PHYS404 Notes (Fall 2021)

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1 Lecture Notes

Let us consider 3 interesting physical systems. The first is a block of copper, the second is a glass of water, and the third is a baby. How much can we explain about these systems using something like the Schrodinger Equation? These all have about 10^{23} particles, and it isn't viable to use the equation to analyze these systems. For the copper block, we can identify that it is copper, but it has a catch, if we for example heat up the block of copper and phase transition it from solid to liquid to vapor to plasma, we can't understand this with the SE. We are missing the interaction between the system of the candle and the copper block. For the second system, we solve the equation and find that we identify it as ice, which is very off. For the third system, we have no idea what we get when we solve for the baby as a system.

This is why we need statistical mechanics and thermodynamics. In the 19th century, people began with macroscopic properties that could be measured, such as mass M, number of atoms N, the pressure P, the volume V, etc. From these, we do the best we can to infer the energy U of the system. From that, we obtain the entropy S, and from that, we get the temperature T.

In the late 19th century, Boltzmann, Maxwell, and Gibbs applied classical physics and statistics, but it is difficult, and incomplete. This is not the approach we are using.

A better approach is to take some basic quantum ideas plus one new physical law, which gives us statistical mechanics and thermodynamics. This approach is much simpler than the other two methods.

1.1 Chapter 1

We begin with a model system. The system is a lattice of N points, each of which can have a spin of either up or down. There is no interaction between the points, they just interact with the external field. We will use this model system to learn some statistics. We have the multiplicity function, $g(N, N_\uparrow)$, which represents how many ways to have $N_\uparrow$ have spin up out of N (Given $N_\uparrow$ and N, we can immediately determine $N_\downarrow$).

We then move to a general system, which can be anything, with an insulating and impermeable boundary. All we know about the system is the multiplicity function g, and we can then see how the quantities like entropy and temperature appear.

Suppose we have a loop of current I, with a normal $\hat{n}$. If we put it in a magnetic field, there will be a torque on it. If it has an area of A, and there is a field at an angle θ from the normal, there is the magnetic moment $\vec{m} = IA \cdot \hat{n}$. It can be shown that the energy U in the system takes the form $-\vec{m} \cdot \vec{B} = |m||B| \cos\theta$.

Electrons have a magnetic moment (hard to think about it as a current loop because they're point particles):

$$|\vec{m}_e| = m_e = \frac{e\hbar}{2\mu}$$

where μ is the mass of the electron. If we put this in a magnetic field $\vec{B}$, there are two energies:

$$U = \pm m_e B$$

This is known as a two-level system. These are the only two energies that we can get, we have quantized energy levels.

Another example of this is copper atoms in a lattice. Each copper atom has some energy U_{Cu}, and we can sprinkle in some Zinc into the lattice, each of which has energy U_{Zn}.

Let us look at a model macroscopic system. We have a bunch of sites, labelled from 1 to N. Each site can have either a spin up or spin down. They don't interact with each other, they only interact with the external field $\vec{B}$. A specific arrangement of these spins is called a microstate (just a distinct quantum state). The question we want to ask is how many microstates there are. There are 2^N different combinations (N spots and 2 ways to fill each spot). Another way to do this is to generate a sort of "tree" of the different spin configurations. From this we can see the exponential growth of the number of spin conditions. Thus we have 2^N distinct microstates for the system.

We can now ask what the energies of each of the microstates are. An up spin has energy $U = -mB$ and a down spin has an energy of $U = -(-mB) = mB$. To get the energy of a microstate, we add up the energies of each of the spins:

$$U = \sum_{i=1}^{N} -m_i B$$

Where $m_i = \pm m$ based on the spin. We can rewrite this as

$$U = B\sum_{i=1}^{N} -m_i = -MB$$

Where $M = \sum_{i=1}^{N} m_i$, or the total magnetic moment. This is a macroscopic variable, while m_i is a microscopic variable.

How many distinct M values are there? This is the same as asking how many different macrostates there are. To do this, we start with in all up state, which has total magnetic moment Nm. If we now flip one to down, we are left with a total magnetic moment $M = (N-2)m$. Flipping two gets $M = (N-4)m$. Eventually, we are left with all downs and we have $M = -Nm$. When N is even, there are $\frac{N}{2}$ macrostates with positive M, and the same number of negative macrostates, and then the macrostate with net spin 0. This gets $N+1$ states total.

For odd N we have one more of each signed state, and no 0 state:

$$\frac{N+1}{2} \times 2 = N + 1$$

Thus no matter the sign of N, we have the same number of macrostates, $N+1$.

We have shown that we have 2^N distinct microstates and $N+1$ distinct macrostates. The ratio of macrostates to microstates goes to 0 very rapidly (2^N grows incredibly fast, while $N+1$ does not).

For $N = 10$,

$$\frac{10+1}{2^{10}} = 0.01$$

If we look at the energy, we see that U is proportional to M, and thus states are highly degenerate in M and U. We have that N is the total number of spins, and let $N_\uparrow$ be the number of spins that are up. Similarly, let $N_\downarrow$ be the number of spins that are down. By definition, $N = N_\uparrow + N_\downarrow$. We can define something that represents how far we deviate from the 50/50 split:

$$N_\uparrow = \frac{N}{2} - S \qquad N_\downarrow = \frac{N}{2} - S$$

We can rewrite the energy:

$$U = -Bm(N_\uparrow - N_\downarrow)$$

Let us look at the spin difference (also known as the spin excess):

$$N_\uparrow - N_\downarrow = 2s$$

The factor of 2 is annoying. We can ask the question, how many microstates have a given value of s. This is the multiplicity function $g(N, s)$. For example, $g(4, 2) = 1$ (Only 1 state can be all up spins). One way to find g is to use the binomial expansion:

$$(\uparrow + \downarrow)^N$$

But we can do it another way as well.

Let us begin with all spins down. This is the only possible way to do this, so $g = 1$. If we flip 1 arrow, there are N possible places that we can flip the arrow, so we have $g = N$. If we want to flip two, we have N spots for the first arrow, and then $N - 1$ spots for the second one, giving us $g = N(N - 1)$. We keep doing this until we reach N up:

$$g(N, N_\uparrow) = N(N-1)(N-2)\ldots(N - N_\uparrow + 1)$$

However, this over counts, because the order in which we flip the arrows does not matter. We remove the over counting by dividing by $N_\uparrow!$.

$$g(N, N_\uparrow) = \frac{N(N-1)(N-2)\ldots(N - N_\uparrow + 1)}{N_\uparrow!}$$

Let's do a summary. We have a set of N sites that can each be either up or down spin. A specific arrangement of these states is called a microstate. If we add up all the magnetic moments, we get M, the total magnetic moment. A specific value of M is a macrostate. There are 2^N microstates, and $N + 1$ macrostates. It should also be noted that $N + 1 << 2^N$, the number of microstates rapidly outpaces the number of macrostates. $N_\uparrow$ and $N_\downarrow$ are the number of up spins and down spins respectively. We also have that

$$N_\uparrow = \frac{1}{2}N + s \quad N_\downarrow = \frac{1}{2}N - s$$

And

$$N_\uparrow - N_\downarrow = 2s$$

Where $2s$ is the spin excess. We can also write the total moment with this:

$$M = (N_\uparrow - N_\downarrow)m = 2sm$$

And the total energy:

$$U = -2smB$$

We have $g(N, s)$, the multiplicity function, which is the number of microstates with value s:

$$g(N, s) = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{\left(\frac{1}{2}N + s\right)!\left(\frac{1}{2}N - s\right)!}$$

Suppose we now turn the magnetic field off, $B = 0$. All the states (micro and macro) have $U = 0$. We can ask what $\langle s \rangle$ is, the average value of s:

$$\langle s \rangle = \frac{\sum_s g(N,s)s}{\sum_s g(N,s)}$$

This is essentially a weighted average. However, this sum is a pain to compute for large systems (when you have a lot of states), because of the factorials. We have an approximation that can help this. We have that

$$n! = n(n-1)(n-2)\dots 1$$

Also recall that $\ln(ab) = \ln a + \ln b$. We can then take the log of both sides to convert this product into a sum:

$$\ln(n!) = \ln(n(n-1)(n-2)\dots 1)$$

This goes from product to sum, which we then convert to an integral. We have

$$\ln(n!) = \ln(1) + \ln(2) + \dots + \ln(n)$$

We can plot each of these terms and then make upper and lower bounds on the sum:

$$\ln(n!) = \sum \ln(n) < \int_1^n \ln x \, dx$$

This integral is

$$n \ln n - n + 1$$

If we then exponentiate this, we should have a good approximation of $\ln(n!)$.

A different way to do this is the Stirling formula:

$$\ln(n!) = \frac{1}{2}\ln(2\pi) + n\ln n - n + \frac{1}{2}\ln n + \frac{1}{12n} + \dots$$

We can then exponentiate this to get back the $n!$:

$$n! = (2\pi)^{1/2} n^n e^{-n} n^{1/2} e^{\frac{1}{12n}+\dots} = (2\pi n)^{1/2} n^n e^{-n+\frac{1}{12n}+\dots}$$

This gets a much more usable representation of the factorial.

We now have a way to rewrite the factorials that we were using in our multiplicity function. We can now plug in our representation into $g(N,s)$ (dropping the higher order terms). It is a painful process, but the result is much more useful than the factorial form:

$$g(N,s) \approx \left(\frac{2}{\pi N}\right)^{1/2} 2^N e^{-2s^2/N}$$

This is an example of the central limit theorem, where the binomial distribution in the limit of large N turns into a Gaussian distribution. We can also much more easily compute averages with this form.

If we let $N = 10$ and $s = 0$, the exact value of $g(N,s)$ is

$$\frac{10!}{5!5!} = 252$$

Now using the approximation:

$$\left(\frac{2}{10\pi}\right)^{1/2} 2^{10} = 258.37$$

This is a pretty good approximation (something like .24 percent error.)

If we take the important part of the multiplicity function, the $e^{-2s^2/N}$ term, we see that we have a Gaussian, symmetric around the x-axis. To find how fast it falls off, we can find a $\tilde{s}$ such that $g(N, \hat{s}) = g(N, 0)e^{-1}$. We then have

$$\frac{2\tilde{s}^2}{N} = 1$$

Which then gets us that

$$\tilde{s}^2 = \frac{N}{2}$$

We care about the fractional width, so we can divide by s^2:

$$\frac{\tilde{s}}{s} = \sqrt{\frac{1}{2N}}$$

We see that the width gets smaller and smaller as the value of N increases. Thus we see that if N is of order 10^{22}, the width will be roughly 10^{-11}. On a fractional basis, most quantum states (microstates) are near the mean.

We often look at average values:

$$\langle s^\alpha \rangle = \frac{\sum s^\alpha}{\sum 1}$$

Where both sums are over ever quantum state. However it is often easier to use the multiplicity function and convert the sums into integrals:

$$\langle s^\alpha \rangle = \frac{\int_{-\infty}^{\infty} s^\alpha g(N, s)\, ds}{\int_{-\infty}^{\infty} g(N, s)\, ds}$$

The basic integral is for $s^\alpha = 0$:

$$I_0 = \int_{-\infty}^{\infty} e^{-x^2}\, dx$$

We can swap out the variable for another since they're equivalent, and then square I_0:

$$I_0^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-x^2} e^{-y^2}\, dxdy$$

If we now put together the exponentials and swap to polar:

$$= \iint_{-\infty}^{\infty} e^{-(x^2+y^2)}\, dxdy = \int_0^{2\pi}\int_0^{\infty} e^{-r^2} r\, drd\theta = 2\pi\frac{1}{2}\int_0^{\infty} e^{-r^2} 2r\, dr$$

$$= \pi$$

Thus we have that $I_0 = \sqrt{\pi}$. Let us now look at even powers multiplied into the integral:

$$I_{2l} = \int_{-\infty}^{\infty} x^{2l} e^{-x^2}\, dx$$

To do this, we use the fact that if we know $\int e^{-x^2}\,dx$, then we know $\int e^{-\alpha x^2}\,dx$, via $u=\sqrt{\alpha}x$:

$$\int e^{-\alpha x^2}\,dx=\sqrt{\frac{\pi}{\alpha}}$$

If we take the partial derivative with respect to α, we see that we just drop down a factor of x^2

$$I_{2l}=\int x^{2l}e^{-x^2}\,dx=\sqrt{\pi}\frac{1}{2}\cdot\frac{3}{2}\dots\frac{2l-3}{2}\cdot\frac{2l-1}{2}$$

We can then do the odd powers:

$$\int x^{2l+1}e^{-x^2}\,dx$$

But since x^{2l+1} is odd, integrating it against a symmetric region gives 0:

$$\int x^{2l+1}e^{-x^2}\,dx=0$$

We can also do the integral by splitting it:

$$I_{2l+1}=2\int_0^\infty x^{2l+1}e^{-x^2}\,dx$$

This is done via integration by parts generally:

$$I_{2l+1}=1\cdot 2\cdot 3\dots(l-1)l=l!$$

We had previously stated that

$$g(N,s)=g(N,0)e^{-2s^2/N}$$

The average value for s will be 0, since s is an odd function

$$\langle s\rangle=\frac{\int g(N,0)se^{-2s^2/N}}{\int g(N,0)e^{-2s^2/N}}=0$$

Instead we look at

$$\sqrt{\langle s^2\rangle}=s_{rms}$$

We can compute $\langle s^2\rangle$:

$$\langle s^2\rangle=\frac{\int g(N,0)s^2e^{-2s^2/N}\,ds}{\int g(N,0)e^{-2s^2/N}\,ds}=\frac{\int s^2e^{-2s^2/N}\,ds}{\sqrt{\frac{\pi N}{2}}}=\frac{N}{4}\sqrt{\frac{N\pi}{2}}\sqrt{\frac{2}{N\pi}}=\frac{N}{4}$$

Note that if we tried this for $\langle s\rangle$, we'd get 0, because the integral is of the form

$$\int_{-\infty}^{\infty}xe^{-x^2}\,dx=0$$

So we have that $\langle s^2\rangle=\frac{N}{4}$, and $N_\uparrow-N_\downarrow=2s$. We can see that $\langle(2s)^2\rangle=N$. If we divide both sides by N^2, to get the average of the fractional spin excess squared:

$$\left\langle\left(\frac{2s}{N}\right)^2\right\rangle=\frac{1}{N}$$

Then we have the root mean square fractional excess $\mathcal{F}$:

$$\mathcal{F}=\left(\frac{2s}{N}\right)_{rms}=\frac{1}{\sqrt{N}}$$

1.1.1 Key Ideas For Chap. 1

We began with a system with N sites that can have either spin up or spin down in a magnetic field, with energy $U_i = -mB$. There are 2^N possible microstates/quantum states, and $N+1$ macrostates. The total magnetic moment M is the sum of the moments:

$$M = \sum_{i=1}^{N} m_i$$

The total energy of the system is

$$U = B\sum_{i=1}^{N} -m_i = -MB$$

The multiplicity function $g(N,s)$defines the number of different ways you can arrange the sites to get a certain total spin, or the number of microstates in a certain macrostate. The formula for g is given as

$$g(N,s) = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{(\frac{1}{2}N+s)!(\frac{1}{2}N-s)!} \approx \left(\frac{2}{\pi N}\right)^{1/2} 2^N e^{-2s^2/N}$$

We then moved on to how to compute Gaussian integrals.

1.2 Chapter 2

The fundamental assumption for statistical mechanics is that **a closed system is equally likely to be in any accessible quantum state.** From this, everything in statistical mechanics follows.

