

Reading

This week we'll work on chemical potential and the Gibbs distribution which is covered in K&K chapter 5.

Parting Shot on Oscillators

Before we get to the main part of this week's material, let's have a quick recap on oscillators.

If we have an oscillator of frequency ω , its energy levels are spaced by $\hbar\omega$. If this oscillator is in thermal equilibrium at temperature τ , then if $\hbar\omega < \tau$, its average energy is τ . If $\hbar\omega > \tau$, its average energy is exponentially "killed off" and it's not too gross of an approximation to say that it's 0. This happens because of the quantized states. Energy can only be exchanged with the oscillator in units of $\hbar\omega$ and when this is larger than a thermal energy, the heat reservoir almost never gets enough energy together to excite the oscillator.

We know the energy of the oscillator, and all we have to do is count up how many oscillators there are in order to find the total energy of the system.

For blackbody radiation, the number of modes is proportional to $\omega^3 (\int \omega^2 d\omega)$, and all these modes are excited up to the maximum ω where $\hbar\omega = \tau$. So the energy in blackbody radiation is proportional to τ^4 .

In the case of lattice vibrations, we again have a number of modes proportional to ω^3 , but there are a finite number, so if we run out of modes before we reach the maximum ω of an excited oscillator, then every mode has energy τ and the total energy is $3N\tau$ (where $3N$ is the number of modes). If we don't run out of modes before we reach the maximum ω of an excited oscillator, then the situation is just like that with blackbody radiation and the energy is proportional to τ^4 . These two cases correspond to high and low temperatures and give heat capacities which are constant or proportional to τ^3 for high and low temperatures. By the way, the fact that molar heat capacities of solids are usually $3R$ at room temperature (R is the gas constant) is called the law of Dulong and Petit.

Finally, when we considered Johnson noise in a resistor, we made use of a one dimensional cavity, where the number of modes is proportional to $\omega (\int d\omega)$ and we considered the low temperature limit and found the energy proportional to $\tau d\omega$.

Basically, we know the energy of the modes and we count the modes. All the factors of π , \hbar , etc., come out as a result of the proper bookkeeping when we do the counting.

Integrals Related to Planck's Law

Judging by experience with previous classes, some (maybe many) of you are wondering just how one goes about doing the integral

$$\int_0^{\infty} \frac{x^2 dx}{\exp(x) - 1}.$$

The first thing to note is that doing integrals is an art, not a science. You've probably learned a number of techniques for doing integrals. However, there is never a guarantee that an arbitrary expression can be integrated in closed form, or even as a useful series. Some expressions you just have to integrate numerically!

Let's see what we can do about

$$I_n = \int_0^{\infty} \frac{x^n dx}{\exp(x) - 1},$$

where n need not be an integer, but I think we'll need $n > 0$. The first thing to do is to try and look it up! I like Dwight, *Tables of Integrals and other Mathematical Data*, 4th edition, 1964, MacMillan. (Actually, I bought mine when I was an undergraduate in the late 60's. It seems that they were coming out with a new edition every 10 years, so maybe it's up to the seventh edition by now!) Anyway, in my edition of Dwight, there is entry 860.39:

$$\int_0^{\infty} \frac{x^{p-1} dx}{e^{ax} - 1} = \frac{\Gamma(p)}{a^p} \left[1 + \frac{1}{2^p} + \frac{1}{3^p} + \dots \right] = \frac{\Gamma(p)}{a^p} \zeta(p),$$

and this is basically the integral we're trying to do.

