Physics 12c Notes

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Contents

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[*] With minor corrections by Michael Beverland (a current TA for the course)

1 Tuesday, March 30, 2010

1.1 Introduction

Ph12c, Statistical Mechanics. Administrative details are the same as last term, except that there is one new grader. Same professor, different material. These details are on the course website

`http://www.theory.caltech.edu/~preskill/ph12c/`.

Textbook is Thermal Physics by Kittel and Kroemer. In contrast to Liboff, this is a very good book. Therefore, many of the problems will be assigned from the book.

Thermal physics has two components: **Thermodynamics** and **Statistical Mechanics**.

Thermodynamics deals with concepts of heat, energy, work, temperature, and, most centrally, entropy. It has the benefit of being summarized in 3-4 fundamental laws. It has applications to phases of matter like gases and liquids, chemical reactions, cell biology, black holes. A central concept of thermodynamics is irreversibility, the arrow of time. There is a difference between future behavior and past behavior. This doesn't appear in Newton's laws or Schrödinger's equation, but arises from thermodynamics. The central mathematical tools we need in thermodynamics are total and partial derivatives (unlike last term, we won't see much linear algebra). Unlike Newton's laws, which were corrected by quantum theory, thermodynamics is more of an exact science. Einstein called it the most robust of the physical sciences.

Statistical mechanics dates back to the 19th and 20th century. Its goal is to explain/derive thermodynamics from the microscopic laws of physics. Its main mathematical tool is probability theory applied to many degrees of freedom. For instance, a box containing gas has on the order of Avogadro's number of molecules, and comparable numbers of degrees of freedom. Instead of considering each possible molecule, we can compose an ensemble of macroscopic states and take averages to get key statistical quantities, like energy, volume, etc. This allows us to predict macroscopic behavior without precise knowledge of the microscopic state. Large fluctuations from the average behavior is extraordinarily unlikely. The common example is the probability of all air molecules in a box accumulating randomly in one corner of the box.

Probability theory arises in statistical mechanics because we can't obtain complete knowledge of the microscopic state of the system. Even if we knew the microscopic state, we would still average over the microscopic details of the state when computing expected observations. The main mathematical tools are probability theory and combinatorics (or put less pretentiously, counting).

This course will focus on statistical mechanics, but we will also address thermodynamics.

1.2 Counting States

We often specify certain macroscopic properties, then count microstates consistent with those properties. For instance, we try to count microstates within a certain energy gap, say, between $\mathcal{E}$ and $\mathcal{E} + \Delta\mathcal{E}$. There will still be many possible microstates. We will typically assume in statistical mechanics that these possible microstates at approximately the same energy are equally likely, since we have no reason to prefer one to another. It's a hard assumption to justify in detail, which isn't completely solved, but we won't focus on that and will just assume it is true.

Now we have a probability distribution: The probability of any one microstate is $\frac{1}{\text{total number of microstates}}$. We can then use probability theory to make predictions about the average behavior of other macroscopic observables. In quantum mechanics, it makes sense to count individual microstates because our energy levels are discrete. It makes less sense in classical mechanics. As we consider larger and larger systems, we will know the macroscopic properties to greater and greater accuracy (the law of large numbers).

As an example, consider a fair coin. Flipping it once, the total number of heads is 0 with probability 1/2 and 1 with probability 1/2. Flipping it twice, we get 0 heads 1/4 of the time, 1 head 1/2 of the time, and 2 heads 1/4 of the time. Flipping it 3 times, we get 0 heads 1/8 of the time, 1 head 3/8 of the time, 2 heads 3/8 of the time and 3 heads 1/8 of the time. Flipping it many times, $N \gg 1$ times, the probability distribution approaches a normal (Gaussian) distribution with mean $N/2$ and standard deviation proportional to $\sqrt{N}$, which gets small compared to N as N gets large.

This is an example of the central limit theorem. Suppose you have any probability distribution. If you sample N times from this probability distribution and sum the outcomes, consider the probability distribution of this sum. The central limit theorem says that this probability distribution approaches a Gaussian distribution, with a width that becomes narrower compared to N.

Because this is a physics class, not a math class, let's pick a physical example. Consider a magnet, which has many atoms, each with a magnetic moment (spin) that can point either up or down. Mathematically, this is equivalent to a coin flip because we assume the two spins are equally probable. The total magnetization $M = (N_\uparrow - N_\downarrow)m$, where m is the magnetic moment of a single spin. Let $2s = N_\uparrow - N_\downarrow$, since if we flip one spin, this number changes by 2. Let $g(N,s)$ denote the number of microstates in the N-site magnet, with spin excess $2s$.

We can imagine turning on an external magnetic field pointing upwards, making the ↑ spins more energetically favorable: $\mathcal{E}_\uparrow = -mB$ and $\mathcal{E}_\downarrow = mB$. The total energy is then given by $(-mB)N_\uparrow + mbN_\downarrow = -mB(N_\uparrow - N_\downarrow) = -(2s)mB$.

To calculate $g(N,s)$, we need to do a binomial expansion: $(\uparrow + \downarrow)^N$, yielding 2^N possible states (all equally likely if we don't specify s). Then we want the total number with $N_\uparrow = \frac{1}{2}N + s$ and $N_\downarrow = \frac{1}{2}N - s$, so $g(N,s) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{(\frac{1}{2}N+s)!(\frac{1}{2}N-s)!}$. We can think of this as counting the number of permutations of the N spins, divided by the number of permutations that interchange up spins with each other and down spins with each other.

Now how does that narrow Gaussian arise? We will make several approximations. First, $s \ll N$. Then there's the Stirling approximation for the factorial: $N! = (2\pi N)^{1/2} N^N \exp(-N + \frac{1}{12N} + O(\frac{1}{N^2}))$. We can ignore the $\frac{1}{12N} + O(\frac{1}{N^2})$ terms for N large. We won't derive this, but it is derived in an appendix in the book. Apart from the $\sqrt{2\pi N}$ term, we can understand this in this way: $N! = \prod_{m=1}^N m$, so $\log N! = \sum_{m=1}^N \log m \approx \int_1^N dm \, \log m = (m \log m - m)|_1^N = N \log N - N$. We need a more careful approximation to get the right prefactor, but this at least explains the $N^N \exp(-N)$ terms.

Applying the Stirling approximation to our binomial, we get

$$\begin{aligned} g(N,s) &= \frac{(2\pi N)^{1/2} N^N e^{-N}}{\left[\pi N(1+\frac{2s}{N})\right]^{1/2} \left[\frac{N}{2}(1+\frac{2s}{N})\right]^{\frac{N}{2}(1+\frac{2s}{N})} e^{\frac{N}{2}(1+\frac{2s}{N})} \left[\pi N(1-\frac{2s}{N})\right]^{1/2} \left[\frac{N}{2}(1-\frac{2s}{N})\right]^{\frac{N}{2}(1-\frac{2s}{N})} e^{\frac{N}{2}(1-\frac{2s}{N})}}. \\ &= (2\pi)^{-1/2} 2N^{-1/2} \left[1 - \left(\frac{2s}{N}\right)^2\right]^{-1/2} 2^N \left(1 + \frac{2s}{N}\right)^{-\frac{N}{2}(1+\frac{2s}{N})} \left(1 - \frac{2s}{N}\right)^{-\frac{N}{2}(1-\frac{2s}{N})}. \end{aligned}$$

To understand the last two factors, let's take a log:

$$\log\left[\left(1+\frac{2s}{N}\right)^{-\frac{N}{2}(1+\frac{2s}{N})}\right] = -\frac{N}{2}\left(1+\frac{2s}{N}\right)\log(1+\frac{2s}{N}).$$

Then using the expansion $\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3$, we cut off after the quadratic term. We get approximately

$$-\frac{N}{2}\left(1+\frac{2s}{N}\right)\left(\frac{2s}{N}-\frac{2s^2}{N^2}+\cdots\right) = -\frac{N}{2}\left(\frac{2s}{N}+\frac{2s^2}{N^2}+\cdots\right).$$

Then when we take the log of the other term, we get the same thing with s replaced by $-s$, getting $-\frac{N}{2}\left(-\frac{2s}{N}+\frac{2s^2}{N^2}+\cdots\right)$. When we multiply these, we add their logs to get $-\frac{2s^2}{N}$ and higher powers.

Therefore, putting this all together, the $\left[1-\left(\frac{2s}{N}\right)^2\right]^{-1/2}$ term is approximately 1, so we get

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

This is a Gaussian, as desired. It is centered at 0, and drops to $\frac{1}{e}$ of its peak value when $\frac{2s^2}{N}=1$, or $s=\sqrt{\frac{N}{2}}$. If we normalize by dividing by N, it drops to $\frac{1}{e}$ of the peak value at $\frac{s}{N}=\frac{1}{\sqrt{2N}}$. Therefore, as N gets large, the average magnetization becomes more narrowly distributed near 0.

Also notice that if we divide by the total number of spins 2^N, we get the probability distribution:

$$P(N,s) = \frac{1}{2^N}g(N,s) = \left(\frac{2}{\pi N}\right)^{1/2}\exp\left(-\frac{2s^2}{N}+\cdots\right).$$

We can check the normalization. Normally, we would want to take the sum from $s=-N/2$ to $N/2$, but let's replace this with the infinite integral. It won't be much different because as s changes by 1, the argument of the exponential won't change, and the tail ends of this Gaussian will be very small (spins near $\pm N/2$ are very unlikely). Recall from last term that $\int_{-\infty}^{\infty} dx e^{-Ax^2} = \sqrt{\frac{\pi}{A}}$. We then calculate this Gaussian integral:

$$\int_{-\infty}^{\infty} ds\, P(N,s) = \left(\frac{2}{\pi N}\right)^{1/2}\int_{-\infty}^{\infty} ds\, e^{-2s^2/N} = 1,$$

as desired.

To get a feel for the typical fluctuations away from zero, we calculate the mean square deviation. Of course, the probability distribution is symmetric about 0, so $\langle s\rangle = 0$. Recall from last term that $\int_{-\infty}^{\infty} dx\, x^2 e^{-x^2} = \frac{\sqrt{\pi}}{2}$. Then another Gaussian integral can get us the variance:

$$\langle s^2\rangle = \left(\frac{2}{\pi N}\right)^{1/2}\int ds\, e^{-2s^2/N}s^2 = \left(\frac{2}{\pi N}\right)^{1/2}\left(\frac{N}{2}\right)^{3/2}\int dx e^{-x^2}x^2 = \frac{N}{4}.$$

Therefore, the average value of the spin excess is $\langle(2s)^2\rangle = N$. So the typical fluctuations will be on the order of $\sqrt{N}$. So if you flip a coin 10^{22} times, perhaps an appropriate number of spins a typical magnet has, you expect that the total spin will be on the order of 10^{11}. If you bet a penny on the outcome of each spin, you would stand to win or lose on the order of a billion dollars. But if we look at the total spin, 10^{11} is pretty small compared with 10^{22}.

Magnetized magnets will have spins aligned, so $M \sim Nm$, or $10^{22}m$ in this case. For unmagnetized magnets, $|M| \sim \sqrt{N}m \approx 10^{11}m$. This is 10^{11} times smaller, so it will be measured as zero by an experimentalist.

We can also ask questions like this: What is the probability that the spin excess is around $2s \approx 10^{12}$, around 10 times larger than the standard deviation. The exponential in our Gaussian is $e^{-(2s)^2/2n} \approx e^{-50} \approx 10^{-21}$. So these fluctuations are extremely rare. That's the central idea of statistical mechanics, that mean behavior is very well approximated.

2 Thursday, April 1, 2010

Last time we learned about differences between Ph12b and Ph12c. He left out one of the most important ones: Instead of having a midterm, we're going to have a series of pop quizzes. The first is today, so take out a piece of paper and number from 1 to 10, and list the 10 laws of thermodynamics, which you should know from your required reading.

April Fool. We were actually looking at a magnet, with N spins of magnetic moment m. The total spin was given by $M = (N_\uparrow - N_\downarrow)m = 2sm$, where $N = N_\uparrow + N_\downarrow$. We considered large $N \gg 1$, and $N \gg |s|$. Then using Stirling's approximation, we obtained $P(N,s) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-2s^2/N}$. Then $\left\langle (2s)^2 \right\rangle = N = \left\langle (N_\uparrow - N_\downarrow)^2 \right\rangle$. Therefore, $\frac{\Delta(2s)}{N} = \frac{1}{\sqrt{N}} \to 0$ as $N \to \infty$.

This is going to provide a model for us: Fluctuations away from mean value will typically be small compared to the value itself.

2.1 Temperature

We will be seeking to explain this observation: A hot body and a cold body are in contact, and heat flows from the hot body, lowering its temperature, to the cold body, raising its temperature.

How do we model this? Our fundamental assumption: For a closed system, all accessible states of the system are equally likely. Closed means that the total energy U and total number of particles N are fixed. As for accessible, we don't want to consider processes that occur on unreasonable timescales. For instance, the air molecules in the room could collapse into a black hole, but that will take way too long to occur. Or a chemical transformation could occur, like graphite transforming into diamond. But we assume those don't happen because they would require average times in excess of those we observe.

Let g be the multiplicity of accessible microstates, a function of U and N. Then the probability of a given state is $1/g$. If we have some macroscopic property X of the system, the expected value of X is $\langle X \rangle = \sum_{\text{microstate}} P(\text{microstate}) X(\text{microstate})$. We expect that fluctuations of X far from $\langle X \rangle$ will be very rare.

Suppose we have two systems, system 1 and system 2, each with associated N_i, U_i and g_i. The multiplicity of a joint state with with N_1, N_2, U_1, U_2 will be $g_{12}(N_1, N_2, U_1, U_2) = g_1(N_1, U_1) g_2(N_2, U_2)$ which is proportional to the probability of observing the macrostate with N_1, N_2, U_1, U_2. The total number and energy are $N = N_1 + N_2$ and $U = U_1 + U_2$. If the two systems are in thermal contact, they can exchange energy (U_1 and U_2 can change, but U is constant) but not particles. The total number of accessible microstates is then $g(N,U) = \sum_{0 \le U_1 \le U} g_1(N_1, U_1) g_2(N_2, U - U_1)$. The probability of observing the system with N_1, N_2, U_1, U_2 is $P(N_1, N_2, U_1, U_2) = g_{12}(N_1, N_2, U_1, U_2)/g(N,U)$. If $N_1, N_2 \gg 1$, this function is sharply peaked near some average value $\hat{U}_1$. This is the "most probable configuration" or "equilibrium configuration".

Let's differentiate to find the peak:

$$\begin{aligned} dg_{12} = d(g_1 g_2) &= \left(\left.\frac{\partial g_1}{\partial U_1}\right|_{N_1} dU_1 \right) g_2 + g_1 \left(\left.\frac{\partial g_2}{\partial U_2}\right|_{N_2} dU_2 \right) \\ 0 &= \left(\left.\frac{\partial g_1}{\partial U_1}\right|_{N_1} g_2 - g_1 \left.\frac{\partial g_2}{\partial U_2}\right|_{N_2} \right) dU_1 \end{aligned}$$

Dividing by g_1 and g_2, we get $\frac{1}{g_1} \left.\frac{\partial g_1}{\partial U_1}\right|_{N_1} = \frac{1}{g_2} \left.\frac{\partial g_2}{\partial U_2}\right|_{N_2}$, or $\left.\frac{\partial}{\partial U_1} \ln g_1\right|_{N_1} = \left.\frac{\partial}{\partial U_2} \ln g_2\right|_{N_2}$.

This makes it natural to define the *entropy* $\sigma(N,U) = \ln g(N,U)$. We have $\sigma = \sigma_1 + \sigma_2$, and $\left.\frac{\partial \sigma_1}{\partial U_1}\right|_{N_1} = \left.\frac{\partial \sigma_2}{\partial U_2}\right|_{N_2}$. This is in the "most probable configuration."

Therefore,

1. U_1 wants to increase if $\frac{\partial}{\partial U_1} g_1 g_2 > 0$, or $\left.\frac{\partial \sigma_1}{\partial U_1}\right|_{N_1} - \left.\frac{\partial \sigma_2}{\partial U_2}\right|_{N_2} > 0$. In this case, energy flows from system 2 to system 1.
2. U_1 wants to decrease if $\frac{\partial}{\partial U_1} g_1 g_2 < 0$, or $\left.\frac{\partial \sigma_1}{\partial U_1}\right|_{N_1} - \left.\frac{\partial \sigma_2}{\partial U_2}\right|_{N_2} < 0$. In this case, energy flows from system 1 to system 2.

It then is natural to define the *temperature* τ by $\frac{1}{\tau} = \left.\frac{\partial \sigma}{\partial U}\right|_N$. Then $d(\sigma_1 + \sigma_2) = \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) dU_1$, and equilibrium is given by $\tau_1 = \tau_2$. Then

1. If $\tau_2 > \tau_1$, U_1 increases to increase $\sigma_1 + \sigma_2$. Heat flows from 2 to 1.
2. If $\tau_1 > \tau_2$, U_2 increases to increase $\sigma_1 + \sigma_2$. Heat flows from 1 to 2.

Dimensions: τ has dimensions of energy, and σ is dimensionless. We convert temperature to units of degrees Kelvin by Boltzmann's constant: $\tau = k_B T$, where $k_B = 1.4 \times 10^{-16}$ erg/°K and T is the "conventional" temperature. Entropy can similarly be expressed in conventional units as $S = k_B \sigma$, in units of erg/K. Then we still have $\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_N$.

How sharp is the multiplicity peak? Let's return to the magnet example. We had $N_\uparrow - N_\downarrow = 2s$ and $g(N,s) = g(N,0)e^{-2s^2/N}$. Then consider two systems with spins s_1 and s_2 in a magnetic field B which favors one of the spins. If we insulate from the environment, the total energy, and therefore spin $s = s_1 + s_2$, must be constant. Then the entropy is $\sigma = \ln(g_1 g_2) = \ln g_1(N_1, 0) g_2(N_2, 0) - \frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}$. The peak $\hat{s}_1$ is determined by $\frac{\partial \sigma}{\partial s_1} = 0$. Substituting $s_2 = s - s_1$, this implies $-\frac{4s_1}{N_1} + \frac{4(s-s_1)}{N_2}$, or $\hat{s}_1/N_1 = \hat{s}_2/N_2$, so $\hat{s}_1 = \frac{sN_1}{N_1+N_2} = \frac{sN_1}{N}$.

What is the entropy at this maximum? $\sigma_{\max} = \text{const} - 2\left[N_1(s_1/N_1)^2 + N_2(s_2/N_2)^2\right] = \text{const} - 2(N_1 + N_2)(s/N)^2 = \text{const} - 2s^2/N$. To determine the peak sharpness, suppose $s_1 = \hat{s}_1 + \delta$. We Taylor expand about $\hat{s}_1$:

$$\sigma(\hat{s}_1 + \delta) = \sigma(\hat{s}_1) + \sigma'(\hat{s}_1)\delta + \frac{1}{2}\sigma''(\hat{s}_1)\delta^2 + \cdots.$$

Now $\frac{\partial^2 \sigma}{\partial s_1^2} = -4\left(\frac{1}{N_1} + \frac{1}{N_2}\right) = -4\frac{N_1+N_2}{N_1 N_2}$. Therefore, we approximate $\sigma(\hat{s}_1 + \delta) = \text{const} - \frac{2N}{N_1 N_2}\delta^2 + \cdots$. So

$$g_1 g_2 = e^\sigma = \text{const} \cdot \exp\left[-\frac{2N}{N_1 N_2}\delta^2 + \cdots\right].$$

(This is a different constant from before; it includes the $-2s^2/N$ because that is fixed.) As an example, if $N_1 = N_2 = \frac{1}{2}N$, the deviation is $\exp\left[-\frac{4s^2}{N_1}\right]$. Consider $N_1 = 10^{22}$ and $\delta/N_1 = 10^{-10}$. Then the multiplicity compared to the peak value is $\exp(-4(10^{-10})^2 10^{22}) = e^{-400} = 10^{-174}$, extraordinarily unlikely.

One thing this discussion explains is the origin of irreversibility: Conceivably, heat flow could be reversed, but the probability is exceedingly unlikely.

We have been considering the modal state as equilibrium. This is justified through the central limit theorem, which always produces a symmetric Gaussian.

2.2 Boltzmann Distribution

Temperature applies to a closed system, e.g. when a closed system has two parts in thermal contact. It also applies to an open system, that is, one in contact with its environment. To model that, we'll consider a system with two parts. One will be much larger than the other, called the reservoir, denoted R, with associated large N_R and U_R. Our system is S but might not necessarily be very large.

For instance, the system S can be a single atom with two "orbitals", at energies $\mathcal{E}_1 < \mathcal{E}_2$. We want the probability that the system occupies orbital 1 or orbital 2. Since the multiplicities for the system are each 1, we have $\frac{P(\mathcal{E}_1)}{P(\mathcal{E}_2)} = \frac{g_R(U_0-\mathcal{E}_1)}{g_R(U_0-\mathcal{E}_2)} = \exp[\sigma_R(U_0-\mathcal{E}_1) - \sigma_R(U_0-\mathcal{E}_2)]$. Expand this entropy in a power series:

$$\sigma_R(U_0-\mathcal{E}_1) = \sigma_R(U_0) - \mathcal{E}_1 \left.\frac{d\sigma_R}{dU}\right|_{U=U_0} + \frac{1}{2}\mathcal{E}_1^2 \left.\frac{d^2\sigma_R}{dU^2}\right|_{U=U_0} + \cdots$$
$$\sigma_R(U_0-\mathcal{E}_2) = \sigma_R(U_0) - \mathcal{E}_2 \left.\frac{d\sigma_R}{dU}\right|_{U=U_0} + \frac{1}{2}\mathcal{E}_2^2 \left.\frac{d^2\sigma_R}{dU^2}\right|_{U=U_0} + \cdots$$

Now $\frac{d\sigma_R}{dU} = \frac{1}{\tau}$, which is an intensive quantity. Quadratic and higher order terms will vanish as the size of the Reservoir increases; for instance, $\dfrac{d^2\sigma_R}{dU^2} \sim \frac{1}{\text{system size}}$. Therefore, we get

$$\frac{P(\mathcal{E}_1)}{P(\mathcal{E}_2)} = \exp\left(-\frac{\mathcal{E}_1-\mathcal{E}_2}{\tau}\right) = \frac{e^{-\mathcal{E}_1/\tau}}{e^{-\mathcal{E}_2/\tau}}.$$

Therefore, $\boxed{P(\mathcal{E}_s) \propto e^{-\mathcal{E}_s/\tau}}$, the Boltzmann factor. To normalize, define $Z(t) = \displaystyle\sum_s e^{-\mathcal{E}_s/\tau}$, where the sum is over all accessible microstates so we get $\boxed{P(\mathcal{E}_s) = \dfrac{e^{-\mathcal{E}_s/\tau}}{Z}}$. We'll talk more about the Boltzmann distribution next week.

