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# 1 Free Energy and Chemical Thermodynamics

## 1.1 Free Energy as Available Work

There are four quantities that are important:

$$H \equiv U + PV$$

$$F \equiv U - TS$$

$$G \equiv U - TS + PV$$

$F$  is the total energy minus the heat you can get for free from an environment at temperature  $T$ . In other words, this is the energy that we *have* to provide if we're "creating" the system from thin air. Alternatively, if we are annihilating the system, the maximum amount of energy extracted is given by  $F$ .

If the system is in an environment with constant pressure and temperature, then the work we do to create it is given by the Gibbs free energy  $G$ . **Need some intuition on what these actually mean again.**

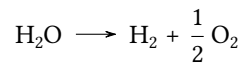
In most systems, we won't really be concerning ourselves with creating/annihilating, so we'll look at changes in these quantities:

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$$

Now, since  $Q \leq T\Delta S$  (with equality when the process is quasistatic, then we have the relationship that  $F \leq W$  at constant  $T$ . (where the  $T\Delta S$  formula applies). A similar argument can be made for  $G$ , where we have  $G \leq W_{\text{other}}$ , where this denotes the extraneous work done on the system, that is not from the environment. As a rule of thumb, if we don't care about the energy the environment provides, then we use  $G$  instead of  $F$ .

## 1.2 Fuel Cells

Consider the chemical reaction:



Looking up  $\Delta H$  values gives us 289 kJ, meaning that we need to supply this amount of energy (somehow) in order for the reaction to proceed. Not all of this energy needs to be supplied by us though, we can use the environment to do some of it for us. To figure out how much we need, we compute the change in entropy and calculate  $T\Delta S$ , which will be the energy supplied by the environment. Once we have that, then  $H - T\Delta S$  (which is  $G$ ) will tell us how much energy we need to supply. For this particular reaction, that works out to be 237 kJ.

In general, just look at the chemical reaction, determine  $\Delta H$  and  $\Delta S$ , then use these quantities to calculate  $\Delta G$ , simple.

## 1.3 Thermodynamic Identities

Recall the formula for  $dU$ :

$$dU = TdS - PdV + \mu dN$$

We can create similar equations for  $dH$ , using the knowledge that  $H = U + PV$ :

$$dH = dU + PdV + VdP$$

(note that we need to take the product rule with  $PV$ , which gives us the two terms.) Now we substitute  $dU$  into this equation, so we get:

$$dH = TdS + VdP + \mu dN$$

This tells us how  $H$  changes with respect to other thermodynamic quantities. Similarly, we can do this for  $F$  :

$$dF = -SdT - PdV + \mu dN$$

holding  $V$  and  $N$  constant gives us:

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}$$

The same can be done for  $G$ , and its respective quantities. If we have a mixture of multiple particles in our system, then recall that we replace  $\mu dN$  by  $\sum_i \mu_i dN_i$ , and so to calculate  $\mu$ , then we have:

$$\mu_1 = \left( \frac{\partial G}{\partial N_1} \right)_{T,P,N_2} \quad \mu_2 = \left( \frac{\partial G}{\partial N_2} \right)_{T,P,N_1}$$

## 2 Boltzmann Statistics

### 2.1 Boltzmann Factor

Essentially deals with a system in contact with a reservoir of energy  $E$ . The reservoir has to have a specified temperature. Because the system is interacting with its environment, then we can relate the probability of our particle being in one state to another:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = e^{[S_R(s_2) - S_R(s_1)]/k}$$

Then use the thermodynamic identity  $dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R)$  (note that the signs of  $PdV$  and  $\mu dN$  are flipped, because we are looking from the reservoir's perspective. We will now neglect these two terms for the time being (generally  $PdV$  is small, and we'll add  $dN$  back later), so this gives us:

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$$

To get the probability, divide by the partition function  $Z$  :

$$P(s) = \frac{1}{Z} e^{-E(s)/kT}$$

To get  $Z$ , we note that:

$$1 = \sum_s \frac{1}{Z} e^{-E(s)/kT} \implies Z = \sum_s e^{-E(s)/kT}$$

so  $Z$  is the **sum of all boltzmann factors**.

### 2.2 Average (Expected) Values

The average value of any state variable  $X$  with  $X(s)$  being the value at state  $s$ , then we have:

$$\bar{X} = \sum_s X(s)P(s) = \frac{1}{Z} \sum_s \sum_s X(s)e^{-\beta E(s)}$$

Note that  $\beta = \frac{1}{kT}$ . Then, to calculate the energy, we have:

$$\bar{E} = \sum_s E(s)P(s)$$

then, we can calculate the total energy  $U$  by using the formula  $U = N\bar{E}$ .