Suppose we have a baby. When a system is closed, we assume that the baby is in an insulated box, with no energy transfer in or out, with nothing moving in or out. If we have a spin system in the ground state in a box, and we smack the box with enough energy to flip 1 spin, it is equally likely to be in any of the states with 1 spin flipped.

Suppose we have a box with a spin state, with $g(N,s)$ states. The probability that we are in a single microstate given that we are in a macrostate will be

$$P_{microstate} = \frac{1}{g(N,s)}$$

For example if we know that the energy of a 4 spin system requires one spin to be down and the rest up, then the probability is $\frac{1}{4}$, as there are 4 states with only 1 spin down.

If we have a quantum system with some fixed energy U, then only certain quantum states have energy U, and all those states are equally likely (if they are accessible). If there are g such states, each one has a probability

$$P = \frac{1}{g}$$

The average of some property x of the system can be computed using this probability:

$$\langle x \rangle_{microstate} = \sum_{microstates} x_{microstate} \cdot P = \frac{1}{g} \sum_{microstates} x_{microstate}$$

This is called an ensemble average, as we are looking at an ensemble of all the different possible states (as opposed ot a time average, which takes a system, time evolves it, and then looks at the average).

If we have a 3d quantum oscillator, the solution has 3 quantum numbers:

$$E_{n_x,n_y,n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega$$

Where the ns are 0 and positive integers.

If we have a drink in a glass, and we have an ice cube, energy conservation states that we could see the ice cube getting colder while the drink gets warmer, but we never see this. Its because of this principle of probability that we just stated.

Suppose we have 2 spin systems, one with a hinge on the bottom right corner, called $\mathcal{S}_2$, and a system with a hinge on the top left corner, with a thermally conductive plate on an inside wall. We then open the two hinges and smack the two systems together. How does the energy of the combined system change?

Each system has some initial value of N, s, and U. There are a couple different cases of what could happen. The first is that nothing happens. The second is that something happens. If nothing happens, the two systems are said to be in thermal equilibrium to begin with. Note that the total energy will never change:

$$U = U_1 + U_2$$

Recall that $U = -2smB$, so we have that

$$U_1(N_1, s_1) + U_2(N_2, s_2) = U(N, s)$$

We also have that the total number of particles in the system is constant:

$$N = N_1 + N_2$$

Using the definition of the energy:

$$-2s_1mB - 2s_2mB = -2smB$$

And we see that we have

$$s = s_1 + s_2$$

This says that the total spin excess will be the sum of the spin excesses of the original systems.

What is the multiplicity function for this new system? When we have them separate, we can see that the number of ways we can do this is

$$g(N, s) = g_1(N_1, s_1)g_2(N_2, s_2)$$

We can then sub in $s_1 + s_2 = s$, and sum over all values of s_1:

$$g(N, s) = \sum_{s_1} g_1(N_1, s_1)g_2(N_2, s - s_1)$$

We are summing over s_1 because when we join the two systems we add more systems. If we then plot each term in the series against s_1, we have a very sharp Gaussian distribution, with a peak at the most likely s_1, which we call $\hat{s}_1$. For a sharp distribution, $\hat{s}_1$ is very close to the average, $\langle s_1 \rangle$.

We can find the peak in the distribution by taking the derivative and finding when it is 0, being careful to do it with respect to s_1:

$$\frac{\partial g(N,s)}{\partial s_1} = \frac{\partial}{\partial s_1}\left[g_1(N_1,s_1)g_2(N_2,s-s_1)\right]_{s,N_1,N_2}$$

$$= \frac{\partial}{\partial s_1}\left[g_1(N_1,s_1=0)e^{-2s_1^2/N_1}g_2(N_2,s_2=0)e^{-2(s-s_1)^2/N_2}\right]_{s,N_1,N_2}$$

Let us look at the derivative of the log of some function:

$$\frac{\partial}{\partial x}\ln(f(x,\dots)) = \frac{1}{f}\frac{\partial f}{\partial x}$$

Note that both sides have the same maxima and minima, and so we can take the log of a function and take the derivative and set that to 0 to find the extrema:

$$\frac{\partial}{\partial s_1}\left[\frac{-2s_1^2}{N_1} - \frac{2s(s-s_1)^2}{N_2}\right] = 0$$

This defines the most likely value $\hat{s_1}$:

$$\frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2} = \frac{\hat{s}}{N}$$

This is the condition for equilibrium, if we start this way, we stay this way.

This is why heat flows from hot to cold, as the states in which it works the other way around are extremely unlikely, nigh on impossible.

Let's generalize these ideas to some system. Suppose we have a system with N particles/molecules, contained in some insulating box. Inside the box we have a heat conducting wall. Particles cannot move through the wall, but energy can. Suppose chamber 1 has N_1 particles and chamber 2 has N_2 particles, and the overall system has total energy U, with the chambers having energies U_1 and U_2 respectively. We know that $g(N,U) = \sum g(N_1,U_1)g(N_2,U_2)$, $U_1 + U_2 = U$. We want to find the largest product in this sum.

This is essentially an optimization problem. We can create some differential:

$$dg = \frac{\partial}{\partial U_1}\left(g_1(N_1,U_1)g_2(N_2,U_2)\right)_{N_1,N_2,U_2} dU_1 + \frac{\partial}{\partial U_2}\left(g_1(N_1,U_1)g_2(N_2,U_2)\right)_{N_1,N_2,U_1} dU_2 = 0$$

We can take these derivatives:

$$dg = g_2\left(\frac{\partial g_2}{\partial U_1}\right)_{N_1,N_2,U_2} dU_1 + g_1\left(\frac{\partial g_2}{\partial U_2}\right)_{N_1,N_2,U_1} dU_2 = 0$$

Now using the fact that we have energy conservation due to the insulation:

$$U_1 + U_2 = U \to dU_1 + dU_2 = 0 \to dU_2 = -dU_1$$

Now plugging this last relationship into our differential we have

$$g_2 \frac{\partial g_1}{\partial U_1} = g_1 \frac{\partial g_2}{U_2}$$

This is the equilibrium condition, if this is true, no energy will flow. Rewriting this:

$$\frac{1}{g_1}\frac{\partial g_1}{\partial U_1} = \frac{1}{g_2}\frac{\partial g_2}{\partial U_2}$$

This is the condition for thermal equilibrium. Note that this can be written as

$$\frac{\partial}{\partial U_1}(\ln g_1) = \frac{\partial}{\partial U_2}(\ln g_2)$$

Let us define a quantity $\sigma = \ln g$. This is a dimensionless form of the entropy. With this, the condition for equilibrium is

$$\frac{\partial \sigma_1}{\partial U_1} = \frac{\partial \sigma_2}{\partial U_2}$$

We say that

$$\frac{1}{\tau} = \frac{\partial \sigma}{\partial U}$$

Where τ is temperature in units of energy. We will show that

$$k_B T = \tau$$

and $k_B \sigma = S$, where S is the conventional entropy. Combining these two, we get

$$k_B \ln g = S$$

Suppose we have 2 isolate systems separate from each other, each with their own energies, number of molecules, and multiplicity function. If we move some energy from the first system to the second system while still keeping them isolated, the first system now has energy $U_1 - \Delta U$, and the second system has energy $U_2 + \Delta U$. How does the total entropy change when we do this energy transfer? The multiplicity of the system is

$$g = g_1 g_2$$

The total entropy of the system is then

$$\sigma = \ln g = \ln(g_1 g_2) = \ln g_1 + \ln g_2 = \sigma_1 + \sigma_2$$

We can compute the change in entropy:

$$\Delta\sigma = \left(\frac{\partial \sigma_1}{\partial U_1}\right)\Delta U_1 + \left(\frac{\partial \sigma_2}{\partial U_2}\right)\Delta U_2 = \frac{1}{\tau_1}(-\Delta U) + \frac{1}{\tau_2}(\Delta U)$$

$$\Delta\sigma = \left(\frac{1}{\tau_2} - \frac{1}{\tau_1}\right)\Delta U = \left(\frac{\tau_1 - \tau_2}{\tau_1 \tau_2}\right)\Delta U$$

We can see that if $\tau_1 > \tau_2$ and we move some energy from system 1 to 2, the entropy change $\Delta\sigma > 0$. Also note that if σ increases, then so does g, meaning that more states become accessible. Similarly, if $\tau_1 < \tau_2$, then $\Delta\sigma < 0$, and the number of states decreases. If $\tau_1 = \tau_2$, then $\Delta\sigma = 0$.

If we put the two systems together, and allow only energy to transfer:

$$g_{comb} = \sum_{\Delta U} g_1(N_1, U_1)g_2(N_2, U_2)$$

Note that we know $g_{comb} > g$, because all the terms are positive and g appears in the sum somewhere. Thus we also have

$$\sigma_{comb} = \ln g_{comb} \geq \ln g = \sigma$$

This is the law of increase of entropy. In an isolated system, when an internal constraint is removed, the entropy increases or stays the same. This is the Second Law of Thermodynamics, spontaneous processes either increase the entropy or keep the entropy equal.

So far in chapter 2, we have used an isolated system, with nothing going in or out of the system. This isolated system is known as the microcanonical ensemble. We solve problems by first specifying what is fixed, such as U and N. From there, we calculate how many quantum states have that particular U and N, $g(U, N)$. From there we can compute the entropy $\sigma = \ln(g(U, N))$, and then compute $\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N$, where τ is the temperature. The fundamental assumption is that the probability in an isolated system of achieving a certain microstate is $P = \frac{1}{g}$. The average value of some quantity x is

$$\langle x \rangle = \sum_s P_s x_s = \frac{1}{g}\sum_s x_s$$

Where we are summing over all accessible quantum states.

We also had that the σ in an isolated system increases or stays the same if an internal constraint is removed. An example of this is the system of a box with a conducting wall placed in the middle of the box.

1.2.1 Laws of Thermodynamics

Theorem 1.1. *The 0th law of thermodynamics is that temperature exists, and if* $T_1 = T_2$*, and* $T_2 = T_3$*, then* $T_1 = T_3$*. This defines thermal equilibrium.*

Theorem 1.2. *The 1st law of thermodynamics is that heat is a form of energy. Including heat, energy is conserved.*

Theorem 1.3. *The 2nd law of thermodynamics has three different formulations. The first (Clausius) states that it is impossible to transfer heat from a low temperature to a high temperature without other energetic consequences.*

Kelvin's statement is that it is impossible to convert heat completely into work.

The third, modern formulation is that in a closed system, σ *increases or stays the same.*

Let us discuss the first law. If we have a magic device, with some energy going in, and some energy leaving, then E_{out} cannot be greater than E_{in} in state, $E_{in} = E_{out}$ (provided that the system is steady-state, things are no longer changing).

In 1618, Robert Fludd thought of a system with a high water reservoir and a low water reservoir, and a water wheel between the two, pumping water up into the top reservoir from the lower one.

This is a perpetual motion machine of the first kind, and it violates the first law, energy is not conserved.

A Kelvin machine is a machine that takes in heat and spits out work, and according to Kelvin's statement, we must have some other output other than just work, we can't have 100% efficiency. Note that you can have 100% efficiency when converting work to heat, just not the other way around.

Suppose we have a machine that is taking us from a low τ to a high τ, and thus takes in some heat Q_1 and spits out some heat Q_2. By Clausius's statement, we can't have $Q_2 = Q_1$ unless we have some work input W. This is why we have to plug in air conditioners, we can't just move from low to high without having to put in some work.

An example perpetual motion machine of the 2nd kind is a steam ship that takes in water and spits out ice cubes from the back. Since the ice cubes have less energy, this should create some energy to power the ship. However, this violates the second law. This actually also lowers the entropy of the universe.

1.2.2 Canonical Ensemble

If we are at the beach in Paestum, Italy, we are very clearly not in a closed system, it is an open system. We don't know how to deal with this one, but we do know how to deal with a fixed energy system. We create a big isolated system, and place a subsystem surrounded by heat conducting walls, and place the beach at Paestum in the subsystem. We call the outer system a reservoir $\mathcal{R}$. The total system has some energy U_0, meaning that the reservoir has energy $U_0 - \varepsilon$, and the system $\mathcal{S}$ has energy ε.

Thus we have some functions

$$g_{\mathcal{R}}(U_0 - \varepsilon) \quad g_{\mathcal{S}}(\varepsilon)$$

The combined multiplicity function is

$$g = \sum_{\varepsilon} g_{\mathcal{R}}(U_0 - \varepsilon) g_{\mathcal{S}}(\varepsilon)$$

Since the two are in equilibrium, their temperatures are the same, $\tau_{\mathcal{R}} = \tau_{\mathcal{S}}$.

The first brilliant trick we can pull is to suppose $\mathcal{S}$ is in a single quantum state s, and thus $g_{\mathcal{S}} = 1$, which specifies the energy ε, turning the multiplicity function into

$$g_s = g_{\mathcal{R}}(U_0 - \varepsilon_s)$$

This number is proportional to the probability that $\mathcal{S}$ is in the quantum state s:

$$g_s \propto P_s$$

To turn this into an equality, we could divide by g (the total number of states), but let's not do this. We know that this is true of any state, such as state 1:

$$g_1 = g_{\mathcal{R}}(U_0 - \varepsilon_1) \propto P_1$$

We can now divide g_s by g_1:

$$\frac{P_s}{P_1} = \frac{g_{\mathcal{R}}(U_0 - \varepsilon_s)}{g_{\mathcal{R}}(U_0 - \varepsilon_1)}$$

Solving this for P_s:

$$P_s = P_1 \frac{g_\mathcal{R}(U_0 - \varepsilon_s)}{g_\mathcal{R}(U_0 - \varepsilon_1)}$$

We now use the fact that $g = e^\sigma$:

$$= P_1 \frac{e^{\sigma_\mathcal{R}(U_0 - \varepsilon_s)}}{e^{\sigma_\mathcal{R}(U_0 - \varepsilon_1)}}$$

If $U_0 \gg \varepsilon_s$:

$$\sigma_\mathcal{R}(U_0 - \varepsilon_s) = \sigma_\mathcal{R}(U_0) - \left(\frac{\partial \sigma_\mathcal{R}(U)}{\partial \varepsilon_s}\right)_{U_0} \varepsilon_s + \dots$$

Note that this second term is $\frac{1}{\tau}$:

$$\sigma_\mathcal{R}(U_0 - \varepsilon_s) = \sigma_\mathcal{R} - \frac{\varepsilon_s}{\tau} + \dots$$

Inserting this back into the expression for P_s:

$$P_s = P_1 \frac{e^{\sigma_\mathcal{R}(U_0) - \frac{\varepsilon_s}{\tau}}}{e^{\sigma_\mathcal{R}(U_0) - \frac{\varepsilon_1}{\tau}}} = P_1 \frac{e^{-\varepsilon_s/\tau}}{e^{-\varepsilon_1/\tau}}$$

Now using the fact that if we sum over all quantum states, the probability sums to 1:

$$\sum P_s = 1$$

$$\frac{P_1}{e^{-\varepsilon_1/\tau}} \sum_s e^{\varepsilon_s/\tau} = 1$$

$$\boxed{P_1 = \frac{e^{-\varepsilon_1/\tau}}{\sum e^{-\varepsilon_s/\tau}}}$$

The quantity $e^{-\varepsilon/\tau}$ is known as the Boltzmann factor. Note that this is the probability of being in quantum state 1, not the probability of being in a state with energy ε_1. For any single state s:

$$P_s = \frac{e^{-\varepsilon_s/\tau}}{\sum_s e^{-\varepsilon_s/\tau}}$$

The denominator $\sum_s e^{-\varepsilon_s/\tau}$ is known as Z, the partition function. It is called that because it tells us how the probability is partitioned across the different states (since they aren't all equally likely).