3 Tuesday, April 6, 2010

Recall from last time: We considered a closed system with number of states $g(N,U)$. Entropy was defined as $\ln g(N,U) = \sigma(N,U)$. Temperature is defined as $\tau = \left(\dfrac{\partial\sigma}{\partial U}\right)_N$.

We considered two systems with N_1 and N_2 particles, and energies U_1 and U_2 where $U = U_1 + U_2$ is held constant. The system will seek the more probable configuration, i.e. maximize the entropy. We have $d\sigma = \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) dU_1$. Therefore, energy will flow from one side to the other until reaching equilibrium at $\tau_1 = \tau_2$.

Furthermore, if $N_1, N_2 \gg 1$, after leaving the systems to reach equilibrium, the typical fluctuations about $\tau_1 = \tau_2$ are small: If $\delta U_1 = U_1 - \hat{U}_1$, $\langle \delta U_1^2 \rangle \propto \frac{N_1 N_2}{N_1+N_2}$, so the standard deviation scales as $\sqrt{N}$, while the energy scales as N.

We also considered an open system with a large reservoir in thermal contact with our system. We considered the case where there are a small number of states at energies $\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \ldots$, and we argued that the probability that the system is in microstate s is $P(\mathcal{E}_s) \propto e^{-\mathcal{E}_s/\tau}$ where $\mathcal{E}_s$ is the energy of the microstate and τ is the reservoir temperature. Doesn't this contradict our assumption that all states are equally likely? No, because this is true for a closed system. The combination of both the system and the reservoir are closed. Adding energy to the reservoir increases the number of states in the reservoir, making lower energy systems more likely. (We also used a linear approximation of the entropy of the reservoir with slope $1/\tau$ in our calculation, which is justified if the reservoir is sufficiently large.)

When we say proportional in $P(\mathcal{E}_s) \propto e^{-\mathcal{E}_s/\tau}$, we mean up to an overall normalization factor, which is known as the *partition function* $Z(\tau) = \sum_s e^{-\mathcal{E}_s/\tau}$. Then the probability of energy $\mathcal{E}_s$ is $\frac{1}{Z(\tau)} e^{-\mathcal{E}/\tau}$, so $\sum_s P(\mathcal{E}_s) = 1$. This result is true no matter the size of the system, large or small as long as it is in thermal contact with a large reservoir with temperature τ.

The probability that the system has energy $\mathcal{E}$ when in contact with a reservoir of temperature τ is given by $P_{system}(\mathcal{E}) = g_{system}(\mathcal{E}) \frac{1}{Z(\tau)} e^{-\mathcal{E}/\tau}$. For a large system, the probability distribution of the system energy is going to be narrowly distributed.

The average system energy is $U = \langle \mathcal{E} \rangle = \sum_s \mathcal{E}_s P(\mathcal{E}_s) = \sum_s \frac{\mathcal{E}_s e^{-\mathcal{E}_s/\tau}}{Z}$. Then we notice that $\frac{d}{d\tau}Z(\tau) = \sum_s \frac{\mathcal{E}_s}{\tau^2} e^{-\mathcal{E}_s/\tau}$. Comparing this to U, we see $U = \frac{\tau^2}{Z}\frac{d}{d\tau}Z(\tau) = \tau^2 \frac{d}{dt} \ln Z(\tau)$.

We now defend the assertion that these equations are useful by deriving the ideal gas law. Before doing that, we need some preliminaries:

3.1 Pressure

Pressure, as we know, is force per unit area. We can think of this, equivalently, considering a piston pushing on one face of a gas: $W = F dx = PA dx = -P dV$. In a closed system, this implies that $dU = -P dV$.

To apply what we know about statistical mechanics, we want to consider very slow changes (aka reversible changes). We want to be able to continue to assume that the system can reach all accessible states over the period of time in which it changes. We won't discuss the magnitudes of the corresponding timescales, but intuitively, it needs to be slow enough.

Here we consider two types of slow/reversible changes: Adiabatic (isentropic) changes occur in systems which remain thermally isolated, as in a closed system. Isothermal changes occur in systems which remain in contact with a very large reservoir during the change. Why are adiabatic changes isentropic?

We think of the different energy levels in the system to be functions of the volume, which increase in energy with decreasing volume. If the system is thermally isolated, the probabilities will remain the same, since there are the same number of accessible states, so the entropy is fixed.

Therefore, we write $P = -\left(\frac{\partial U}{\partial V}\right)_\sigma$, that is, the change in U with changes in V holding σ fixed. Think of it as writing U as a function of σ and V (and N if we want, but we won't be changing N for another week or so). Also recall that we have $\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_V$, or $\tau = \left(\frac{\partial U}{\partial \sigma}\right)_V$. Combining these,

$$dU = \tau\, d\sigma - P\, dV,$$

the *thermodynamic identity.* The first term corresponds to the heat flow and the second to the work done on the system.

Now let's think of σ as a function of U and V. We have $\tau\, d\sigma = dU + P dV$, so $\left(\frac{\partial \sigma}{\partial U}\right)_V = \frac{1}{\tau}$ (which we already knew) and $\left(\frac{\partial \sigma}{\partial V}\right)_U = \frac{P}{\tau}$. Of course, we can still convert to the usual temperature and entropy by Boltzmann's constant: $dU = T\, dS - P\, dV$.

3.2 (Helmholtz) Free Energy

Consider the Boltzmann distribution, $P(\mathcal{E}_s) \propto e^{-\mathcal{E}_s/T}$, with many closely-spaced energy levels, i.e. when the system is large. A region of energy $U \to U + dU$ has approximately $g(U)dU = e^{\sigma(U)}dU$ number of microstates. Then the probability of the energy lying in this region is approximately $dU \exp(\sigma(U) - U/\tau)/Z(\tau)$ where

$$Z(\tau) = \sum_s e^{-\mathcal{E}_s/\tau} = \int dU\, g(U) e^{-U/\tau} = \int dU\, \exp(\sigma(U) - U/\tau).$$

When the system size is large, as usual, we expect a narrow peak in $\exp(\sigma(U) - U/\tau)$ as a function of U for fixed τ. The peak occurs where the first-order change in $e^{-(U - \sigma(U)\tau)/\tau}$ with respect to U is zero, i.e. $0 = \frac{d}{dU}(U - \sigma\tau) = 1 - \frac{\tau}{\tau_S}$, i.e. the temperature of the system matches the temperature of the reservoir (we already knew this).

The peak in $\exp(\sigma(U) - U/\tau)$ occurs where $U - \tau\sigma(U)$ is stationary with respect to U. We can define a function of temperature as follows: $F(\tau) = [U(\tau) - \tau\sigma(U(\tau))]$, where $U(\tau)$ is the value of U which makes

$U - \tau\sigma(U)$ stationary for a given τ. We get probability $e^{-F(\tau)/\tau}$. Indeed, we started with $U - \tau\sigma(U)$, which is a function of both τ and U, but by evaluating this at the value of U which makes $U - \tau\sigma(U)$ stationary, which makes this just a function of the temperature. [This general strategy is called the Legendre transform and is used commonly in thermodynamics.] The function $F(\tau)$ is known as the *Helmholtz free energy.*

Let's analyze F: $dF = dU - \tau\, d\sigma - \sigma\, d\tau$. But $dU = \tau\, d\sigma - PdV$. Combining these, we have

$$dF = -P\, dV - \sigma\, d\tau.$$

We can understand from this relation why F is called the free energy. If a system is in contact with a reservoir at constant temperature the free energy tells us how much energy can be reversibly converted into work ($P\, dV$ is the work done by the system on its surroundings).

Taking partial derivatives of this provides us with expressions for pressure and entropy in terms of F: $\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$ and $\left(\frac{\partial F}{\partial V}\right)_T = -P$.

We can write the free energy in terms of the partition function: $Z(\tau) = \sum_s e^{-\mathcal{E}_s/\tau} \approx \max \exp(\sigma - U/\tau) \approx e^{-F(\tau)/\tau}$. Therefore, $F = -\tau \ln Z(\tau)$.

3.3 Classical Ideal Gas

Consider a one-particle gas (we'll add more particles later) in a cubic box with side length L and volume L^3. This was a problem from Ph12b, except that in Ph12b, the world was one-dimensional.

The orbitals are the energy eigenstates of Hamiltonian: $\hat{H} = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) = -\frac{\hbar^2}{2m}(\partial_x^2 + \partial_y^2 + \partial_z^2)$. Impose the boundary condition that the wavefunction vanishes at the edges of the box, i.e. $x, y, z \in \{0, L\}$. The problem is separable, so the eigenstates are

$$\psi(x,y,z) = c \sin\left(\frac{\pi x n_x}{L}\right) \sin\left(\frac{\pi y n_y}{L}\right) \sin\left(\frac{\pi z n_z}{L}\right),$$

where n_x, n_y, n_z are non-zero positive integers. The corresponding energy eigenvalues are $\mathcal{E} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$.

Here we make a classical approximation: We assume that we can replace the sum in the partition function by an integral, i.e. the Boltzmann factor does not change very much as we increase n_x by 1. This corresponds to the assumption that the de Broglie wavelength of the particle is small compared to the size of the box.

Now we just need to compute an integral, a Gaussian integral in fact (our favorite). Writing $\alpha = \frac{\hbar^2\pi^2}{2mL^2}\frac{1}{\tau}$, the partition function for 1 particle in the box is

$$Z_1 = \sum_s e^{-\mathcal{E}_s/\tau} \approx \int_0^\infty dn_x\, dn_y\, dn_y\ \exp(-\alpha(n_x^2 + n_y^2 + n_z^2))$$

This decomposes into three one-dimensional integrals. Since we know that $\int_0^\infty dn\, e^{-\alpha n^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \sqrt{\frac{\pi}{4\alpha}}$, we get

$$Z_1 \approx \left(\frac{m\tau L^2}{2\pi\hbar^2}\right)^{3/2} = n_Q V,$$

since $V = L^3$. Writing $n_Q = \frac{1}{L_Q^3}$, where L_Q is approximately the wavelength, we have $L_Q^2 = \frac{2\pi\hbar^2}{m\tau}$. The classical approximation is $\alpha \ll 1$, or $L \gg L_Q$.

Now let's compute the average energy:

$$\langle U \rangle = \tau^2 \frac{d}{d\tau} \ln Z_1 = \frac{3}{2}\tau^2 \frac{d}{d\tau} \ln \tau = \frac{3}{2}\tau = \frac{3}{2}k_B T.$$

4 Thursday, April 8, 2010

4.1 Boltzmann Factor and Free Energy

Recall: We were considering a system in contact with a reservoir at constant temperature. We defined the free energy $F(\tau)$ as the maximum of $U-\tau\sigma(u)$ over possible U, i.e. $(U-\tau\sigma(U))|_{dU/d\sigma=\tau}$. Then $F=\tau\log Z$. We calculated a version of the thermodynamic identity for the free energy: $dF=-\sigma\,d\tau-P\,dV$, that is, $\left(\frac{\partial F}{\partial\tau}\right)_V=-\sigma$ and $\left(\frac{\partial F}{\partial V}\right)_T=-P$.

Therefore, by the commutativity of partial derivatives, $\left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right)_T=\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_V$, so we have $\left(\frac{\partial\sigma}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V$. This is an example of a *Maxwell relation*; all are derived in a similar way.

4.2 Ideal Gas

We then considered a particle in a cubic box of side length L. Then the partition function of one particle is $Z_1=\sum_s e^{-\mathcal{E}_s/\tau}=\sum_{n_x,n_y,n_z}\exp\left(-\frac{\hbar^2}{2m\tau}\left(\frac{\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2)\right)$. In the classical regime, a short wavelength approximation, the prefactor in the exponent $\frac{\hbar^2}{2m\tau}\left(\frac{\pi}{L}\right)^2\ll 1$. The Hamiltonian is $H=p^2/2m$.

Then we defined the *quantum concentration* $n_Q=\left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}=\frac{1}{L_Q^3}$. We computed the average energy:

$$U=\langle\mathcal{E}\rangle=\tau^2\frac{d}{d\tau}\ln Z_1=\frac{3}{2}\tau^2\frac{d}{d\tau}\ln\tau=\frac{3}{2}\tau=\frac{3}{2}k_BT.$$

Now, we're going to put multiple particles in the box, $N\gg 1$. We still assume that the concentration is more dilute than the quantum concentration: letting $n=N/V$, $n\ll n_Q$.

Let's consider the particles as distinguishable. Then the total energy for particles in states $(s_1,\dots,s_n)$ is $\mathcal{E}=\mathcal{E}(s_1)+\cdots+\mathcal{E}(s_N)$, so $e^{-\mathcal{E}/\tau}=\prod_{i=1}^N e^{-\mathcal{E}(s_i)/\tau}$. To find the partition function, we sum over all the s_i:

$$Z_N=\sum e^{-\mathcal{E}/\tau}=\sum_{s_1}\cdots\sum_{s_n}e^{-\mathcal{E}/\tau}=\left(\sum_{s_1}e^{-\mathcal{E}(s_1)/\tau}\right)\cdots\left(\sum_{s_N}e^{-\mathcal{E}(s_N)/\tau}\right)=Z_1^N=(n_QV)^N.$$

This allows us to compute thermodynamic quantities:

$$\begin{aligned}
U&=\tau^2\frac{\partial}{\partial\tau}\ln Z_N=N\tau^2\frac{\partial}{\partial\tau}\ln Z_1=\frac{3}{2}N\tau\\
F&=-\tau\ln Z=-N\tau\ln(n_QV)\\
P&=-\left(\frac{\partial F}{\partial V}\right)_T=-\frac{\partial}{\partial V}(-N\tau\ln V+\text{const})_T=\frac{N\tau}{V}\\
PV&=N\tau=Nk_BT\text{ (ideal gas law)}\\
\sigma_N&=-\frac{\partial}{\partial\tau}[-N\tau\ln(n_QV)]_V=N\ln(n_QV)+\frac{3}{2}N,
\end{aligned}$$

where $n_Q=\left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$. Now, the ideal gas law and calculation of average energy can be computed using classical means, but there is something funny abour this last epxression. For instance, it isn't extensive; σ_N does not scale with N. Writing $n=N/V$, $V=N/n$, so

$$\sigma_N=N\ln(n_Q/n)+\frac{3}{2}N+N\log N=N\ln V+N\ln n_q+\frac{3}{2}N.$$

This is surprising: If we have two systems, with particle number and volume (N_1, V_1) and (N_2, V_2). Initially there's a barrier separating the gases, then we remove the barrier. Initially, the nonextensive terms are $N_1 \ln V_1 + N_2 \ln V_2$, and finally, $\sigma = (N_1 + V_1)\ln(V_1 + V_2)$. The change in entropy is

$$\Delta\sigma = \sigma_f - \sigma_i = N_1 \log\left(\frac{V_1 + V_2}{V_1}\right) + N_2 \log\left(\frac{V_1 + V_2}{V_2}\right) = (N_1 + N_2)\log 2 = N \log 2,$$

if we assume that $V_1 = V_2$. Indeed, the number of states for each particle doubles, so the total number of states is mulitplied by 2^N, as we got. If the particles on each side are different (nitrogen and oxygen, for instance), this is what we would expect. But if we have the same gas, this is a contradictory result. Gibbs decided that we can't make these assumptions, as the entropy will not increase by $N \log 2$.

These formulas are actually wrong; they don't agree with experiment. The problem is that we can't pretend that the particles are distinguishable. Having one particle in orbitals 1 and 2 is the same whichever particles we have. We have to count again. [There will also be difficulties when $n \sim n_Q$ which describes *quantum gases*, basically, gases in the quantum regime.]

In the classical regime, though, we have $n \ll n_Q$, and there will be many more orbitals than particles: $e_1^\sigma = n_Q V = \frac{n_Q}{n} N \gg N$. Then if we think of starting to put some particles in the orbitals. We may assume that it is not probable that any orbitals will be doubly occupied, i.e. the N particles are in different orbitals. Therefore, our original count was $N!$ times too large, and $(Z_N)_{\text{indist}} = \frac{1}{N!} Z_1^N$. Therefore, $\ln(Z_N)_{\text{indist}} = (\ln Z_N)_{\text{dist}} - \ln N!$, and $\ln N! = N \ln N - N$, so this removes the factor of $N \ln N$ that was nonlinear. This also allows us to compute $(F_N)_{\text{indist}} = (F_N)_{\text{dist}} + \tau \ln N!$. Therefore, $U = \tau^2 \dfrac{\partial}{\partial \tau} \ln Z$ and $P = -\left(\dfrac{\partial F}{\partial V}\right)_T$ are unchanged. It's okay; we didn't have a problem with those. The entropy becomes

$$(\sigma_N)_{\text{indist}} = N[\log(n_Q/n) + 5/2].$$

This is extensive, as we expect.

4.3 Entropy of mixing

There is always this tradeoff between maximizing entropy and minimizing energy, and we always have to balance between those two desiderata. Consider an example of mixing two molten metals A and B, then cooling them down. If they mix together, that would increase the entropy since there are many possible states, but it will probably also increase the energy becauase like atoms fit together more favorably.

Suppose there are N atoms in all, xN B atoms and $(1-x)N$ A atoms. The multiplicity is $g(N, x) = \binom{N}{xN}$. Taking a log, we get

$$\begin{aligned}\sigma(N, x) &= \ln g(N, x) = N \ln N - N - xN \ln(xN) + xN - (1-x)N \ln[(1-x)N] + (1-x)N \\ &= N \ln N - xN \ln x - xN \ln N - (1-x)N \ln(1-x) - (1-x)N \ln N = N[-x \ln x - (1-x)\ln(1-x)].\end{aligned}$$

Since $0 < x < 1$, $\ln x < 0$, so this is a sum of two nonnegative terms.

Now we make an approximation: x is small, i.e. $-\ln x \gg 1$. Then the $(1-x)\ln(1-x)$ term will be very small compared the other terms, so $\sigma(N, x) \approx -Nx \ln x$. The free energy is then $F = U - \tau\sigma = \text{const} + (Nx)\mathcal{E} + N\tau x \ln x$. We want to find the fraction x that minimizes F, as this will be the most probable configuration. Differentiating, $\dfrac{\partial F}{\partial x} = N(\mathcal{E} + \tau + \tau \ln x) = 0$, so $\mathcal{E} + \tau + \tau \ln x = 0$ and solving for x, $\ln x = -1 - \mathcal{E}/\tau$, so $x = \frac{1}{e} e^{-\mathcal{E}/\tau}$.

Of course, if we add too many B atoms, they will start to cluster and leave some dissolved in the A atoms. This also assumes that you allow the system to reach equilibrium. If you cool it quickly enough, it might fail to reach its most probable state. Another consequence is that it is very hard to purify a metal, because there are so many possible mixed configurations.

5 Tuesday, April 13, 2010

5.1 Planck Distribution

Consider a cubical box of side L, with conducting sides and a vacuum inside.

Planck hypothesized that photon energy came in units of $\hbar\omega$. Since photons are indistinguishable, this means that the probabilities are just the Boltzmann factors over the partition function: $P(s) = \frac{e^{-s\hbar\omega/\tau}}{Z}$, where $Z = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} = \frac{1}{1-e^{-\hbar\omega/\tau}}$. Let's compute the average energy: $\langle\mathcal{E}\rangle = \hbar\omega\langle s\rangle$, and $\langle s\rangle = \sum_{s=0}^{\infty} s\cdot P(s) = \frac{1}{Z}\sum_{s=0}^{\infty} se^{-s\hbar\omega/\tau}$, which requires some more complicated manipulations to compute. Instead, let's use the formula

$$\begin{aligned} U &= \tau^2\frac{\partial\log Z}{\partial\tau} = \frac{\tau^2}{Z}\frac{\partial Z}{\partial\tau} \\ &= \frac{\tau^2}{Z}\frac{\partial}{\partial\tau}\frac{1}{1-e^{-\hbar\omega/\tau}} \\ &= \frac{\tau^2}{Z}\frac{e^{-\hbar\omega/\tau}\frac{\hbar\omega}{\tau^2}}{(1-e^{-\hbar\omega/\tau})^2} \\ \langle\mathcal{E}\rangle &= \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1} \end{aligned}$$

Note that as $\tau\to\infty$, $\langle\mathcal{E}\rangle = \tau$, which matches the classical result. As $\tau\to 0$, $\langle\mathcal{E}\rangle\to\hbar\omega e^{-\hbar\omega/\tau}$.

How do we solve for the electric field within the cavity? We must satisfy the equation $\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{E} = 0$. We assume that such an equation is separable, so $\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathcal{E}_x = 0$, and then $\mathcal{E}_x = f(x)g(y)h(z)$. Similarly for y, z.