### 2.2.1 Paramagnetism

Consider a dipole having spin up energy  $\mu B$  and spin down energy  $-\mu B$ . Then, for a singular dipole:

$$Z = \sum_s e^{\beta E(s)} = e^{-\beta \mu B} + e^{\beta \mu B} = 2 \cosh(\beta \mu B)$$

The average energy is calculated as:

$$\bar{E} = \sum_s E(s)P(s) = -\mu B \tanh(\beta \mu B)$$

So in total, we have  $U = -N\mu B \tanh(\beta \mu B)$ . There's also an alternate way to calculate the mean energy:

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

The total magnetization can then be calculated by scaling the average magnetization:

$$\bar{\mu}_z = \sum_s \mu_z(s)P(s) = \mu P(\uparrow) - \mu P(\downarrow) = \mu \tanh(\beta \mu B) \implies M = N\bar{\mu}_z = N\mu \tanh(\beta \mu B)$$

Problem 6.22 looks good as practice

## 2.3 Equipartition Theorem

Suppose we have a system whose energy is given by a quadratic function  $E(q) = cq^2$ , where  $q$  represents any state variable (coordinate, momentm, etc). Then, the partition function is:

$$Z = \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta cq^2} = \frac{1}{\Delta q} \sum_q e^{-\beta cq^2} \Delta q$$

Now, since  $\Delta q$  is very small, then we can interpret this as an integral (when can we no longer do this?). Therefore we have:

$$Z = \frac{1}{\Delta q} \int_{-\infty}^{\infty} e^{-\beta cq^2} dq = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx = \frac{1}{\Delta q} \sqrt{\frac{\pi}{\beta c}} = C\beta^{-1/2}$$

Then, taking the average energy is easy:

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{2} \beta^{-1} = \frac{1}{2} kT$$

## 2.4 Maxwell Speed Distribution

We know that the root mean squared distribution:

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

This is nice, but we now want to calculate the proportion of molecules that are travelling at a given speed. Given a distribution  $D(v)$ , the probability that our particle is within  $v_1$  and  $v_2$  is:

$$P(v \in [v_1, v_2]) = \int_{v_1}^{v_2} D(v) dv$$

The distribution function can be written as:

$$D(v) \propto (\text{probability of having velocity } \vec{v}) \times (\text{number of vectors with speed } v)$$

The first factor is (proportional to) the Boltzmann factor:

$$(\text{probability of having velocity } \vec{v}) \propto e^{-mv^2/2kT}$$

Recall that having a speed  $v$  means having energy  $\frac{1}{2}mv^2$ , which explains the exponent. To calculate the number of velocity vectors with velocity  $v$ , we imagine the surface of a sphere in velocity space, and the set of velocity vectors with speed  $v$  lives on the surface of that sphere with radius  $v$ . This is due to the fact that on a surface of a sphere, the magnitude of the velocity vector is always going to be  $v$ . Therefore:

$$(\text{number of vectors with speed } v) \propto 4\pi v^2$$

Combining the two now gives:

$$D(v) = C \cdot 4\pi v^2 e^{-mv^2/2kT}$$

The constant  $C$  is just the constant that ensures that the integral over all space is 1, so at the end of all the algebra, we get:

$$D(v) = \left( \frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}$$

This is the **Maxwell distribution**. Knowing the distribution, we can now calculate the average speed:

$$\bar{v} = \sum_v v D(v) dv = \int_0^\infty v D(v) dv = \sqrt{\frac{8kT}{\pi m}}$$

## 2.5 Partition Functions and Free Energy

Here we will prove that the equation  $F = -kT \ln Z$  is true. To do this, we start with the definition of  $F = U - TS$ , and recall the thermodynamic identity

$$\left( \frac{\partial F}{\partial T} \right)_{V,N} = -S$$

We can write  $S$  in terms of the first equation, so

$$\left( \frac{\partial F}{\partial T} \right)_{V,N} = \frac{F - U}{T}$$

This is a differential equation for  $T$ , and from here we will show that  $F = -kT \ln Z$  obeys this differential equation and also shares the same initial condition at  $T = 0$ . Let  $\tilde{F} = -kT \ln Z$ , so then we have:

$$\frac{\partial \tilde{F}}{\partial T} = -k \ln Z - kT \frac{\partial}{\partial T} \ln Z = -k \ln Z - kT \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z = \frac{U}{kT^2}$$