We've talked about the gamma function, $\Gamma(z)$, see lecture 5. The Riemann Zeta function is

$$\zeta(s) = \sum_{k=1}^{\infty} \frac{1}{k^s},$$

where $\text{Re}(s) > 1$. The function can be defined for other values of s , but this series requires $\text{Re}(s) > 1$. A good reference book for special functions is Abramowitz and Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, US Government Printing Office. If you look up the zeta function in this handbook, you'll find lots of cool stuff. For example,

$$\zeta(s) = \prod_{\text{primes } p} \frac{1}{1 - 1/p^s}.$$

The zeta function establishes a connection between number theory and function theory! Other things you'll find in A&S are various integral representations, representations in

terms of Bernoulli and Euler polynomials (if you don't know what these are, they're also discussed in A&S), special values, and tables of values. For example $\zeta(0) = -1/2$, $\zeta(1) = \infty$, $\zeta(2) = \pi^2/6$, and $\zeta(4) = \pi^4/90$. $\zeta(3)$, needed for the integral at the top of the page, does not have a simple value. Instead, we find it in a table, $\zeta(3) = 1.2020569\dots$

Can we write I_n in the form suggested by Dwight?

$$\begin{aligned}
 I_n &= \int_0^\infty \frac{x^n dx}{\exp(x) - 1}, \\
 &= \int_0^\infty \frac{x^n e^{-x} dx}{1 - e^{-x}}, \\
 &= \int_0^\infty x^n e^{-x} \sum_{m=0}^\infty e^{-mx} dx, \\
 &= \int_0^\infty x^n \sum_{m=0}^\infty e^{-(m+1)x} dx, \\
 &= \sum_{m=0}^\infty \int_0^\infty x^n e^{-(m+1)x} dx, \\
 &= \sum_{m=0}^\infty \frac{1}{(m+1)^{n+1}} \int_0^\infty ((m+1)x)^n e^{-(m+1)x} d((m+1)x), \\
 &= \sum_{m=0}^\infty \frac{1}{(m+1)^{n+1}} \int_0^\infty y^n e^{-y} dy, \\
 &= \sum_{m=0}^\infty \frac{1}{(m+1)^{n+1}} \Gamma(n+1), \\
 &= \Gamma(n+1) \sum_{m=1}^\infty \frac{1}{(m)^{n+1}}, \quad (m \text{ now starts at } 1) \\
 &= \Gamma(n+1) \zeta(n+1),
 \end{aligned}$$

in agreement with Dwight.

If you need to numerically evaluate $\zeta(s)$, you can just start summing the series. Suppose you've summed the inverse powers from 1 to $M-1$. You should be able to show (make some sketches) that $\int_M^\infty dx/x^s = 1/[(s-1)M^{(s-1)}]$ is less than remainder of the sum and $\int_M^\infty dx/(x-1)^s = 1/[(s-1)(M-1)^{(s-1)}]$ is greater than the remainder of the sum. You can use the average of these two integrals as an estimate of the remainder of the sum and half their difference as a bound on the numerical error. (Actually the error will be quite a bit smaller!). As an example, consider $\zeta(2) = \pi^2/6 = 1.64493\dots$. The sum of the first 10 terms, $1 + 1/4 + 1/9 + 1/16 + \dots + 1/100 = 1.5497677\dots$. The two integrals are just $1/11 = 0.09090909\dots$ and $1/10 = 0.1$. Their average is $0.09545454\dots$ and half their

difference is 0.004545..., so numerically we can be pretty sure that the value is within 0.00455 of 1.64522. In fact, we actually miss by only 0.00028!

The Chemical Potential

Recall in lectures 2 and 3 we discussed two systems in *thermal* (microscopic exchange of energy), *volume* (macroscopic exchange of energy), and *diffusive* (exchange of particles) equilibrium. By requiring that the entropy be a maximum, we found that

$$d\sigma = \frac{1}{\tau} dU + \frac{p}{\tau} dV - \frac{\mu}{\tau} dN ,$$

where μ is the *chemical potential* and N is the number of particles.

In other words,

$$\mu = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U,V} .$$

We can also rewrite the differential relation above in the form

$$dU = \tau d\sigma - p dV + \mu dN ,$$

from which we deduce

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{\sigma,V} .$$

Adding a particle to a system changes its energy by μ .