The boundary conditions give $\vec{E}_{\|} = 0$, so $h(0) = h(L) = 0$, $g(0) = g(L) = 0$ and $f'(0) = f'(L) = 0$. Therefore, the solutions are given by

$$\begin{aligned} E_x &= E_{x0}\cos(k_x x)\sin(k_y y)\sin(k_z z)e^{i\omega t} \\ E_y &= E_{y0}\sin(k_x x)\cos(k_y y)\sin(k_z z)e^{i\omega t} \\ E_z &= E_{z0}\sin(k_x x)\sin(k_y y)\cos(k_z z)e^{i\omega t}, \end{aligned}$$

where $k_x = \frac{\pi}{L}n_x$, $k_y = \frac{\pi}{L}n_y$, and $k_z = \frac{\pi}{L}n_z$, with the n_x, n_y, n_z nonnegative integers, with at most one of them zero. Additionally, we must satisfy $\vec{\nabla}\cdot\vec{E} = 0$, or $k_x E_{x0} + k_y E_{y0} + k_z E_{z0} = 0$, i.e. the vectors $\vec{E}_0 = (E_x, E_y, E_z)$ and $\vec{k} = (k_x, k_y, k_z)$ are perpendicular. Then to satisfy the differential equation, we need $\omega^2 = c^2\left\|\vec{k}\right\|^2 = \frac{c^2\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$.

We want to approximate the mean energy $U = \sum_{\text{modes}}\langle\mathcal{E}\rangle$. Due to polarization, this is $2\sum_{n_x,n_y,n_z}\langle\mathcal{E}\rangle$. Because energy is not quickly varying in n (we know this because ω is multplied by $\hbar$, which is small), we can replace this sum with an integral: $2\int_0^\infty\int_0^\infty\int_0^\infty dn_x\,dn_y\,dn_z\,\frac{\hbar\omega}{e^{\hbar\omega}-1}$. We then switch to spherical coordinates: Letting $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$, a shell at radius n has volume $4\pi n^2\,dn$, but we're only concerned with one octant since $n_x, n_y, n_z > 0$. Therefore, we get

$$U = 2\frac{4\pi}{8}\int_0^\infty n^2\,dn\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}.$$

Now we get $\omega^2 = \frac{c^2\pi^2}{L^2}n^2$, so $\omega = \frac{c\pi n}{L}$, or $n = \frac{L}{c\pi}\omega$. This yields

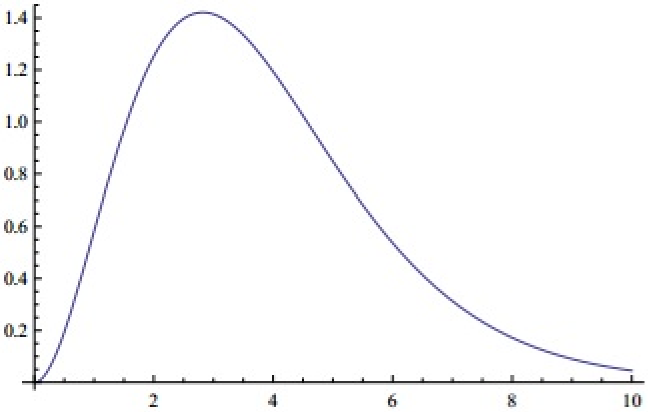
$$U = \pi\left(\frac{L}{c\pi}\right)^3\int_0^\infty \omega^2\,d\omega\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1} = \frac{L^3\hbar}{c^3\pi^2}\int_0^\infty\frac{\omega^3 d\omega}{e^{\hbar\omega/\tau}-1} = \frac{L^3\tau^4}{c^3\hbar^3\pi^2}\underbrace{\int_0^\infty\frac{x^3\,dx}{e^x-1}}_{\pi^4/15}$$

$$U = \frac{\pi^2}{15c^3\hbar^3}V\tau^4.$$

We have written $L^3 = V$ because we claim that this holds for all volumes, not just cubes. The energy density is then given by $\frac{U}{V} = \frac{\pi^2}{15c^3\hbar^3}\tau^4$. We also want the distribution:

$$\frac{U}{V} = \int_0^\infty\frac{\hbar}{c^3\pi^2}\frac{\omega^3\,d\omega}{e^{\hbar\omega/\tau}-1} = \int_0^\infty U_\omega(\tau)\,d\omega,$$

where $U_\omega(\tau) = \frac{\hbar}{c^3\pi^2}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}$. This distribution is shown below:



The maximum can be calculated to be around when $\frac{\hbar\omega_0}{\tau} \approx 2.82$. This increases with τ, Wein's law. Actually, for $\tau_2 > \tau_1$, the entire distribution is larger at each frequency.

For $\hbar\omega/\tau \ll 1$, we get $U_\omega(t) = \frac{\omega^2\tau}{c^3\pi^2}$. This is just a parabola, and matches the classical result. If extrapolated to high ω the classical result would have unbounded $U_\omega(\tau)$, which would cause the total energy density to be infinite, which is clearly absurd. This was the ultraviolet catastrophe, which made Planck's work more interesting since it does not predict the infinite energy density found in the purely classical analysis.

We haven't actually talked about blackbody radiation yet. Planck imagined a small hole with area A in the box where photons (energy) could escape. Consider some small solid angle $d\Omega$. Drawing a cylinder outward from the hole with length $c\,dt$, the volume is $uAc\cos\theta\frac{d\Omega}{4\pi}$, where $u = U/V$ is the energy density. We integrate over the solid angle, but the only angle that matters is θ, so consider an annulus on the sphere between angles θ and $\theta + d\theta$. It has surface area $2\pi\sin\theta\,d\theta = 2\pi d(\cos\theta)$. Now we integrate from $\cos\theta = 0$ to $\cos\theta = 1$, getting

$$dU = \frac{1}{2}\int_0^1 uAcdt\cos\theta\,d(\cos\theta), \quad J = \frac{dU}{A\,dt} = \frac{1}{4}cu = \frac{\pi^2}{60c^2\hbar^3}\tau^4.$$

The constant $\frac{\pi^2}{60c^2\hbar^3} = \sigma_B$ is the Stefan-Boltzmann constant. Make sure you use the one with the fundamental temperature τ rather than with the traditional temperature T; that one differs by a factor of k_B^4.

Also note that we can get the energy density lost at certain frequencies: $J_\omega = \frac{1}{4}cu_\omega = \frac{c}{4V}U_\omega(\tau)$.

What is a blackbody? Anything that absorbs all incident radiation. The sun is an example, but it's not perfect because it's not at constant temperature, and there are spectral lines due to atomic absorptions. Are we blackbodies? Well, there are problems that ask you to assume so.

For non-blackbodies, we can also examine the absorption and emission coefficients: a_ω is the energy the body absorbs at ω over the energy incoming at ω, and e_ω is the energy the body emits at ω over the energy that a black body emits at ω. For a blackbody, of course, $a_\omega = e_\omega = 1$.

Now suppose we plug our blackbody's hole with some other material. The energy it absorbs from the blackbody is $a_\omega \frac{c}{4} u_\omega$, and the energy it returns to the blackbody is $e_\omega \frac{c}{4} u_\omega$. Therefore, at equilibrium, $a_\omega = e_\omega$, even for non-blackbodies.

Plank's derivation assumes that only discrete energy levels occur for each mode of light. This was a controversial hypothesis, since the wave nature of light had been well-established. Planck regarded it merely as a working hypothesis, not a theory of the nature of light. Around this time, the photoelectric effect was also explained by Einstein as matching this particle nature of light.

Also, when we chose to discretize energy with $\mathcal{E} = s\hbar\omega$, we can think of this as similar to the quantum harmonic oscillator, with a $\frac{1}{2}\hbar\omega$ term. When we examine phonons on Thursday, this will come up.

Doesn't having photons contradict our assumption that the number of particles is fixed? One consequence is that photons are not conserved. In the language we'll see later, the chemical potential of a photon is zero.

6 Thursday, April 15, 2010

Recall our setup: s photons have energy $\mathcal{E} = s\hbar\omega$. The probability of being in state s is $P_\omega(s) = \frac{e^{-s\hbar\omega/\tau}}{1-e^{-\hbar\omega/\tau}}$, average number of photons is $\langle s \rangle_{\omega,\tau} = \frac{1}{e^{\hbar\omega/\tau}-1}$, and the average energy is $\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}$. Considering our volume as a cube with side length L, we calculated that the energy density is

$$u = \frac{U}{V} = \frac{\pi^2}{15}\frac{1}{(\hbar c)^3}\tau^4 = \int d\omega\, U_\omega, \text{ where } u_\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}.$$

For the classical limit, $\omega < c\tau$, we get $u_\omega \approx \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{\hbar\omega/\tau} = \frac{\omega^2}{\pi^2 c^3}\tau$. This is known as the *Rayleigh-Jeans Law.* Since it makes no reference to $\hbar$, we might expect to derive it classically, and indeed this can be done.

There's a problem, though. Notice that $\langle \mathcal{E} \rangle_{\omega,\tau} = \frac{\hbar\omega}{\hbar\omega/\tau} = \tau$, so the energy stored in each mode with $\omega/\tau \ll 1$ is τ. If there were infinitely many such modes, then the energy would be infinite: $\int^\infty d\omega U_\omega = \infty$. This became known as the *ultraviolet catastrophe.*

We can imagine that this problem was used to show that classical physics was wrong and quantum might be right, but that's not historically what happened. In fact, Einstein derived the Rayleigh-Jeans law and found the ultraviolet catastrophe, and remarked that Planck had already resolved this problem.

Let's talk about blackbodies now. A blackbody, as we defined last time, absorbs all light incident on it. The energy flux density is $J = \frac{1}{A}\frac{d\mathcal{E}}{dt} = \frac{1}{4}c\frac{U}{V} = \frac{\pi^2}{60}\frac{1}{\hbar^3 c^2}\tau^4 = \sigma_B (k_B \tau)^4$, where σ_B is the Stefan-Boltzmann constant.

What about the case of a "gray body", one that absorbs only some of the light incident on it? We suppose that $e(\omega) \le 1$ is the emission coefficient, and $a(\omega)$ is the absorption coefficient. At a constant equilibrium temperature, we need $a(\omega) = e(\omega)$.

6.1 Theory of Phonons

Suppose we have a crystal lattice composed of particles which each sit in the middle of a local potential well. We think of the vibrating crystal as a system of couple harmonic oscillators. There will be normal modes with frequencies $\{\omega_i\}$.

In the case of the quantum harmonic oscillator, we had a sequence of modes with energy gap $\hbar\omega$, i.e. the nth energy mode has energy $\mathcal{E}_n = n\hbar\omega$. The phonon case is analogous to the energy of n noninteracting particles, each with frequency ω and energy $\hbar\omega$.

Phonons (sound) are like photons (light), except:

(1) There are 3 polarizations, not 2. You can additionally have longitudinal polarizations with sound. We will assume that the speed of sound is the same for each of these modes.

(2) There is a minimum wavelength corresponding to the size of the crystal.

A mode will have a wavenumber $\vec{k}$ and frequency $\omega(\vec{k})$. We make the approximation that the dispersion relation is $\omega^2 = v^2\vec{k}^2$, where v is the speed of sound. This assumes the dispersion is isotropic and linear in k, which is valid for long wavelengths compared to the particle spacing. Since the particles are what is moving, we can't imagine a mode with wavelength 1/10 of the particle spacing, since there's nothing to capture that fine structure. There must therefore be an upper limit of allowed k (corresponding to a minimum wavelength).

Another way to see this minimum wavelength is to consider N particles, which have $3N$ degrees of freedom, so there will be $3N$ normal modes. We can count the number of modes in another way. Considering the modes as $\vec{k} = \frac{\pi}{L}\vec{n}$ where $\vec{n} = (n_1, n_2, n_3)$ is a triple of nonnegative integers. Then the number of modes can be approximated by an integral again: $3\left(\frac{L}{\pi}\right)^3 \frac{1}{8}\int_0^{k_{\max}} 4\pi k^2\,dk = \frac{3}{2}\frac{L^3}{\pi^2}\frac{1}{3}k_{\max}^3 = 3N$, so with $V = L^3$, $k_{\max}^3 = 6\pi^2 N/V = k_D^3$, known as the *Debye wavenumber.* Then if a is the interparticle spacing, $V/N = a^3$, and $k_{\max} = \frac{2\pi}{\lambda_{\min}} \sim \frac{2\pi}{a}$ and the minimum wavelength is around a. So we can see this bound as either a minimum wavelength or a maximum wavenumber.

We continue the same discussion as we had with the Planck setup. The energy is then given by $U = \frac{3L^3}{2\pi^2}\int_0^{k_{\max}} dk\,4\pi k^2\,\langle\mathcal{E}(k)\rangle$. We also have the dispersion relation $\omega = vk$. The average energy is given by Planck as $\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1} = \frac{\hbar vk}{e^{\hbar vk/\tau}-1}$.

Writing $x = \frac{\hbar vk}{\tau}$, or $k = \frac{\tau}{\hbar v}x$, we get

$$U/V = \frac{3}{2\pi^2}\left(\frac{\tau}{\hbar v}\right)^4 \hbar v\int_0^{x_D} dx\,\frac{x^3}{e^x-1}.$$

Writing $x_D = \theta/\tau$, we have $\theta = \hbar v k_D = \hbar\omega_D$ is the *Debye temperature.*

6.1.1 Low-Temperature Limit

Consider the low-temperature limit. Then $x_D = \theta/\tau \gg 1$, or $\frac{\hbar\omega_D}{\tau} \gg 1$. Since the integrand $\frac{x^3}{e^x-1}$ gets very small for large x, we can extend our integral from 0 to ∞ with only a small error. Then compute that $\int_0^\infty dx\,\frac{x^3}{e^x-1} = \frac{\pi^4}{15}$ ("as all fans of the Riemann zeta function know").

Now we write $\theta^3 = (\hbar v)^3 k_D^3 = (\hbar v)^3 6\pi^2 N/V$. We will subsitute this in to get rid of the $\hbar$. Then we have

$$\begin{aligned} \frac{U}{V} &= \frac{3}{2\pi^2}\frac{\tau^4}{(\hbar v)^3}\frac{\pi^4}{15} = \frac{\pi^4}{10\pi^2}\frac{\tau^4}{(\hbar v)^3}\frac{(\hbar v)^3 6\pi^2 N/V}{\theta^3} \\ \frac{U}{V} &= \frac{N}{V}\frac{3}{5}\pi^4\frac{\tau^4}{\theta^3} \\ U &= \frac{3\pi^4}{5}N\tau^4/\theta^3, \end{aligned}$$

which applies for $\tau/\theta \ll 1$. This is known as the *Debye T^3 law* because energy varies as τ^4. Actually, the T^3 describes the heat capacity, the temperature derivative of energy: $c_V = \left(\frac{\partial U}{\partial\tau}\right)_V = \frac{12\pi^4}{5}N\tau^3/\theta^3$.

Experimentally, this works well in the $\theta_D/k_B \sim 200 - 600$°K range when compared to the exponential at $T \lesssim 100$°K.

6.1.2 High-Temperature Limit

We also have the high temperature limit, $\theta/\tau \ll 1$. Now we approximate the integrand by $\frac{x^3}{e^x-1} \approx \frac{x^3}{x} = x^2$. The integral is then $\int_0^{x_D} dx\, x^2 = \frac{1}{3}x_D^3$. Then

$$\frac{U}{V} = \frac{3}{2\pi^2}\frac{\tau^4}{(\hbar v)^3}\frac{1}{3}\left(\frac{\theta}{\tau}\right)^3 = \frac{3N\tau}{V} \implies U = 3N\tau.$$

This is analogous to the Rayleigh-Jeans law. Note that $\langle \mathcal{E}(\omega)\rangle = \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1} \sim \tau$, so we can explain this law as saying that each of the $3N$ modes has energy τ stored in it. Experimentally, this means that the specific heat is $c_v = 3N$, the *Law of Dulong and Petit* (1819). It was explained by Boltzmann in 1876 as "equipartition." Einstein was the first to examine the quantum corrections of the low-temperature limit, but he used too crude a model (assuming all modes were equal, rather than behaving as a Planck distribution), and Debye six years later redid the calculation, yielding the T^3 law.

6.2 Chemical Potential

What's chemical about it? Well, it's useful in chemistry, applying to equilibrium concentrations of chemical reactions. The word potential is used in the same sense as potential energy. The context is a natural extension of our discussion: We had two systems in thermal contact, so they could exchange energy. If they were at temperatures $\tau_1 > \tau_2$, then energy will flow from 1 to 2.

Our new setup has two systems, both kept at temperature τ by a reservoir. The systems have volumes V_1 and V_2 and particle number N_1 and N_2. The total number of particles $N = N_1 + N_2$ is fixed. The chemical potential is analogous to temperature in that if two systems have chemical potentials $\mu_1 > \mu_2$, particles will move from 1 to 2.

We'll call this kind of contact where particles can move *diffusive contact.* Particles will continue to flow until they reach equilibrium with $\mu_1 = \mu_2$. There will be a most probable configuration, depending on the ambient temperature τ, where the numbers of particles will be approximately $\hat{N}_1$ and $\hat{N}_2$. As before with temperature and energy, typical fluctuations about the equilibrium will be small compared with the total numbers of particles.

The most probable configuration at a fixed temperature τ is determined by minimizing free energy $F(\tau, V, N)$. The total free energy is the sum of the free energies of each system, so $F = F_1(\tau, V_1, N_1) + F_2(\tau, V_2, N_2)$. We are keeping τ, V_1, V_2 fixed, so small changes in free energy $dF = \left(\frac{\partial F_1}{\partial N_1}\right)_{\tau,V_1} dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right)_{\tau,V_2} dN_2 = 0$ in equilibrium. Since total particle number is fixed, $dN_2 = -dN_1$. Therefore, define the chemical potential $\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$. The equilibrium condition is then $dF = (\mu_1 - \mu_2)dN_1 = 0$, or $\mu_1 = \mu_2$.

Again, we want to minimize free energy, so $dF = (\mu_1 - \mu_2)dN_1 < 0$. If $\mu_1 > \mu_2$, $dN_1 < 0$ and particles flow from system 1 to system 2.

In chemical potential analyses, we usually distinguish between "internal" and "external" contributions. We'll illustrate this with some examples.

First consider two ideal gases (1) and (2) separated vertically by a height Δh in the gravitational field of the earth g. Then there are two contributions to the energy: the gravitational potential energy, which we label as external, and the kinetic energy of the ideal gas, which we label as internal. To be in diffusive equilibrium, $0 = \mu_1 - \mu_2 = (\Delta\mu)_{\text{int}} + (\Delta\mu)_{\text{ext}}$. Then we get $(\Delta\mu)_{\text{ext}} = mg\Delta h$, and we'll calculate $(\Delta\mu)_{\text{int}}$ next week. We'd have to balance these two effects.

For another example, consider two metals with a battery producing a voltage difference of ΔV between them. The chemical potential of electrons will have a contribution of $\mu_{\text{ext}} = e\Delta V$.

7 Tuesday, April 20, 2010

We want to analyze chemical potential in the same way as temperature. First, there is an alternative formula for the chemical potential: Indeed, consider fixed V: Then first order change in $F = U - \tau\sigma$ yields $dF = \left(\frac{\partial U}{\partial \sigma}\right)_N d\sigma + \left(\frac{\partial U}{\partial N}\right)_\sigma dN - \tau d\sigma - \sigma d\tau$. Then $\tau = \left(\frac{\partial U}{\partial \sigma}\right)_N$, so those terms cancel. Then keep temperature fixed, so $\left(\frac{\partial U}{\partial N}\right)_\sigma = \left(\frac{\partial F}{\partial N}\right)_\tau = \mu$.

This yields a new, more general thermodynamic identity:

$$dU = \tau d\sigma - pdV + \mu dN.$$

A third formulation is to fix U and V in this identity, so $0 = \tau d\sigma + \mu dN$ and $\frac{\partial \sigma}{\partial N} U, V = -\frac{\mu}{\tau}$.

7.1 Internal and External Chemical Potential

Consider a system with two gases in a gravitational field g at a height difference Δh. Then we consider gravity as an external influence, and the external chemical potential is $\Delta\mu_{\text{ext}} = mg\Delta h$. The total free energy has two components: internal, the free energy cost of changing particle number in absence of external influence, and external, the potential energy per particle due to the external influence.

Let's consider our favorite example: the ideal gas. The partition function was given by

$$Z_N = e^{-F/\tau} = \frac{1}{N!} Z_1^N = \frac{1}{N!}(n_Q V)^N, \quad n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}.$$

where n_Q is the quantum concentration of the particles. Then free energy is given by $F = -\tau \ln Z = -\tau[N \ln Z - \ln N!]$. To compute the chemical potential, we can take a derivative, or we can just take the difference between the free energy of $N-1$ particles and N particles. This is

$$\mu(T, V, N) = F(T, V, N) - F(T, V, N-1) = -\tau \left[\ln Z_1 - \ln \frac{N!}{(N-1)!}\right] = \tau \ln(N/Z_1) = \tau \ln(n/n_Q),$$

where $n = N/V$ is the concentration. Therefore, if we establish diffusive contact between two gases, say of the same species so they have the same quantum concentration, then particle number flows from high n to low n, or high $P = n\tau$ to low P.

Let's use this to model how the atmospheric pressure varies as a function of height above sea level, to see if we can breathe at the top of Mount Everest. We'll assume an isothermal model, which is not a great approximation, but not that bad because we're talking about absolute temperatures. (Mount Everest might be 40 degrees colder, but that's only around 15%.)

The total chemical potential is $\mu_{\text{ideal gas}} + \mu_{\text{external}} = \tau \ln(n/n_Q) + mgy$, where m is the mass of an oxygen molecule. Think of it as a series of bands at different altitudes, which are in diffusive equilibrium with their nearest neighbors. This implies that the chemical potential at each height is constant, $\mu(h) = \mu_0$. Therefore, $\tau \ln(n/n_Q) = \mu - mgy$, so $n = n_Q e^{\mu/\tau} e^{-mgy/\tau} = n(0)e^{-mgy/\tau}$. We might have been able to guess this formula because it looks like a Boltzmann factor.

For a temperature of 300 K, we get $\frac{mgy}{\tau} \approx 1$ for $y = 8$ km, so $n \propto e^{-y/8 \text{ km}}$. Since Mount Everest is around 8.7 km altitude, the oxygen partial pressure is expected to drop off to around $1/e$ of its sea-level value, which is pretty accurate.

7.2 Gibbs Factor and Gibbs Sum

If we want to continue our program of analyzing temperature, the next step is to analyze a system in contact with a large reservoir which is in both thermal and diffusive equilibrium.