Therefore:

$$\frac{\partial \tilde{F}}{\partial T} = -k \ln Z - kT \frac{U}{kT^2} = \frac{\tilde{F} - U}{T}$$

So it follows the same differential equation as  $F$ . Then, looking at  $T = 0$ , we have  $F = U = U_0$ , since all excited states should limit to 0. The partition function does the same thing, and so all we get is the ground state term, so therefore:

$$\tilde{F}(0) = -kT \ln Z(0) = U_0 = F(0)$$

Hence, we have  $F = -kT \ln Z$ .

## 2.6 Partition Function for Composite Systems

How do we derive the general partition function? We just multiply them together, as long as they are noninteracting. For instance, for two identical particles, we have:

$$Z_{\text{total}} = Z_1 Z_2$$

where  $Z_1$  is the partition function for particle 1, and  $Z_2$  for particle 2. This holds as long as the particles don't interact with one another. We also need the case that the particles are distinguishable. If they are indistinguishable, then simply taking the product is incorrect because we end up overcounting the number of states we have in our system. In general then, we'd have to divide by a factor of the number of permutations of the particles in the indistinguishable case, whereas the distinguishable case is relatively easy:

$$Z_{\text{total}} = \begin{cases} Z_1 Z_2 \cdots Z_N = \prod_i Z_i & \text{noninteracting, distinguishable} \\ \frac{1}{N!} Z_1^N & \text{noninteracting, indistinguishable} \end{cases}$$

Note that the indistinguishable case is still not exactly correct, since we haven't eliminated the possibility that the energies of the particles could be the same when we divided by  $N!$ . This will be handled in the next chapter.

## 2.7 Ideal Gas Revisited

Consider an ideal gas with identical particles, then we have the partition function

$$Z = \frac{1}{N!} Z_1^N$$

Then, we need to calculate  $Z_1$  (the partition function for a single molecule). To find  $Z_1$ , first look at the Boltzmann factor:

$$e^{-E(s)/kT} = e^{-E_{\text{tr}}(s)/kT} e^{-E_{\text{int}}(s)/kT}$$

$E_{\text{tr}}(s)$  is the translational energy and  $E_{\text{int}}(s)$  is the internal energy (rotational, for example) for the state  $s$ . Then, we can just write  $Z_1 = Z_{\text{tr}} Z_{\text{int}}$ . First, we look at all the possible translational states of a molecule. For a particle in a box, there are only a defined number of states:

$$\lambda_n = \frac{2L}{n} \implies p = \frac{h}{\lambda_n} = \frac{hn}{2L} \implies E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2}$$

So now that we have  $E_n$ , we can calculate  $Z_{1d}$ , the partition function for a molecule in 1D:

$$Z_{1d} = \sum_n e^{-E_n/kT}$$

And if the energy levels are close together (which is the case when  $L$  or  $T$  are large enough), then we can treat this as an integral over  $dn$ :

$$Z_{1d} = \int_0^\infty e^{-h^2 n^2 / 8mL^2 kT} dn = \sqrt{\frac{2\pi mkT}{h^2}} L = \frac{L}{\ell_Q}$$

where  $\ell_Q$  is the **quantum length**, defined as:

$$\ell_Q = \frac{h}{\sqrt{2\pi mkT}}$$

Consequently, then, we can calculate the full translational partition function by doing the same but now over all directions  $x, y, z$ :

$$Z_{\text{tr}} = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-E_{n_x}/kT} e^{-E_{n_y}/kT} e^{-E_{n_z}/kT} = \frac{L_x}{\ell_Q} \frac{L_y}{\ell_Q} \frac{L_z}{\ell_Q} = \frac{V}{\ell_Q^3}$$

we define the quantum volume to be  $v_Q = \ell_Q^3$ , so we have  $Z_{\text{tr}} = \frac{V}{v_Q}$ . Therefore, we can now combine this with  $Z_1 = Z_{\text{tr}}Z_{\text{int}}$  to get:

$$Z_1 = \frac{V}{v_Q} Z_{\text{int}}$$

Then, for  $N$  molecules we use the formula derived in the previous section:

$$Z = \frac{1}{N!} \left( \frac{V Z_{\text{int}}}{v_Q} \right)^N$$

As a side note, we then have  $\ln Z = N[\ln V + \ln Z_{\text{int}} - \ln N - \ln v_Q + 1]$ , which will come up later. Now that we have  $Z$ , we can compute all the properties of an ideal gas, and we'll find that everything lines up exactly with what we had predicted earlier. For instance, the total energy follows the equipartition theorem:

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = U_{\text{int}} + \frac{3}{2} NkT$$

[Review the actual derivation for how to differentiate.](#) Taking the derivative of this result also gives the heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U_{\text{int}}}{\partial T} + \frac{3}{2} Nk$$

We can also calculate  $F = -kT \ln Z = -NkT[\ln V - \ln N - \ln v_Q + 1] + F_{\text{int}}$ , so then we have:

$$P = -\left( \frac{\partial F}{\partial V} \right)_{T,N} = \frac{NkT}{V}$$

Similarly, we have:

$$S = Nk \left[ \ln \left( \frac{V}{Nv_Q} \right) + \frac{5}{2} \right] - \frac{\partial F_{\text{int}}}{\partial T}, \quad \mu = -kT \ln \left( \frac{V Z_{\text{int}}}{Nv_Q} \right)$$

Neglecting the internal terms, these results match what we had earlier.

## 3 Quantum Statistics

### 3.1 Gibbs Factor

One thing we did at the beginning of the previous section was derive the relation:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = e^{[S_R(s_2) - S_R(s_1)]/k}$$

Then, with the assumption that  $PdV$  is small and  $dN = 0$ , we were able to derive:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = e^{[E(s_2) - E(s_1)]/k}$$

Now, we'll relax the condition and let  $\mu dN \neq 0$ . Now we have:

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{-[E(s_2) - \mu N(s_2)]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$$

Now, the exponent is called a Gibbs factor, similar to how the one without the  $\mu N$  term was called the Boltzmann factor:

$$\text{Gibbs factor} = e^{-[E(s) - \mu N(s)]/kT}$$

Now, the probability is calculated by again inserting a normalization constant:

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-[E(s) - \mu N(s)]/kT}$$

where  $\mathcal{Z}$  is called the **Grand partition function**. If there are multiple particles, then we have to sum over the particles individually, so if there were two, then we'd have  $e^{-[E(s) - \mu_A n_A(s) - \mu_B n_B(s)]/kT}$  as the exponent.

### 3.2 Bosons and Fermions

Now we'll investigate the situation where identical particles actually do occupy the same energy state, where our equation for  $Z = \frac{1}{N!} Z_1^N$  no longer works, since the  $N!$  was derived from removing the multiplicity only if the particles are in different states. When they are allowed to occupy the same state, there are more copies that we need to get rid of. In fact, the  $N!$  gets rid of too many states, since two particles that occupy the same state should be counted as one state, but by dividing by  $N!$  we are actually getting rid of "half" of those states too.

So what happens when  $Z_1$  is on the same order as  $N$  (in other words, our earlier analyses don't apply)? We first consider a "system" consisting of a single particle state (not a particle) **what is meant by this?**. Consider a particle in a box, whose occupied energy is  $\epsilon$ . When the state is unoccupied, then the energy is zero, and when  $n$  states occupy it, then it has energy  $n\epsilon$ . Therefore, the probability that the state is occupied by  $n$  particles is

$$\mathcal{P}(n) = \frac{1}{\mathcal{Z}} e^{-(n\epsilon - \mu n)/kT} = \frac{1}{\mathcal{Z}} e^{-n(\epsilon - \mu)/kT}$$

We get the exponents from the fact that we have  $E(s) - \mu N(s)$  as a general exponent, so when  $s$  is the condition that we have  $n$  particles, then  $E(s) = n\epsilon$  and  $N(s) = n$ , giving us a  $n\epsilon - \mu n$  in the exponent.

If we have Fermions, then  $n$  can only be 0 or 1 (since no two Fermions can occupy the same state), so therefore:

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT}$$

So therefore, we can now calculate the "occupancy", or the average number of particles in any given state:

$$\bar{n} = \sum_n n \mathcal{P}(n) = \frac{e^{-(\epsilon - \mu)/kT}}{1 + e^{-(\epsilon - \mu)/kT}} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

**Is this the occupancy of this particular state  $n$ ? i.e. we'd have to calculate this for all states, or is this somehow calculating for all  $n$ ?**