Let's do a problem. Suppose we have a 2 level system, which has two energy levels, 0, corresponding to state 1, and ε which corresponds to states 2 and 3.

$$Z = 1 + e^{-\varepsilon/\tau} + e^{-\varepsilon/\tau} = 1 + 2e^{-\varepsilon/\tau}$$

The probability that we are in the ground state:

$$P_1 = \frac{1}{1 + 2e^{-\varepsilon/\tau}}$$

And the probability that we are in state 2:

$$P_2 = \frac{e^{-\varepsilon/\tau}}{1 + 2e^{-\varepsilon/\tau}} = P_3$$

We see that

$$\lim_{\tau\to 0} P_1 = 1$$

And the limit for P_2:

$$\lim_{\tau\to 0} = 0$$

As $\tau \to \infty$, we see that $P_3 = \frac{1}{3}$, and notably $P_1 = P_2 = P_3 = \frac{1}{3}$. We see that the system settles into the ground state at low temperatures, but at high temperatures all the states are equally likely. In the microcanonical ensemble the probability of a state P_s was

$$P_s = \frac{1}{g(U)}$$

Whereas in the canonical ensemble the probability is

$$P_s = \frac{e^{-\varepsilon_s/\tau}}{\sum_s e^{-\varepsilon_s/\tau}}$$

Where the denominator is also known as Z, the partition function.

Let's now find the average energy:

$$U = \langle \varepsilon_s \rangle = \sum_s P_s \varepsilon_s = \frac{2\varepsilon e^{-\varepsilon/\tau}}{1 + 2e^{-\varepsilon/\tau}} = \frac{2}{e^{\varepsilon/\tau} + 2}$$

Where we have multiplied both the top and bottom by $e^{\varepsilon/\tau}$. As we take the limit as $\tau \to \infty$, we see we approach $\frac{2}{3}\varepsilon$, and as $\tau \to 0$ we approach 0. These make sense as at infinite temperature, we have equally likely probabilities in each state, so we just have an unweighted average of the energies, giving us $\frac{2}{3}\varepsilon$. If we approach 0 temperature, then we are always in the ground state, which has energy 0, so this checks out as well.

If we look at Z:

$$Z = \sum_s e^{-\varepsilon_s/\tau}$$

And we take the derivative with respect to τ:

$$\frac{\partial Z}{\partial \tau} = \frac{1}{\tau^2} \sum_s \varepsilon_s e^{-\varepsilon_s/\tau}$$

Thus we have that

$$\tau^2 \frac{\partial Z}{\partial \tau} = \sum_s \varepsilon_s e^{-\varepsilon_s/\tau}$$

Putting this back in:

$$\boxed{U = \tau^2 \frac{\partial}{\partial \tau}(\ln Z)}$$

1.2.3 Thermodynamics (Microcanonical)

Suppose we have an insulating box with a frictionless piston in it. There is a gas with volume V and energy U, and the piston has area A. There is some force caused by the gas pressing against the piston, as well as the force either pushing or pulling on the piston. We can sum up the forces:

$$\sum F = F_{ext} + PA = 0$$

If this is true, the piston is not accelerating, and $v = 0$. In this equilibrium state, $F_{ext} = -PA$. If we let the piston move a little bit, the work done by the force F_{ext} on the system is $dW = F \cdot dx$:

$$dW = -PA\,dx$$

The change in the volume of the system is $A\,dx = dV$. This tells us that

$$-PdV = dW$$

If we instead move the piston instantly, we still have a pressure differential, and the volume and pressure are no longer well defined. This is an irreversible process.

Take a similar system with a stationary piston, and instead insert some heat into the gas dQ. Recall that the condition for equilibrium is

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_V$$

at constant volume, and we can do a small change:

$$dU = \tau d\sigma$$

This must be dQ, as this is the only way we can change the energy in the system:

$$dU = \tau d\sigma = dQ$$

This is reversible and keeps the volume constant. We can then combine the piston movement and the heat increase:

$$dU = \tau d\sigma - PdV$$

$$dU = dQ + dW$$

Note that this only holds for reversible processes. Suppose we want to find the temperature of the system if we know the energy and we know that the change in volume is constant, we can divide everything by $d\sigma$, and then compute the derivatives, noticing that since volume is held constant, we have just one term left:

$$\left(\frac{\partial U}{\partial\sigma}\right)_V = \tau$$

and likewise

$$\left(\frac{\partial U}{\partial V}\right)_\sigma = -P$$

1.2.4 Heat Capacities

Conservation of energy (1st law) tells us that we can either add heat or do work to add energy to the system:

$$dU = dQ + dW$$

And the combined first and second laws tell us that

$$dU = \tau d\sigma - PdV$$

We can define the heat capacity:

$$C = \frac{\partial Q}{\partial \tau}$$

The heat capacity is defined under specific conditions. We can solve for dQ in the expression for dU:

$$dQ = dU + PdV$$

$$\frac{\partial Q}{\partial \tau} = \frac{\partial U}{\partial \tau} + P\frac{\partial V}{\partial \tau}$$

Where we are holding some unknown quantity constant in all of these derivatives. If we choose that quantity to be the volume, we get

$$C_V = \left(\frac{\partial U}{\partial \tau}\right)_V$$

If we let the quantity be pressure instead:

$$C_P = \left(\frac{\partial U}{\partial \tau}\right)_P + P\left(\frac{\partial V}{\partial \tau}\right)_P$$

1.2.5 Helmholtz Free Energy

We have the temperature in terms of the derivative of the energy with respect to the entropy, and the pressure as the derivative of the energy with respect to the volume at constant entropy, both of which are not great variables. Instead, we can change the independent variables:

$$d(\tau\sigma) = \tau d\sigma + \sigma d\tau$$

Now solving this for $\tau d\sigma$:

$$\tau d\sigma = d(\tau\sigma) - \sigma d\tau$$

Inserting this into the first law:

$$dU = d(\tau\sigma) - \sigma d\tau - PdV$$

Now rewriting:

$$d(U - \tau\sigma) = -\sigma d\tau - PdV$$

The independent variables for this equation are temperature and volume. This quantity is called $F = U - \tau\sigma$, and is known as the Helmholtz free energy, $F(\tau, V)$.

What are some properties of F? F represents the amount of energy in the system that is available to do work at constant temperature:

$$dF = -\sigma d\tau - PdV$$

where in this case $d\tau = 0$:

$$dF = -PdV$$

Another property is that in the canonical ensemble we specify τ and V, and thus if they are specified, $dF = 0$, as $d\tau$ and dV are 0. $dF = 0$ implies that we are at an extremum, and it can be shown that we are actually at a minimum for F. We can get σ and P:

$$-\left(\frac{\partial F}{\partial \tau}\right)_v = \sigma \qquad -\left(\frac{\partial F}{\partial V}\right)_\tau = P$$

We know that $F + \tau\sigma = U$, and we can use the nice property that we had, $U = \tau^2 \frac{\partial}{\partial \tau}(\ln Z)$:

$$F - \tau\left(\frac{\partial F}{\partial \tau}\right)_V = \tau^2 \frac{\partial}{\partial}(\ln Z)$$

This is a first order differential equation in terms of F. We can try a trick:

$$\frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right)_V = -\frac{1}{\tau^2}F + \frac{1}{\tau}\frac{\partial F}{\partial \tau}$$

We can also compute a different free energy, by doing a Legendre transformation on PdV instead of $\tau d\sigma$:

$$d(PV) = VdP + PdV$$
$$dU = \tau d\sigma + VdP - d(PV)$$
$$d(U + PV) = \tau d\sigma + VdP$$

This is known as the enthalpy, and is represented with H. If we do a Legendre transformation on both terms, we have what is known as the Gibb's free energy. If we combine the fact that $F = U - \tau\sigma$ and $U = \tau^2 \frac{\partial}{\partial \tau} \ln Z$, we have that

$$F + \tau\sigma = \tau^2 \frac{\partial}{\partial \tau} \ln Z$$

Now using the relationship $dF = -\sigma d\tau - PdV$ and then solving for σ:

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

We are left with the differential equation

$$F - \tau\left(\frac{\partial F}{\partial \tau}\right)_V = \tau^2 \frac{\partial}{\partial}(\ln Z)$$

If we compute the derivative $\frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right)$:

$$\tau^2 \frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right) = F - \tau\left(\frac{\partial F}{\partial \tau}\right)_V$$

Inserting this back into the original equation:

$$\frac{\partial}{\partial \tau}\left(\frac{F}{\tau}\right) = -\frac{\partial}{\partial \tau}(\ln Z)$$

Now integrating this:

$$\frac{F}{\tau} = -\ln Z + f(V)$$

It can be shown that $f(V) = 0$, leaving us with

$$F = -\tau \ln Z$$

We can use this to write the partition function:

$$Z = e^{-F/\tau}$$

1.3 Ideal Gas

Suppose we have a cube with side length l, with 1 molecule with mass M inside it. If we first look at the 1D case, with a particle trapped between two walls, with infinite potential outside the walls and 0 potential inside the well. The 1D TISE is

$$-\frac{\hbar^2}{2M}\frac{d^2\Psi}{dx^2} + V\Psi = \varepsilon\Psi$$

Inside the box, we have a simpler equation:

$$-\frac{\hbar^2}{2M}\frac{d^2\Psi}{dx} = \varepsilon\Psi$$

And outside the box we have boundary conditions $\Psi(0) = \Psi(L) = 0$. We can see that the solution to this diffeq will be

$$\Psi(x) = A\sin(kx) + B\cos(kx)$$

Using the boundary conditions, $\Psi(0) = 0 = B\cos(0)$, which gives us that $B = 0$. We also know that $A\sin(kL) = 0$, so we know that $kL = n\pi$, for $n = 1, 2, 3, \ldots$. We now have Ψ, so we can plug this into the diffeq and solve for the energy:

$$-\frac{\hbar^2}{2M}\left[-k_n^2 A\sin(k_n x)\right] = \varepsilon A\sin(k_n x)$$

$$\varepsilon_n = \frac{\hbar^2}{2M}k_n^2 = \frac{\hbar^2}{2M}\left(\frac{n\pi}{L}\right)^2$$

These are the allowed energies in the system, with corresponding states

$$\Psi = A\sin\left(\frac{n\pi x}{L}\right)$$

This sets us up to solve for the thermodynamics of the 1D case, but we care about the 3D case. If we solve it, the states are

$$\Psi = A\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)$$

And the energy becomes

$$\varepsilon(n_x, n_y, n_z) = \frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2(n_x^2 + n_y^2 + n_z^2)$$

If we make a table of the different possibilities of n_x, n_y, and n_z, the value of ε, and the multiplicity g, we start with the all 1 state, which has energy 3 and degeneracy 1.

What does the partition function for this look like in the high temperature limit?

$$Z = \sum_{n_x, n_y, n_z} e^{-\frac{\hbar^2}{2M}\frac{\pi^2}{L^2\tau}(n_x^2 + n_y^2 + n_z^2)}$$

If we let $\alpha^2 = \frac{\hbar^2}{2M}(\frac{\pi}{L})^2\frac{1}{\tau}$, we can write the partition function as

$$\sum e^{-\alpha^2(n_x^2+n_y^2+n_z^2)}$$

For the microcanonical isolated system, we did QM to get the states, and then we found the multiplicity function. From this, we can find the entropy via a logarithm. The expression $\sigma = \ln g$ tells us that the entropy is dimensionless, and the definition of τ is in units of energy.

For the next system we did, the open system (canonical system), we had a thermal reservoir at some given temperature, and we once again did QM to get the states. We then sum over all states to get the partition function, and all the physics follows from that.

1.4 Chapter 3.5: The classical limit

We begin with phase space, where we look at any system in terms of its momenta and positions. For example, the harmonic oscillator has total energy $\frac{1}{2}kx^2 + \frac{1}{2}mv^2$, or $E = \frac{p^2}{2m} + \frac{1}{2}kx^2$. This plots out an ellipse in phase space.

When we expand this to N partiles in d dimensions, this becomes and $2Nd$ dimensional problem, giving an $2Nd$ dimensional integral. To fix this, they made up a quantity called the basic unit of action, $\frac{1}{h^{2Nd}}$.

If we are at high "quantum numbers", from the Schrodinger equation:

$$\oint_{\text{constant energy}} p\,dx = nh \qquad n \in \mathbb{Z},\, n \gg 0$$

This is a statement that the orbits in phase space are quantized.

In summary, we had an attempt to generalize the Bohr model, which said that

$$\oint p_x\,dx = nh$$

And the claim was that this area of a closed curve in phase space was quantized, n can only be integers. This represents concentric circles of expanding radius when plotted in phase space. This is the Bohr-Sommerfeld quantization. What does this have to do with stat mech? For each component of p_x and component of position x, a state in phase space is Nd dimensional, where N is the number of particles, and d is the number of variables. Each point in phase space has a "volume" h^{Nd}.

In the canonical ensemble, we have the partition function:

$$Z = \sum_s e^{-\varepsilon_s/\tau}$$

we know that at high τ, we can approximate the partition function sum as an integral:

$$Z = \sum e^{-\varepsilon/\tau} \approx \int\int \cdots \int e^{\varepsilon/\tau}\, ds$$

We have $2Nd$ integrals:

$$= \iiint_{2Nd} e^{-H/\tau}\, d\vec{p}\, d\vec{q}$$

This has units, so we divide by the volume h^{Nd}:

$$Z = \frac{1}{h^{Nd}} \iiint_{2Nd} e^{-H/\tau}\, d\vec{q}\, d\vec{q}$$

Where we are integrating over every single variable in the system (q represents all of the coordinates), and H is the classical Hamiltonian of the system.

Let's look at 1 particle in a 3d box. Classically speaking, we can think of this as just a ball in a box. To get the partition function out, we realize that we have an integral over 6 variables, with the momenta going over all real numbers and the positions going over the bounds of the box ($0 \to L$):

$$Z = \int_{p_x}\int_{p_y}\int_{p_z}\int_{x}\int_{y}\int_{z} \exp\left(-\frac{\frac{-\vec{p}\cdot\vec{p}}{2M}}{\tau}\right) dx\, dy\, dz\; dp_x\, dp_y\, dp_z$$

Where we have computed the Hamiltonian $\frac{1}{2}mv^2 + V$, where the potential is always 0.

$$= \int_{p_x}\int_{p_y}\int_{p_z}\int_{x}\int_{y}\int_{z} \exp\left(-\frac{p_x^2}{2M\tau}\right)\exp\left(-\frac{p_y^2}{2M\tau}\right)\exp\left(-\frac{p_z^2}{2M\tau}\right) dx\, dy\, dz\; dp_x\, dp_y\, dp_z$$

We can move terms around, and we see that we are left with a bunch of integrals of the form

$$I = \int_{\mathbb{R}} \exp\left[-\frac{p_j^2}{2M\tau}\right] dp_j$$

If we let $\frac{p_j^2}{2M\tau} = u^2$, we are left with

$$I = \sqrt{2M\tau}\int_{\mathbb{R}} \exp(-u^2)\, du = \sqrt{2\pi M\tau}$$

And we know that

$$\iiint_0^L dx\, dy\, dz = L^3 = V$$

In the end, the partition function for the classical particle in a box is

$$Z = \sqrt{2M\pi\tau}V$$

But we forgot the unit removing term, $\frac{1}{h^3}$:

$$Z = \frac{\sqrt{2\pi M\tau}}{h^3}V$$

Which can be written as

$$Z = \left(\frac{2\pi M\tau}{h^2}\right)^{3/2} V = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} V$$

Let's look at another problem. Suppose we have a spring with spring constant k attached to a wall and a mass M. The Hamiltonian will be

$$H = \frac{1}{2}Mv^2 + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

We can write down the partition function:

$$Z = \frac{1}{h}\int_{\mathbb{R}}\int_{\mathbb{R}} \exp\left[\left(\frac{p^2}{2m} + \frac{1}{2}kx^2\right)\frac{1}{\tau}\right]\, dp\, dx$$

$$= \frac{1}{h}\iint_{\mathbb{R}} \exp\left[-\frac{p^2}{2m\tau}\right]\exp\left[-\frac{1}{2\tau}kx^2\right]\, dp\, dx = \frac{1}{h}\sqrt{2m\tau\pi}\sqrt{\frac{2\tau\pi}{k}}$$

It can be shown that this simplifies down into

$$Z = \frac{\tau}{\hbar\omega}$$

The quantum result for this same system is

$$Z_{\text{quantum}} = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

We may be confused as to why they are different, but we have to realize that the classical result is the high τ limit. If we make $\tau \to \infty$ in the quantum approximation, we see that it approaches the classical limit.