Recall that to increase its energy, a system in thermal contact with a reservoir had to take energy from the reservoir. Let's generalize to compare two particle numbers and energies:

$$\frac{P(N_1,\mathcal{E}_1)}{P(N_2,\mathcal{E}_2)} = \frac{g_R(N_0-N_1,U_0-\mathcal{E}_1)}{g_R(N_0-N_2,U_0-\mathcal{E}_2)} = \exp[\sigma_R(N_0-N_1,U_0-\mathcal{E}_1)-\sigma_R(N_0-N_2,U_0-\mathcal{E}_2)].$$

We can now, as before, expand in a power series, and the superlinear terms will vanish as the reservoir becomes large. We get approximately

$$\exp\left[-(N_1-N_2)\left(\frac{\partial\sigma_R}{\partial N}\right)_U-(\mathcal{E}_1-\mathcal{E}_2)\left(\frac{\partial\sigma_R}{\partial U}\right)_N\right]=\exp[((N_1-N_2)\mu-(\mathcal{E}_1-\mathcal{E}_2))/\tau].$$

Therefore, the probability $P(N,\mathcal{E})\propto e^{(N\mu-\mathcal{E})/\tau}$. This effect is more complicated than the temperature, since μ can be positive or negative.

Now we normalize as before: $P=\frac{1}{\mathfrak{z}}e^{(N\mu-\mathcal{E})/\tau}$, where $\mathfrak{z}=\sum_s e^{(N_s\mu-\mathcal{E}_s)/\tau}$ is the *Gibbs sum*. We can then get average statistics using $\langle X\rangle=\sum_s X(s)P(s)$. For instance, the average number of particles is

$$\langle N\rangle=\frac{1}{\mathfrak{z}}\sum_s N_s e^{(N_s\mu-\mathcal{E}_s)/\tau}=\frac{\tau}{\mathfrak{z}}\left(\frac{\partial\mathfrak{z}}{\partial\mu}\right)_\tau.$$

For particle number $\bar{N}$, we choose a chemical potential μ such that $\langle N\rangle_{\mu,\tau}=\bar{N}$. As usual, for a large system, fluctuations in particle number relative to the total $\delta N/\bar{N}\ll 1$.

7.2.1 Example: Impurity in a Doped Semiconductor

For instance, say there is a phosphorus atom in a silicon semiconductor. Does the phosphorus give up an electron to the electron gas? There is an ionization energy I which is the energy cost of removing an electron from P. Taking into account spin, there are three states we need to analyze: ionized ($\mathcal{E}=0$, $N=0$), and not ionized ($\mathcal{E}=-I$, $N=1$), with two states of spin up and spin down.

For this system, $\mathfrak{z}=1+2e^{(\mu+I)/\tau}$. The probability of ionization is then $\frac{1}{\mathfrak{z}}=\frac{1}{1+2e^{(\mu+I)/\tau}}$. If $\mu+I>0$, as $\tau\to 0$, the probability of ionization goes to 0. The key comparison is how "hungry" the semiconductor is for electrons compared to the ionization energy of the phosphorus atom. With the Fermi electron gas that we'll learn about later, we can estimate μ.

7.3 Johnson-Nyquist Noise in Electrical Circuits

Consider an electrical circuit with a nonzero temperature. We'll treat the circuit as an ideal resistor R with no external potential applied. There will be thermal fluctuations which produce minute voltages, which we measure with a voltmeter. We filter the frequencies to obtain a Fourier analysis, Fourier tranforming the voltage $V(t)$. Keeping only a band from the transform $\hat{V}(\omega)$, we Fourier tranform back, getting $[V(t)]_{\text{filtered}}$. Of course, the average will be 0, but the mean square will be $\langle[V^2(t)]_{\text{filtered}}\rangle=4(k_BT)R\,dt$. This is what Johnson discovered experimentally and Nyquist explained. It is derived under the assumption that $\frac{\hbar\omega}{kT}=\frac{hf}{kT}\ll 1$.

There's a bit of electrical engineering lore that goes into this: All resistors can be treated as a coaxial cable with a characteristic impedance of R. If we put a resistor at one end with resistance R (impedance matching), then all the incident power will be absorbed. In thermal equilibrium, the power dissipated in the circuit will equal the power delivered by the transmission line.

Analyzing as we did in Ph12a, give the cable length L, so the wavenumber of the nth mode is $k_n=\frac{\pi}{L}n$. With propogation speed v, the dispersion relation is $\omega=kv$, so $\omega_n=\frac{\pi v}{L}n$. The average energy is then $\langle\mathcal{E}(\omega)\rangle=\frac{\hbar\omega}{e^{\hbar\omega}-1}\approx\tau$. Energy is then

$$U=\sum_{\omega_n}\langle\mathcal{E}(\omega_n)\rangle=\frac{L}{\pi v}\int d\omega\,\tau=\frac{2L}{v}\tau\int df.$$

Therefore, power is given by $\frac{1}{2}v\frac{U}{L} = \tau\int df$. So a frequency bandwidth of width df has energy τ. Power is $\left\langle [I^2]_{\text{filtered}}\right\rangle R$. Now since our coaxial cable has impedance R, the total resistance is $2R$ so $V = 2IR$ and we get $\tau df = \frac{\left\langle [V^2]_{\text{filtered}}\right\rangle}{4R}$, which Nyquist found.

To get a feel for the scales of these fluctuations, for $R = 50\,\Omega$, $T = 300$ K, and $\Delta f = 1$ MHz, $\left\langle V^2\right\rangle^{1/2} \approx 1$ μV. This has consquences for electrical signaling; if you watch for a microsecond, the signal must have energy greater in magnitude than 1 μV. Actually, the latest electrical signals bump up against the quantum barrier.

Next time we'll look at quantum gases, both the Fermi gas and the quantum bosonic gas.

8 Thursday, April 22, 2010

Last time we had examined chemical potential and generalized the thermodynamic identity to include changes in the number of particles:

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

From this expression, we see that one way to express μ is $\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$. We saw two other expressions: $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$.

We talked about the case of the ideal gas and computed the chemical potential in the classical regime as $\mu = \tau\ln(n/n_Q)$. We considered the case of a (not necessarily large) system in both thermal and diffusive contact with a large reservoir with chemical potential μ and temperature τ. We used this to describe the probability of being in the state $(N, \mathcal{E})$ as $\frac{1}{\mathfrak{z}}e^{(N\mu-\mathcal{E})/\tau}$, where $\mathfrak{z} = \sum_s e^{(N\mu-\mathcal{E})/\tau}$ is the Gibbs sum (of Gibbs factors).

Part of the reason we are interested in the chemical potential is as a useful tool in understanding the quantum ideal gases, gases outside the classical regime. Recall what we mean by ideal: The particles are non-interacting. We think of a series of particle orbitals which are filled with particles. Suppose the orbitals are $a = 0, 1, 2, \dots$ and the particles are $i = 1, \dots, N$. We can denote a state as $(a_1, a_2, a_3, .., a_N)$ meaning particle 1 is in orbital a_1 etc. By an ideal gas, we mean that $U = \sum_{i=1}^{N}\mathcal{E}(a_i)$.

We discovered that this estimate overcounts, because particles are in fact indistinguishable. In the classical regime, i.e. there are many more orbitals than particles, so we ignore the possibility of multiple occupancy of orbitals and suppose each orbital can only have 0 or 1 particle. Then we had simply overcounted by a factor of $N!$ since there are $N!$ ways to arrange the N particles in N orbitals.

Moving to the quantum regime, we need to consider the possibility that more than one particle is in the same of orbital. For each orbital, we count the number of particles in each, labeling a configuration as $(n_0, n_1, n_2, \dots)$, where $n_a = 0, 1, 2, \dots$.

8.1 Fermions and Bosons

This would work, except we're sort of lying. There are actually two types of indistinguishable particles, bosons and fermions. One of the features of quantum mechanics we didn't get to in Ph12b is the quantization of angular momentum. Particles have intrinsic angular momentum (called spin), which can be either $\hbar n$, making them bosons, or $\hbar(n + \frac{1}{2})$, making them fermions, where n is an integer. Another way to examine this is the operator $\hat{R}(e_z, 2\pi)$ which rotates by 2π radians about some axis e_z. This doesn't change bosons: $|\psi\rangle \mapsto |\psi\rangle$, but it does change fermions: $|\psi\rangle \mapsto -|\psi\rangle$. Of course, when we rotate by 4π, we get the identity: $\hat{R}(e_z, 4\pi) = \hat{I}$. This is "illustrated" by holding an object outwards in one's arm and rotating the object by 2π, which twists the arm.

There are other ways in which this difference arises. An operation that only exchanges two particles' positions fixes the wavefunction for bosons but negates it for fermions. That is, for bosons, $\psi(x_1, x_2) = \psi(x_2, x_1)$, while for fermions, $\psi(x_1, x_2) = -\psi(x_2, x_1)$. For bosons, the wavefunction is symmetric, and for fermions, it is antisymmetric. Yet another way: If we have an orbital, any number of bosons can occupy it. But for fermions, only one particle can be put in the orbital. This is called the *Pauli exclusion principle.*

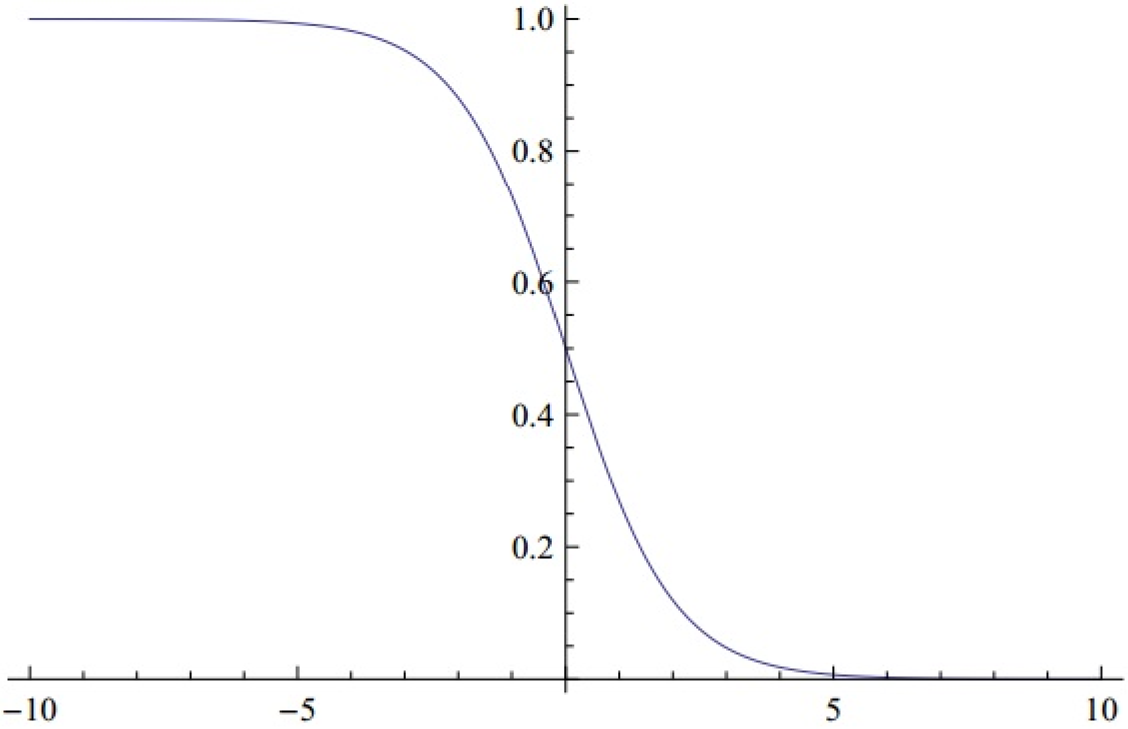
We can derive the Pauli exclusion principle from the exchange property. Considering placing two particles a and b in two orbitals x_1 and x_2, we have $\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2) \pm \psi_a(x_2)\psi_b(x_1)$, a $+$ for bosons and a $-$ for fermions. If $a = b$, these two terms cancel out for fermions, $\psi(x_1, x_2) = \psi_a(x_1)\psi_a(x_2) - \psi_a(x_2)\psi_a(x_1) = 0$, so there is no probability that a state will have two fermions in the same orbital.

We can also relate the 2π rotation property to the exchange property, known as the connection between spin and statistics: If the spin is $\hbar n$, $\hat{R}(e_z, 2\pi) = \hat{I}$, and if the spin is $\hbar(n + \frac{1}{2})$, $\hat{R}(e_z, 2\pi) = -\hat{I}$. So why is exchange equivalent to rotation by 2π? When Feynman was asked this question, he took off his belt (and Feynman was pretty skinny, so this always made it a little bit edgy whether his pants would fall down, less of an issue for Preskill :P). Holding the belt by the two ends, he would exchange the two ends, introducing a twist of 2π in the belt.

Another explanation uses spacetime diagrams and antiparticles. We denote worldlines of regular particles as lines in spacetime going forward with time, and antiparticles as the same lines going backward with time. Then pair creation and annhilation are illustrated as a worldline changing directions in time. Considering a picture with an exchange performed, with worldlines crossing. We can redraw this using pair annihilation and creation, then separate the worldlines. See the online lecture notes for the diagrams. This makes it equivalent to the rotation of one of the particles by 2π and propogation of the other. Since the coefficient of this transformation is either ± 1 but continuously varies, these must have the same coefficient, 1 in bosons and -1 in fermions.

8.2 Fermi-Dirac Statistics

We now return to the fermion system in a big reservoir, where each orbital has 0 or 1 particle in it. Considering a single orbital, the Gibbs sum is $\mathfrak{z} = \sum e^{(N\mu - \mathcal{E})/\tau} = 1 + e^{(\mu - \mathcal{E})/\tau}$. Then the expectated number of particles is $f(\mathcal{E}) = \langle N \rangle_{\mathcal{E}} = \frac{e^{(\mu-\mathcal{E})/\tau}}{1+e^{(\mu-\mathcal{E})/\tau}} = \boxed{\frac{1}{1 + -e^{-(\mathcal{E}-\mu)/\tau}}}$. This is known as the Fermi-Dirac distribution function, even though it's an expectation value. This is because we'll be examining a system with many orbitals. If we graph this against $\mathcal{E}$, we get the following graph:



At $\mathcal{E} = \mu$, $f(\mathcal{E}) = 1/2$, and how quickly it approaches 1 and 0 on either side depends on τ. At $\tau = 0$, it approaches a step function, which makes sense because the lowest energy state will have all of the smallest energy orbitals occupied.

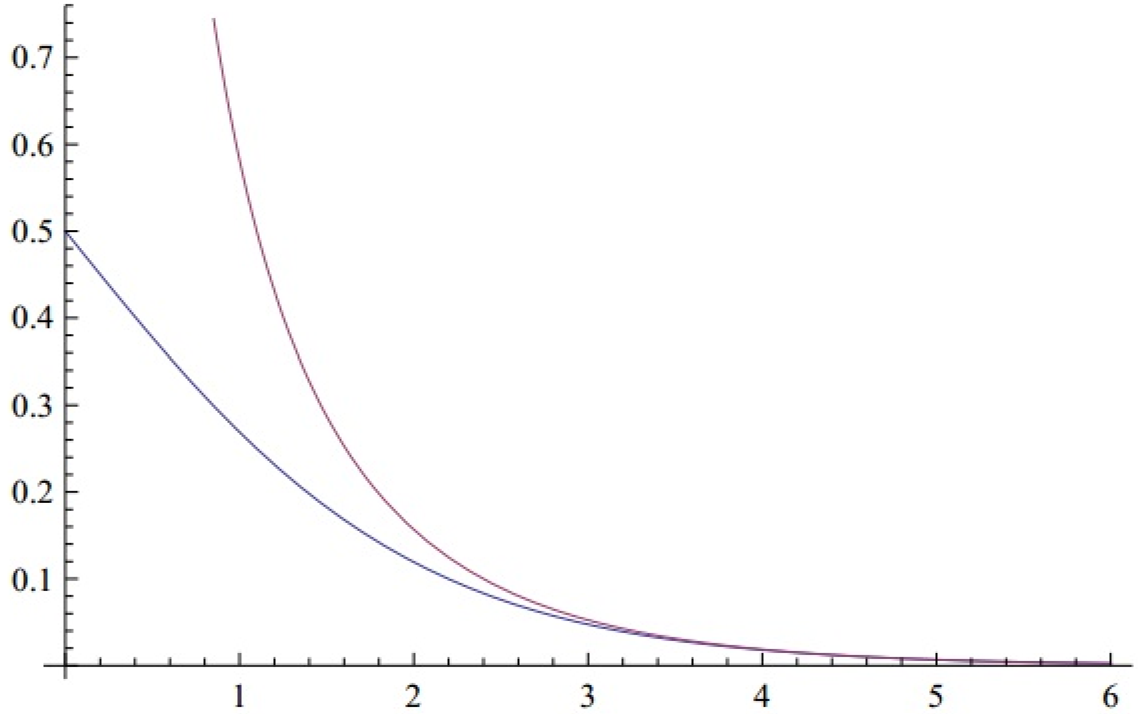
8.3 Bose-Einstein Statistics

Consider one orbital again. If there are N particles in the orbital, the energy is $E = N\mathcal{E}$, so $\mathfrak{z} = \sum_{N=0}^{\infty} e^{N(\mu-\mathcal{E})/\tau} = \frac{1}{1-e^{(\mu-\mathcal{E})/\tau}}$. Then $f(E) = \langle N \rangle_E = \frac{1}{\mathfrak{z}} \sum_{N=0}^{\infty} N e^{N(\mu-\mathcal{E})/\tau}$. In this and other contexts, it is useful for refer to the quantity $e^{\mu/\tau} = \lambda$ as the "activity." Substituting, we get

$$\begin{aligned} f(E) &= \frac{1}{\mathfrak{z}} \sum_{N=0}^{\infty} N\lambda^N e^{-N\mathcal{E}/\tau} = \frac{1}{\mathfrak{z}} \lambda \frac{d\mathfrak{z}}{d\lambda} \\ &= (1-\lambda e^{-\mathcal{E}/\tau}) \frac{\lambda e^{-\mathcal{E}/\tau}}{(1-\lambda e^{-\mathcal{E}/\tau})^2} = \frac{\lambda e^{-\mathcal{E}/\tau}}{1-\lambda e^{-\mathcal{E}/\tau}} \\ &= \frac{1}{\lambda^{-1} e^{\mathcal{E}/\tau} - 1} = \frac{1}{e^{(\mathcal{E}-\mu)/\tau} - 1}. \end{aligned}$$

Notice that this is very similar to $f(\mathcal{E})$ from the Fermi-Dirac distribution, except for the minus sign. We call $f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/\tau} \pm 1}$ the Fermi-Dirac distribution if there is a $+$ and the Bose-Einstein distribution if there is a $-$ sign.

Graphing the Bose-Einstein distribution, it blows up near $\mathcal{E} = \mu$. As $\mathcal{E}$ gets large, though, $e^{(\mathcal{E}-\mu)/\tau} \gg 1$, and the distributions are nearly identical and equal to $e^{(\mu-\mathcal{E})/\tau} = \lambda e^{-\mathcal{E}/\tau}$, the product of the activity and the Boltzmann factor. This is the classical regime, the right side of the graph below.



All of this was done with the correct counting of states, and thus is valid in both classical and quantum regimes. We can rederive our final expression for the chemical potential where we made the strange approximation of dividing by $N!$ when the concentration was small compared with the quantum concentration. This time, that assumption tells us that the vast majority of the orbitals will have energies in the classical regime, so we approximate the distribution function by $f(\mathcal{E}) = \lambda e^{-\mathcal{E}/\tau}$. Summing over states with energy $\mathcal{E}$, we have $N = \langle N \rangle = \sum \lambda e^{-\mathcal{E}/\tau}$. The activity is constant, so we just get $N = \lambda Z_1$, where Z_1 is the single-particle partition function that we have already computed as $Z_1 = V n_Q$, where $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$ is the quantum concentration. Then $n = \frac{N}{V} = \lambda n_Q$, so $\lambda = n/n_Q = e^{\mu/\tau}$, or $\mu = \tau \ln(n/n_Q)$, as desired.

8.4 Thermodynamics of a classical ideal gas

8.4.1 Isothermal Expansion/Compression (reversible)

Consider a gas at constant temperature τ with a piston to compress or expand it. The ideal gas law gives $pV = N\tau$. Then $p_f/p_i = V_i/V_f$ as pV is constant.

How does the entropy change? Our formula gives $\sigma = N\ln(n_Q V/N + 5/2)$, so $\sigma_f - \sigma_i = N\ln(V_f/V_i)$. This makes sense: As the gas expands, there will be more accessible states, which increases the entropy.

How much work is done? $W = \int p\,dV = \int_{V_i}^{V_f} dV\,\frac{NT}{V} = N\tau\ln(V_f/V_i) = \tau\Delta\sigma$.

How much heat flows? Energy doesn't change, so $0 = \int dU = \int \tau\,d\sigma - \int p\,dV = \tau\Delta\sigma - W$, so $W = \tau\Delta\sigma$ and work done equals heat flow. More generally, $dU = dQ - dW$, the heat flow *in* minus the work done *by* the system.

This is just conservation of energy, but we label it the *first law of thermodynamics*. If we reverse this process, isothermally expanding then compressing, for instance, the total work done and heat flow are both zero.

8.4.2 Isentropic (Adiabatic) Expansion/Compression (reversible)

Now we isolate the system, so the heat flow is zero: $dQ = \tau d\sigma = 0$. Since $n_Q \propto \tau^{3/2}$, we have $\sigma = N(\ln V\tau^{3/2} + \text{const}) = \text{const}$, so $V\tau^{3/2}$ is constant. Thus $\tau_f/\tau_i = (V_i/V_f)^{2/3}$. By the ideal gas law, $P_f/P_i = (V_i/V_f)^{5/3}$. In other words, $PV^{5/3}$ is constant, or $pV = \text{const}V^{-2/3}$, so $d(pV) = -\frac{2}{3}(pV)\frac{dV}{V} = -\frac{2}{3}pdV$. Therefore, the work done is $\int pdV = \int -\frac{3}{2}d(pV) = -\frac{3}{2}N(T_f - T_i) = \Delta U$ (since there is no heat flow).