**This is the value of  $\bar{n}$  for a particular state; we'll take into account all states later**

This is the **Fermi-Dirac distribution**, which tells us that:

$$\bar{n}_{\text{FD}} = \frac{1}{e^{(\epsilon - \mu)/kT} + 1}$$

If we have bosons instead of fermions, then we have to sum over all possible  $n$ :

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT} + e^{-2(\epsilon - \mu)/kT} + \dots = \frac{1}{1 - e^{-(\epsilon - \mu)/kT}}$$

The average number of particles is then:

$$\bar{n} = \sum_n n \mathcal{P}(n) = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x}$$

where  $x = (\epsilon - \mu)/kT$ . Therefore, we have:

$$\bar{n}_{\text{BE}} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$$

which is the **Bose-Einstein distribution**

### 3.3 Degenerate Fermi Gases

We are now going to consider the case where the Boltzmann statistics that we generally apply to an ideal gas, primarily the assumption that  $V/N \gg v_Q$  is not true, and that instead  $V/N \ll v_Q$ . This applies to cases such as conduction electrons in metals, where the volume per conduction electron is very small. At this scale, the temperature

(not really room temperature, temperature as defined in terms of the change in entropy relative to energy) is very low. Here, we'll first look at the case where  $T = 0$ , then ask what happens when  $T \approx 0$ .

At  $T = 0$ , then our Fermi-Dirac distribution becomes a step function, and this means that all the states less than  $\mu$  are completely occupied. **Does this also mean that all states larger than  $\mu$  have occupancy of 0? Yes!** Here,  $\mu = \epsilon_F$ , which is called the Fermi energy. At these temperatures where states below  $\epsilon_F$  are occupied states above aren't, we consider these **degenerate gases**.

To calculate  $\epsilon_F$ , we first assume that the electrons are free particles (a pretty good assumption for metals), and confined to a volume of  $V = L^3$ . Then, we have the discretization of states as a result of limited wavelengths:

$$\lambda_n = \frac{2L}{n}, \quad p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$$

Therefore, in all three dimensions, we have one for each dimension so:

$$p_i = \frac{hn_i}{2L} \implies \epsilon = \frac{|\vec{p}|^2}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

So basically, all triplets  $(n_x, n_y, n_z)$  that generate an energy less than  $\epsilon$  will be an allowed state. To count the number of states, then, we just have to find the number of states in this eighth-sphere. If the  $n$  corresponding to  $\epsilon$  is  $n_{\max}$  i.e.:

$$\epsilon_F = \frac{h^2 n_{\max}^2}{8mL^2}$$

Then, this means that the total number of states is going to be (roughly) the volume of the sphere (the factor of 2 is to account for two spins):

$$N = 2 \cdot \frac{1}{8} \cdot \frac{4\pi n_{\max}^3}{3} = \frac{\pi n_{\max}^3}{3}$$

Therefore, this gives us the equation:

$$\epsilon_F = \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3}$$

To calculate the total energy of the system, we just sum over the energies of all the states in all states:

$$U = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(\vec{n}) = 2 \int \int \int \epsilon(\vec{n}) dn_x dn_y dn_z$$

**Is the reason why we're not accounting for any kind of "number of particles" term because these are electrons (hence fermions), so the occupation is either 1 or 0, and the fact that at  $T = 0$ , the states below  $\epsilon_F$  are guaranteed to be filled? Also yes!** At the end of the day, we're left with the equation:

$$U = \pi \int_0^{n_{\max}} \epsilon(n) n^2 dn = \frac{3}{5} N \epsilon_F$$

**Note that the  $n^2$  term comes from switching the integral from Cartesian to polar.** So we get that the average energy (divide by  $N$ ) of the electrons is  $\frac{3}{5}\epsilon_F$ . For metals, the Fermi energy is typically *much higher* when compared to the thermal energy ( $kT$ ), and the temperature at which  $kT$  is equal to  $\epsilon_F$  is called the **Fermi temperature**:

$$T_F = \frac{\epsilon_F}{k}$$

This temperature is generally high enough that metals become gases before this temperature is reached. Now that we have  $U$ , we can figure out  $P$  using the identity:

$$P = - \left( \frac{\partial U}{\partial V} \right)_{S,N} = \frac{2}{3} \frac{U}{V}$$

This is called the **degeneracy pressure**. This pressure is what keeps the matter from collapsing in on itself, and is *solely* a product of the Pauli exclusion principle, and not the electrostatic repulsion between electrons. The degeneracy pressure is not directly computable, instead we compute the bulk modulus:

$$B = -V \left( \frac{\partial P}{\partial V} \right)_T = \frac{10}{9} \frac{U}{V}$$