Let's do a summary for this section we just did. For high temperature, we can construct a partition function by taking the Boltzmann factor with the Hamiltonian, integrating over the "canonically conjugate variables", momenta and positions, rather than summing:

$$Z = \frac{1}{h^{Nd}}\int\cdots\int e^{-H/\tau}\,(d\vec{p})(d\vec{x})$$

This doesn't work for low temperatures, and actually it doesn't even work all the time in the high temperature limit either.

1.5 Chapter 4: Photons and Phonons

Imagine we have a string instrument. As we excite the string, we generate waves by the combination of normal modes. What if we have a coaxial cable, and we short both ends, we generate standing EM waves inside the cable. How do we apply statistical mechanics to systems like this?

Suppose we find the modes, indexed by n, with no wave being $n = 0$, and the first standing wave being $n = 1$, etc. This is the first step, finding the mode of the system.

We then quantize the modes. For each mode n, we then find Z_n. We then use the fact that the total partition function is the product over all modes of the partition functions:

$$Z = \prod_n Z_n$$

If we try to do this for string, we know that each standing wave can be represented by a sin:

$$y = A\sin(kx)\sin(\omega t)$$

We can then plug in the boundary conditions:

$$y(0) = 0 \quad y(L) = 0 \to \sin(kL) = 0 \to kL = n\pi,\ n = 1, 2, 3, \dots$$

This give us the allowed modes, and we also know that $\omega_n = k_n c$, where c in this case is the speed of the wave.

Now if we take one of the modes, and we zoom in on a little piece of it, it can be shown that mass of the little piece is $\rho\Delta x$, and in the y direction we have $\rho\Delta x\ddot{y}$. The point is that the tension in the section of the string is proportional to $-y$. We just need to know the frequency. We now know that $\varepsilon_{n,s} = (s + \frac{1}{2})\hbar\omega_n$. We know that $\omega_n = n\frac{\pi}{L}c$.

The convertion is now to say that we don't care where the 0 is, so we drop the factor of $\frac{1}{2}$ (which is scary because our ω_ns are all different):

$$\varepsilon_{s,n} = s\hbar\omega_n$$

We can then write out Z_n:

$$Z_n = \sum_{s=0}^{\infty} e^{-s\hbar\omega_n/\tau} = \frac{1}{1 - e^{-\hbar\omega_n/\tau}}$$

Where we have used the geometric series sum. We can then put the total partition function together:

$$Z = \prod_{n=1}^{\infty} Z_n$$

But remember that we almost always take the log of the partition function, so we can remember log rules and that we split the log of products into the sum of the logs:

$$\ln Z = \ln Z_1 + \ln Z_2 + \dots = \sum_{n=1}^{\infty} \ln Z_n$$

Which is the same as

$$\ln Z = \sum_n \ln\left(\frac{1}{1 - e^{-\hbar\omega_n/\tau}}\right) = -\sum_n \ln\left(1 - e^{-\frac{\hbar}{\tau}\frac{\pi c}{L}n}\right)$$

We can then approximate this as an integral:

$$= -\int_0^{\infty} \ln\left(1 - e^{-\frac{\hbar\pi c}{L\tau}n}\right)\, dn$$

If we collapse the exponent into something called x, we have that

$$\ln Z = \frac{-L\tau}{\hbar\pi c}\int_0^{\infty} \ln(1 - e^{-x})\, dx$$

If we plug this integral into a solver or something, we find that the integral is equal to $-\frac{\pi^2}{6}$:

$$\ln Z = \frac{L\tau\pi}{6\hbar c}$$

If we then use the thermodynamic identity

$$dU = \tau d\sigma - PdV \to dF = -\sigma d\tau - PdV$$

And the fact that $F = -\tau \ln Z$:

$$F = \frac{-\pi}{6}\frac{L\tau^2}{\hbar c}$$

And we note that PdV is the force that the string exerts, and is thus the same as fdL, force times distance. This tells us that

$$-\left(\frac{\partial F}{\partial \tau}\right)_L = \sigma = \frac{\pi}{3}\frac{L\tau}{\hbar c}$$

We can also find the force:

$$\left(\frac{\partial F}{\partial L}\right)_\tau = \frac{\pi}{6}\frac{\tau^2}{\hbar c}$$

We then use the fact that

$$U = \tau^2 \frac{\partial}{\partial \tau}\ln Z = \frac{\pi}{6}\frac{L\tau^2}{\hbar c}$$

We have just solved a 1D model for Black Body radiation, which is a 3D model. The process is the same, finding the modes is harder in 3D.

If we had instead taken the classical limit of the integrand when computing $\ln Z$, and just taken the high τ limit, we have that

$$e^{-\hbar\omega/\tau} \approx 1 - \frac{\hbar\omega}{\tau} + \dots$$

We then plug this into the integral:

$$\ln Z = \int_0^\infty \ln \frac{\tau}{\hbar\omega}\, dn$$

Now recalling that $\omega = \frac{n\pi c}{L}$, we obtain that

$$\ln Z = \int_0^\infty \ln\left(\frac{L\tau}{\pi c n}\right) dn$$

This integral diverges, and we see that in the classical limit, the guitar string has infinite energy.

What if we instead of integrating over n integrate over ω? We know that $n = \frac{L\omega}{\pi c}$, and thus $dn = \frac{L}{\pi c}\, d\omega$. This makes the integral

$$\ln Z = \frac{L}{\pi c}\int_0^\infty \ln\left(\frac{1}{1 - e^{-\hbar\omega/\tau}}\right) d\omega$$

If we now use the fact that $U = \tau^2 \frac{\partial}{\partial\tau}\ln Z$:

$$U = \tau^2 \frac{L}{\pi c}\frac{\partial}{\partial \tau}\int_0^\infty \ln\left(\frac{1}{1 - e^{-\hbar\omega/\tau}}\right) d\omega$$

If we then move the derivative inside the integral we are left with

$$U = \frac{L\hbar}{\pi c}\int_0^\infty \frac{e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}}\omega\, d\omega$$

We can rewrite this:

$$U = \frac{L\hbar}{\pi c}\int_0^\infty \frac{\omega}{e^{\hbar\omega/\tau} - 1}\, d\omega$$

$$U = \int_0^\infty \frac{L\hbar}{\pi c}\frac{\omega}{e^{\hbar\omega/\tau}-1}\,d\omega$$

This tells us the energy per unit frequency for the oscillator. This is the spectral density of the oscillator. If we now choose to take the classical limit of the integrand, we see that

$$U_{classical} = \int_0^\infty \frac{L\tau}{\pi c}\,d\omega$$

This is called white noise, Johnson noise, or Nyquist noise:

$$\Delta U = \left(\frac{L\tau}{\pi c}\right)\Delta\omega$$

Note that this only holds in the high frequency case.

How do we do this problem in 3D? Suppose we create a hollow cube with side lengths L made of sheet metal plates. It has a tiny hole in it, nd this generates a black body, where light can go in but it is not likely to leave. This is an ideal absorber, since light goes in but doesn't go out, but it is also an ideal emitter, since it emits in a different way than it absorbs. We can measure the analogue of the spectral density for temperature of this black-body radiator. We would find the modes by using a result from EM (which we won't derive here):

$$\begin{aligned}
E_x &= E_{x0}\sin(\omega t)\cos\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}\\
E_y &= E_{y0}\sin(\omega t)\sin\frac{n_x\pi x}{L}\cos\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}\\
E_z &= E_{z0}\sin(\omega t)\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\cos\frac{n_z\pi z}{L}
\end{aligned}$$

Where the sines and cosines change due to the boundary conditions of the system, and the ns are integers. It also must satisfy the wave equation:

$$\nabla^2\vec{E} = \frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2}$$

Where this is actually 3 vector equations (the del squared is applied to a different component in each equation, so we have one equation for each direction). We then get that

$$\omega_n = \frac{c\pi}{L}\sqrt{n_x^2+n_y^2+n_z^2}$$

Where n is shorthand for n_x,n_y,n_z. Each mode has energy

$$E_{n,s} = s\hbar\omega_n$$

To then get the partition function, we sum over all s and compute the Boltzmann factors:

$$Z_n = \sum_s e^{-s\hbar\omega_n/\tau} = \frac{1}{1-e^{-\hbar\omega_o/\tau}}$$

The total Z is the product of these individual Zs:

$$Z = \prod_{n_x,n_y,n_z} Z_n$$

Now taking the log of this:

$$\ln Z = \sum_n \ln Z_n = 2\iiint_0^\infty \ln\left(\exp\left(-\frac{\hbar c\pi}{L\tau}(n_x^2+n_y^2+n_z^2)^{1/2}\right)\right)\,dn_x\,dn_y\,dn_z$$

We add a factor of 2 because there are 2 possible polarization states. We can switch to spherical coordinates:

$$dn_x\,dn_y\,dn_z = \frac{1}{8}(4\pi n^2\,dn)$$

Where the $\frac{1}{8}$ is added because we are doing this over just 1 octant of space.

$$\ln Z = \pi\int_0^\infty n^2\,dn\ln\frac{1}{1-\exp\left(-\frac{\hbar c}{L\tau}n\right)}$$

We now let $\frac{\hbar c\pi}{L\tau}n = u$:

$$= \left(\frac{L\tau}{\hbar c\pi}\right)^3\pi\int_0^\infty u^2\ln\frac{1}{1-\exp(-u)}\,du$$

If we put this all together, we get that

$$\ln Z = \frac{\pi^5}{45}\left(\frac{L\tau}{\pi\hbar c}\right)^3$$

Now computing the free energy:

$$F = -\tau\ln Z \propto \tau^4 V$$

We can then compute the entropy

$$\sigma = \frac{4\pi}{45}V\left(\frac{1}{\hbar c}\right)^3\tau^3$$

And the pressure as well:

$$P = \frac{\pi^2}{45}\left(\frac{1}{\hbar c}\right)^3\tau^4$$

This is the radiation pressure.

Finally, computing the energy:

$$U = \frac{\pi^2}{45}V\left(\frac{1}{\hbar c}\right)^3\tau^4$$

From these equations we can see that

$$PV = \frac{1}{3}U$$

For classical particles, we generally find that

$$PV = \frac{2}{3}U$$

We can also solve this another way:

$$\ln Z = \int_0^\infty \pi\ln\left[\frac{1}{1-\exp\left(\frac{\hbar\omega_n}{\tau}\right)}\right]n^2\,dn$$

We know that $n = \frac{L\omega}{c\pi}$, so it can be shown that

$$\frac{U}{V} = \int_0^\infty \frac{\hbar}{\pi^2 c^3} \left(\frac{\omega^3}{\exp(\frac{\hbar\omega}{\tau}) - 1} \right) d\omega$$

If we take a small $d\omega$, we have a spectral density:

$$\frac{U_\omega}{V} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{\tau}\right) - 1}$$

This is a measurable quantity. If we have a box of photons, and we collimated a beam from them, and sent the beam through a diffraction grating, after which we place a bolometer. If we plot the spectral density as a function of ω, we see that we get something similar to the black-body radiation curve. The peak of the function can be computed numerically:

$$\frac{\hbar\omega_{max}}{k_B T} \approx 2.82$$

As a consequence of the fundamental assumption, we believe that the entropy is a maximum at equilibrium, so we can look at an isolated system with a wall. This wall can be changed to have different properties, which we will change over time.

We have an axiom that σ_s is a maximum at thermal equilibrium, and is the sum of the entropies of the two subsystems:

$$\sigma_s = \sigma_1 + \sigma_2$$

We begin with a barrier that can conduct heat. We have that the change in the total entropy is

$$\Delta\sigma_s = \Delta\sigma_1 + \Delta\sigma_2$$

We have 3 pairs of variables, N, V, and U. Let energy flowing from system 1 to system 2 be a positive change in energy. From this we have that

$$\Delta\sigma = \left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1,V_1} (-\Delta U) + \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2,V_2} (\Delta U)$$

The change in entropy at equilibrium is 0, and

$$\frac{1}{\tau_1} = \left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1,V_1} = \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2,V_2} = \frac{1}{\tau_2}$$

In case B, we have that the barrier can conduct heat and can move. System 2 gains some ΔV. We have that the change in entropy is

$$\Delta\sigma = \left(\frac{\partial\sigma_1}{\partial U_1}\right)_{N_1,V_1} (-\Delta U) + \left(\frac{\partial\sigma_2}{\partial U_2}\right)_{N_2,V_2} (\Delta U) + \left(\frac{\partial\sigma_1}{\partial V_1}\right)_{N_1,U_1} (-\Delta V) + \left(\frac{\partial\sigma_2}{\partial V_2}\right)_{N_2,U_2} (\Delta V)$$

Where we have added in a varying volume for both systems. This gets us a second condition for equilibrium:

$$\left(\frac{\partial\sigma_1}{\partial V_1}\right)_{N_1,U_1} = \left(\frac{\partial\sigma_2}{\partial V_2}\right)_{N_2,U_2}$$

We know that $dU = \tau d\sigma - PdV$, which we can solve for $d\sigma$:

$$d\sigma = \frac{dU + PdV}{\tau}$$

Now finding $\frac{d\sigma}{dV}$:

$$\left(\frac{\partial \sigma}{\partial V}\right)_U = \frac{1}{\tau}\left(\frac{\partial U}{\partial V} + P\frac{\partial V}{\partial V}\right) = \frac{P}{\tau}$$

This tells us that the pressures are equal at equilibrium (because τ is already equal), giving us that

$$\tau_1 = \tau_2 \quad P_1 = P_2$$

For the third phase, suppose we let the wall also be semipermeable, one type of particles can flow through but not the other. We then have a permeable, movable, and heat conducting wall. The change in entropy is the same 4 terms as the previous case, but we also add in the fact that N_1 and N_2 can vary:

$$\begin{aligned}\Delta\sigma = &\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1,V_1}(-\Delta U) + \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2,V_2}(\Delta U)\\ &+\left(\frac{\partial \sigma_1}{\partial V_1}\right)_{N_1,U_1}(-\Delta V) + \left(\frac{\partial \sigma_2}{\partial V_2}\right)_{N_2,U_2}(\Delta V)\\ &+\left(\frac{\partial \sigma_1}{\partial N_1}\right)_{U_1,V_1}(-\Delta N) + \left(\frac{\partial \sigma_2}{\partial N_2}\right)_{N_2,V_2}(\Delta N)\end{aligned}$$

This is a new equilibrium condition, known as diffusive equilibrium.

$$d\sigma = \frac{1}{\tau}dU + \frac{P}{\tau}dV + \mu dN$$

Now lets talk about what μ means by doing some macroscopic and microscopic examples. We begin by computing the free energy dF:

$$dU = \tau d\sigma - PdV + \mu dN$$

$$d(\tau\sigma) = \sigma d\tau + \tau d\sigma$$

$$dU = d(\tau\sigma) - \sigma d\tau + PdV + \mu dN$$

$$d(U - \tau\sigma) = \mu dN - PdV - \sigma d\tau$$

$$dF = \mu dN - PdV - \sigma d\tau$$

Now computing the value for μ:

$$\frac{dF}{dN} = \mu\frac{dN}{dN} - P\frac{dV}{dN} - \sigma\frac{d\tau}{dN}$$

$$\boxed{\mu = \left(\frac{dF}{dN}\right)_{V,\tau}}$$

μ is the Helmholtz free energy of a particle that we are adding to the system at constant τ and V.