Again, the process can be reversed, and the system goes back to its original configuration. The last process, free expansion of a gas, we'll look at next time; it is not reversible and has to be treated differently.

9 Tuesday, April 27, 2010

Recall: We've looked at isothermal and isentropic compression/expansion of the ideal gas. In isothermal changes, $U = \frac{3}{2}N\tau$, so if τ is constant, U is constant, so $dU = dQ - dW = 0$. In isentropic changes, there is no heat flow, so $dU = -dW$. We saw that both of these processes were reversible; if we isothermally expand and then isothermally compress, there is no net heat flow, work done, change in internal energy, or change in entropy. Similarly, if we isentropically expand and then isentropically compress, there is no net heat flow, work done, change in internal energy, or change in entropy. This is in contrast to the next case we consider.

9.0.3 Free Expansion (irreversible)

Example: Membrane separates two chambers with a vacuum in one, but is punctured, so the gas moves quickly from one chamber to the other. It occurs so rapidly that we can ignore the surroundings. No work is done and there is no heat flow, so there is no change in internal energy: $\Delta Q = \Delta W = \Delta U = 0$. It's an ideal gas, so $\tau_f = \tau_i$. The pressure and volume change, though, inversely as $p_f/p_i = V_i/V_f$.

What happens if we try to reverse this process? We can follow the free expansion by quasi-static compression, isothermal or isentropic. First consider isothermal compression. Recall the formula for entropy: $\sigma = N[\ln(n_Q V/N) + \frac{5}{2}]$ It's isothermal so $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$ doesn't change. Therefore, $\sigma = N\ln V + \text{const}$.

This formula tells us that in free expansion, there's a change in the entropy of the gas of $\Delta\sigma = N\ln(V_f/V_i)$. What isn't true is that $Q \neq \int \tau\, d\sigma$ and $W \neq -\int p\, dV$. Both of these are zero, but the integrals are not.

Subsequent isothermal compression will reduce the entropy of the system back to the initial value as V changes from V_f to V_i. But isothermal changes do net work on the system, and there is net heat flow. Thus for the combined process of free expansion followed by isothermal compression, the entropy of the system $\Delta\sigma_S = 0$, but the entropy of the reservoir $\Delta\sigma_R > 0$ since heat flows out of the system into the reservoir. In all, the entropy increases: $\Delta_{S+R} > 0$.

Isentropic compression from V_f to V_i will increase the temperature, and the internal energy increases. This makes the net change in the entropy of the system from before the free expansion at V_i to after the free expansion and isentropic compression $\Delta_S > 0$. The reservoir $\Delta\sigma_R = 0$, but the total entropy $\Delta_{S+R} > 0$.

These two examples illustrate the *second law of thermodynamics*, which says that the total entropy $\Delta_{S+R} \geq 0$, with equality for reversible processes.

9.1 Ideal Fermi Gas

Ideal, as usual, means the particles don't interact. The internal energy is $U = \sum_i N_i\mathcal{E}_i$ where the sum is over orbitals i. We no longer assume that the gas is dilute, $n \ll n_Q$.

9.1.1 Degenerate Fermi gas

Let's start at zero temperature. Taking the limit as $\tau \to 0$, $f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/\tau}+1}$, and we get a step function: $f(\mathcal{E}) = 1$ for $\mathcal{E} < \mu$ and $f(\mathcal{E}) = 0$ for $\mathcal{E} > \mu$. We call $\mu(\tau = 0) = \mathcal{E}_F$ the *Fermi energy.* Each orbital below the Fermi energy gets occupied, and each orbital above the Fermi energy is unoccupied.

We've counted states before with fixed boundary conditions; let's also consider periodic boundary conditions: Our solutions will be $\psi(x,y,z) = e^{i\vec{k}\cdot\vec{x}}$, and with $\psi(x+L,y,z) = \psi(x,y,z)$, $k_x = \frac{2\pi}{L}n_x$, and similarly $k_y = \frac{2\pi}{L}n_y$ and $k_z = \frac{2\pi}{L}n_z$, where n_x, n_y, n_z are integers. Unlike the previous case, these can be positive or negative, not just positive. Summing n_x, n_y, n_z over all integer values, we transform into a Riemann approximation of an integral over k: $\left(\frac{L}{2\pi}\right)^3 \sum_{n_x,n_y,n_z} \left(\frac{2\pi}{L}\right)^3 = \frac{L^3}{(2\pi)^3}\int d^3k = \frac{V}{(2\pi)^3}\int d^3k$. Since $p = \hbar k$, we count the number of orbitals as $\int dn = \frac{V}{(2\pi\hbar)^3}\int d^3p = \frac{1}{h^3}\int d^3x d^3p$. This brings up the easy-to-remember statement that $1/h^3$ is the density of states per unit of (x,p) phase space. In D dimensions, this generalizes to the number of orbitals being $\frac{1}{h^D}\int d^Dx d^Dp$.

Let's return to the degenerate (zero temperature) Fermi gas. We're going to consider the particles as electrons, making the rather dubious assumption that electrons don't interact. The only feature of electons that we'll use is that they exist in one of two spin states. This provides a factor of 2 out front in the number of filled orbitals: $N = 2\int_0^{k_F} \frac{V}{(2\pi)^3}\, d^3k$. Now k_F is the maximum $\left|\vec{k}\right|$ for filled orbitals. We're integrating over the sphere, getting $N = \frac{2V}{(2\pi)^3}\int_0^{k_F} 4\pi k^2\, dk = \frac{V}{\pi^2}\int_0^{k_F} k^2\, dk = \frac{V}{3\pi^2}k_F^3$. We can use this to solve for $k_F^3 = 3\pi^2 N/V = 3\pi^2 n$.

Since they're nonrelativisic particles, we can write their energy as $\mathcal{E} = p^2/2m = \frac{\hbar^2}{2m}k^2$, so $\mathcal{E}_F = \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$.

Now let's compute the energy U_0 of the ground state. We have to sum energies up to the Fermi energy:

$$\begin{aligned}
U_0 &= 2\frac{V}{(2\pi)^3}\int_0^{k_F} d^3k\, \frac{\hbar^2 k^2}{2m} = 2\frac{V}{(2\pi)^3}\int_0^{k_F} dk (4\pi k^2)\frac{\hbar^2}{2m}k^2 = \frac{V}{\pi^2}\frac{\hbar^2}{2m}\int_0^{k_F} dk\, k^4 \\
&= \frac{V}{\pi^2}\frac{\hbar^2}{2m}\frac{1}{5}k_F^5 = \left(\frac{V}{3\pi^2}k_F^3\right)\frac{3}{5}\frac{\hbar^2}{2m}k_F^2 = \frac{3}{5}N\mathcal{E}_F \\
U_0/N &= (3/5)\mathcal{E}_F.
\end{aligned}$$

There's now another way to compute quantities in the ground state. For the whole system, $X = \sum_i f(\mathcal{E}_i)X_i = \int d\mathcal{E}\mathcal{D}(\mathcal{E})f(\mathcal{E})X(\mathcal{E})$, where $\mathcal{D}(\mathcal{E})$ is the density of orbitals per unit of energy. We can calculate this. First, $\int dN = \frac{V}{(2\pi\hbar)^3}\int d^3p = \frac{V}{(2\pi\hbar)^3}\int dp\, 4\pi p^2$. For a nonrelativisitic particle, $p^2 = 2m\mathcal{E}$, so $dp = d\sqrt{2m\mathcal{E}} = \sqrt{2m}\frac{1}{2}\mathcal{E}^{-1/2}d\mathcal{E}$. We get

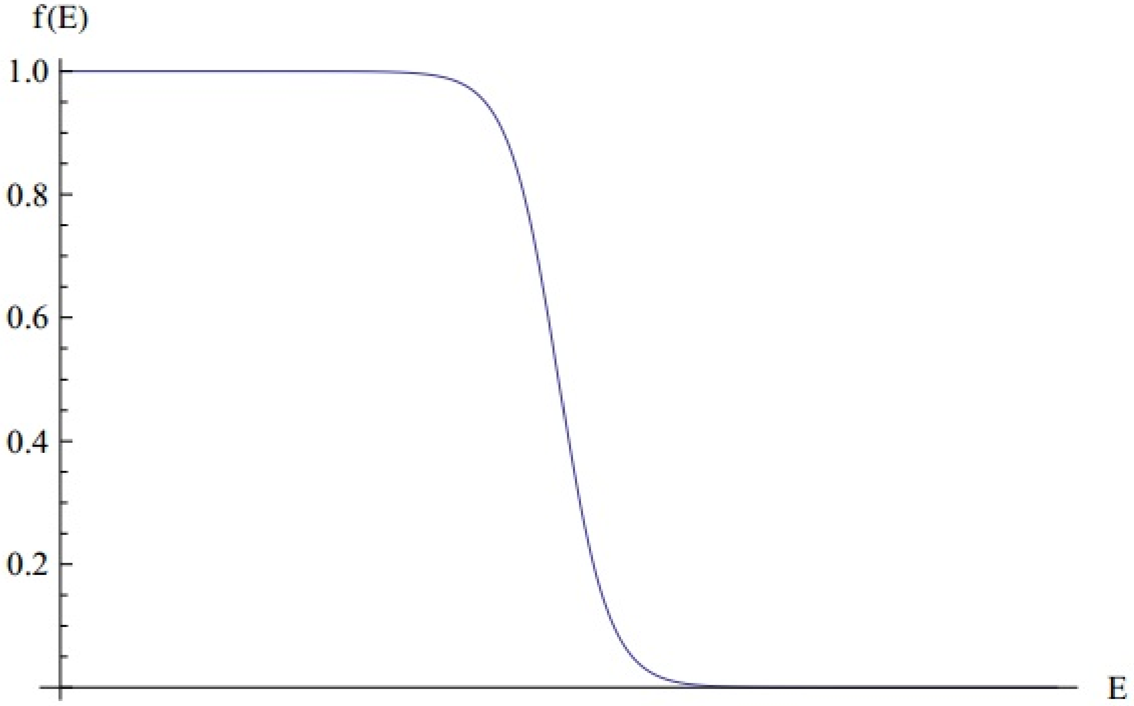
$$\frac{V}{(2\pi\hbar)^3}4\pi p^2 dp = \frac{V}{(2\pi\hbar)^3}4\pi(2m\mathcal{E})\sqrt{2m}\frac{1}{2}\mathcal{E}^{-1/2}\, d\mathcal{E}$$

Therefore, the density of states is

$$\mathcal{D}(\mathcal{E}) = (\text{spin factor})\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mathcal{E}^{1/2}.$$

9.1.2 Nearly degenerate Fermi gas

Now let's consider low temperature: $\tau \ll \mathcal{E}_F$. The step function gets slightly curved. The distribution is of the form $\frac{1}{e^x+1} = \frac{1}{2} - \frac{1}{2}\frac{e^x-1}{e^x+1} = \frac{1}{2} - \frac{1}{2}\frac{e^{x/2}-e^{-x/2}}{e^{x/2}+e^{-x/2}} = \frac{1}{2} - \frac{1}{2}\tanh(x/2)$, where $x = \frac{\mathcal{E}-\mu}{\tau}$, the deviation of energy from chemical potential in units of temperature.



$f(\mathcal{E})$ still varies from 1 to 0 over a small range of energies. We therefore assume that the density of states is approximately constant around this point, $\mathcal{D}(\mathcal{E}) \approx \mathcal{D}(\mathcal{E}_F)$.

Now we argue that the chemical potential does not change when we increase the temperature. At least, we argue that the linear term in the power series expansion of μ in τ is null. Normally, we would expect to have to either change the particle number or the chemical potential when we change the temperature, but we claim that these effects are not large when we increase the temperature a small amount above 0.

Now $N = \int d\mathcal{E}\mathcal{D}(\mathcal{E})f(\mathcal{E})$, so $\dfrac{dN}{d\tau} = \int d\mathcal{E}\mathcal{D}(\mathcal{E})\dfrac{\partial}{\partial\tau}f(\mathcal{E}) = \mathcal{D}(\mathcal{E}_F)\int d\mathcal{E}\dfrac{\partial}{\partial\tau}f(\mathcal{E})$. We compute that $\dfrac{\partial}{\partial\tau}f = \dfrac{\partial x}{\partial\tau}\dfrac{\partial}{\partial x}f(x) = -\frac{\mathcal{E}-\mu}{\tau^2}\left(-\frac{1}{4}\operatorname{sech}^2\left(\frac{x}{2}\right)\right)$, which is a product of an odd and an even function of x, hence odd. Therefore, it integrates to 0 and at a fixed chemical potential, the number of particles involved remains constant when we change the temperature among small values.

Intuitively, this is saying that the little bit we've rounded off the top of our distribution function matches the rounded part we've added, and as long as they are at comparable energies (low temperature), they'll have similar orbital densities.

Let's use these computations to get the heat capacity. The energy is $U = \int d\mathcal{E}\mathcal{D}(\mathcal{E})f(\mathcal{E})$, so keeping the volume fixed, the heat capacity is

$$\begin{aligned} c = \frac{dU}{d\tau} &= \int d\mathcal{E}\,\mathcal{E}\mathcal{D}(\mathcal{E})\mathcal{E}\frac{\partial f}{\partial\tau} = \tau\mathcal{D}(\mathcal{E}_F)\int\frac{d\mathcal{E}}{\tau}\left[\frac{\mathcal{E}-\mathcal{E}_F}{\tau}+\mathcal{E}_F\right]\frac{\partial f}{\partial\tau}\tau \\ c &= \tau\mathcal{D}(\mathcal{E}_F)\int_{-\infty}^{\infty} dx\,x\frac{1}{4}x\operatorname{sech}^2(x/2) \\ \left(\frac{\partial U}{\partial\tau}\right)_V &= \frac{\pi^2}{3}\tau\mathcal{D}(\mathcal{E}_F). \end{aligned}$$

That integral can be computed with knowledge of the Riemann zeta function, or you can just use Mathematica. We can relate this to the particle number: $N = \int_0^{\mathcal{E}_F} d\mathcal{E}\,\mathcal{D}(\mathcal{E}) \propto \mathcal{E}_F^{3/2}$. Then $\left.\dfrac{dN}{d\mathcal{E}}\right|_{\mathcal{E}=\mathcal{E}_F} = \mathcal{D}(\mathcal{E}_F)$, so

$\mathcal{D}(\mathcal{E}_F) = \frac{3}{2}\frac{N}{\mathcal{E}_F}$. Therefore, $c = \frac{\pi^2}{2}N(\tau/\mathcal{E}_F)$.

10 Thursday, April 29, 2010

We can think of the expression $c = \frac{\pi^2}{2}N(\tau/\mathcal{E}_F)$ as a power series expansion in the dimensionless variable $\tau/\mathcal{E}_F$, with the first nonzero term.

10.1 Heat capacity in metals

Recall Debye theory's τ^3 law: $c_V = A\tau^3$, where $A = \frac{12\pi^4}{5}N\theta^{-3}$. There are also effects of electron-electron repulsion on the this result, but those effects can actually be adjusted for by changing the mass of the electron by a factor around 1.

Let's consider potassium, which has density $n = 13 \times 10^{22}$ cm^{-3}. There is around 1 electron per atom. The Fermi energy is $\mathcal{E}_F = 2.1$ eV, comparable to the Rydberg energy. Converting this to a temperature, we get 24,000 K, so $\tau/\mathcal{E}_F \approx .01$ and this is a nearly degenerate electron gas. Then the heat capacity is $c = \gamma\tau + A\tau^3$, where $\gamma = \frac{\pi^2}{2}\frac{N}{\mathcal{E}_F}$. Also, $\theta \approx 91$ K.

What does Debye theory predict? It will be linear at small τ and cubic at large τ. We expect a cross-over where the terms are comparable, i.e. $\gamma = A\tau^2$, or $\left(\frac{\tau}{\theta}\right)^2 \approx \frac{5}{24\pi^2}\frac{\theta}{\mathcal{E}_F} \approx .008$, i.e. $\tau \approx 1$ K. Therefore, Debye theory should work down to a degree Kelvin, but below that the linear term dominates. This is indeed what we observe.

We have to adjust the γ by a factor of order 1, i.e. $\gamma = \gamma_{calc} \times O(1)$. The reason is that we should have used an effective mass for the electron, because the electrons in the system reside in energy bands and are not free, so that the energy is given by $\mathcal{E} = \hbar^2k^2/(2m_{eff})$ where $m_{eff} = m \times O(1)$. This comes into γ since $\gamma = \frac{\pi^2}{2}\frac{N}{\mathcal{E}_F} = \frac{\pi^2}{2}\frac{N\,2m_{eff}}{\hbar^2(3\pi^2 n)^{2/3}}$, which explains why the result we wrote before is out by a factor $O(1)$.

10.2 White Dwarfs and Neutron Stars

A white dwarf is a possible endpoint of stellar evolution for stars like the sun. One of the first observed examples was the binary companion of Sirius. We know from the orbital dynamics that Sirius B has a mass of around $M_\odot \approx 2 \times 10^{33}$ g. We can calculate the luminosity and temperature and use the Stefan-Boltzmann law to compute the radius, as $R \approx 20,000$ km. This is actually quite small; the sun has a radius of $\mathbb{R}_\odot \approx 700,000$ km. The density is then $M/V \approx 20$ kg cm^{-3}, around 20,000 times as dense as the sun.

Let's try to model this. Suppose the white dwarf is uniform. Given that density, the Fermi energy is 3×10^5 eV, which is much greater than the Rydberg energy. Translated into a temperature, this is very hot, 3×10^9 K, which is much greater than the surface temperature, so the white dwarf is nearly degenerate.

What determines the radius of a white dwarf? Gravitational collapse wants to pull it inwards, but the degeneracy that results when the star is compressed, increasing the Fermi energy, actually pushes outwards. The size is a result of this competition.

The gravitational energy is $-GM^2/R$. The electron kinetic energy is $U \sim N\mathcal{E}_F \sim N\frac{\hbar^2}{m_e}\left(\frac{N}{V}\right)^{2/3} = \frac{\hbar^2}{m_e}\frac{N^{5/3}}{R^2}$. We make one more approximation to relate N to the mass: We'll have 1 electron per proton, and a comparable number of neutrons perhaps, but that's just a factor of 2 or so, so $N \sim \frac{M}{m_p}$, where m_p is the mass of the proton. Then the total energy is given by

$$E = \frac{\hbar^2}{m_e}\left(\frac{M}{m_p}\right)^{5/3}\frac{1}{R^2} - \frac{GM^2}{R}.$$

Therefore, this has a stable equilibrium at a radius on the order

$$R_{WD} \sim \frac{1}{\sigma M^2}\frac{\hbar^2}{m_e}\left(\frac{M}{m_p}\right)^{5/3} = \frac{\hbar^2}{Gm_e m_p^{5/3}}M^{-1/3}.$$

Therefore, as the mass of the dwarf increases, it gets smaller. We might think that the dwarf can just increase in mass without limit. But we've been ignoring something that matters: The electrons are going to go relativistic. In fact, their rest mass is 511 keV, and we found the Fermi energy for the companion of Sirius as 300 keV, so it might not even be a good approximation here.

Let's analyze that relativistic limit. We have $\mathcal{E} = \sqrt{p^2c^2 + m^2c^4}$. In the extreme relativistic limit, $\mathcal{E} = pc = \hbar kc$. The density is $\frac{N}{V} = \int_0^{k_F} \frac{d^3k}{(2\pi)^3} \sim k_F^3$. The energy density is $\frac{U}{V} = \int_0^{k_F} \frac{d^3k}{(2\pi)^3} \hbar kc = (\hbar c)k_F^4$, so the electron kinetic energy is $U = \hbar cV(N/V)^{4/3} \sim \hbar cN^{4/3}\frac{1}{R}$. This varies as $1/R$, not $1/R^2$ as before. The total energy is $E = \frac{\hbar cN^{4/3}}{R} - \frac{GM^2}{R}$. The star will collapse when these coefficients are comparable: $GM^2 \sim \hbar cN^{4/3} \sim \hbar c\left(\frac{M}{m_p}\right)^{4/3}$, or $M^{2/3} \sim \frac{\hbar c}{G}m_p^{-4/3}$. Therefore, $M \sim \left(\frac{\hbar c}{G}\right)^{3/2}\frac{1}{m_p^2}$. That fraction is actually in units of mass, the Planck mass: $\frac{\hbar c}{G} \sim (10^{-5}\text{ g})^2 = M_{\text{Planck}}^2$. Planck actually claimed that one could write mass in terms of elementary constants before discovering the constant that bears his name. Anyways, we can compute the limit, known as the Chandra(sekhar) limit $M_{\text{Chandra}} \sim \frac{M_{\text{Planck}}^3}{m_p^2} \sim 10^{33}\text{ g} \sim M_\odot$.

There are two things to do this analysis correctly: Use the actual estimate for energy, not the relativistic limit, and use the fact that the density varies with radius. Chandrasekhar did this estimate, and he got a mass of $1.4M_\odot$.

So what happens if the mass exceeds the Chandra mass? Well, with relativistic electrons, the reaction $p + e \to n + \nu_e$ occurs. This removes a lot of the electrons, and the star will continue to collapse. Or will it? Neutrons are fermions, too! So we can go through the same analysis. The number of neutrons will again be about $M/m_p \approx M/m_n$. There's a Chandrasekhar limit again, at around 1 solar mass again. Since the neutron is 1800 times heavier, the radius is going to be 1800 times smaller as before, around 10 km if the companion of Sirius's companion. We can't really ignore nucleon interactions, so if we redo the calculations, we get a mass of around $3M_\odot$.