Of course, the entropy is not a completely natural variable to work with as a dependent variable. To get around this, we use the Helmholtz free energy which we've previously defined as a function of temperature and volume. We now extend the definition to include particle number. In particular, consider the free energies of two systems in contact with a reservoir at temperature τ . We allow these two systems to exchange particles until equilibrium is established. The free energy of the combined system is

$$F = F_1 + F_2 ,$$

where the subscripts refer to the individual systems. The free energy will be a minimum at constant temperature and volume. The change in free energy due to particle exchange is

$$dF = dF_1 + dF_2 = \left(\frac{\partial F_1}{\partial N_1} \right)_{\tau,V} dN_1 + \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau,V} dN_2 .$$

We want $dF = 0$ at minimum and, since the total number of particles is constant, we have $dN_1 = -dN_2$ which means that

$$\left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V} = \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V} = \mu.$$

This constitutes yet another definition of the chemical potential. Is it the same chemical potential we've already defined? Yes, provided the free energy continues to be defined by

$$F = U - \tau\sigma.$$

Then when the particle number changes, we have

$$\begin{aligned} dF &= dU - \tau d\sigma - \sigma d\tau, \\ &= \tau d\sigma - p dV + \mu dN - \tau d\sigma - \sigma d\tau, \\ &= -\sigma d\tau - p dV + \mu dN, \end{aligned}$$

and it's the same chemical potential according to either definition.

By the way we defined the chemical potential, it must be the same for two systems in diffusive and thermal contact, once they've reached equilibrium. What if the two systems in diffusive contact do not have equal values of the chemical potential? Since

$$dF = dF_1 + dF_2 = \mu_1 dN_1 + \mu_2 dN_2,$$

there will be a flow of particles in order to minimize F . If $\mu_1 > \mu_2$, then $dN_1 < 0$ and $dN_2 = -dN_1 > 0$, so particles flow from the system with the higher chemical potential to the system with the lower chemical potential.

To summarize,

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

Getting a Feel for the Chemical Potential

The chemical potential is another one of those thermodynamic quantities that seems to appear by magic. In order to gain intuition about the chemical potential, you will probably have to see it in action and work with it for a while.

To start this process, note that adding a particle to a system requires that the energy of the system be changed by μ while the entropy and volume are kept constant. Better yet, the free energy changes by μ while the temperature and volume are kept constant.

Why might adding a particle to a system change the system's energy? There are at least two reasons. There might be macroscopic fields around (such as gravitational or electromagnetic fields) in which the particle has an ordinary potential energy (mgh or $e\Phi$ for example). In addition when a particle is added to a system at temperature τ , it must acquire a thermal energy which depends on τ and other parameters of the system. In other words the change in energy upon adding a particle can be due to both macroscopic fields and microscopic thermal effects.

The distinction made in K&K between the external, internal and total chemical potentials is just a division into the macroscopic, microscopic, and total contributions to the energy upon adding a particle.

Let's find the chemical potential of the classical, ideal, monatomic gas. Recall in lecture 7, we found,

$$\begin{aligned} U &= \frac{3}{2}N\tau, \\ F &= -N\tau \left(\log \frac{n_Q}{n} + 1 \right), \\ \sigma &= N \left(\log \frac{n_Q}{n} + \frac{5}{2} \right), \\ n_Q &= \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2}, \\ n &= \frac{N}{V}. \end{aligned}$$

Of the thermodynamic potentials U , F , and σ above, only F is expressed in terms of its natural independent variables τ , V , and N . Let's find μ by differentiating F with respect to N while keeping τ and V constant.

$$\begin{aligned} \mu &= \left(\frac{\partial F}{\partial N} \right)_{\tau, V} = \frac{\partial}{\partial N} \left(-N\tau \left(\log \frac{n_Q V}{N} + 1 \right) \right), \\ &= -\tau \left(\log \frac{n_Q V}{N} + 1 \right) + \tau, \end{aligned}$$

$$\begin{aligned}
 &= -\tau \log \frac{n_Q V}{N}, \\
 &= \tau \log \frac{n}{n_Q}.
 \end{aligned}$$

Note that for a typical gas, the concentration n is quite small compared to the quantum concentration, n_Q , perhaps a part in 10^6 to a part in 10^5 . So we expect $\mu = -14\tau$ to -11τ . If μ gets close to zero, then the concentration is approaching the quantum concentration and the classical treatment is no longer valid.