Let us take two isolated systems with defined temperatures, and defined μ, with $\mu_2 > \mu_1$. If we lift system 1 a height of h, what happens to the system we lifted? If we lift it slowly, this is a reversible process, so the entropy doesn't change (the number of accessible quantum states does not change). The volume does not change, but we add mgh to each of the particles, giving a change of

$$\Delta U = Nmgh$$

This change in energy has to equal $\Delta\mu$, since V and σ are constant. This means that when we are adding a single particle:

$$(F_{N+1} - F_N)_{\tau,V} = \mu$$

Suppose $\mu_1 + \Delta Nmgh = \mu_2$. This means it takes the same energy to add a particle to the lifted system 1 as it does to add the same particle to the second system. μ is a (chemical) potential energy. This gets us that

$$\mu_{tot} = \mu_{internal} + E_p$$

Where E_p is the external potential energy.

Let's do an example. Say we have the Earth, and we push Lobb off the Earth as he is screaming. We want to find how far away he has to get until we can't hear him scream. The Earth has a radius R, and we can model the atmosphere with radius r. We have an air molecule at the edge of the atmosphere and at the surface of the Earth, in equilibrium with each other. We assume that τ is a constant (this model is the isothermal atmospher model). We say that $\mu_{internal}(\tau, n_R) + E_p(R) = \mu_{internal}(\tau, n_r) + E_p(r)$, where n represents the density. We know that gravitational potential is $-\frac{Gm_e m}{r}$ plus a constant.

1.6 Chapter 5

1.6.1 Grand Canonical Ensemble

We have been using the grand canonical ensemble, by taking the microcanonical ensemble with a subsystem with conducting walls and a single porous wall. We have a fixed V, a fixed τ, and a fixed μ. The probability that you will be in a single quantum state P_s is given by

$$P_s = \frac{\exp\left(\frac{N\mu - \varepsilon_{s(N)}}{\tau}\right)}{\sum_N \sum_{s(N)} \exp\left(\frac{N\mu - \varepsilon_{s(N)}}{\tau}\right)}$$

Where the denominator is known as the grand sum, and is represented by η. To find the average value of N:

$$\langle N \rangle = \frac{\sum_{ANS} N \exp[(N\mu - \varepsilon_{s(N)})/\tau]}{\sum_{ANS} \exp[(N\mu - \varepsilon_{s(N)})/\tau]}$$

Where we have abbreviated the double sum as a single sum (ANS means all numbers and states). We would like to write out the numerator in terms of the denominator, which we have done before for the canonical case. We notice that taking a derivative will drop down a factor of N:

$$\langle N \rangle = \tau \frac{\partial}{\partial \mu} \ln(\eta)$$

To get the average value of the energy:

$$\langle \varepsilon_s \rangle = \frac{\sum_{ANS} \varepsilon_s \exp[(N\mu - \varepsilon_{s(N)})/\tau]}{\eta}$$

We can do a similar trick, and we see that

$$\langle \varepsilon_s \rangle = [\tau^2 \frac{\partial}{\partial \tau} + \tau\mu \frac{\partial}{\partial \mu}] \ln \eta$$

If we write the thermodynamic identity:

$$dU = \tau d\sigma - PdV + \mu dN$$

For our new system, V is fixed, and τ and μ are determined by the reservoir. This is not the energy that we want for the system, we want the natural variables to be μ, V, and τ. We want to do a Legendre transformation to get a new free energy called Ω:

$$d(\tau\sigma) = \sigma d\tau + \tau d\sigma \quad d(\mu N) = N d\mu + \mu dN$$

$$dU = -PdV + d(\tau\sigma) - \sigma d\tau + d(\mu N) - N d\mu$$

$$d(U - \tau\sigma - \mu N) = -PdV - \sigma d\tau - N d\mu = d\Omega$$

This is known as the grand potential, also sometimes known as the Landau potential (he didn't develop it though). We also have the relationship that

$$\Omega = -\tau \ln \eta$$

Let's do an example, by looking at silicon. Pure Si is an insulator, with valence 4. If we insert something like phosphorous, which has valence 5, if we sandwich the P between two Silicon atoms, we have an excess electron. Our system is the one phosphorous atom, with the reservoir being all the Silicon. Now instead of being an insulator, we have an conductor, but not a great one. This is a semiconductor. We have 3 states, labelled from 1 to 3. State 1 is the electron being detached. State 2 is the electron is attached with spin up, and state 3 is the electron being spin down and attached.

In this case, N for state 1 is 0, and 1 for states 2 and 3. The energy for the first state is 0, and $-I$ for the other two states, where I is the ionization energy of the atom.

The probability that the electron is ionized or detached is

$$P_1 = \frac{\exp[(N_1\mu - \varepsilon_1)/\tau]}{\sum_N \sum_s \exp[(N\mu - \varepsilon_{s(N)})/\tau]}$$

$$= \frac{1}{1 + \exp[(\mu + I)/\tau] + \exp[(\mu + I)/\tau]} = \frac{1}{1 + 2\exp\left(\frac{\mu+I}{\tau}\right)}$$

For P-doped Si, $\mu + I \gg \tau$, so we have that

$$P_1 \approx \frac{1}{2} \exp\left[-\frac{\mu + I}{\tau}\right]$$

We see that there is a very strong temperature dependence in the probability of ionization.

1.7 Chapter 6: Fermions and Bosons

For a classical physicist, a hollow box with a particle in it can be treated like a ball bouncing around the box, and for a quantum physicist, we have a state function ψ that obeys the Schrodinger equation. The function has 3 state quantum numbers, n_x, n_y, and n_z. If the particle is a spin-1/2 particle, we also have an either up spin or down spin. Thus the quantum state is determined by 3 quantum numbers and the spin of the particle.

We will treat one quantum state as our system, and treat all the other quantum states as the reservoir. For example, we could take the state $(3, 1, 5), \Uparrow$ as the system, and take all other states to be the reservoir. Since the state can be either occupied or not, we have to use the grand canonical ensemble.

The spatial part of the quantum state is called an orbital (in this case ψ).

Let us first look at a 2 identical particle state. If we mathematically swap the two particles, we have that

$$\psi(1, 2) = \pm\psi(2, 1)$$

This is nice, because then $|\psi|^2$ remains the same. We cannot tell these two electrons apart. If they're $-$, they're known as Fermions, and if they're $+$ they're known as Bosons.

We cannot have more than one Fermion in one quantum state, while we can have as many Bosons as the physics allows in the quantum state.

Let us start with Fermions, like electrons. Given 1 orbital (Note, this is not a 1 particle system, this is just looking at 1 orbital), what is the average of the number of particles in the state?

$$\begin{aligned}\langle N_s\rangle &= \frac{\sum_N \sum_s N \exp[(N\mu - \varepsilon_s)/\tau]}{\sum_N \sum_s \exp[(N\mu - \varepsilon_s)/\tau]} \\ &= \frac{0 + \exp[(\mu - \varepsilon_s)/\tau]}{1 + \exp[(\mu - \varepsilon_s)/\tau]}\end{aligned}$$

Where we have two possibilities, with $N = 0$ we have no electron in the quantum state and thus the energy ε_s is 0, and the case where there is a Fermion in the state, which gives us $N = 1$ and $\varepsilon_s = \varepsilon_s$. We can multiply by the inverse of the exponential in the numerator:

$$\langle N_s\rangle = \frac{1}{\exp[(\varepsilon - \mu)/\tau] + 1}$$

We call this f_s, and it is known as the Fermi Distribtuion function.

We can plot this function, and in the low τ limit we see that we actually get a step function! In fact, at $\tau \to 0$, we have that we can sum over all the orbitals to get the total number of particles, $\sum \langle N_s\rangle = \langle N\rangle$.

Note that we have disregarded spins, so we would have to multiply by 2.

If we increase the temperature, we get a more curved shape in the step function (note that all the curves will intersect the point defined by when $\varepsilon_s = \mu$). For example, temperatures slightly above 0 still look roughly like a step function, just with slight curves right before the drop from 1 to 0.

For Bosons, we no longer have the constraint that we can have only either 0 or 1 in the state:

$$\langle N_s\rangle = \frac{\sum_N \sum_s N \exp[(N\mu - \varepsilon_s)/\tau]}{\sum_N \sum_s \exp[(N\mu - \varepsilon_s)/\tau]}$$

When we have more than 1 boson in the state, we have to increase the energy accordingly, so when we have 2 bosons, we have that ε_s is doubled. We can write the denominator as

$$\eta = \exp[(N\mu - N\varepsilon_{s0})/\tau] = \sum_N \left[\exp[(\mu - \varepsilon)/\tau]\right]^N$$

We can see that if $(\mu - \varepsilon) < 0$ then it converges to

$$\eta = \frac{1}{1 - \exp[(\mu - \varepsilon)/\tau]}$$

Via the geometric series ($\sum r^k = \frac{1}{1-r}$).

Let's do a little retrospective.

In an isolated system, the probability of a quantum system is $P_s = \frac{1}{g(\varepsilon)}$.

If we change the system to have conducting walls, we no longer fix U, and fix the temperature with a reservoir, and the probability of being in a quantum state is the Boltzmann factor over the partition function:

$$P_s = \frac{e^{-\varepsilon_s/\tau}}{Z}$$

Where $Z = \sum_s e^{-\varepsilon_s/\tau}$. We can use these with $F = -\tau \ln Z$ where $dF = -\sigma d\tau - PdV$ and $F = U - \tau\sigma$.

We can also change the isolated system into a system with walls that allow particle movement as well, giving the grand canonical ensemble:

$$P = \frac{e^{\frac{N\mu - \varepsilon_s}{\tau}}}{\eta}$$

Where $\eta = \sum_s \sum_N e^{\frac{N\mu - \varepsilon_s}{\tau}}$, the sum of all the Gibb's factors. There is a free energy Ω:

$$\Omega = U - \tau\sigma - \mu N$$

And we have the relationship $\Omega = -\tau \ln \eta$.

If we have 1 spatial wavefunction, we can compute $\langle N \rangle$ for Fermions (0 or 1) and for Bosons (0, 1, 2, 3, ...). When we did the Fermion case, we got

$$\langle N \rangle_{fermions} = f = \frac{1}{\exp[(\varepsilon - \mu)/\tau] + 1}$$

We then started with the Boson case, where we found that

$$\eta = \sum_N \sum_s \exp[(N\mu - \varepsilon_s)/\tau] = \sum_N \exp[(N\mu - N\varepsilon)/\tau] = \sum_N (\exp[(\mu - \varepsilon)/\tau])^N = \frac{1}{1 - \exp[(\mu - \varepsilon)/\tau]}$$

We really want to find $\langle N \rangle_{bosons}$:

$$\langle N \rangle_{bosons} = \frac{\sum_{ANS} N e^{(N\mu - N\varepsilon)/\tau}}{\eta}$$

We see we want to pull down a factor of N in the grand sum, so we use the classic trick and take a derivative of the grand sum with respect to μ, and after doing some algebra, we find that

$$\langle N\rangle_{bosons} = f_B = \frac{1}{\exp[(\varepsilon-\mu)/\tau]-1}$$

We see that it is similar to the fermion case, except we have a minus instead of a plus.

Taking a side trip to prove the relationship that we have:

$$\frac{\partial\eta}{\partial\mu} = \sum_N \frac{N}{\tau}\exp[(N\mu - N\varepsilon)/\tau] = \frac{1}{\tau}\sum_N N\exp[(N\mu - N\varepsilon)/\tau]$$

From this we have $\frac{\tau\frac{\partial\eta}{\partial\mu}}{\eta} = \langle N\rangle$, and this is by definition the derivative of the log:

$$\langle N\rangle = \tau\frac{\partial}{\partial\mu}\ln\eta$$

We see that we have derived

$$f_\pm = \frac{1}{\exp(\frac{\varepsilon-\mu}{\tau})\pm 1}$$

The average value of the number of particles in a single quantum state is given by this distribution function. What happens when two particles are very unlikely to be in the same state, or when this function is small? If $f_\pm \ll 1$, it doesn't really matter whether we're talking aobut Fermions or Bosons. This occurs when $\exp(\frac{\varepsilon-\mu}{\tau}) \gg 1$. In this limit, we get the classical limit:

$$f = \exp\left(\frac{\mu-\varepsilon}{\tau}\right) = e^{\frac{\mu}{\tau}}e^{\frac{\varepsilon}{\tau}} = \lambda\exp\left(-\frac{\varepsilon}{\tau}\right)$$

where λ is known as the activity, or the fugacity in old books. It is a measure of how many particles a system can transfer.

To get the total number of particles:

$$\langle N_{total}\rangle = \sum_s \lambda\exp(-\frac{\epsilon_s}{\tau})$$

This term is just the partition function Z_1 for a single particle.

$$\langle N\rangle = \lambda Z_1 = \exp\left[\frac{\mu}{\tau}\right]Z_1 = \exp\left[\frac{\mu}{\tau}\right]V\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$$

Where we call $n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$ the quantum concentration. We can solve this for μ:

$$\tau\ln\frac{n}{n_Q} = \mu$$

Where we have condensed $\frac{\langle N\rangle}{V}$ into n, the density.

We can from this prove that $G = N\mu$.

Suppose that we shift all the chemical potentials by some amount, such as if we picked the sample up.

$$\mu = \Delta + \tau\ln\frac{n}{n_Q}$$

If we account for spin I in the potential, from QM, each orbital has $2I+1$ angular momentum states. And we find that

$$\langle N_{total}\rangle = \lambda V\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}(2I+1)$$

Once we have μ, we have $dF = -\sigma d\tau - PdV + \mu dN$, and we can solve for μ:

$$\left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \mu$$

We can integrate this with respect to N:

$$\int\left(\frac{\partial F}{\partial N}\right)dN = F(\tau,V) = \int \mu\, dN$$

$$\int \mu\, dN = \int \tau[\ln N + \ln p]\, dN$$

Where we have put all the junk that we use for dimensions into p. We can then integrate:

$$\int \mu\, dN = \tau(N\ln N - N)$$

From this, we find that

$$F = N\tau\left[\ln\left(\frac{N}{Vn_Q}\right) - 1\right]$$

We can then find an expression for σ in an ideal gas:

$$\sigma = N\left[\ln\frac{n_Q}{n} + \frac{5}{2}\right]$$

with $n = \frac{N}{V}$ and $n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$. This is the Sackur-Tetrode result, developed in 1912.

