu B(s_1+s_N)/2} \sum_{s_2=\pm1} \cdots \sum_{s_N=\pm1} e^{-\beta E(s_1,s_2)-\beta E(s_2,s_3)-\cdots-\beta E(s_{N-1},s_N)} \quad (10.69)\\
&= e^{\beta\mu B(s_1+s_N)/2} \sum_{s_2=\pm1} e^{-\beta E(s_1,s_2)} \sum_{s_3=\pm1} e^{-\beta E(s_2,s_3)} \sum_{s_4=\pm1} e^{-\beta E(s_3,s_4)} \cdots\\
&= e^{\beta\mu B(s_1+s_N)/2} \left(\mathbf{T}^{N-1}\right)_{s_1,s_N} \quad (10.70)
\end{aligned}$$

where

$$\mathbf{T} = \begin{pmatrix} e^{-\beta E(1,1)} & e^{-\beta E(1,-1)} \\ e^{-\beta E(-1,1)} & e^{-\beta E(-1,-1)} \end{pmatrix} \quad (10.71)$$

$$(10.72)$$

is referred to a transfer matrix. Each transfer matrix completely accounts for the four possible states that any pair of sites can have, and plays a role similar to the quantum mechanical transfer matrix in finite square well calculations: each multiplication of the matrices transfers from one domain to the next. Dirac notation can still be used here, with

$$Q[s_1, s_N] = e^{\beta\mu B(s_1+s_N)/2} \sum_{s_2,\ldots,s_{N-1}} \langle s_1|\mathbf{T}|s_2\rangle\langle s_2|\mathbf{T}|s_3\rangle \cdots \langle s_{N-1}|\mathbf{T}|s_N\rangle \quad (10.73)$$

We can evaluate the partition function exactly by diagonalizing $\mathbf{T}$, with

$$\mathbf{T} = \mathbf{P}^T\mathbf{\Lambda}\mathbf{P} \qquad Q_N(s_1, s_N) = (\mathbf{P}^T\Lambda^{N-1}\mathbf{P})_{s_1,s_N} \quad (10.74)$$

We can use this to finally determine the exact partition function

$$Q_N = \sum_{s_1=\pm1} \sum_{s_N=\pm1} e^{\beta\mu B(s_1+s_N)/2} Q_N(s_1, s_N) = \mathbf{v}^T\mathbf{P}^T\Lambda^{N-1}\mathbf{P}\mathbf{v} \quad (10.75)$$

with

$$\mathbf{v}(s) = \begin{pmatrix} e^{+\beta\mu B/2} \\ e^{-\beta\mu B/2} \end{pmatrix} \quad (10.76)$$

This is exact, but somewhat tedious to compute due to the boundary terms which we expect will be unimportant in the limit of $N \gg 1$. A common method for computing the partition function is to prescribe periodic boundary conditions, where an additional virtual bond between s_1 and s_N is inserted. This will produce an inextensive change in the free energy which can be neglected for $N \to \infty$. For the periodic boundaries, we simply must insert an additional factor of $\mathbf{T}$ in the calculation, and it is straightforward to show that

$$Q_N = Tr(\mathbf{T}^N) \tag{10.77}$$

removing any need for the endpoint terms described by vv. Switching to periodic boundary conditions makes the problem somewhat simpler, because we no longer need to determine the eigenvectors of the matrix $\mathbf{T}$ in the diagonalization, we only need the eigenvectors. Note that this methodology depends only on the fact that there are discrete nearest neighbor interactions. The transfer between sites must be memoryless, a requirement shared by Markov chains. In a Markov process, the lack of memory means the state at any time can be written as the previous state times a matrix summarizing the probability of moving between different states. Here, the transfer matrix is not normalized and thus is not a probability matrix, but the mathematics is similar. Constructing a transfer matrix that takes all possible interactions into account may be larger (e.g. a $\sqrt{N} \times \sqrt{N}$ matrix for the 2-D Ising model, which we will not discuss), but is always possible. It's only useful, of course, if one can extract useful information from the transfer matrix. We can do that now.