Suppose we wanted to calculate the chemical potential by differentiating the entropy. We express the entropy in terms of its natural independent variables U , V , and N ,

$$\begin{aligned}
 \sigma &= N \left(\log \frac{n_Q}{n} + \frac{5}{2} \right), \\
 &= N \left(\log \left(\left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \frac{V}{N} \right) + \frac{5}{2} \right),
 \end{aligned}$$

substitute $\tau = 2U/3N$,

$$= N \left(\log \left(\left(\frac{mU}{3\pi\hbar^2} \right)^{3/2} \frac{V}{N^{5/2}} \right) + \frac{5}{2} \right).$$

Now differentiate with respect to N , multiply by $-\tau$, and replace U with $3N\tau/2$,

$$\begin{aligned}
 \mu &= -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U,V}, \\
 &= -\tau \frac{\partial}{\partial N} \left[N \left(\log \left(\left(\frac{mU}{3\pi\hbar^2} \right)^{3/2} \frac{V}{N^{5/2}} \right) + \frac{5}{2} \right) \right], \\
 &= -\tau \left[\left(\log \left(\left(\frac{mU}{3\pi\hbar^2} \right)^{3/2} \frac{V}{N^{5/2}} \right) + \frac{5}{2} \right) - \frac{5}{2} \right], \\
 &= -\tau \log \frac{n_Q V}{N}, \\
 &= \tau \log \frac{n}{n_Q},
 \end{aligned}$$

the same as we obtained before.

Since we're having so much fun playing with the mathematics, suppose we wanted to find the chemical potential by differentiating the energy. This should be done at constant entropy and volume. The Sackur-Tetrode formula for the entropy is fairly messy to solve for the temperature, so we may not want to rewrite the energy in closed form as a function of the entropy, volume and number of particles. Instead, we can write the energy as a

differential involving dN and $d\tau$ and find the relation between these differentials which makes the entropy change vanish. This will be left as a homework problem. Needless to say, one gets the same expression for the chemical potential that we've already derived.

As an example of a macroscopic contribution to the chemical potential, consider our atmosphere which exists in the gravitational field of the Earth. Suppose the atmosphere consists of a single kind of atom of mass m , is isothermal, and is in equilibrium. Then the chemical potential must be the same everywhere in the gas. At height h above the zero level for the gravitational potential, there is a contribution mgh from the gravitational field. This means

$$\mu = \text{Constant} = \tau \log \frac{n}{n_Q} + mgh ,$$

or

$$n(h) = n(0)e^{-mgh/\tau} .$$

so the concentration decreases exponentially with altitude. With the ideal gas law, $p/\tau = N/V = n$, so the pressure also decreases exponentially with altitude. We can write

$$p(h) = p(0)e^{-h/h_0} ,$$

where $h_0 = \tau/mg = kT/mg = RT/Mg$, is called the *scale height* of the atmosphere. R is the gas constant, and M is the molar mass. If we take, $T = 300$ K, $M = 28$ g (appropriate for Nitrogen molecules), and $g = 980$ cm s^{-2} , we find $h_0 \approx 9$ km. There are several problems with this simple model. First, the atmosphere is stirred by winds, so it is not in equilibrium. However, this is important only in the first few miles above sea level. At higher altitudes, the atmosphere is approximately isothermal, but with a considerable colder temperature, about 230 K according to the plot in K&K. Also, each molecule should have a slightly different scale height, with the lighter molecules having a large scale height (and being more likely to completely evaporate from the Earth).