When a white dwarf collapses to a neutron star, it releases an energy of $\frac{GM^2}{R} \sim 10^{53}$ ergs. It's a supernova! Where does that energy go? Most of it is carried away by neutrinos. But since they have to go through a mass of nuclear density, they bounce around a bit, imparting some energy in blowing up the star. Before we were born, in 1987, there was a supernova in the Large Magellanic Clouds that was close enough for us to detect with our neutrino detectors.

Why is it so bright? This is a rather difficult question. Around 1987, people were trying to model supernovae, but weren't succeeding very much.

What happens if the neutron star collapses? We get a black hole. This occurs when the gravitational potential energy is comparable to the rest mass, i.e. $\frac{GM^2}{R} \sim Mc^2$, or $R_{\text{Schwarzchild}} = \frac{2GM}{c^2} = 3$ km for a star of solar mass. You won't see it any more with ordinary telescopes, but you might see some gravitational waves. It has to collapse asymmetrically, though. Just like with electromagnetic radiation, a radially symmetric collapse does not have a dipole moment, so it doesn't release radiation. You need a dipole or quadrupole moment.

10.3 Ideal Bose Gas

Let's first consider $\tau = 0$. Since degeneracy is not a problem, the distribution function of occupancy will be a spike at $\mathcal{E}_0$, the smallest energy orbital. At small τ, there are a lot of particles in the lowest orbital and a few in higher energy orbitals. The fraction of particles in the ground state will be $O(1)$. When this is the case, we say that we have a *Bose-Einstein condensate* (BEC).

A natural way to express the feature that the temperature is small is the following: Quantum behavior dominates when $n \sim n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$.

Question: Our distribution is not very different from the Planck distribution. Why don't we get a BEC for photons? Answer: It's different because photon number is not conserved, but here we're considering a conserved number of particles.

Let's put the lowest energy orbital at $\mathcal{E} = 0$. The Bose-Einstein distribution was $f(\mathcal{E}) = \frac{1}{e^{(\mathcal{E}-\mu)/\tau} - 1}$. Then

$f(0) = N_0(\tau) = \frac{1}{e^{-\mu/\tau}-1} \gg 1$. This is the number of particles in the lowest energy orbital. We approximate $\frac{1}{e^{-\mu/\tau}-1} \approx -\frac{\tau}{\mu}$. In order for this to be large, we need μ negative but close to zero.

Now we can solve for the chemical potential given N_0: $\mu = -\tau/N_0$. We can also solve for the number of particles in excited states:

$$N_e = \int_0^\infty d\mathcal{E}\, \mathcal{D}(\mathcal{E}) f(\mathcal{E}, \tau, \mu)$$

where $\mathcal{D} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mathcal{E}^{1/2}$, for spinless nonrelativistic particles in 3D, and $f(\mathcal{E},\tau,\mu) = \frac{1}{e^{(\mathcal{E}-\mu)/\tau}-1} = \frac{1}{\lambda^{-1}e^{\mathcal{E}/\tau}-1} \sim \frac{1}{e^{\mathcal{E}/\tau}-1}$ since μ is close to zero. Then we get

$$N_e(\tau) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty d\mathcal{E}\,\frac{\mathcal{E}^{1/2}}{e^{\mathcal{E}/\tau}-1}.$$

Substituting with $x = \mathcal{E}/\tau$, $\mathcal{E}^{1/2} = \tau^{1/2}x^{1/2}$ and $d\mathcal{E} = \tau dx$, so we get

$$N_e(\tau) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\tau^{3/2}\int_0^\infty d\mathcal{E}\,\frac{x^{1/2}}{e^x-1}.$$

Now $\frac{N_e(\tau)}{V} = n_e(\tau) = 2.61 n_Q$, where the quantum concentration $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$. This makes sense as long as the total number of electrons in the ground state here is less than the total number of electrons. It's also derived on the assumption that $N_0(\tau) \gg 1$.

11 Tuesday, May 4, 2010

11.1 Bose-Einstein Condensation

Recall: For bosons, the expected occupancy of an orbital of energy $\mathcal{E}$ is $f(\mathcal{E}) = \dfrac{1}{e^{(\mathcal{E}-\mu)/\tau}-1}$. That's the Bose-Einstein distribution. For convenience, define the ground orbital to have energy 0.

If the temperature were zero, we would put all of the particles in the ground state. This makes a distribution peaked sharply at 0. If we increase the temperature by a small amount, we'll still get a sharp spike at 0 and then a continuous energy distribution above that. What does a spike mean? It means that $\frac{N_0}{N} > 0$ even as $N \to \infty$.

This distribution is similar to the Planck distribution, except for the spike, and the fact that the particles are nonrelativistic, unlike Planck's relativistic photons. Also, we want to conserve the number of particles, so the chemical potential must change with τ. Our spike requires that $N_0 \approx \frac{-\tau}{\mu} \to \infty$ as $N \to \infty$, which means that $\mu \to 0$, so $\lambda = e^{\mu/\tau} \to 1$.

Let's find the temperature at which the Bose-Einstein condensation occurs. We should have $N_e(\tau) + N_0(\tau) = N$. We'll compute N_e assuming $\mu = 0$, and when that equals N, we'll have the *Einstein temperature* τ_E, the critical temperature so BEC occurs for $\tau < \tau_E$.

To compute the number of particles in the excited states, we as usual convert the sum to an integral: $N_e(\tau) = \int_0^\infty d\mathcal{E}\,\mathcal{D}(\mathcal{E})f(\mathcal{E},\tau)$. We've worked out that $\mathcal{D}(\mathcal{E}) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mathcal{E}^{1/2}$ for nonrelativistic ($\mathcal{E} = p^2/2m$) spinless bosons in 3D space. The distribution function $f(\mathcal{E},\tau) = \frac{1}{e^{\mathcal{E}/\tau}-1}$. The integral is then

$$N_e(\tau) = \int_0^\infty d\mathcal{E}\,\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mathcal{E}^{1/2}\frac{1}{e^{\mathcal{E}/\tau}-1}.$$

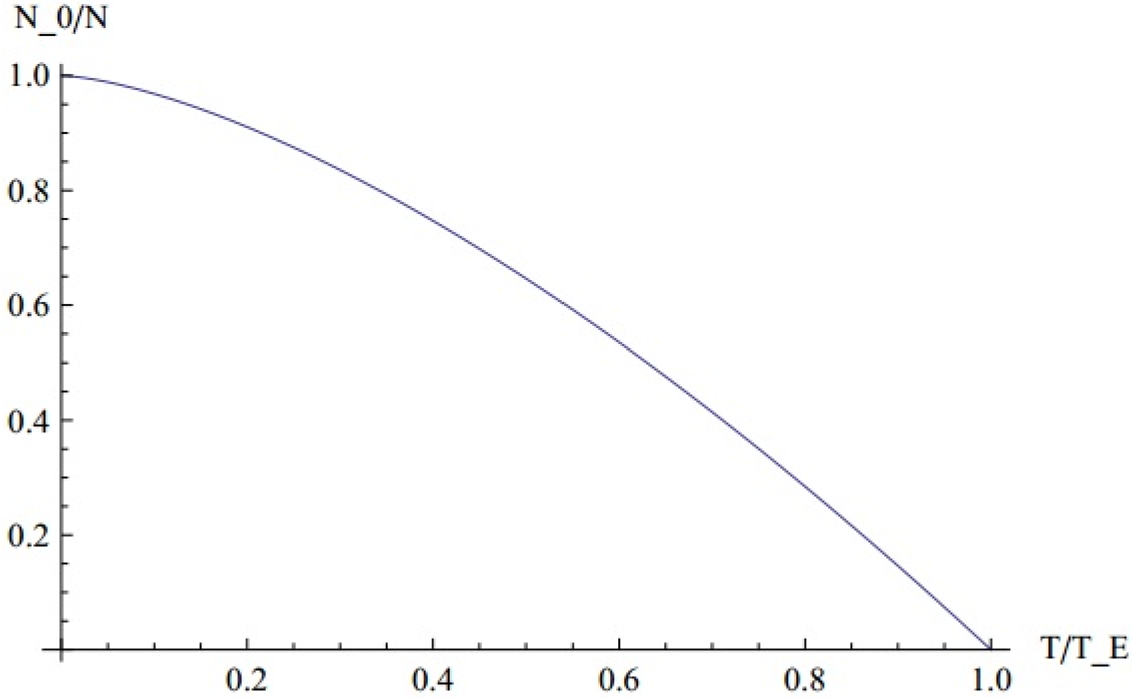
With $x = \mathcal{E}/\tau$, $\mathcal{E}^{1/2} = \tau^{1/2}x^{1/2}$ and $d\mathcal{E} = \tau\, dx$, this becomes

$$N_e(\tau) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\tau^{3/2}\underbrace{\int_0^\infty dx\,\frac{x^{1/2}}{e^x-1}}_{1.306\sqrt{\pi}} = \frac{V}{4\pi^{3/2}}2^{3/2}\left(\frac{m\tau}{\hbar^2}\right)^{3/2}(1.306) = V(2.61)n_Q,$$

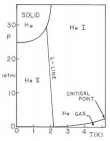
where again $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$ is the quantum concentration. Therefore, the excited concentration is $n_e = 2.61 n_Q$, when we assume that $\mu \approx 0$, i.e. we are looking at a Bose-Einstein condensate.

The critical temperature is attained when $n_e = n$. Solving, we get $\tau_E = \frac{2\pi\hbar^2}{m}\left(\frac{n}{2.61}\right)^{2/3}$. In other words, as $\left(\frac{m\tau}{\hbar^2}\right)^{3/2} \sim k^3$, the wavenumber. We've determined that Bose-Einstein condensation occurs when this is comparable to $n \sim \frac{1}{r^3}$ where r is the typical distance between neighboring particles. In other words, BEC occurs when the de Broglie wavelengths of the particles are comparable to the distances between them, i.e. their wavepackets start overlapping.

At $\tau < \tau_E$, our peak is $\frac{n_0}{n} = 1 - \frac{n_e}{n} = 1 - \left(\frac{\tau}{\tau_E}\right)^{3/2}$. This is plotted below:



Until 15 years ago, the main example of a Bose-Einstein condensation was liquid helium. Here we have $n^{-1} = 273$ cm^3 mol-1, and $m = 6.6 \times 10^{-24}$ g. We compute the Einstein temperature as $T_E = 3.1$ K. Something strange does happen with liquid helium at low temperature, but it occurs at 2 degrees, not 3. It becomes a superfluid, known as liquid helium II. The phase diagram is below.



Helium II flows without resistance. This is rather complicated, but a simplified explanation says that superfluid flow is a result of particles occupying the ground orbital and normal fluid flow is a result of particles being in excited orbitals.

We can test this hypothesis that this has to do with BEC by looking at other isotopes of helium. Helium-3 consists of fermions, since there are an odd number of particles, and it doesn't become superfluidic until 10^{-3} K. Why does this happen? The atoms pair up, forming a BEC.

A superfluid does not generally occur for an ideal gas of nonrelativistic bosons. Interactions are important. Usually particle motion is impeded by viscosity. Elementary excitations in the fluid scatter off moving objects. We can model this with usual kinematics. Conservation of energy gives $\frac{1}{2}MV^2 = \frac{1}{2}MV'^2 + \mathcal{E}$ and $M\vec{V} = M\vec{V}' + \vec{p}$. Dotting this last relation with itself, $M^2V'^2 = M^2V^2 + p^2 - 2M\vec{V}\cdot\vec{p} = M^2V^2 - 2M\mathcal{E}$, so $\mathcal{E} = \vec{V}\cdot\vec{p} - p^2/2M$. In the limit of large M, $\mathcal{E} = \vec{V}\cdot\vec{p} \le Vp$.

Therefore, scattering is not allowed if $\mathcal{E}_p > pV$. Therefore, there's a critical velocity $V_c = \min(\mathcal{E}_p/p)$ under which no scattering of large particles occurs. To predict a superfluid, we need this critical velocity to be nonzero. Normally, $\mathcal{E}_p = p^2/2m$, so $\mathcal{E}_p/p = p/2m$, which can get arbitrarily small, so there is no superfluidity. In other words, the dispersion relation of $\mathcal{E}_p$ plotted against p needs to approach a line with nonzero slope as p gets small. How do we get the dispersion relation? We have to consider (1) the hard core interaction between helium-4 atoms, and (2) Bose-Einstein statistics. And that's how it's done.

As he said, before 15 years ago, and the book is older than 15 years, this was the only example. Experimental physicists have gotten very good recently at cooling atomic gases. Because they're so proud of this, they call this *ultracold atomic gases*. There are a couple sources available on the website with more information. The BEC homepage was put together by Cornell and Wieman, and it has a tutorial letting you cool the gases yourself. There's also a review article by Wolfgang Ketterle.

How did they get so good at cooling gases? They used rubidium (Cornell and Wieman) or sodium (Ketterle), which have a critical temperature of a few micro degrees Kelvin at a concentration of 10^{14} cm^{-3}. They trapped the particles with an inhomogeneous magnetic field. Another strategy is called "optical molasses" involving shooting lasers at the atoms. Tune the lasers so that the atoms that are moving towards the light see a blue-shifted light, which you make more similar to the absorption band of the atom. Then it will re-radiate nearly uniformly, so on average it slows down. You can use this with laser cooling to get down to 100 microkelvin. After that, they used evaporative cooling. It's important that you allow the particles to re-equilibrate, so they fall into the ground state, so you have to go slow enough for that. But you can't go too slow, since you don't want to lose all the particles. If you do all of this right, you'll get down to 1 microkelvin, and 10^7 or so molecules are in the ground state.

So after getting this cold enough, we can compare to our predictions for Bose-Einstein condensation. Or can we? The biggest difference is that we now have an external potential, like a trapping harmonic well, not just a box. So let's redo the theory for a harmonic oscillator.

The Hamiltonian is $H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2}m\omega_0^2(x^2 + y^2 + z^2)$. This separates into three harmonic oscillators. The energy will depend on three nonnegative integers: $E(n_x, n_y, n_z) = \hbar\omega_0(n_x + n_y + n_z)$. Actually, there should be a $\frac{3}{2}$ there too, but we subtract it off to make the ground state have 0 energy.

The distribution function is

$$N_e(\tau) = \sum_{n_x,n_y,n_z} \frac{1}{e^{\hbar\omega_0(n_x+n_y+n_z)\tau} - 1},$$

where we assume $\mu = 0$. Let's assume that $\frac{\hbar\omega_0}{\tau} \ll 1$. This allows us to approximate this sum by an integral. It becomes

$$\left(\frac{\tau}{\hbar\omega_0}\right)^3 \int_0^\infty dxdydz\, \frac{1}{e^{x+y+z} - 1},$$

where $x = \hbar\omega_0 n_x/\tau$ and y and z are similar. Denoting this big integral as I, a constant, we have $\tau_E = \hbar\omega_0 N^{1/3} I^{-1/3}$, and $I^{-1/3} \approx .94$. Below this temperature, we get $N_e/N = (\tau/\tau_E)^3$.

How do we relate these two equations for the Einstein temperature? For an ideal gas, $T_E \sim \frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3}$ and for the harmonic well, $T_E \sim \hbar\omega_0 N^{1/3}$. We claim that these answers agree in order of magnitude. To do so, we need to have a notion of volume for the harmonic well. Suppose that $E_n = n\hbar\omega_0 \sim T_E$. Then the size of the nth orbital will be an estimate for the volume. We have $(\Delta x)^2 = n\frac{\hbar}{m\omega_0}$, so the volume is $V \sim (\Delta x)^3 \sim \left(\frac{n\hbar}{m\omega_0}\right)^{3/2}$. Then $\frac{N}{V} = N\left(\frac{m\omega_0}{n\hbar}\right)^{3/2}$, so $\left(\frac{N}{V}\right)^{2/3} \sim N^{2/3}\frac{m\omega_0}{n\hbar}$. The computation for the ideal gas is then $T_E \sim \frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3} \sim \hbar\omega_0\frac{N^{2/3}}{n} \sim \hbar\omega_0 N^{1/3}$.

The thermal deviations from the mean position is given by $(\Delta x)_{\text{thermal}} = \sqrt{n}\sqrt{\frac{\hbar}{m\omega_0}}$, and the width of the ground state is $(\Delta x)_0 = \sqrt{\frac{\hbar}{m\omega_0}}$, so $\frac{(\Delta x)_0}{(\Delta x)_{\text{thermal}}} = N^{-1/6}$. This means that for a big gas, the population distribution at high temperatures is much wider than the BEC width, which is the width of the ground state. Check out the tutorial on the BEC homepage and try to see this result.

12 Thursday, May 6, 2010

One complicated setup that Ketterle discusses in his article on BEC is colliding two Bose-Einstein condensates. The result is similar to the two-slit experiments we talked about last term.

If you shine a laser on a BEC, it creates in effect a periodic potential. Since the BEC is already mostly in the ground state, the atoms will fill each potential well, and you can control it so there is one atom per well. This creates an artifical crystal, and you can measure its properties.

12.1 Heat Engine

We have a system S which can be coupled with one of two reservoirs: R_h at temperature τ_h and R_l at temperature τ_l, where $\tau_h > \tau_l$. We couple S with R_h, transferring heat Q_h into the system, then couple S with R_l, transferring heat Q_l out of the system.

By conservation of energy, $dU = \bar{d}W + \bar{d}Q$. We put bars through the d's to denote that these are not conserved quantities. U is conserved, so if you integrate, $\oint dU = U_f - U_i = 0$. Similarly, volume is conserved, $\oint dV = V_f - V_i = 0$. The work $\oint p dV$, though, does not have to be zero. Indeed, we can consider loops in $p - V$ space which enclose some area, and the integral will be the area enclosed. That's the work done. We can say the same things about the heat.

We're going to consider a cycle of the heat engine. A guiding idea is that the entropy is nondecreasing. In a cycle, the system's entropy will return to its initial value, but the entropy gained or lost at the high and low temperature reservoirs must be nonnegative. In fact, we will make the heat engine operate reversibly, so the entropy change is zero. Therefore, $Q_h = \tau_h \Delta\sigma$ and $Q_l = \tau_l \Delta\sigma$ (we've defined Q_h as heat drawn into the system and Q_l as heat drawn out of the system), so $Q_h/Q_l = \tau_h/\tau_l$. In a cycle, $\Delta U = 0$, so the work done is $W = Q_h - Q_l = Q_h(1 - \tau_l/\tau_h) = \frac{\tau_h - \tau_l}{\tau_h} Q_h$.

We then define the efficiency of the conversion of heat to work as the fraction of heat drawn from the high temperature reservoir that is converted to useful work: $\eta = \frac{W}{Q_h} = \frac{\tau_h - \tau_l}{\tau_h} = \eta_C$, known as the Carnot efficiency, because it was discovered by Kelvin. This is the best conversion possible: If it was irreversible, the entropy would be increasing, which would make $\eta < \eta_C$.

This is reversible, and the reverse process is a refrigerator. We move heat against its temperature gradient by using work. There is work W done and heat Q_l in, and heat Q_h out. The efficiency is given by $\gamma = Q_l/W$. Then the work needed is $W = Q_h - Q_l = (\tau_h/\tau_l - 1)Q_l = \frac{\tau_h - \tau_l}{\tau_l} Q_l$, so $\gamma = \frac{Q_L}{W} = \frac{\tau_l}{\tau_h - \tau_l} = \gamma_C$, the Carnot efficiency of a heat pump. Again, this is achieved if the cycle is reversible.

Another version of the same setup is to heat a room by cooling the outdoors. This gives us a different perspective on the efficiency. Now we care about $\frac{Q_h}{W} = \frac{Q_h}{(1 - \tau_l/\tau_h)Q_h} = \frac{\tau_h}{\tau_h - \tau_l}$. This is greater than 1! Why is that? Well, an efficiency of 1 would correspond to $Q_h = W$. This corresponds to taking a gas at 0 degrees Kelvin and heating it up all the way to room temperature. Of course this would be less efficient; we're not taking advantage of the temperature the outside is already at.

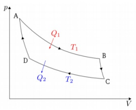
12.2 Carnot Cycle

Let's consider an example of a reversible cycle, a classical ideal gas. There will be four "strokes" in the cycle: two isothermal strokes, in contact with the two reservoirs R_h and R_l, and two isentropic (isolated) strokes to change the temperature to match τ_h and τ_l. We couldn't bring a system in contact with a reservoir without them being at the same temperature; that would be irreversible.

Graphing σ against τ, the result is a rectangle, traversed counterclockwise. Step 1 is isothermal expansion in contact with R_h. Step 2 is isolated adiabatic expansion, which cools the system to T_l. Step 3 is isothermal compression in contact with R_l. Step 4 is isolated adiabatic compression, which heats the system to T_h.

By the thermodynamic identity, as $\oint dU = 0$, the work done is $W = \oint p dV = \oint \tau d\sigma = (\tau_h - \tau_l)\Delta\sigma$.

Let's graph this in $p-V$ space. Wikipedia has this image:



Let's analyze each case.

(1) Isothermal expansion: $p_f/p_i = V_i/V_f$, and the work done is $W = \int p dV = \int_{V_i}^{V_f} dV \, \frac{N\tau_h}{V} = N\tau_h \ln(V_f/V_i)$. The energy is $U = \frac{3}{2}N\tau$.

(2) Isentropic expansion: Entropy is constant, so $N\tau^{3/2}$ is constant, or $V^{5/2}p^{3/2}$ is constant, or $p \propto V^{-5/3}$, which describes the curve in $p-V$ space. Work done is then $W = \frac{3}{2}N(\tau_h - \tau_l)$.

(3) Isothermal compression: By the same logic as 1, $W = -N\tau_l \ln(V_f/V_i)$.

(4) Isentropic compresion: Work is the opposite from isentropic expansion, $W = \frac{3}{2}N(\tau_l - \tau_h)$.

Net work done is then $N(\tau_h - \tau_l)\ln(V_f/V_i)$. Well, we have to justify the claim that V_f/V_i is the same for the isothermal strokes. Well, $\sigma \propto \ln V$, so the change in entropy is $\Delta\sigma = \ln(V_f/V_i)$, which must be the same for each of the isothermal steps.