It's tedious but straightforward to diagonalize the matrix

$$\mathbf{T} = \begin{pmatrix} e^{\beta J+\beta\mu B} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J-\beta\mu B} \end{pmatrix} \tag{10.78}$$

$$\lambda_\pm = e^{\beta J}\left[\cosh(\beta\mu B) \pm \sqrt{\sinh^2(\beta\mu B) + e^{-4\beta J}}\right] \tag{10.79}$$

so that the partition function for a 1D ising model with periodic boundary conditions is

$$Q_{periodic} = Tr(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N \approx \lambda_+^N \tag{10.80}$$

in the limit of $N \to \infty$, since $\lambda_+ > \lambda_-$. We then have

$$M(B,T) = \frac{1}{\beta}\frac{\partial \log(Q)}{\partial B} = \frac{N\mu \sinh(\beta\mu B)}{\sqrt{\sinh^2(\beta\mu B) + e^{-4\beta J}}} \tag{10.81}$$

Now, there's a bit of a problem here... $M(0,T) = 0$ for all $T > 0$. Spontaneous magnetization *does not* occur for one dimensional ising systems (above absolute zero, anyway), despite the prediction of the mean field approach! There is actually no critical behavior in the 1D Ising model, despite all of the work that we put into the mean field theory.

It turns out that we can in fact determine the behavior of the ising model exactly in two dimensions in the absence of a field. We can do this by defining transfer matrices, as we just discussed. Instead of having a 2 × 2 matrix, the Transfer Matrices must incorporate the statistics of each *row* simultaneously. This means the transfer matrices must be $n \times n$ where $n = \sqrt{N}$ is the number of rows (or columns) of the square matrix. Onsager managed to show that the 2D Ising model *does* exhibit a second order phase transition at a finite critical temperature $T_c = 4J/k_B$ (as is predicted by the mean field theory). Despite that qualitative success, the quantitative features of the mean field approach are quantitatively incorrect:

$$\begin{aligned} \alpha = \alpha' &= 0 \qquad \text{(correct)} && (10.82)\\ \beta &= \frac{1}{8} \neq \frac{1}{2} && (10.83)\\ \gamma = \gamma' &= \frac{7}{4} \neq 1 && (10.84) \end{aligned}$$

We've seen that the mean field approach didn't recover the exact results. The failure of the mean field approximation arises from the fact that fluctuations are ignored on the mean field level, which are not negligible. It turns out that in greater than four dimensions, these fluctuations *can* be neglected and the mean field theory is exact. This arises from the Ginzburg Criterion, which requires that $\langle m \rangle^2 \gg \langle (m - \langle m \rangle)^2 \rangle$ (that is, fluctuations are significantly smaller than the mean magnetization). This can be rewritten as $\langle m \rangle^2 \gg \chi k_B T$ (the thermal energy multiplied by the response of the system to a perturbation), which can be calculated on the mean field to scale as $|t|^{(d-4)/2}$. If $d < 4$, the entire system is consumed by fluctuations near the critical point, and the mean field approach will necessarily fail. If $d > 4$, fluctuations vanish near the critical point, and the mean field methods will be appropriate.

10.5 Landau's Phenomenological free energy (Pathria 12.9)

10.5.1 Phase Transitions

The reason that two systems can have the same universality class is that the shape of their free energies are similar near the critical points. In the Ising and VdW cases, we did not work out the free energies explicitly, but both systems can be used by studying what's referred to as Landau's phenomenological free energy. For any system we have an *order parameter* (sometimes called a reaction coordinate): an observable that we measure as we vary the other parameters. The mean magnetization $m(t)$ the order parameter for the Ising model. In the absence of an external field, the free energy $\psi[m(t), t]$ is a function solely of the magnetization and temperature, and near the critical point we assume $m \ll 1$. This means we can expand

$$\psi \sim \psi_0(t) + r(t)m^2 + s(t)m^4 + \cdots \qquad (10.85)$$

where the first and third order terms must vanish, because the system is invariant under the exchange $m \to -m$ in the absence of an external field. We can minimize the free energy to find that