### 3.3.1 Small Nonzero Temperatures

Earlier we looked at  $T = 0$ , but now we're going to concern ourselves with  $T \approx 0$ , or basically in the case where we have a small but nonzero  $T$ . At some temperature  $T$ , all particles can acquire thermal energy equal to  $kT$ . However, because we're dealing with a degenerate Fermi gas, not all particles have the ability to acquire all that energy (since the states that they would be jumping into would be occupied already). Hence, the only particles that we care about are within  $kT$  of the Fermi energy, and this number must also scale with  $N$ . Therefore:

$$\text{additional energy gained} \propto (\text{number of affected electrons}) \times (\text{energy acquired}) = NkT \times kT = N(kT)^2$$

We'll see later on that the added energy should be:

$$U_{\text{add}} = \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F}$$

And so the total energy  $U$  is now:

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F}$$

Then, the heat capacity is the derivative of this quantity with respect to  $T$ :

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\pi^2 N k^2 T}{2 \epsilon_F}$$

### 3.3.2 Density of States

Going back to the integral for the energy:

$$U = \pi \int_0^{n_{\text{max}}} \epsilon(n) n^2 dn$$

we're going to change variables from  $n$  to energy  $\epsilon$ :

$$n = \sqrt{\frac{8mL^2}{h^2}} \sqrt{\epsilon} \implies dn = \sqrt{\frac{8mL^2}{h^2}} \frac{1}{2\sqrt{\epsilon}} d\epsilon$$

Then, the energy integral becomes:

$$U = \int_0^{\epsilon_F} \epsilon \left[ \frac{\pi}{2} \left( \frac{8mL^2}{h^2} \right)^{3/2} \sqrt{\epsilon} \right] d\epsilon$$

The term in the square brackets represents the number of single-particle states per unit energy. Therefore, to compute the total energy, then we have to sum over the energy  $\epsilon$ , then multiply that by the total number of single-particle states to get the total energy. **Why does this equation not take into account whether the state is actually occupied?**

The **density of states** is  $g(\epsilon)$ , and it is written as:

$$g(\epsilon) = \frac{\pi(8m)^{3/2}}{2h^3} V \sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon}$$

The first representation is nicer, since it implies the correct dependencies: that  $g(\epsilon)$  doesn't depend on  $N$ , but instead depends linearly on  $V$  and proportional to  $\sqrt{\epsilon}$ . For an electron gas (remember, these are fermions), then finding the total number of particles is just equal to integrating the density of states:

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad (T = 0)$$

If  $T$  is nonzero, then we have to multiply  $g(\epsilon)$  by the probability that each state is occupied, so in other words by the Fermi-Dirac distribution. Therefore:

$$N = \int_0^{\infty} g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) d\epsilon = \int_0^{\infty} g(\epsilon) \frac{1}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon$$

Then, to get the total energy, we just multiply this integrand by an extra  $\epsilon$  **why?**

$$U = \int_0^{\infty} \epsilon g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) d\epsilon = \int_0^{\infty} \epsilon g(\epsilon) \frac{1}{e^{(\epsilon-\mu)/kT} + 1} d\epsilon$$

## 3.4 Blackbody Radiation

### 3.4.1 Ultraviolet Catastrophe

Classically, we think of radiation as a continuous field, and when confined to a box, we restrict the possible waves to be *standing waves* **are these standing waves with respect to the ends, or just "waves" for now?**, with frequencies  $f = c/\lambda$ . Each oscillator has two (**quadratic?**) degrees of freedom, meaning that each possible wave carries energy  $2\frac{1}{2}kT$ . Since there are infinitely many possible waves that can be within the box (infinitely many wavelengths), then there should be theoretically an infinite amount of energy within that box. This, of course, cannot be true! This is called the **ultraviolet catastrophe**

### 3.4.2 Planck Distribution

The solution is to impose the fact that a harmonic oscillator can't just have arbitrary energy, but instead can only have discrete amounts of energy:

$$E_n = 0, hf, 2hf, \dots$$

Therefore, the partition function (a sum of all  $e^{-\beta E(s)}$ ) is going to be:

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + \dots = \frac{1}{1 - e^{-\beta hf}}$$

Therefore, the average energy is:

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{hf}{e^{hf/kT} - 1}$$

And since energy is quantized in units of  $hf$ , then we know that since  $\bar{E} = N\epsilon$ , then we know that the average number of units of energy is given by

$$\bar{n}_{pl} = \frac{1}{e^{hf/kT} - 1}$$

This is called the **Planck distribution**

### 3.4.3 Photons

Photons can also be considered particles, and are bosons (**how do we know this?**), so their distribution follows the Bose-Einstein distribution:

$$\bar{n}_{BE} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}$$

Here  $\epsilon = hf$ , the energy per mode. In order for this  $\bar{n}_{BE}$  to properly model photons in a box, then it must match the plank distribution, which means that  $\mu = 0$  for photons.