The pressure is given by

$$P = \frac{N\tau}{V}$$

We know that $F = U - \tau\sigma$, and from this we know that $F + \tau\sigma = U$, and then solving for U, we have that

$$U = \frac{3}{2}N\tau = \frac{3}{2}PV$$

We see that U depends "only" on τ, not P or V.

Let's do some thermodynamics. We have the thermodynamic identity

$$dU = \tau d\sigma - PdV$$

where we have assumed that N is constant. We can put the heat on one side of the equation:

$$\tau d\sigma = dU + PdV$$

If we add a measured amount of heat to a system, and we want to find how much τ increases by. We have constant P. We have that $(\frac{\partial Q}{\partial \tau})_P = C_P$, so we can take the derivative with respect to τ on both sides:

$$\tau\left(\frac{\partial\sigma}{\partial\tau}\right)_P = C_P = \left(\frac{\partial U}{\partial\tau}\right)_P + P\left(\frac{\partial V}{\partial\tau}\right)_P = \frac{3}{2}N + N = \frac{5}{2}N$$

If we wanted, we could compute C_V, which is $\left(\frac{dQ}{d\tau}\right)_V$, which in this case is $\frac{3}{2}N$. For the ideal gas, we have that

$$C_P = C_V + N$$

We can actually work out a general relationship between the two:

$$C_P = C_V - \tau \frac{\left(\frac{\partial V}{\partial \tau}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_\tau}$$

This is a general statement, this holds for all substances, the only assumption we have made is the thermodynamic identity.

$$dU = \tau d\sigma - PdV$$

Now let's use the fact that the order in which we take the second derivative does not matter:

$$\frac{\partial^2 U}{\partial \sigma \partial V} = \frac{\partial^2 U}{\partial V \partial \sigma}$$

And we see that we are left with

$$-\left(\frac{\partial \tau}{\partial V}\right)_\sigma = \left(\frac{\partial P}{\partial \sigma}\right)_V$$

Let's do a little summary. We began with the average number of particles in a single quantum state:

$$\langle N_s \rangle = \frac{1}{\exp[(\epsilon - \mu)/\tau] \pm 1}$$

Where the + represents Fermions and the − represents Bosons. In the classical limit, it doesn't matter whether they are Fermions or Bosons, and we find that

$$\langle N_s \rangle_{\text{classical}} = \exp[(\mu - \epsilon_s)/\tau] = \exp(\mu/\tau)\exp[-\epsilon_s/\tau]$$

We then compute the total number of particles:

$$\langle N \rangle = N = \lambda \sum_s \exp[-\epsilon_s/\tau]$$

Where we have written $\lambda = \exp[\mu/\tau]$. We then notice that the sum is the partition function for a single particle Z_1:

$$N = \lambda Z_1$$

We can then solve this relationship for μ:

$$\lambda = \frac{N}{Z_1} = \exp[\mu/\tau]$$

Taking the log of both sides, we have that

$$\mu = \tau \ln\left(\frac{N}{Z_1}\right)$$

To get other thermodynamic functions, we have the Helmholtz Free Energy:

$$dF = -\sigma d\tau - PdV + \mu dN$$

We can then write μ in terms of F:

$$\left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \mu$$

Integrating both sides:

$$\int_0^N \left(\frac{\partial F}{\partial N}\right)_{\tau,V} dN = F = \int \mu \, dN$$

This leads (via the free energy relationships) to the Sackur-Tetrode equation:

$$\sigma = N\left[\ln\frac{n}{n_Q} + \frac{5}{2}\right]$$

Where n is the density $\frac{N}{V}$ and n_Q is the quantum concentration $\left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$.

Also from the free energy we get that $PV = N\tau$, and that $U = \frac{3}{2}N\tau$.

1.7.1 Transformations of Ideal Gases

Let's take an insulated container with a reservoir at temperature τ. There is a piston being slowly expanded by the gas in the system. We are isothermally and reversibly expanding the gas. What happens when we go from V_i to V_f. We can write down our thermodynamic identity:

$$dU = \tau d\sigma - PdV$$

Where we have let N be constant. What happens to the energy in the system? Since $U = \frac{3}{2}N\tau$, we see that nothing happens. Why is this happening? Well since the volume changes, the pressure must decrease, since $PV = N\tau$. The right side is constant, and thus the left must also be constant. Heat flows into the system from the reservoir. The work done on the gas is given by

$$W = \int_{V_i}^{V_f} -PdV = \int_{V_i}^{V_f} -\frac{N\tau}{V}\, dV = -N\tau \ln V\Big|_{V_i}^{V_f} = -N\tau\ln\left(\frac{V_f}{V_i}\right)$$

The heat flow is then

$$Q = N\tau\ln\frac{V_f}{V_i}$$

To find the change in entropy, we have $dU = dQ + dW = \tau d\sigma - PdV$, which gives us that

$$\tau d\sigma = N\tau\ln\frac{V_f}{V_i} \to \Delta\sigma = N\ln\frac{V_f}{V_i}$$

Comparing this to Sackur-Tetrode, we expect

$$N\left[\ln\frac{n_Q}{n} + \frac{5}{2}\right]$$

The only thing thats changing in this system is V, so by Sackur-Tetrode we have that $\sigma \propto N\ln\frac{V}{N}$.

Suppose we have another system, where we have a wall separating the gas from a vacuum, and we have the same reservoir setup. If we all at once remove the wall, the gas will expand all at once. We still have no change in energy U, because τ and N remain constant. We see that the final values for all the variables are the same, and thus we have that the change in entropy is the same in the last case. We see that we can dodge the issue of irreversibility by assuming that the process was reversible, and just looking at the end state. This is because N, τ, σ, U are state functions, they do not care about the path you took to get to the end result, only the end result itself.

1.7.2 Summary of Chapter 6

Lets do a review of chapter 6. We have that the average number of particles in a certain state is given by

$$\langle N_s \rangle = f(\varepsilon_s) = \frac{1}{\exp[(\varepsilon - \mu)/\tau] \pm 1}$$

Where the $+$ is for Fermi gases and the $-$ is for Bose gases. If the ± 1 matters, we have a quantum gas, and it not, then $\exp[(\varepsilon - \mu)/\tau] \gg 1$.

If this is true, then

$$\exp[(\mu - \varepsilon)/\tau] \ll 1$$

Splitting this:

$$\exp[\mu/\tau] \exp[-\varepsilon/\tau] \ll 1$$

We can see that the second term must be less than 1 since its a decaying exponential, so we can also say that

$$\exp[\mu/\tau] \ll 1$$

If this is true,

$$\mu = \tau \ln \frac{n}{n_Q}$$

Where $n = \frac{N}{V}$ and $n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$ (the quantum concentration). We can rewrite and then use the inequality that we have:

$$\frac{\mu}{\tau} = \ln \frac{n}{n_Q} \to \exp[\mu/\tau] = \frac{n}{n_Q} \to \frac{n}{n_Q} \ll 1$$

This tells us that $n \ll n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$. Solving this for temperature:

$$\frac{2\pi\hbar^2}{M} n^{2/3} \ll \tau$$

This tells us that there is some characteristic temperature τ_0 above which we can use the classical/high temperature limit.

If all of these things are true, $f(\varepsilon_s) = \exp[(\mu - \varepsilon)/\tau] = \lambda \exp[-\varepsilon/\tau]$, where $\lambda = \exp[\mu/\tau]$. We then say that the total number of particles is

$$\langle N \rangle = \lambda \sum_s \exp[-\varepsilon_s/\tau] = \lambda Z_1$$

This tells us that $\mu = \ln \frac{N}{Z_1}$, and

$$F = \int \mu \, dN$$

And everything follows from this. For 1 dimension, where $\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2$, for $n = 1, 2, 3 \ldots$.

1.8 Chapter 7: Fermi and Bose Gases

1.8.1 Fermi Gases

What about for a Fermi gas, where $\langle N_s \rangle = f = \frac{1}{\exp[(\varepsilon-\mu)/\tau]+1}$. What we want is the ground state in 1D. We have that $\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n_x^2$. If we plot this, we see that it is a step function, 1 until we reach a point where the occupancy is 0, and we have 0. If we have many particles, we keep this shape, and just make the function closer and closer to continuous. The energy at which we drop to 0 is known as the Fermi energy ε_F. This is the chemical potential at 0 temperature (because we hit 0 when $\tau \to 0$ and $\varepsilon \gg \mu$).

We have been neglecting spins so far, so to account for this, we see that we have some maximum value of n_x, so we have

$$2n_{max} = N$$

Where that factor of two comes from the spins, and this equals the total number of particles in the system. For 1D, we have that

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n_{max}^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2\left(\frac{N}{2}\right)^2$$

For 3 dimensions, its a bit more detailed, but its the same process as the 1D case:

$$\varepsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

where we have that $n_i \geq 1$. We collapse the constants into 1 constant, $n^2 = n_x^2 + n_y^2 + n_z^2$. If we plot the large n limit, we have a sphere of radius n_F. This is known as a Fermi surface. We need to count how many points are inside the sphere, and then multiply by 2 to get the spin factors too. If we take an arbitrary point, and make a cube that reaches halfway to its nearest neighbor, we have a cube of unit volume. Each orbital takes up a unit amount of volume. The volume of the Fermi surface is

$$2\frac{1}{8}\frac{4}{3}\pi n_F^3 = N$$

Where the 2 comes from the spin factors, and the $\frac{1}{8}$ comes from the fact that we are only in the first octant. Note that we are also hiding a $\frac{1}{1}$ for the density of the surface.

Now solving for n_F:

$$n_F = \left(\frac{3N}{\pi}\right)^{1/3}$$

Now finding the Fermi energy (We can just plug into the energy expression that we have):

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2\left(\frac{3N}{\pi}\right)^{2/3}$$

We can rewrite this (using the fact that $\left(L^{2/3}\right)^{2/3} = L^2$):

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

This is the 3D Fermi ground state, at $\tau = 0$. Suppose we want to know the ground state energy. We want to add the energies for every coordinate inside the surface:

$$U_0 = 2 \sum_{n_x^2+n_y^2+n_z^2 \leq n_F} \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

where the 2 is a spin factor, and we are essentially adding up the energy in shells up until the edge of the Fermi surface. We can convert this to an integral for large n, because the difference between the shells is very small:

$$= 2 \iiint_0^{n_F} \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)\, dn_x\, dn_y\, dn_z$$

We can do this more easily in spherical:

$$U_0 = 2\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \frac{1}{8}\int_0^{n_F} 4\pi n^4 dn$$

Where we have added a $\frac{1}{8}$ because we are only in one octant. This gives us

$$U_0 = \frac{\hbar^2\pi}{2m}\left(\frac{\pi}{L}\right)^2 \left[\frac{n^5}{5}\right]_0^{n_F}$$

$$= \frac{\pi}{5}\frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n_F^5$$

Recalling the definition of ε_F, we find that

$$\boxed{U_0 = \frac{3}{5}N\varepsilon_F}$$

We can define the Fermi temperature:

$$k_B T_F = \varepsilon_F$$

Let's talk about the density of states. Suppose we want to look at the average value of some quantity $\langle X \rangle$:

$$\langle X \rangle = 2 \sum_{n_x, n_y, n_z = 0}^{\infty} X_n f(\varepsilon_n)$$

Where the 2 is from the spin factor. We can convert the sum to an integral:

$$= \iiint_0^{\infty} X_n \frac{1}{\exp[(\varepsilon - \mu)/\tau] + 1}\, 2\, dn_x\, dn_y\, dn_z$$

This $2\, dn_x\, dn_y\, dn_z$ is the number of states in some infinitesimal cube in the space. The 2 is the density of states in n_x, n_y, n_z space.

We can also talk about a different density. We can change to spherical:

$$2\, dn_x\, dn_y\, dn_z = 2 \times \frac{4}{8}\pi n^2\, dn = \pi n^2\, dn$$

This tells us that $\pi n^2\,dn$ is the number of states at radius n in a shell of thickness dn. This is also a form of density of states. Recalling that we have

$$\varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 n^2$$

We can convert our density using energy:

$$n = \sqrt{\frac{2m}{\hbar^2}\left(\frac{L}{\pi}\right)^2 \varepsilon_n} = n$$

If we take the derivative on both sides to get dn on the right side:

$$\sqrt{\frac{2m}{\hbar^2}\left(\frac{L}{\pi}\right)^2}\frac{1}{2}\varepsilon_n^{-1/2}\,d\varepsilon = dn$$

Now plugging this into $\pi n^2\,dn$:

$$\boxed{D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}}$$

This is known as the density of states, and is the number of states per unit energy. As a summary, lets write out the different expressions that we have

$$\langle X\rangle = \sum_{n_x=0}^{\infty}\sum_{n_y=0}^{\infty}\sum_{n_z=0}^{\infty} 2X_n f(\varepsilon_n)$$

$$\langle X\rangle = \iiint_0^\infty X_n f(\varepsilon_n)\,2\,dn_x\,dn_y\,dn_z$$

$$\langle X\rangle = \int_0^\infty X_n f(\varepsilon_n)\frac{2}{8}4\pi n^2\,dn$$

$$\langle X\rangle = \int_0^\infty X_n f(\varepsilon_n)\,\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}\,d\varepsilon$$

Let us now look at $\langle N\rangle$. We have that $X_n = 1$:

$$\langle N\rangle = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{1}{\exp[(\varepsilon-\mu)/\tau]+1}\varepsilon^{1/2}\,d\varepsilon$$

If we let $\exp[\mu/\tau] = \lambda$ once again, we have

$$\langle N\rangle = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{e^{1/2}}{\lambda^{-1}e^{\varepsilon/\tau}+1}\,d\varepsilon$$

We can now do a usub, and let $u = \frac{\varepsilon}{\tau}$. This gets us that $\frac{du}{d\varepsilon} = \frac{1}{\tau}$, and thus $d\varepsilon = \tau du$:

$$\langle N\rangle = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\tau^{3/2}\int_0^\infty \frac{u^{1/2}}{\lambda^{-1}e^u+1}$$

The classical limit would be to say that the 1 is negligible and we would be able to pull the λ out. This integral is a function of λ, and is a special function. This integral evaluates to

$$\int_0^\infty \frac{u^{1/2}}{\lambda^{-1}e^u + 1} = -\frac{3}{4}\sqrt{\pi}\,\mathrm{Li}_{3/2}(-\lambda)$$

Where Li is the polylogarithm of order $\frac{3}{2}$.

Another useful relationship is the Sommerfeld expansion:

$$\mu = \varepsilon_F - \frac{1}{3}\left(\frac{\pi}{2}\right)^2\frac{\tau^2}{\varepsilon_F} + \dots$$

for $\tau \ll \varepsilon_F$.