$$\frac{\partial \psi}{\partial m} = r(t)m + 2s(t)m^3 = 0 \tag{10.86}$$

which means that $m = 0$ or $m = \pm\sqrt{-r(0)/2s(0)}$ at equilibrium. This is not an immediately useful result since we do not know the functional form of r or s, but importantly it means that the non-trivial solutions exist only if r has the opposite sign of s. That is, this free energy will exhibit spontaneous magnetization if $r(t)$ changes sign when $t = 0$ (i.e. $s(t)$ is an odd function of t) while $s(t)$ does not change sign (i.e. $s(t)$ is an even function of t). In order to use this phenomenological free energy to study the Ising model, it is useful to take a simple anzatz that satisfies the known critical exponent of $\beta = 1/2$, with the simplest form $r(t) = rt$ and $s(t) = s$ constant. This ensures that $m(t) \sim -\sqrt{t}$, but is not the only choice one could make and is not justified by anything more than its simplicity. Note that the fourth order term was necessary to prevent the system from blowing up to $m \to \infty$ once $r(t)$ changed signs, which is generally true for any free energy model: the free energy must be large for extreme values of the order parameter, else the system will diverge.

In the Ising model, and external field can be introduced by adding an additional term to the free energy:

$$\psi(B, t) = \psi_0(t) + \frac{mB}{k_B T} + rtm^2(B, t) + sm^4(B, t) \tag{10.87}$$

entering the free energy coupled to the magnetization linearly, with no additional terms in the energy. This is because $k_B T \partial\psi/\partial B = m$ is how the magnetization is computed, and if B affected any other terms in the free energy this relationship would not hold true. Defining $h = B/k_B T$, we have

$$\begin{aligned}
\psi &\sim -hm + q(t) + r(t)m^2 + s(t)m^4 && (10.88)\\
\frac{\partial \psi}{\partial m} = 0 &= -h + 2rtm + 4sm^3 && (10.89)\\
\chi &= \frac{\partial^2 \psi}{\partial h^2} = \frac{\partial m}{\partial h} = \left(\frac{\partial h}{\partial m}\right)^{-1} = \frac{1}{2rt + 12sm^2} && (10.90)
\end{aligned}$$

which, for $m \sim t^{1/2}$, scales as t^{-1} on either side of the transition but with different coefficients. Of course, we also find that $h \sim m^3$ at $t = 0$ as well. We've thus recovered the expected scaling laws using a very simple expansion on the free energy, choosing the scaling of the free parameters to satisfy the known scaling laws (except for the heat capacity, which is left as an exersise).

10.5.2 First order transitions

Landau theory adequately describes second order phase transitions, since nontrivial solutions suddenly appear when $t < 0$ and disappear when $t > 0$, with those nontrivial solutions approaching $m(t) \to 0$ as $t \to 0^-$ (and of course is =0 at $t = 0^+$). The interpretation of the second order transition is clear for a symmetric free energy: the nontrivial roots of the polynomial transition from imaginary to real as t passes through 0 from above, converging on zero at $t = 0$. A second order transition has a continuous change in the thermodynamic variables, while a first order change has a discontinuity in the thermodynamic variables. This is where the term 'first order' comes from: the first (or second) derivative of the free energy is discontinuous.

First order transitions require two elements: first that non-trivial solutions suddenly emerge, and second that they do not pass through 0. $\psi \sim \psi_0 + hm + rtm^2 + sm^4 + \cdots$. A linear term will not be able to produce such a root if $r(t)$ vanishes at $t = 0$: while a solution $m = |h/4s|^{1/3}$ or $m = -|h/4s|^{1/3}$ (depending on the sign of h) will exist, the solution $m = 0$ is *no longer* a solution, so a discontinuous change in the magnetization will not occur. That is not true for a cubic term in the free energy: if $\psi = \psi_0 + rtm^2 + wm^3 + sm^4$, $m = 0$ is always a free energy minimum and there will be two additional roots ($m = -3w/8s \pm \sqrt{(3w/8s)^2 - rt/2s}$) which transition from imaginary to real and nonzero at some finite value of t. This means that at some critical temperature there will be a jump from the solution $m = 0$ to a real-valued root $m \neq 0$, a first order transition.