The Planck distribution gives us the distribution of particles in any given mode of the EM field, so we can use this distribution to figure out not only the total energy but also the total number of photons in our box. First, consider the case in 1 dimension. Here, if the "box" is of length  $L$ , then the allowed wavelengths are:

$$\lambda = \frac{2L}{n}; \quad p = \frac{hn}{2L}$$

where  $n$  denotes the mode that we're talking about. Then, because they are photons, we have:

$$\epsilon = pc = \frac{hcn}{2L}$$

In three dimensions, then our momentum becomes a vector  $\vec{p}$ , so the energy  $\epsilon$  is going to be  $c$  times the magnitude of the momentum vector:

$$\epsilon = c\sqrt{p_x^2 + p_y^2 + p_z^2} = c\sqrt{\left(\frac{h}{2L}\right)^2 (n_x^2 + n_y^2 + n_z^2)} = \frac{hcn}{2L}$$

the last  $n$  represents the magnitude of the  $\vec{n}$  vector. With the energy of every mode determined, we can now determine the total energy, by multiplying  $\epsilon$  with the occupancy of that state:

$$U = \sum_{n_x, n_y, n_z} \epsilon \bar{n}_{pl}(\epsilon) = \sum_{n_x, n_y, n_z} \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1}$$

Converting this summation into an integral (**why can we do this?**), we now have:

$$U = \int_0^\infty dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin \theta \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1}$$

### 3.4.4 Planck Spectrum

Computing the integral is easier if we change variables into:

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\epsilon^3/(hc)^3}{e^{\epsilon/kT} - 1} d\epsilon$$

Then, the integrand is basically the energy density per unit photon energy, also called the **spectrum**:

$$u(\epsilon) = \frac{\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}$$

Evaluating this integral, it's more useful if we make another substitution of  $u = \epsilon/kT$  (to make the exponent on  $e$  nicer), so we have:

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

### 3.4.5 Total Energy

The previous integral evaluates to  $\pi^4/15$ , so the total energy density is given by:

$$\frac{U}{V} = \frac{8\pi^5(kT)^4}{15(hc)^3} \implies U = \frac{8\pi^5(kT)^4 V}{15(hc)^3}$$

Note the dependence on  $T^4$ . Now, we can figure out  $C_V$ :

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 4\alpha T^3$$

where  $\alpha$  just absorbs all the constants. Then, since this works for all  $T$ , we can now integrate  $C_V$  to find  $S$ :

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = \frac{32\pi^5}{45} V \left( \frac{kT}{hc} \right)^3 k$$

As I understand it, this integral comes from the fact that  $T = \frac{dU}{dS}$  so  $dU = TdS$ , thne if  $dU = C_V dT$ , then we have  $TdS = C_V dT$  where we can get the integral. But this implies that  $PdV = 0$ . Is this true?

## 4 Questions

Alongside the red text, questions below:

- I noticed that your treatment of Debye solids is very different than the one from Schroeder. Should we study both, or is one of the approaches good enough?
- Same question as above but for Bose-Einstein condensates.
- The Hamiltonian in problem 3 on homework 10: Do we just use that for  $\epsilon$  to find the occupation numbers?
- Part b of problem 7: how do I argue this? Could we argue that  $g(\epsilon)$  is the problem?

## 5 Topic List

### 5.1 Multiplicity and Entropy

Multiplicity is defined as  $\Omega$ , where it defines the number of possible states our system can be in, given that it has energy  $E$ . The multiplicity is useful because when we count the total number of states, we just have to sum over all the multiplicities corresponding to all the energies. Further, the probability of our system existing in any possible state is given by:

$$\text{probability} = \frac{\Omega(n)}{\Omega(\text{all})}$$

where  $\Omega(\text{all})$  refers to the sum of all microstates. This idea for the multiplicity explains why we see gases mixed after left out for a while, since we expect that they exist in the most likely microstate (i.e. the one with the most possibilities). This is one way of phrasing the second law of thermodynamics.