12.3 Second Law of Thermodynamics

The great minds of thermodynamics bequeathed to us several equivalent formulations of the second law of thermodynamics. Here's another: It is not possible to extract heat $Q > 0$ from a reservoir and convert it to work without producing waste heat (unless a $\tau = 0$ reservoir is available). Consequently, all reversible engines operating between reservoirs at positive temperatures τ_h and τ_l must have the same efficiency.

Why does the second statement follow from the first? If two reversible heat engines 1 and 2 each expel heat Q_l. The first takes in heat Q_h and produces work $W = Q_h - Q_l$, while the second is less efficient: It takes in heat $Q_h - \Delta W$ and produces work $W - \Delta W$. But these are reversible, so we can run the less efficient heat engine backwards to make a refrigerator that takes in work $W - \Delta W$ and heat Q_l and produces heat Q_h. Now hook these two together. The net effect is to take in heat ΔW and produce work ΔW, a perfect conversion of heat into useful work.

In short, the first law of thermodynamics says "You can't win," while the second law says "You can't even break even, except at absolute zero." Well, there's a third law, which says "You can't reach aboslute zero," which seals our doom.

The hero of this subject was the engineer Carnot, who in his entire career wrote one paper, in 1824, called "Reflections on the Motive Power of Fire." He died six years later. It was a remarkable paper, quite ahead of his time, but it was ahead of his time and Kelvin rediscovered it later. Since he was such a nice guy, we named our temperature scale after Kelvin (for other reasons, too).

13 Tuesday, May 11, 2010

13.1 Gibbs Free Energy

This has applications in chemistry and related fields. Our system will be "open to the atmosphere." This means that the system is in contact with a reservoir which has a constant temperature τ and pressure p. We can think of this as a piston pushing down on the system, which can be moved when the system volume changes. This will change our energy accounting, since work is needed to move the piston.

This is just another way in which contact can be established between two systems. Previously, we've talked of thermal contact, in which energy is exchanged, and diffusive contact, in which particles are exchanged. Here we're considering what we call mechanical contact, in which volume is exchanged.

We previously derived $dW = dU - dQ = dU - \tau d\sigma$. Recall that in an isothermal setting, this can be written as $\bar{d}W = d(U - \tau\sigma) = dF$, where we use the $\bar{d}$ to remind ourselves that work is not a conserved quantity. If we want to talk of the available work, we have to subtract off the mechanical work done on the system: $\bar{d}W = -pdV$. Therefore, the available energy is $\bar{d}W' = \bar{d}W + pdV = d(F + pdV) = dG$, where

$$G = F + pV = U - \tau\sigma + pV$$

is the *Gibbs free energy.* Recall that these things are derived in reaching the most probable configuration, i.e. maximizing $\sigma_S + \sigma_R$. When we only had thermal contact, energy was conserved, so $dU_S = -dU_R$. Therefore, we derived that $d(\sigma_S + \sigma_R) = \left(\frac{1}{\tau_S} - \frac{1}{\tau_R}\right) dU_S = 0$, which means that the temperatures are equal in equilibrium: $\tau_S = \tau_R$.

Now we're also doing the same thing with mechanical contact. Again, total volume is preserved, so $dV_S = -dV_R$. Remember that pressure is $p = -\left(\frac{\partial F}{\partial V}\right)_\tau$. If we analogously consider the change in the Helmholtz free energy, $d(F_S + F_R) = -(p_S - p_R)dV_s$. When we find the most probable configuration, we will have maximized the total Helmholtz free energy, so we will have pressure equilibrium: $p_S = p_R$. Another way to say this is that $G = F + pV$ will be minimized as a function of the system variables. In that most probable configuration, the temperature and pressure of the system will match the temperature and pressure of the reservoir, and Gibbs free energy is a function of that temperature and pressure.

What are we doing mathematically? When we change what our independent variable is, this is a Legendre transform. We started with $U(\sigma, V)$ and replaced it with $F(\tau, V)$, then replaced that with $G(\tau, p)$.

Let's consider the first step, and ignore the volume. We had $U(\sigma)$, but we more directly control the temperature. Recall that $\tau = \frac{dU}{d\sigma}$. In order to do this, we need to assume that $\frac{dU}{d\sigma}$ is monotonic (1-1) as a function of σ, which implies that $U(\sigma)$ must be convex.

We then take $F(\tau) = (U - \tau\sigma)|_{\text{stationary wrt } \sigma}$. The convexity of $U(\sigma)$ guarantees that there will be a solution where the slopes of U and $\tau\sigma$ are equal.

How does F change when we change τ? We have $dF = d(U - \tau\sigma) = dU - \tau d\sigma - \sigma d\tau$. To first order, we chose τ so that $dU - \tau d\sigma = 0$ and $dF = -\sigma d\tau$, or $\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$.

The other step is exactly the same, but we're trading in volume for pressure. We write $G(\tau, p) = (F(\tau, V) + pV)|_{\text{stationary wrt } V}$. Again, we write $dG = dF + pdV + Vdp$. Because we chose the volume so that this expression is stationary, we're left with $dG = Vdp$, or $\left(\frac{\partial G}{\partial p}\right)_\tau = V$.

A thermodynamic identity that describes this situation is $dG = -\sigma d\tau + Vdp + \mu dN$. At equilibrium, the pressure, temperature, and particle number.

What could this non-mechanical work be? It could be "chemical work" needed to move particles from low to high concentration. This would make the work done $W = (\mu_2 - \mu_1)\Delta N$. This is just an example of 'non-mechanical work.'

There's a close relationship between Gibbs free energy and chemical potential. We need to distinguish between extensive and intensive properties. Extensive properties scale linearly with the size of the system, i.e. σ, U, V, N. Intensive quantities are independent of system size, i.e. τ, p, μ. Notice that the ratio of any two extensive quantities is intensive. For instance, the energy per particle $u = U/N$ is intensive, so we can express it as a function of intensive quantities: $u(\sigma/N, V/N)$. Similarly, the free energy per particle $f(\tau, V/N) = F(\tau, V, N)/N$. Finally, the Gibbs free energy is $g(\tau, p) = G(\tau, p, N)/N$.

From the thermodynamic identity, $\mu = \left(\frac{\partial G}{\partial N}\right)_{\tau,p}$. But the last expression gives us $\frac{\partial G}{\partial N} = g$, so $\mu = g$. Therefore, we can write $G = N\mu(\tau, p)$.

Suppose that there are many species of particles, each with its own chemical potential. For an individual species, $\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{\tau,p,N_j}$. Then we can consider $G(N_1, N_2, \ldots, \tau, p) = N_1 g(N_2/N_1, N_3/N_1, \ldots, \tau, p)$.

Therefore, G is homogeneous in the N_i of degree 1, or $G(\lambda N_1, \lambda N_2, \ldots, \tau, p) = \lambda G(N_1, N_2, \ldots, p, \tau)$. Take a derivative in λ of both sides. We get $G(N_1, N_2, \ldots, \tau, p) = \sum_i N_i \left(\frac{\partial G}{\partial N_i}\right) = \sum_i N_i \mu_i$. Recall that each of the μ_i are intrinsic, so they can depend on τ, p, and any ratios of particle numbers.

13.2 Gibbs Free Energy in Chemistry

We consider chemical equilibrium for the system at "atmospheric pressure" and "room temperature." To be concrete, consider a reaction: $H_2 + Cl_2 \longleftrightarrow 2\,HCl$. We can consider this reaction as $({}_1)H_2 + ({}_1)Cl_2 + (-2)HCl = 0$, or in general, $\sum_i \nu_i A_i = 0$, where A_i is the species and ν_i is the quantity. This gives us a new way to change the N_i, but only with $dN_i \propto \nu_i$.

The most probable configuration will maximize the Gibbs free energy: $dG = 0 = \sum_i \mu_i dN_i$, or equivalently, $\boxed{\sum_i \mu_i \nu_i = 0}$.

To see the consequences of this, we're going to treat the species as ideal gases. First we have to generalize that discussion. Our formulas for the ideal gas assumed it was monatomic. The formulas change because there are different contributions to the partition function due to internal degrees of freedom, for anything more complicated, like the diatomic gases we're considering here.

Recall that we computed the Gibbs sum for a single orbital as $\mathfrak{z} = \sum \lambda^n e^{-n\mathcal{E}/\tau}$ (where the sum over n is just $n = 0, 1$ for Fermions, and $n = 0, 1, 2, ..., \infty$ for Bosons). In the classical regime, we assumed that there was no multiple occupancy, so we approximated this power series by the first two terms: $\mathfrak{z} \approx 1 + \lambda e^{-\mathcal{E}/\tau}$. We also need to consider internal degrees of freedom, so molecules can vibrate and rotate, and we should include binding energy in the energy accounting used to compute the Boltzmann factor $e^{\mathcal{E}/\tau}$.

Of course, we don't have to worry about those things with the empty orbital; it will only affect the second term. So we get $\mathfrak{z} \approx 1 + \lambda e^{-\mathcal{E}/\tau} \sum_{\text{internal}} e^{-\mathcal{E}_{\text{int}}/\tau} = 1 + \lambda_{\text{eff}} e^{-\mathcal{E}/\tau}$, where $\lambda_{\text{eff}} = \lambda Z_{\text{int}}$ and $Z_{\text{int}} = \sum_{\text{internal}} e^{-\mathcal{E}_{\text{int}}/\tau}$. So everything is the same except we replace λ by λ_{eff}.

Then the particle number $N = \lambda_{\text{eff}} n_Q V = \lambda Z_{\text{int}} n_Q V$. Therefore, writing $\lambda = e^{-\mu/\tau} = \frac{n}{n_Q Z_{\text{int}}}$, so $\mu = \tau \ln\left(\frac{n}{n_Q Z_{\text{int}}}\right)$.

The internal partition function can be split up according to the different contributions to its energy: $Z_{\text{int}} = \sum_{\text{int}} e^{-\mathcal{E}_{\text{int}}/\tau} = e^{-E_0/\tau} Z_{\text{vib}} Z_{\text{rot}}$. Let's consider the vibrational partition function for a diatomic gas, which is just a harmonic oscillator with a reduced mass and spring constant. Then $Z_{\text{vib}} = \sum_n e^{-n\hbar\omega/\tau} = \frac{1}{1 - e^{-\hbar\omega/\tau}}$. This is approximately 1 for $\tau \ll \hbar\omega$ and $\tau/\hbar\omega$ for $\tau \gg \hbar\omega$.

The effect on chemical potential will be logarithmic: $\mu = \tau(\ln n - \ln c)$ where $c = n_Q Z_{\text{int}} = c(\tau)$. Plugging in μ_i and dividing by τ gives $0 = \sum_i \nu_i (\ln n_i - \ln c_i)$. Taking the exponential of both sides, $\boxed{\prod_i n_i^{\nu_i} = \prod_i c_i^{\nu_i} = K(\tau)}$, which is the equilibrium constant. This is known as the "law of mass action."

Let's use a simple example: $H + H \longleftrightarrow H_2$, or $(-2)H + ({}_1)H_2 = 0$. The law of mass action would tell us that $[H_2]/[H]^2 = K(\tau) = \frac{(n_Q Z_{\text{int}})_{H_2}}{(n_Q Z_{\text{int}})_H^2}$. The quantum concentation is, as always, $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2} \propto m^{3/2}$. Therefore, $K(\tau) \approx \frac{(n_Q)_{H_2}}{(n_Q)_H} \approx 2^{3/2} = 2^{3/2} e^{E_{\text{BE}}/\tau} \frac{1}{(n_Q)_H} (Z_{\text{vib}} Z_{\text{rot}})_{H_2}$, or

$$\frac{[H_2]}{[H]} = 2^{3/2} e^{E_{\text{BE}}/\tau} (Z_{\text{vib}} Z_{\text{rot}})_{H_2} \frac{[H]}{(n_Q)_H}.$$

There's going to be competition between the hydrogen wanting to bind to reduce the Boltzmann factor and the hydrogen wanting to dissociate to increase the entropy. We now have enough information to solve, with the additional conservation of hydrogen atoms: $[H] + 2[H_2] = C$. Then $K[H]^2 + \frac{1}{2}[H] - \frac{1}{2}C = 0$, so $[H] = \frac{1}{2K}\left[-\frac{1}{2} + \sqrt{\frac{1}{4} + 2KC}\right] = \frac{1}{4K}\left(\sqrt{1 + 8KC} - 1\right)$. When $KC \ll 1$, $1 + 8KC \approx 1 + 4KC$ and $[H] \approx C$. Then $\frac{[H_2]}{[H]} = K[H] = KC \ll 1$ and the atomic hydrogen dominates.

14 Thursday, May 13, 2010

14.1 Phase Transitions

This is one of the most active and most interesting aspects of modern physics. Generally speaking, a phase transition is a large quantitative change in the system's state resulting from a small change in a system variable. An example is water, which can exist in three phases: ice, liquid, and steam. In high school, we probably learned that there are three phases of matter, but in reality there are many different phases that physicists study. Here are some examples:

- Ferromagnetism: Below some critical temperature $\tau < \tau_c$, iron magnetizes. Above the critical temperature, iron does not magnetize.
- Superfluidity of helium-4.
- Superconductivity: Below a critical temperature, current flows without resistance; above, there is resistance as usual.
- Liquid Crystals: Below a critical temperature, there is orientational order (a preferred direction results).

Mathematically, a phase transition results from discontinuities in some parameter. Everything is derived from the derivatives of the partition function $Z = \sum e^{-\mathcal{E}/\tau}$. This can only occur (at least formally) when the system size is taken to be infinite. This might seem to make the topic academic, but finite systems tend to be very large, so there can be a discontinuity to within our accuracy. Discontinuities are 'rounded out' slightly in finite systems.

One approach used to study phase transitions is to find universal properties of them, which apply to many different systems and materials. Physicists also try to derive quantitative predictions (for example, the critical temperatures) from a microscopic model.

There will be conditions (temperature and pressure) when multiple phases coexist. These correspond to the lines on a phase diagram. There are a few important points on a phase diagram such as that of water: At the triple point (316 degrees Kelvin, 458 mm Hg), all three can coexist. Past the critical point (at 647 degrees Kelvin and 218 atmospheres for water), the discontinuity between liquid and gas loses its discontinuity.

We can understand the critical point by considering a $p-V$ diagram. There is a hill-shaped region wherein the isotherms are actually horizontal, corresponding to latent heating. Above this region, the isotherms act normally.

14.2 Coexistence of phases

Gas and liquid occur in thermal, pressure, and diffusive equilibium. Therefore, the pressure, temperature, and chemical potentials have to be equal. Can we derive anything about the slope of the coexistence curve?

The chemical potential is $\mu_l(p,\tau) = \mu_g(p,\tau)$. To first order in small quantities, we expand $\mu_l(p+dp, T+dT) = \mu_g(p+dp, T+dT)$, so $\left(\frac{\partial \mu_l}{\partial p}\right)_T dp + \left(\frac{\partial \mu_l}{\partial T}\right)_p dT = \left(\frac{\partial \mu_g}{\partial p}\right)_T dp + \left(\frac{\partial \mu_g}{\partial T}\right)_p dT$. Therefore, the slope is

$$\frac{dp}{d\tau} = \frac{\left(\frac{\partial \mu_l}{\partial T}\right)_p - \left(\frac{\partial \mu_g}{\partial T}\right)_p}{\left(\frac{\partial \mu_g}{\partial p}\right)_T - \left(\frac{\partial \mu_l}{\partial p}\right)_T}.$$

Now remember that the Gibbs free energy is $G(\tau, p, N) = N\mu(\tau, p)$. Therefore, $\left(\frac{\partial G}{\partial p}\right)_{\tau,N} = V$ and $\left(\frac{\partial G}{\partial \tau}\right)_{p,N} = -\sigma$. With the volume per particle $v = V/N$ and entropy per particle $s = \sigma/N$, we get that along the coexistence curve, $\dfrac{dp}{d\tau} = \frac{s_g - s_l}{v_g - v_l}$. These are usually both positive, so the slope is positive. We can get the volumes from the density, and the entropies from the latent heat: $L = \tau \Delta s$ is the heat per particle needed to transform a liquid to a gas. Therefore, the slope is given by $\dfrac{dp}{d\tau} = \frac{L}{\tau \Delta v}$, where Δv is the difference in the volume per particle for the gas and the liquid. This is known as the *Clausius-Clapeyron equation.* Of course, it also applies to other phase coexistences.

For instance, applying this to the water-ice transition, since ice floats, i.e. $\Delta v < 0$, while the entropy is positive (you have to add heat to melt the ice). This means that we can ice skate, since at higher pressure, they coexist at a lower temperature.

14.3 van der Waals Equation of State

Speaking of ice skating, they do it in Holland, and a physicist from Holland was van der Waals, so let's seamlessly transition to talking about him. We'll be considering a nonideal gas for the first time (gasp!).

van der Waals suggested that particles have a small attractive force between them, but they repel each other very strongly for very small distances.

Crudely, he assumed that the presence of molecules precluded placing more atoms in the same spot, and there is some excluded volume, so we replace V with $V - N\delta$. Additionally, the attraction decrease the energy by $\Delta U = \frac{1}{2} \sum_{ij} V(\vec{v}_i - \vec{v}_j) = \frac{1}{2} \int d^3x \, d^3y \, n(\vec{x}) n(\vec{y}) V(\vec{x} - \vec{y})$. If we assume uniform density, $n(\vec{x})$ is constant, and we get $n^2 V \frac{1}{2} \int d^3x V(\vec{x})$. This will be negative, so let $-a = \frac{1}{2} \int d^3x V(\vec{x})$, so $\Delta U = -aN^2/V$.

The new free energy is given by $F_{\text{vdW}} = F_{\text{ideal}}(V - N\delta) - aN^2/V == -N\tau \ln n_Q \left(\frac{V - N\delta}{N} - aN^2/V \right)$. Then the pressure is

$$p = -\left(\frac{\partial F}{\partial V} \right)_{\tau, N} = \frac{N\tau}{V - Nb} - \frac{aN^2}{V^2}.$$

The ideal gas law, usually $pV = N\tau$, becomes

$$\boxed{\left(p + \frac{N^2}{V^2} a \right) (V - Nb) = N\tau}.$$

Don't take this equation too seriously; it's a crude approximation that only works for dilute gases.

We're going to work with it where it doesn't apply, near phase transitions. This relates the numbers a and b, which are not physically measurable, to macroscopic measurable values. If we want to solve the van der Waals equation of state for volume, we have to solve a cubic equation:

$$\left(V^2 + \frac{N^2 a}{p} \right) (V - Nb) = \frac{N\tau V^2}{p}$$
$$V^3 - \left(Nb - \frac{N\tau}{p} \right) V^2 + \frac{N^2 a}{p} V - \frac{N^3 ab}{p} = 0.$$

This equation can have either one or three real roots. The critical point corresponds to the transition between one and three roots. Indeed, graphing pressure against volume, there are three roots below the critical pressure and one above, and the isotherms curve back on themselves.

At the critical isotherm, we get three degenerate solutions, so our equation becomes $(V - V_c)^3 = 0$. We can expand that equation and match the coefficients to get the critical parameters. We have $(V - V_c)^3 = V^3 - 3V^2 V_c + 3V V_c^2 - V_c^3$. Therefore,

$$Nb + NT_c/p_c = 3V_c$$
$$\frac{Na^2}{p_c} = 3V_c^2$$
$$\frac{N^3 ab}{p_c} = V_c^3.$$

Solving for the critical values, $V_c = 3Nb$, $p_c = a/27b^2$, and $\tau_c = 8a/27b$. We can scale everything by these values, getting

$$\left(\frac{V}{V_c} - \frac{Nb}{V_c}\right)\left(\frac{p}{p_c} + \frac{V_c^2}{V^2}\frac{N^2 a}{V_c^2 p_c}\right) = \frac{\tau}{\tau_c}\frac{N\tau_c}{V_c p_c}$$

$$\boxed{\left(\frac{V}{V_c} - \frac{1}{3}\right)\left(\frac{p}{p_c} + 3\frac{V_c^2}{V^2}\right) = \frac{8}{3}\frac{\tau}{\tau_c}}.$$

This is important enough to have a name, called the *law of corresponding states.* Don't believe this, because our model is not very accurate.

What does a bending-backwards $p - V$ plot mean? How could $\dfrac{dp}{dV} > 0$? It would have to be unstable: The pressure decreases with the volume!

Let's also analyze the free energy: It will have to be at a minimum, which means $dF = 0$, but also $d^2F \geq 0$. We have $dF = \left[\left(\dfrac{\partial F_S}{\partial V}\right)_\tau - \left(\dfrac{\partial F_R}{\partial V}\right)_\tau\right] = (p_R - p_S)dV_S = 0$, and $d^2F = \dfrac{\partial}{\partial V_S}(p_R - p_S) \approx -\dfrac{\partial p}{\partial V_S} \geq 0$. Therefore, when the pressure is decreasing with volume, we're actually at an unstable equilibrium. What happens? We'll talk about that next time.

Incidentally, thermal contact also has the same phenomenon, saying that heat capacity has to be positive.

15 Tuesday, May 18, 2010

15.1 First Order Phase Transitions

Last time, we started with the van der Waals equation of state, and rewrote everything in terms of the critical volume, temperature and pressure. With $\hat{V} = V/V_c$, $\hat{p} = p/p_c$, and $\hat{\tau} = \tau/\tau_c$, $(\hat{V} - \frac{1}{3})(\hat{p} + 3\hat{V}^{-2}) = \frac{8}{3}\hat{\tau}$.

Also recall that when we graphed p against V that the critical situation arose when the isotherm slope is zero, but not a maximum or minimum. Below this point, we had a region in which the volume was multivalued as a function of pressure. In this region, we had $dp/dV > 0$, which means that the system is unstable. Since $p = -\left(\dfrac{\partial F}{\partial V}\right)_\tau$, this means that $\left(\frac{\partial^2 F}{\partial V^2}\right)_\tau < 0$. It's a stationary point in the free energy, but a maximum.

Let's plot the free energy against volume. We have $F = -\int_{\text{isotherm}} p\, dV + \text{const}$. $dp/dV > 0$ means that over some region, the system will be concave down.