10.5.3 Correlations in Landau Theory

A final example of the power of Landau's theory is to show that it can also make predictions about correlation lengths: the length scale over which the state of one particle can affect other particles. The original expression for the free energy has a homogeneous magnetization for the system, m, which does not vary spatially. The Landau theory can be modified to incorporate spatial variations in the same spirit of the original approximation. Assuming all interactions are purely local, variations in the free energy should enter into the free energy as some function of $\nabla m(\mathbf{r})$ (essentially, a nearest neighbor interaction). Since the sign of m still can't enter into the free energy (since there's no preferred direction), the simplest assumption is that fluctuations will enter the free energy as $|\nabla m|^2$. In this case, the free energy looks like

$$\psi = \psi_0 + \int d^d\mathbf{r}\left(c|\nabla m(\mathbf{r})|^2 + r_1 t m^2(\mathbf{r}) + s_0 m^4(\mathbf{r})\right) \tag{10.91}$$

$\psi[m(\mathbf{r})]$ is now a functional of the magnetizaton m. To compute the correlation function, we can perturb a single point by adding a field $B(x) = b\delta(x)$ and computing its affect on other points in the system. This leads to the perturbed free energy

$$\psi_b = \psi_0 \int d^d r \Big(c|\nabla m|^2 + r_1 t m^2(\mathbf{r}) + s_0 m^4(\mathbf{r}) + b\delta(\mathbf{r}) m(\mathbf{r}) \Big) \tag{10.92}$$

We can take the functional derivative of the free energy to find the equilibrium value of $m(\mathbf{r})$. You did this without the inclusion of a derivative in a previous homework set, and we can compute the variational derivative of the gradient squared as

$$\begin{aligned} \frac{\delta \int d^d |\nabla f(\mathbf{r})|^2}{\delta f(\mathbf{r}')} &= \lim_{\epsilon \to 0} \frac{\delta \int d^d [|\nabla (f(\mathbf{r}) + \epsilon \delta(\mathbf{r} - \mathbf{r}'))|^2 - |\nabla f(\mathbf{r})|^2]}{\epsilon} \qquad (10.93) \\ &= 2 \int d^d \mathbf{r} (\nabla f(\mathbf{r})) \cdot (\nabla \delta(\mathbf{r} - \mathbf{r}')) = -2\nabla^2 f(\mathbf{r}') \qquad (10.94) \end{aligned}$$

This leads to the equilibrium magnetization given a perturbation of strength b at the origin satisfying

$$\Big[- c\nabla^2 + rt + 2sm_b^2(\mathbf{r}) \Big] m_b(\mathbf{r}) + \frac{b}{2}\delta(\mathbf{r}) = 0 \tag{10.95}$$

This equation is the same as Pathria 12.11.21 (up to unknown constants), but using a very different route to get there. Assuming the perturbation is small, we can neglect the $m^2(\mathbf{r})$ term and findthe magnetization at a point $\mathbf{r}$ due to a field at some other point $\mathbf{r} = 0$ becomes

$$(\nabla^2 - rt) m(\mathbf{r}) = c'\delta(\mathbf{r}) \qquad - (\mathbf{k}^2 + rt)\hat{m}(\mathbf{k}) \propto c' \qquad m(\mathbf{x}) = \int \frac{d^d\mathbf{k}}{(2\pi)^d} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\mathbf{k}^2 + rt} \tag{10.96}$$

where the second equality is a Fourier transform and the third the final solution. We see immediately by making a change of variables that the functional dependence of r will always be combined with a term looking like $\mathbf{r}/\sqrt{t}$, so the correlation length (the range over which particles a distance $|\mathbf{r}|$ away from the perturbation feel its effect) must satisfy

$$\lambda = |t|^{-\nu} \qquad \nu = \frac{1}{2} \tag{10.97}$$

nu is one of the critical exponents that are usually computed but not discussed specifically for the Ising model in Sec. **??**. Pathria shows this is specifically

$$m(\mathbf{r}) \sim \frac{e^{-|\mathbf{r}|/\lambda}}{|\mathbf{r}|^{(d-1)/2}} \qquad \xi \sim |t|^{-1/2} \tag{10.98}$$

for $|\mathbf{r}| \to \infty$, showing there is an exponential decay in the correlation length. An important aspect of this correlation length is that it diverges as $t \to 0$. That is what we've discussed extensively in previous discussions of criticality: in the limit as $t \to 0$ a perturbation at some point in the system can have an effect infinitely far away, so fluctuations cannot be localized. All length scales start to play a role near a critical point.