1.8.2 Bose Gases

We begin by finding the ground state, for $\tau = 0$, and then we find what happens for $\tau > 0$. We begin with

$$\langle N_s \rangle = f(\varepsilon) = \frac{1}{\exp[(\varepsilon_s - \mu)/\tau] - 1}$$

For Bosons, we ask how many particles will be in the ground state. Suppose we have the $(1,1,1)$ orbital, which has energy $\varepsilon_{111} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2(1+1+1)$. The next level up will be something like $(1,1,2)$, which will have energy $\varepsilon_{112} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2(1+1+4)$. The difference in energy $\Delta\varepsilon$ is given by just subtracting these two:

$$\Delta\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \cdot 3$$

If we then choose our element, such as Helium, He_1, we find that

$$\frac{\Delta\varepsilon}{k_B} \approx 10^{-14}\,\mathrm{K}$$

However this does not take into account the particle transfer from the grand cannonical ensemble. Instead of using the Boltzmann factors to find the probability (from the canonical ensemble we have that $P_s \propto e^{-\varepsilon_s/\tau}$):

$$P \propto e^{-\varepsilon/\tau}$$

We should be using the grand canonical ensemble:

$$P \propto e^{(N\mu - \varepsilon)/\tau}$$

We can write down the wavefunction for the particle

$$\Psi = A\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}$$

The energy that we have been using was

$$\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2(n_x^2 + n_y^2 + n_z^2)$$

We actually shift this energy down by 3, to make the ground state 0:

$$\varepsilon = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2\left[(n_x^2+n_y^2+n_z^2)-3\right]$$

Let us ignore spin for a moment, and state that there are N_0 particles in the ground state. Recall that

$$f(1,1,1) = N_0 = \frac{1}{\exp[(\varepsilon_{111}-\mu)/\tau]} = \frac{1}{\exp[(0-\mu)/\tau]-1} = \frac{1}{e^{-\mu/\tau}-1}$$

We tentatively assume that N_0 is large. We can solve this for μ:

$$\exp(-\mu/\tau) = \frac{1}{N_0}+1$$

Taking the log of both sides:

$$\ln\left(1+\frac{1}{N_0}\right) = -\frac{\mu}{\tau}$$

We approximate this left side as $\frac{1}{N_0}$, as $\ln(1+x)\approx x+\dots$ for small x:

$$\frac{1}{N_0} = -\frac{\mu}{\tau} \to \mu = -\frac{\tau}{N_0}$$

for large N_0. This tells us that the gas does like to cram into the lowest energy state, as the chemical potential is slightly less than the energy of the lowest state, which in this case is $\varepsilon = 0$. As we increase the temperature, we decrease the chemical potential, and we should expect more population in the higher energy levels. We can find the total number of particles:

$$\langle N\rangle_{\text{total}} = \sum_s f(\varepsilon_s)$$

$$= \sum_s \frac{1}{\exp[(\varepsilon-\mu)/\tau]-1} \approx \int_0^\infty D(\varepsilon)\frac{1}{\exp[(\varepsilon-\mu)/\tau]-1}\,d\varepsilon$$

Where D is the density of states. However, there is an issue, that was noticed by Einstein, who claimed that the fermion and boson cases were different:

$$D(\varepsilon)_{\text{bosons}} = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}$$

However, if we plug in $\varepsilon = 0$, we see that we have 0 states, which doesn't make sense. This density ignores the tendency of bosons to be in the ground state. To fix this, we can say that

$$N = N(111) + \int_0^\infty D(\varepsilon)f(\varepsilon)\,d\varepsilon$$

We know that $N(111)$ is, its just N_0, and we clump the rest into a term known as N_e, for the excited states. Thus we have that $N = N_0 + N_e$:

$$N_0 = \frac{1}{\exp(-\mu/\tau)-1} = \frac{1}{\lambda^{-1}-1}$$

We have already gone through and solved this for μ, and we have that

$$\mu = -\frac{\tau}{N_0}$$

for some unknown $N_0(\tau)$. From this, we realize that $\lambda \approx 1$. And we can compute the integral:

$$N_e = \int_0^\infty \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}\frac{1}{\lambda^{-1}\exp(\varepsilon/\tau)-1}\, d\varepsilon$$

Now inserting the fact that $\lambda \approx 1$:

$$\begin{aligned}\frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{\lambda^{-1}\exp[\varepsilon/\tau]-1}\, d\varepsilon \\ = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{\exp[\varepsilon/\tau]-1}\end{aligned}$$

In order to make the integral dimensionless, we change the variable of integration to $\frac{\varepsilon}{\tau}$:

$$= \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \tau^{3/2}\frac{\left(\frac{\varepsilon}{\tau}\right)^{1/2}}{\exp[\varepsilon/\tau]-1}\, d\left(\frac{\varepsilon}{\tau}\right)$$

Note that we cannot make this dimensionless if we put the λ^{-1} back in. We then have that

$$N_e(\tau) = \frac{V}{4\pi^2}\left(\frac{2M\tau}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{x^{1/2}\, dx}{e^x-1}$$

This integral is just some number, we have all the physics outside of the integral, its just a scaling constant. We end up having that $N_e \propto \tau^{3/2}$, and by the relationship $N_0 + N_\varepsilon = N$, with constant N, this tells us that N_0 will be the opposite. This integral ends up being $1.30619\pi^{1/2}$. If we stack everything inside the $\frac{3}{2}$ exponent:

$$\frac{N_e(\tau)}{N} = \left(\frac{\tau}{\left(\frac{N}{2.612V}\right)^{2/3}\frac{2\pi\hbar^2}{M}}\right)^{3/2}$$

This denominator is known as the Einstein temperature, τ_E:

$$\frac{N_e(\tau)}{N} = \left(\frac{\tau}{\tau_E}\right)^{3/2}$$

When $\tau/\tau_E = 1$, the approximation breaks down, but the approximation is remarkably solid even up to this point. Also note that the ground state occupancy average is proportional to $1 - \left(\frac{\tau}{\tau_E}\right)^{3/2}$.

For a sense of scale, for Helium-4, we find that $T_E = k_B\tau_E \approx 3.1K$.

If we tried to get the free energy, we'd find that at this level of approximation we have that $\mu = 0$, and so we need another route to find other quantities.

We can compute

$$\begin{aligned}U = \langle \varepsilon_s\rangle = N_0\varepsilon_0 + \int_0^\infty \varepsilon D(\varepsilon)f(\varepsilon)\, d\varepsilon \\ = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int \varepsilon\varepsilon^{1/2}f(\varepsilon)\, d\varepsilon\end{aligned}$$

After some numerical magic:

$$U = 0.770N\tau\left(\frac{\tau}{\tau_E}\right)^{3/2}$$

If we plot the heat capacity, we see that we have a cusp after the τ_E.

1.9 Chapter 8: Heat and Work

In an isolated system, we have that $\Delta U = 0$ always, but mechanical energy is not conserved, we have transfer of energy into heat energy.

We have looked at a new quantity, $\Delta\sigma \geq 0$, the log of the number of accessible quantum states in the system. In equilibrium, $\Delta\sigma = 0$, and it will increase if you are out of equilibrium moving towards equilibrium.

We define a reversible process as a process that goes from state A to state A, and the entire universe is unchanged. This means that the change in entropy is 0.

Suppose we have a system, and we plot pressure versus volume, with constant N. A point on this plot is a state, with a certain pressure and a certain volume. We can imagine an infinite number of paths between state 1 and state 2, and likewise an infinite number of return paths. This creates some closed loop, which may or may not define a reversible process. We know that

$$\oint dU = 0$$

and that

$$\oint d\sigma \geq 0$$

The total work done on the system in the cycle is given by the area enclosed by the path:

$$W = -\oint P\,dV$$

Recall the thermodynamic identity, which is defined for a reversible process:

$$dU = \tau d\sigma - PdV$$

And more generally:

$$dU = đQ + đW$$

Where $đ$ indicates a path dependence.

In a reversible process, $\tau d\sigma = đQ_{\text{reversible}}$,but in a irreversible process,

$$\tau d\sigma > đQ_{\text{irreversible}}$$

And we have that

$$đQ_{\text{reversible}} > đQ_{\text{irreversible}}$$

We have the opposite relationship for the work (from the expression for dU):

$$đW_{\text{reversible, on the system}} < đW_{\text{irreversible, on the system}}$$

For the work done by the system, we switch signs:

$$đW_{\text{reversible, by the system}} > đW_{\text{irreversible, by the system}}$$

The steam engine was the first heat engine developed. This relied on the heat of steam.

Work can be converted between different types of work, we can convert transform heat into work, like cars do, and we can also transform work into heat, however not all of these have the same properties. Suppose we have a box that we call an engine. To be precise, this is a steady-state engine, it cannot store anything inside of it, so no entropy or energy storage. If the engine is an electrical generator, we put in some mechanical work, and then convert this to electrical work. In the ideal case, we have that $W_{\text{mech}} = W_{\text{elec}}$. In fact, modern electrical generators are really good at being close to the ideal case (otherwise the sheer amount of work going through those generators would cause things to melt). We can then hook up this generator to a motor, which converts electrical work to mechanical work.

A heat engine converts heat into work. We begin with some high temperature, in this case lets use a reservoir at some temperature τ_R. By energy conservation, heat moving from the reservoir into our magic box and then being converted into work will work, but lets calculate the entropy change in the reservoir. We are taking some amount of heat Q:

$$dQ = \tau d\sigma \to \Delta Q = \tau \Delta\sigma \to \Delta\sigma_R = -\frac{Q}{\tau_R}$$

We see that the entropy in the reservoir is decreasing, and since we can't store entropy in the engine, that can't be a solution, so this setup is not allowed. The next step in making a heat engine is to make a new reservoir at a lower temperature than the first one, so we have temperatures τ_H and τ_L. Now we have some heat going into the engine from the high temperature reservoir, some work coming out, and some heat moving into the low temperature reservoir.

We need energy conservation to be correct:

$$W + Q_L = Q_H$$

and then looking at the entropy change in the two reservoirs (and assuming that the process is reversible so the change in entropy must be 0), we know that

$$\Delta\sigma_L + \Delta\sigma_H = 0 \to \frac{Q_L}{\tau_L} - \frac{Q_H}{\tau_H} = 0$$

What we care about in this system is the work in terms of Q_H:

$$\frac{Q_L}{\tau_L} = \frac{Q_H}{\tau_H} \to Q_L = \frac{Q_H \tau_L}{\tau_H}$$

$$W = Q_H - \frac{Q_H \tau_L}{\tau_H} = Q_H\left(1 - \frac{\tau_L}{\tau_H}\right)$$

This tells us that we cannot completely convert heat to work. We can define the efficiency of a heat engine as the ratio of what we want to what it costs us:

$$\boxed{\gamma = \frac{W}{Q_H} = 1 - \frac{\tau_L}{\tau_H}}$$

This is the Carnot efficiency. Note that if we convert τ to T, we see that the k_Bs cancel, and thus the Carnot efficiency can be written in terms of Kelvin temperatures:

$$\gamma_{\text{Carnot}} = 1 - \frac{T_L}{T_H}$$

Real efficiencies are less than or equal to this Carnot efficiency.

This is due to different sources of loss. There will always be some heat flow directly from the high temperature to the low temperature, Q_1. We can compute the change in entropy due to this:

$$\Delta\sigma_1 = \left(-\frac{Q_1}{\tau_H} + \frac{Q_1}{\tau_L}\right) = Q_1 \left[\frac{\tau_H - \tau_L}{\tau_H \tau_L}\right]$$

We decrease the efficiency by increasing the entropy change. We also have a case where the engine is never heated up past some $\tau_{max} < \tau_H$. Essentially, the engine is not being fully heated up to τ_H:

$$\Delta\sigma_2 = Q_H \left[\frac{\tau_H - \tau_{max}}{\tau_H \tau_{max}}\right]$$

We also have the same issue in the heat leaving the engine going into the cold reservoir:

$$\Delta\sigma_3 = Q_L \left[\frac{\tau_{min} - \tau_L}{\tau_{min} \tau_L}\right]$$

We also have issues with the engine itself creating friction or heat.

If we take the Carnot heat engine, and then run the process backwards, putting work into the system, and having heat flow from the cold reservoir to the hot reservoir, we have a refrigerator. In the case of the refrigerator, we are "paying for" the input work, and what we want is the heat change in the low temp reservoir, which means that

$$\gamma_{\text{refrig}} = \frac{Q_L}{W} = \frac{T_L}{T_H - T_L}$$

Note that this can be larger than 1, so this isn't an efficiency, its more of a quality factor.

We also have an ideal heat pump, where we put in work and pump heat from the low reservoir to the high reservoir. We see that by change in entropy, we have that

$$dQ = \tau d\sigma \rightarrow \Delta\sigma_H = \frac{Q_H}{\tau_H} = \Delta\sigma_L = \frac{Q_L}{\tau_L}$$

For a heat pump, we have

$$\gamma_{\text{heat pump}} = \frac{Q_H}{W} = \left(\frac{T_H}{T_H - T_L}\right)$$

Note that this is always greater than 1 (except when the low temp is absolute 0).

We can plot processes on a entropy-temperature diagram, rather than a P-V diagram. We have two points of entropy, σ_H and σ_L, and two values for temperature, τ_l and τ_h. If we connect these to form a rectangle, we have two isothermal processes, and two adiabatic (constant entropy) processes. If we make this cyclic, we will show that we end up in the same place, but we have done some work.

We begin with the first part of the cycle, expanding the gas at constant temperature τ_h, moving from σ_L to σ_H. We can do this expansion by having a slowly moving insulated piston, as well as a reservoir outsidem at τ_h.

For the second part, we change from τ_h to τ_l at constant entropy σ_H. To do this part, we have an isolated box with a slowly moving insulated piston.

For the third part, we want to compress the gas, keeping the temperature at τ_l and moving from σ_H to σ_L. We do this by adding contact to a reservoir of temperature τ_l, slowly pushing in a piston.

For the final section, we want to increase the temperature from τ_l to τ_h, while keeping the entropy at σ_L. We do this by insulating the entire system and pushing the piston in slowly.

Note that for the first two sections, the system is doing work on the piston, and in the second two sections we are doing work on the system.

For the cycle, we can compute

$$\oint dU = 0 \qquad \oint d\sigma = 0$$

The change in entropy is 0 because we can look at the graph and we see that we have no net change in entropy, and the change in energy is 0 because of energy conservation, the change in heat is balanced out by the work that we put into the system.

From the first integral, we have that

$$\oint \tau d\sigma - \oint PdV = 0$$

$$\oint \tau d\sigma = \oint PdV = W$$

This right side is the work done by the system. This integral is the area inside the box, which is $(\sigma_H - \sigma_L)(\tau_h - \tau_l)$. Thus we have that the work done by the system is

$$W = (\sigma_H - \sigma_L)(\tau_h - \tau_l)$$

Or if you do this by splitting the paths, we have that the part from 4 to 1 and 2 to 3 will be 0 (no change in σ), and from 1 to 2 we have $\tau_h(\sigma_H - \sigma_L)$, and from 3 to 4 we have $\tau_l(\sigma_L - \sigma_H)$. Adding these together, we have

$$W = \tau_h(\sigma_H - \sigma_L) + \tau_l(\sigma_L - \sigma_H)$$

Which is the same as the area.

We can look at the change in heat:

$$Q_h = \tau_h(\sigma_H - \sigma_L)$$

and from this we can recover

$$\gamma_c = 1 - \frac{\tau_l}{\tau_h}$$

and we see that this is just the Carnot cycle.

For an ideal gas we have that

$$PV = N\tau$$

and we see that PV is a constant at constant temperature. We can also see that PV^γ for $\gamma = \frac{C_P}{C_V}$ is also a constant at constant entropy. If we draw the Carnot cycle on a P-V diagram, we once again have two isotherms and two adiabats, and we have that during the isotherms we have $PV = N\tau_h$ and $PV = N\tau_l$, and during the adiabats we have $P_1V_1^\gamma$ constant and likewise for P_2 and V_2 for the other adiabat.

1.10 Chapter 10: Phase Transitions

Suppose we have a box of water, with a piston on one side. If we fix the temperature to τ, and we lift the piston, it turns out that we have dense H_2O (liquid) on the bottom, and some less dense H_2O, in the form of vapor, between the liquid and the piston. When we move from liquid to vapor, we have what is known as a phase transition.