The entropy is then defined from this quantity, and since multiplicity gets very big, then we take the natural log to be nice:

$$S \equiv k_B \ln \Omega$$

Note that since  $\Omega$  is a function of  $E$ , then  $S$  is also a function of  $E$ . Entropy is also additive, so if we have two systems  $S_A$  and  $S_B$ , then the entropy of their combination is given as  $S_A + S_B$ .

### 5.2 Enumerating Microstates

This is generally a counting exercise, so just do problems for this.

### 5.3 Relating thermodynamic quantities

Knowing  $\Omega(U)$ , we can go from  $\Omega(U)$  to  $S(U)$  by using  $S(U) = k_B \ln \Omega(U)$ . Then, to get from that to  $T(U)$ , we use the relation:

$$\frac{1}{T} = \frac{\partial S(U)}{\partial U}$$

We write this as  $1/T$  mainly because we define  $S$  to be a function of  $U$ , so it only makes sense that we take  $\frac{\partial S}{\partial U}$  instead of  $\frac{\partial U}{\partial S}$ , even though that would get us  $T$  directly. To get the heat capacity, we use the fact that  $dU = C_V dT$ , so this gets us

$$C_V = \frac{dU}{dT}$$

Generally, we'll be given a formula for  $U$  (for instance, in an ideal gas,  $U = \frac{3}{2}NkT$ ), from which we can just take the partial derivative with respect to  $T$ .

### 5.4 Energy Transfer

To calculate the energy transfer to thermal equilibrium, note that the condition is that  $T_A = T_B$ , and not that their energies are the same. In the case we did on the homework, energy in the system is conserved, so what we can do is first calculate  $U_i$  (the initial energy), and calculate the condition for thermal equilibrium ( $U_B = 2U_A$ ) and from there we conclude that  $U_f = U_B + U_A = 3U_B$ , from which point we can calculate  $U_B$  and consequently  $U_A$  at equilibrium. From there, if we wish, we can then calculate the temperatures.

### 5.5 Ideal Gas Equations

The total energy of a system is dependent on the number of quadratic degrees of freedom, enumerated by  $f$ . Therefore, the total energy  $U$  is given by

$$U = \frac{f}{2}NkT$$

This is the statement of the equipartition theorem. The Ideal gas law is given by

$$PV = NkT$$

### 5.5.1 Process Curves

- Isothermal: constant temperature, Since  $\Delta U = \frac{3}{2}Nk\Delta T$ , then this implies that  $\Delta U = 0$  in this process too. This then means that  $Q = -W = \int P\Delta V$ . We have to
- Adiabatic:  $Q = 0$ , so this implies that  $U = W = \int PdV$ . However, we use the relation that  $PV^\gamma = \text{const.}$  to do our integrals, instead of the ideal gas law. Specifically, we use  $P(V) = \frac{c}{V^\gamma}$ , and then use one of the points in the adiabatic process to eliminate  $c$  later on.
- Isobaric:  $\Delta P = 0$ , so here calculating work is very easy, we can just calculate  $W = -P\Delta V$ . We then calculate  $\Delta U$ , and then solve for  $Q$ . Calculating  $\Delta U$  can be done by noting that because  $\Delta P = 0$ , then  $\Delta U = \Delta(PV) = P\Delta V$ .
- Isochoric:  $\Delta V = 0$ , so here we have  $W = 0$ , and  $Q = \Delta U$ , and we calculate  $\Delta U = \Delta(PV) = P_f V_f - P_i V_i$ .
- **Is there any special reason why  $\Delta(PV) = P_f V_f - P_i V_i$ ? Should we be using that formula for all processes?**

Efficiency is calculated as

$$\epsilon = 1 - \frac{Q_c}{Q_h}$$

for a process operating between reservoirs, with it gaining  $Q_h$  heat and expelling  $Q_c$ . Note that  $Q_h$  goes into the system, and hence is positive, and  $Q_c$  is negative, so it leaves the system. Note that when calculating the efficiency, because  $Q_c$  is negative (as heat leaves the system), in order to calculate the efficiency  $\epsilon$  properly, we need to flip the sign of  $Q_c$ . For a Carnot cycle, the efficiency is

$$\epsilon = 1 - \frac{T_c}{T_h}$$

and we have a theorem that  $\epsilon_{\text{carnot}} > \epsilon$  for any other system.

## 5.6 Two-State Paramagnet