When we take a magnetic material, such as iron, and we look at the average magnetic moment as a function of temperature, we see that as we increase the temperature the moment goes to 0 (at a temperature known as the Curie temperature). We can see that we can demagnetize a magnet by heating it up enough. For iron, $T_C = 1044.0\,°C$, for nickel, $T_C = 631.58\,°C$.

Let's start with a toy model for a ferromagnet. This is the Ising model, made by a student of Heisenberg's. We begin with a bunch of spins on a lattice. We say that if we have only two, the Hamiltonian is equal to

$$H = -JS_1S_2$$

Where S_1, S_2 are ± 1. We can list out the 4 distinguishable states:

$$\uparrow\uparrow \qquad \uparrow\downarrow \qquad \downarrow\uparrow \qquad \downarrow\downarrow$$

which have energies:

$$-J \qquad J \qquad J \qquad -J$$

and we can write out the partition function:

$$Z = \sum_s e^{-\varepsilon_s/\tau} = e^{J/\tau} + 2e^{-J/\tau} + e^{J/\tau} = 4\cosh\left(\frac{J}{\tau}\right)$$

We can see that $\langle s \rangle = 0$ for all temperatures.

Note that the choice of Hamiltonian is just as a model. If we expand the model to more than 2 spins, we can have interaction with only the nearest neighbors. We introduce some notation. For a lattice:

$$H = \sum_{\langle i,j \rangle} -JS_iS_j = \sum_i (\sum_j^n -JS_iS_j)$$

Where n is the number of nearest neighbors, and we sum over all sites i. The angle brackets in the sum means nearest neighbors only, and we don't double count. In 1 dimension, this is solvable at a PHYS404 level. For 2 dimensions, it was solved by Onsager, and is very difficult. The 3 dimensional case is unsolved.

The Ising model has 1D spin, and if we expand this to 2D spins, we have the planar spin or XY model, and if we switch to 3D spins we have what is known as the Heisenberg model.

For the 2D case, when we look at some spin S_i, we have 4 neighbors, labelled S_{j_1} through S_{j_4}. For this spin, the hamiltonian is

$$H_i = -JS_i \sum_j S_j$$

If we sum up all these pieces:

$$H = \frac{1}{2}\sum H_i$$

Where the $\frac{1}{2}$ comes from the removal of double-counting the interactions.

We can use an approximation known as the mean-field approximation (MFA), where we represent each of the neighbor spins using their average value. If the neighbors point in a direction on average, the middle spin will also want to point in that direction:

$$H_i^{MF} = -JS_i \langle S_j \rangle n$$

where n is the number of nearest neighbors. Note that we can write this as

$$= -[J \langle S_j \rangle n]S_i$$

from which we can see that this is similar to the first model we ever used, it takes the place of the magnetic field.

We can write this for any spin:

$$H^{MF} = -J \langle s \rangle nS$$

Finding a partition function for this:

$$Z = \sum_s e^{-\varepsilon/\tau} = e^{-J\langle s \rangle n/\tau} + e^{J\langle s \rangle n/\tau} = 2\cosh\left(\frac{J \langle s \rangle n}{\tau}\right)$$

We can solve for $\langle s \rangle$:

$$\langle s \rangle = \frac{\sum Se^{-H/\tau}}{\sum e^{-H/\tau}} = \frac{e^{Jn\langle s \rangle/\tau} - e^{-Jn\langle s \rangle/\tau}}{e^{Jn\langle s \rangle/\tau} + e^{-Jn\langle s \rangle/\tau}} = \tanh(Jn \langle s \rangle /\tau)$$

Where we have used the fact that $\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}$.

This doesn't have a basic analytic solution. We can define a new variable, $x = Jn \langle s \rangle /\tau$, which means that $\langle s \rangle = \frac{\tau}{Jn}x$. This gets us that

$$\frac{\tau}{Jn}x = \tanh x$$

We now can think about this graphically, because the varying quantity τ is no longer in the tanh. If we plot both sides, for high τ, we have an intersection at only $x = 0$. This means that $\langle s \rangle = 0$, meaning that there is no spontaneous ordering, at high temperatures, magnets demagnetize.

For low τ, we have 3 solutions. Two of these tell us that at a low temperature most of the spins point up or most of them point down. However, we still have the 0 solution. It turns out that for low temperature, $\langle s \rangle = 0$ has lower free energy than $\langle s \rangle \neq 0$, or more importantly, higher entropy, making it a nonphysical solution.

This is something known as spontaneous symmetry breaking, when we cool down, we pick one of the two possible physical states, and if we're in an all up state and at low temperature we have an exponentially low probability to switch to an all down state, we've been essentially trapped into the state.

We pick one of the two states based on external factors, but if we were in a completely isolated system, they would pick at random, with 50/50 probability.

So we can solve this graphically, but what if we assume that x and $\langle s \rangle$ are small, and then taylor expand the hyperbolic tangent:

$$\frac{\tau}{Jn}x = x - \frac{x^3}{3} + \ldots$$

We can see that we have the solution $x = 0$ immediately, and also the solutions

$$x = \pm\sqrt{3\left(1 - \frac{\tau}{Jn}\right)} \propto \langle s \rangle$$

Note that this will only work for when the Taylor expansion is valid, otherwise we have to do it numerically or graphically. Also note that this solution gives us 0 when $\tau = Jn$, which we define as the transition temperature:

$$\tau_c = Jn$$

From this we have that

$$\langle s \rangle \propto \left(1 - \frac{\tau}{\tau_c}\right)^{1/2}$$

And if we compare this to experimental data, we have

$$\langle s \rangle \propto \left(1 - \frac{\tau}{\tau_c}\right)^{0.34}$$

For 1 dimension, this approximation is really wrong.

We had computed that for this mean field model:

$$Z = 2\cosh\frac{J\langle s \rangle n}{\tau}$$

From this we have that

$$F = -\tau \ln Z = -\tau \ln\left[2\cosh\frac{J\langle s \rangle n}{\tau}\right]$$

Let us look at the region where $\langle s \rangle$ is small, because that's what we're interested in:

$$F = -\tau\ln 2 - \frac{\tau}{2}\frac{\tau_c}{\tau}\langle s \rangle^2 = -\tau\ln 2 - \frac{\tau_c}{2}\langle s \rangle^2$$

Where we have used the fact that

$$\ln\cosh y \approx \frac{y^2}{2} + \dots$$

We can compute $\langle s \rangle^2$, it can be either

$$\langle s \rangle^2 = 0, 3\left(\frac{\tau}{Jn}\right)\left(1 - \frac{\tau}{Jn}\right)$$

For the case where $\langle s \rangle = 0$, we have that

$$F_0 = -\tau\ln 2$$

And for the other case:

$$F_1 = -\tau\ln 2 - \frac{3\tau}{2}\left(1 - \frac{\tau}{\tau_c}\right) = -\tau\ln 2 + \frac{3\tau}{2\tau_c}(\tau - \tau_c)$$

We now need to find which one of these is smaller. If F_0 is smaller, then we have no magnetization, and if the other is smaller we have nonzero magnetization. If we plot these two, we see that above τ_c, F_0 is smaller, and below τ_c, F_1 is smaller.

Let's do some thought experiments. Suppose we have some liquid, with a piston applying some force to it. This forces the piston right up against the liquid. The pressure is given by

$$P = \frac{F}{A}$$

If we push harder, the liquid compresses. If we plot the pressure against the inverse density, we use the fact that higher pressure means lower volume, leading to a higher density. Suppose that the system is surronded by a reservoir, so we have an isotherm on the plot. Using the Gibbs free energy:

$$dG = -\sigma d\tau + V dP + \mu dN$$

We had previously worked out that

$$G = N\mu$$

And we also have that

$$V = \left(\frac{\partial G}{\partial P}\right)_{\tau,N} = N\left(\frac{\partial \mu}{\partial P}\right)_{\tau}$$

This gets us that

$$\left(\frac{\partial \mu}{\partial P}\right)_{\tau} = \frac{V}{N}$$

This is known as a equation of state. This gets the inverse density as a function of P and τ only.

For an ideal gas, we can compute $\frac{N}{V}$ by using the fact that $PV = N\tau$, which gets that $\frac{N}{V} = \frac{P}{\tau}$.

Now suppose that we are lifting the piston rather than pushing it in. If the box is insulated, we can't have a vacuum be created, so we have that a vapor must always form, there must be something to apply pressure to the piston. This occurs even when the thing inside the box is a solid and the piston is pushed, there is still a vapor created.

We have some vapor pressure P_v, the temperature τ is fixed due to the external reservoir, and the chemical potential of the liquid and vapor must be the same:

$$\tau_v = \tau_l \quad \mu_v = \mu_l$$

Using the Gibb's free energy:

$$dG = -\sigma d\tau + V dP + \mu dN$$

We have that

$$G(\tau, P, N) = N\mu(\tau, P)$$

Thus the condition for equilibrium is now

$$\mu_l(\tau, P) = \mu_v(\tau, P)$$

At fixed N, we know that $\left(\frac{\partial G}{\partial \tau}\right) = N\left(\frac{\partial \mu}{\partial \tau}\right) = -\sigma$. This tells us that $\frac{\partial \mu}{\partial \tau} < 0$, since the entropy must always be positive. Likewise, we can find that $\left(\frac{\partial \mu}{\partial P}\right) > 0$.

Taking a second derivative:

$$\frac{\partial^2 \mu}{\partial P^2} = \frac{\partial}{\partial P}\frac{1}{n} = -\frac{1}{n^2}\frac{\partial n}{\partial P}$$

Where n is the density. Looking at this, as we increase pressure, the density must increase, so this term is negative overall:

$$-\frac{1}{n^2}\frac{\partial n}{\partial P} < 0$$

Thus we have that μ has a positive first derivative and a negative second derivative. The vapor pressure is defined by the crossing of the μ_l and μ_v curves. We take the minimum crossing, since minimum G means that μ is at a minimum. We have that at a fixed temperature, we have a fixed vapor pressure. Until all of the solid or liquid are gone, the pressure of the vapor will not change. After the solid/liquid has all evaporated, we have a gas now, and thus the pressure will be dictated by the volume.

If we raise the temperature, the region in which we have both a liquid and a vapor decreases, until we hit what is known as the critical point, after which we have only one phase, but this does not occur for a solid and vapor (because there is no distinction between a vapor and liquid when you are looking at just one of them, in the coesxistence region we just have different densities).

We have a family of curves, and we can shift between them, from $\mu(\tau)$ to $\mu(\tau + \Delta\tau)$. One can show that

$$\left(\frac{\partial P}{\partial \tau}\right)_{\text{coexistence}} = \frac{\frac{\sigma_v}{N_v} - \frac{\sigma_l}{N_l}}{\frac{V_v}{N_v} - \frac{V_l}{N_l}}$$

We can rewrite using $\nu = \frac{1}{n}$, and we can define a quantity known as the latent heat, which defines the heat necessary to transform one molecule:

$$\tau\Delta S_{\text{per molecule}} = \Delta Q = L$$

We find that along the coexistence curve:

$$\left(\frac{\partial P}{\partial \tau}\right)_{\text{coexistence}} = \frac{L}{\tau\Delta\nu}$$

This is the Clausius-Claypeyron equation. This equation applies to any 2 phase changes, and is exact, and experimentally tested and correct.

1.11 Review

We begin with the idea of a stationary quantum state, a system whose properties do not change in time, they are energy eigenstates. We have the microcanonical ensemble, which is a completely isolated system. The fundamental assumption of statmech claims that all accessible stationary states are equally likely. If g is the number of accessible states, the degeneracy, the probability of being in a particular state is $P_s = \frac{1}{g}$. This implies that if U is the energy, then

$$\frac{1}{g}\frac{\partial g}{\partial U} = \frac{1}{\tau}$$

And this determines equilibrium, $\tau_1 = \tau_2$ means that they are in equilibrium.

We define a new quantity, $\sigma = \ln g$. In this isolated system, g is a maximum. We also have that $\langle x\rangle = \sum_s x_s P_s$, for some quantity x.

We can then move to an isolated system with a small system inside it that can conduct heat with the system. In the system, we have that

$$P_s = \frac{e^{-\varepsilon_s/\tau}}{\sum_s e^{-\varepsilon_s/\tau}}$$

From this, we can define an average value of some quantity:

$$\langle x\rangle = \frac{\sum_s x\exp(-\varepsilon_s/\tau)}{\sum_s \exp(-\varepsilon_s/\tau)}$$

Note that if we let all the states have the same energy, we are left with just the microcanonical average value. We have the thermodynamic identity:

$$dU = \tau d\sigma - PdV$$

We can use a Legendre transformation $d(xy) = ydx + xdy$ to change the independent variables of the thermodynamic identity:

$$d(\tau\sigma) = \sigma d\tau + \tau d\sigma$$

$$dF = d(U - \tau\sigma) = -\sigma d\tau - PdV$$

We can show that $F = -\tau\ln Z$, and we can also show that $U = \tau^2\frac{\partial}{\partial\tau}\ln Z$. We define the partition function $Z = \sum_s \exp(-\varepsilon_s/\tau)$.

We can solve Black Body radiation using the fact that

$$\omega_n = \frac{n\pi c}{L}$$

and we have that

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

as well as the fact that we have 2 polarizations. We find that

$$Z_n = \sum_s \exp\frac{s\hbar\omega_n}{\tau}$$

This is one mode for the oscillator, so the total partition function is given by

$$Z_{tot} = \prod_n Z_n$$

because energies add, but they are in the exponentials. We move from the sum to something of the form

$$\frac{1}{8}\cdot 2\int_0^\infty \ldots 4\pi n^2\,dn$$

Which shows up a lot when doing 3D cases.

In the high τ limit:

$$Z = \sum_s \exp(-\varepsilon_s/\tau) \to Z_{\text{classical}} = \frac{1}{h^{Nd}}\int\cdots\int \exp(-H/\tau)\,d\vec{p}d\vec{q}$$

Where d is the dimension of the system, and N is the total number of particles. We are integrating over all momentum and position directions. Note that we will have Nd one dimensional integrals.

We have a new way of adding energy to the system, chemical work:

$$dU = \tau d\sigma - PdV + \mu dN$$

We use a new ensemble, the grand canonical ensemble. We have that

$$P = \frac{\exp[(N\mu - \varepsilon_s)/\tau]}{\sum_{ANS} \exp[(N\mu - \varepsilon_S)/\tau]}$$

Where we can let

$$\eta = \sum_{ANS} \exp[(N\mu - \varepsilon_s)/\tau]$$

Also note that this reduces to the microcanonical result.

For fermions and bosons, we have that

$$\langle N_s \rangle = f = \frac{1}{\exp[(\varepsilon - \mu)/\tau]}$$

In the classical ideal gas, we have that the ±1 is gone, and f is small:

$$f = \exp[(\mu - \varepsilon)/\tau] = \lambda \exp(-\varepsilon/\tau)$$

where $\lambda = \exp(\mu/\tau)$. To find the average number of particles in the entire system:

$$\langle N \rangle = \sum_s \lambda \exp(-\varepsilon/\tau) = \lambda Z_1$$

We can find that

$$\tau \ln \frac{\langle N \rangle}{\sum \exp(-\varepsilon_s/\tau)} = \mu$$

From this we can find F, using the fact that $F = \int_0^N \mu \, dN$.

For heat flow processes, we have energy and entropy flow from different temperatures.