But this is only analyzing homogeneous phase. If we consider a mixed state with a portion liquid and a portion gas. This will give a lower free energy. This is why we have phase transitions.

What points does the liquid or gas accumulate at? These coexistent phases have the same pressure. Letting f_i be the Helmholtz free energy per unit volume for each phase, $F = f_1 V_1 + f_2 V_2 = (f_1 - f_2)\Delta V +$ const. On the $F - V$ graph, these points are the tangent points of the tangent line with two points of tangency. The pressure is the slope of this line.

Where are these points on the pressure-volume graph? We can compute the free energy difference between phases 1 and 2 by (a) following the isotherm, and (b) following the straight line between them. (a) gives the area under the isotherm between these points, and (b) gives the area under a line with constant pressure. These must be equal, or equivalently, the curved areas above and below the isotherm are equal.

This method is known as the Maxwell construction. The goal is to predict the (τ, p) pair at the phase transition. We choose the pressure to satisfy this equal-area criterion.

Another method uses Gibbs free energy. In order to coexist, these things need the same chemical potential: $\mu_l = \mu_g$. We maximize G, and $\left(\dfrac{\partial G}{\partial p}\right)_\tau = V$, so graph the volume against pressure, the same graph but inverted. The Gibbs free energy being maximized means that $\int V\, dp = 0$.

What we've been describing is known as a 1st order phase transition. Why is it called this? Well, as a function of p and τ, G is continuous, but its first derivatives are discontinuous. These are $\left(\frac{\partial G}{\partial \tau}\right)_p = -\sigma$, $\left(\frac{\partial G}{\partial p}\right)_\tau = V$. We're saying that $\sigma_{\text{liquid}} \neq \sigma_{\text{gas}}$, so there is a nonzero latent heat, and $V_{\text{liquid}} \neq V_{\text{gas}}$, so there is a density discontinuity.

While the van der Waals model might not actually be a good description of the isotherms, the equal-area construction applies generally to 1st order phase transitions.

15.2 Supercooling and superheating

We can ask what happens if we decrease volume beyond the temperature of the phase transition from the gas phase. There is a region on which the pressure is still decreasing with volume, but we've passed the point at which we expect liquid to form. This can go up until the critical point in the $p - V$ curve, where the pressure reaches a minimum. In other words, this is a local minimum but not a global minimum, and is known as supercooling.

There is an analogous superheating of liquids. What happens? Eventually we get nucleation of droplets for supercooling and nucleation of bubbles of gas for superheating. How long does this take?

Let's consider a small droplet of liquid. It forms a surface, and gas molecules will want to stay in the gas, and liquid molecules will want to stay in the liquid. The discrepancy here is known as surface tension. For a small droplet, the surface tension will cause it to immediately shrink. Eventually, a big enough droplet will form that the surface tension effects are small compared with the free energy change due to the formation of liquid and gas, and the droplet will grow.

The probability of a fluctuation goes as $e^{\Delta\sigma}$, where $\Delta\sigma < 0$. In contact with a reservoir at temperature τ, this makes the probability of fluctuation $e^{-\Delta F/\tau}$, where ΔF is the free energy cost of forming a "critical droplet."

Then the rate of droplet formation goes as (time scale)$^{-1}e^{-\Delta F/\tau}$. We won't be estimating the fundamental time scale, just the other portion. When considering the work done to make a droplet, we have to consider surface tension, too. $dW = -pdV + \gamma dA$, where A is the surface area and $\gamma > 0$ is the surface tension. The free energy difference $f = \frac{F_{\text{gas}} - F_{\text{liquid}}}{V}$. The change in free energy is $\Delta F = -fV + \gamma A$. We have to figure out how these two forces compete and find an optimum. First, to minimize surface area, we consider the droplet to be spherical. Then $V = -\frac{4\pi}{3}R^3$ and $A = 4\pi R^2$, so $(\Delta F) = -\frac{4\pi}{3}R^3 f + 4\pi R^2\gamma$. This is increasing for small R, but then it rapidly falls downwards. The critical radius $R_c = 2\gamma/f$, and the free energy cost to get over this barrier is $\Delta F_c = 4\pi\frac{\gamma^3}{f^2}(-\frac{8}{3} + 4) = \frac{16\pi}{3}\frac{\gamma^3}{f^2}$. The rate goes as $e^{-\Delta F_c/\tau}$, and a supercooled gas or superheated liquid are metastable.

15.3 Second Order Phase Transitions

Recall that first order phase transitions have discontinuities in the first derivatives of Gibbs free energy. We would reasonably guess that second order phase transitions will be discontinuous, but that's actually not the case; that never happens. Instead, in a second order phase transition, the first order derivatives of $G(\tau, p)$ are continuous, but the second order derivatives *diverge*.

What are second order derivatives? Heat capacity is $c_p = \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_p = -\tau\left(\frac{\partial^2 G}{\partial \tau^2}\right)_p$. Another is the compressibility: $k_\tau = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_\tau = -\frac{1}{v}\left(\frac{\partial^2 G}{\partial p^2}\right)_\tau$.

A second order phase transition occurs as $\tau \to \tau_c$. Here, both c_p and k_τ run as $|\tau - \tau_c|^{-\text{power}}$.

In our phase diagram, the phase transition between p and τ have a line of first order phase transitions, and it terminates in a second order phase transition. As you approach the critical point, the first derivatives become continuous and the second derivatives blow up. Indeed, $\frac{dp}{dV} \to 0$ at the critical point, which means that $k_\tau \propto \dfrac{\partial V}{\partial p}$ diverges. Let's examine what's going on in a little more depth at the critical point, and characterize this divergence.

We'll use that van der Waals equation of state again. Recall that in terms of the rescaled variables, $(\hat V - \frac{1}{3})(\hat p + 3\hat V^{-2}) = \frac{8}{3}\tau$. He then did some algebra to express these in terms of the deviation from critical values: $\delta\hat V = \hat V - 1 = \frac{V-V_c}{V_c}$, $\delta\hat p = \hat p - 1 = \frac{p-p_c}{p_c}$ and $\delta\hat\tau = \hat\tau - 1 = \frac{\tau-\tau_c}{\tau_c}$. He got

$$(\delta\hat V)^3 = \left(-\frac{2}{3}\delta\hat p + \frac{8}{3}\delta\hat\tau\right) + \left(-\frac{7}{3}\delta\hat p + \frac{16}{3}\delta\hat\tau\right)\delta\hat V + \left(-\frac{8}{3}\delta\hat p + \frac{8}{3}\delta\hat\tau\right)\delta\hat V^2 - \delta\hat p\delta\hat V^3.$$

We're now going to assume we're near the critical point, so these values are small. We ignore the last two terms on the RHS because they are small compared with the other terms (with an extra $\delta\hat V$ compared with the second term on the right or an extra $\delta\hat p$ compared with the LHS). What we're left with is cubic in $\delta\hat V$.

As our first goal, we want to characterize the volume discontinuity as $\tau \to \tau_c$ from below. Using the Maxwell construction (it's the same graph, just shifted), we have that $\delta\hat p$ is approximately a cubic function in $\delta\hat V$ (ignoring the $\delta\hat p\delta\hat V$ term in the second term of the RHS). Then the equal area principle will be satisfied if the curve intersects the origin, which means that the constant term is zero. Therefore, $-\frac{2}{3}\delta\hat p + \frac{8}{3}\delta\hat\tau = 0$, so $(\delta\hat V)^3 \approx (-4\delta\hat\tau)\delta\hat V$. The solutions corresponding to the liquid and gas are approximately $\delta\hat V = \pm(-4\delta\hat\tau)^{1/2}$, so $\delta\hat V_{\text{gas}} - \delta\hat V_{\text{liquid}} = \frac{V_{\text{gas}}-V_{\text{liquid}}}{V_c} = 4\left(\frac{\tau_c-\tau}{\tau_c}\right)^{1/2}$.

The prefactor of 4 depended exactly on the van der Waals coefficients, which might depend on our specific model, but the square root is more genearlly true, dependent only on the fact that our inflection point is cubic. Indeed, the same exponent appears in many systems... but experimentally we get an exponent of around .32. Well, darn it.

16 Thursday, May 20, 2010

Recall: Near the critical point, with $\delta\hat V = \frac{V-V_c}{V_c}$, $\delta\hat p = \frac{p-p_c}{p_c}$, and $\delta\hat\tau = \frac{\tau-\tau_c}{\tau_c}$ all small,

$$\delta\hat V^3 = (-2/3\delta\hat p + 8/3\delta\hat\tau) + (-7/3\delta\hat p + 16/3\delta\hat\tau)\delta\hat V.$$

Along the phase transition converging to the critical point, the linear term was zero by the Maxwell construction, so $\delta\hat V^3 = (-4\delta\hat\tau)\delta\hat V$, so $\delta\hat V = \pm 2(-\delta\hat\tau)^{1/2}$. Taking the difference between the two solutions, we get $\frac{V_{\text{gas}}-V_{\text{liquid}}}{V_c} = 4\left(\frac{\tau_c-\tau}{\tau_c}\right)^{1/2}$. Recall that this prefactor was dependent directly on our model, but the exponent of 1/2 should be more general.

How does the isothermal compressibility change? $k_\tau = -\frac{1}{V}\left(\dfrac{\partial G}{\partial p}\right)_\tau = \left(\dfrac{\partial p}{\partial V}\right)_\tau$. This should blow up as $\tau \to \tau_c$. Taking the change at constant temperature of our equation,

$$3\delta\hat V^2 d\delta\hat V = -2/3d\delta\hat p - 7/3d\delta\hat p\delta\hat V + (-7/3\delta\hat p + 16/3\delta\hat\tau)d\delta\hat V.$$

Again, we consider these values along the first order phase transition, so $\delta\hat p = 4\delta\hat\tau$. Also, the minimum along the isotherm of $(d\hat p/d\hat V)_\tau$ occurs for $\delta\hat V = 0$. Therefore, $0 = -2/3d\delta\hat p + (-4\delta\hat\tau)d\delta\hat V$, or $\left(\dfrac{\partial\delta\hat p}{\partial\delta\hat V}\right)_\tau = \frac{3}{2}(-4\delta\hat\tau) = -6\delta\hat\tau$. Then $\left(\dfrac{\partial p}{\partial V}\right)_\tau = \frac{p_c}{V_c}\left(\dfrac{\partial\hat p}{\partial\hat V}\right)_\tau = \frac{p_c}{V_c}(-6)\delta\hat\tau$, so $K_\tau^{-1} = -V\left(\dfrac{\partial p}{\partial V}\right)_\tau = 6p_c\left(\frac{\tau-\tau_c}{\tau_c}\right)^{1/2}$. Therefore, the reciprocal of this will blow up like $(\tau-\tau_c)^{-1}$.

This works when $\tau > \tau_c$. When $\tau < \tau_c$, we have the volume discontinuity to worry about. Taking this into account, we have to keep the $3\delta\hat V^2 d\delta\hat V$, and we have $\delta\hat V^2 = -4\delta\hat\tau$. Plugging this in, $3(-4\delta\hat\tau)d\delta\hat V = -2/3d\delta\hat p - (4\delta\hat\tau)(d\delta\hat V)$. Then $\left(\dfrac{\partial\delta\hat p}{\partial\delta\hat V}\right)_\tau = 12\delta\hat\tau$, and $k_\tau^{-1} = -V\left(\dfrac{\partial p}{\partial V}\right)_\tau = 12p_c\left(\frac{\tau_c-\tau}{\tau_c}\right)$ for $\tau < \tau_c$.

Therefore, universally we predict $k_\tau \sim \frac{1}{|\tau-\tau_c|}$, with the prefactor depending on whether $\tau < \tau_c$ or $\tau_c < \tau$.

Unfortunately, experimentally, we find that $V_{\text{gas}} - V_{\text{liquid}} \sim (\tau_c - \tau)^\beta$, but $\beta \approx .32$, not $\beta \approx .5$, and $k_\tau \sim \frac{1}{|\tau-\tau_c|^\gamma}$, but $\gamma \approx 1.3$, not 1.

16.1 Second Order Phase Transitions in Ferromagnets

Without hesitation, we'll make another wrong prediction, but illustrate the universality of these predictions.

The analog of pressure is H, the applied magnetic field, and the analog of volume is M, the magnetization, which is the magnetic moment over the volume. The analog of compressibility is susceptibility, $\chi = \left(\dfrac{\partial M}{\partial H}\right)_\tau$.

For paramagnetic materials, graphing M against H yields a curve like an arctangent. At small fields, M is linear in H, but at high H, we reach "saturation."

Ferromagnets are different: Below the critical temperature $\tau < \tau_c$, there's a discontinuity in M from some large negative value to some large positive value at $H = 0$. This is known as *spontaneous magnetization.* This is analogous to phase transitions with p and V; there is a discontinuity in $\hat{V}$ with change in $\hat{p}$ near $\hat{p} = 0$, and it vanishes for $\tau > \tau_c$. Why is this analogous? The change in work is $dW = -pdV$ in the gas-liquid case, and $dW = VMdH$ in the ferromagnet case.

We can graph H against τ and find that there is a line of first-order phase transitions exactly on $H = 0$, terminating in $(H, \tau) = (0, \tau_c)$. This makes sense, as the change in entropy across this phase transition is zero (they're symmetric).

Let's try to formulate a magnetic analog of the van der Waals model. First, consider noninteracting spins. For a single spin, up and down will be two microstates with energy difference $\Delta E = 2\mu B$, and the higher energy state will be Boltzmann suppressed: $\frac{n_\uparrow}{n_\downarrow} = e^{-2\mu B/\tau}$. Then $\frac{n_\downarrow - n_\uparrow}{n_\uparrow + n_\downarrow} = \frac{1-e^{-2\mu B/\tau}}{1+e^{-2\mu B/\tau}} = \tanh\left(\frac{\mu B}{\tau}\right)$, where n is the number of spins per volume. We get $M = n\mu \tanh(\mu B/\tau)$. This matches our predictions for paramagnets.

To get a ferromagnet, of course, we need to consider interacting spins. We can model this by saying that the magnetic field at each spin is $B_{\text{eff}} = H + \lambda M$, where λ is a coupling parameter. (This would be 4π if we averaged over all of the material, but we're considering the field at the point of each spin.) We're applying "mean-field theory."

So we get $M = n\mu \tanh(\frac{\mu}{\tau}(H + \lambda M))$. Letting $m = \frac{M}{n\mu}$, we get $m = \tanh(\frac{n\mu^2\lambda}{\tau} m)$. First consider $H = 0$. Then there are either 1 or 3 solutions to this equation, depending on the value of $\frac{n\mu^2\lambda}{\tau}$. If it is greater than 1, then the only solution is $m = 0$. If it is less than 1, there are three solutions, one zero, one positive and one negative.

We have spontaneous magnetization, i.e. $M \neq 0$ as $H \to 0$, whenever $\tau < \tau_c = \lambda n \mu^2$. There is no spontaneous magnetization when $\tau > \tau_c$.

Let's consider a nonzero value of H. Solving for M gives a multivalued function just as in our discussion of the gas-liquid phase transition, like a flipped cubic. The stable phases for H in this region are again mixed phases, where some regions are magnetized in one direction and others are magnetized in the other.

We can ask the same questions as we asked before: How does m behave for $\delta\hat{\tau} = (\tau - \tau_c)/\tau_c$ small and negative? Then at $H = 0$, $m = \tanh(m/\hat{\tau})$. Expanding the hyperbolic tangent, $m = \frac{m}{\hat{\tau}} - \frac{m^3}{3\hat{\tau}^3}$. Since $\hat{\tau} = 1 + \delta\hat{\tau}$, and $\delta\hat{\tau}$ is small, we can approximate $\hat{\tau} \approx 1$, and we get $m\left(1 - \frac{1}{\hat{\tau}}\right) = -\frac{m^3}{3\hat{\tau}^3}$, so $m(\delta\hat{\tau}) = -\frac{1}{3}m^3$. Solving, we get $m = \pm\sqrt{3}\left(\frac{\tau_c - \tau}{\tau_c}\right)^{1/2}$. Again, the prefactor depends on this system, but the exponent is universal.

Let's examine the second order phase transition that occurs as $\tau \to \tau_c$. The susceptibility is $\chi = \left(\dfrac{\partial M}{\partial H}\right)_\tau$, and we have $m = \tanh\left(\frac{m}{\hat{\tau}} + \frac{\mu}{\tau}H\right)$. Using the hyperbolic tangent addition formula, $\tanh(A+B) = \frac{\tanh A + \tanh B}{1 + \tanh A \tanh B}$, setting $h = \tanh\frac{\mu H}{\tau}$, $m = \frac{\tanh(m/\hat{\tau}) + h}{1 + h\tanh(m/\hat{\tau})}$, or $h = \frac{m - \tanh(m/\hat{\tau})}{1 - m\tanh(m/\hat{\tau})}$. Expanding the hyperbolic tangents,

$$h \approx \left(m - \frac{m}{\hat{\tau}} + \frac{1}{3}\left(\frac{m}{\hat{\tau}}\right)^3 \right)\left(1 + \frac{m^2}{\hat{\tau}}\right) = m\left(1 - \frac{1}{\hat{\tau}}\right) + m^3\left(\frac{1}{3\hat{\tau}^3} + \frac{1}{\hat{\tau}}\left(1 - \frac{1}{\hat{\tau}}\right)\right).$$

Close to the critical temperature, $\hat{\tau} = 1 + \delta\hat{\tau}$, and we get $h = m\delta\hat{\tau} + \frac{1}{3}m^3$.

Again, we distinguish between $\tau < \tau_c$ and $\tau > \tau_c$. When $\tau > \tau_c$, there is no spontaneous magnetization, and we can approximate $m^2 = 0$, so $\dfrac{\partial h}{\partial m} = \delta\hat{\tau}$. When $\tau < \tau_c$, $m^2 = -3\delta\hat{\tau}$, so $\dfrac{\partial h}{\partial m} = \delta\hat{\tau} - 3\delta\hat{\tau} = -2\delta\hat{\tau}$ (again, we've flipped the sign and doubled it). Then

$$\chi = \frac{\partial M}{\partial H} = \frac{\partial M}{\partial m}\frac{\partial m}{\partial h}\frac{\partial h}{\partial H} = (n\mu)\left(\frac{\mu}{\tau_c}\right)\left(\frac{\partial h}{\partial m}\right)^{-1} = \frac{n\mu^2}{\tau_c} \times \begin{cases} \left(\frac{\tau_c}{\tau - \tau_c}\right) & \tau > \tau_c \\ \frac{1}{2}\left(\frac{\tau_c}{\tau - \tau_c}\right) & \tau < \tau_c. \end{cases}$$

What are the experimental results? Well, as usual, there's good news and bad news. There does appear to be something universal about the properties of second-order phase transitions: $M = (\tau_c - \tau)^\beta$ has $\beta \approx .32$, and $\chi \sim \frac{1}{|\tau - \tau_c|^\gamma}$, and $\gamma \approx 1.3$. So there's something universal going on in both of the cases.

16.2 Landau Theory of Second Order Phase Transitions

Trying our patience more, Professor Preskill is going to derive the wrong answers, $\beta = .5$ and $\gamma = 1$, one more time.

We want to generalize what's going on in these previous two cases, but let's use the language of ferromagnets. The basic idea is that we're minimizing the Helmholtz free energy $F(M, \tau)$, which is an analytic function in M and τ, so we can expand it in terms of a power series. Basically, the function changes from having two minima, one on each side of $M = 0$, and switches to having a minimum at $M = 0$ at $\tau > \tau_c$. We'll continue this on Thursday.

The next homework, on scaling theory, won't be discussed in class until Tuesday, but the problems are self-contained, so we should be fine.

17 Tuesday, May 25, 2010

Today is the last in a series of lectures on second-order phase transitions. We've been using a theory described as "mean-field theory." A couple examples of our source were the van der Waals equation of state, and a theory developed by Weiss for ferromagnetism. We examined the second-order phase transitions at endpoints of phase transitions, for the $V_{\text{gas}} - V_{\text{liquid}}$ and spontaneous magnetization M. These diverged as $(\tau_c - \tau)^\beta$, and we derived $\beta = 1/2$. Similarly, we derived that the magnetizability $\chi = \left(\dfrac{\partial M}{\partial H}\right)_\tau$ and the compressibility $K_\tau \sim -\frac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_\tau$. Both of these go as $\frac{1}{|\tau - \tau_c|^\gamma}$, and we derived $\gamma = 1$.

We now derive a more general model for second-order phase transitions, known as Landau theory. It's simpler, but it's useful to have some examples in mind.

It's useful to have an "order parameter," something that indicates if the temperature is above the critical temperature. We'll denote it by ξ. Then $\xi_0 = 0$ for $\tau \geq \tau_c$, and $\xi_0 \neq 0$ for $\tau < \tau_c$.

We also assume that the Helmholtz free energy is symmetric; it is equal for ξ and $-\xi$: $F(\xi, \tau) = F(-\xi, \tau)$. However, depending on if we remove a field which is pointing in one direction or the other, the preferred field will be one or the other, not equally likely. We call this spontaneously broken symmetry. If this occurs, there are two possible states, $\xi = \pm\xi_0$.

Following Landau, we now assume that $F(\xi, \tau)$ can be expanded as a power series in ξ and $\tau - \tau_c$. Then by the symmetry, there will only be even powers of ξ. Therefore, write

$$F(\xi, \tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 + \cdots.$$

Another assumption of Landau theory is that $g_2(\tau)$ has a zero at $\tau = \tau_c$. Then expanding about $\tau - \tau_c$, we assume generically that $g_2 > 0$ when $\tau > \tau_c$ and $g_2 < 0$ when $\tau < \tau_c$. Then $g_2(\tau) = \alpha(\tau - \tau_c) + O((\tau - \tau_c)^2)$, and $\alpha > 0$. Finally, we assume that $g_4(\tau) > 0$ near $\tau = \tau_c$.

For $\tau > \tau_c$, free energy is concave up in ξ. For $\tau = \tau_c$, the leading term will be quartic, so there will be a minimum at $\xi = 0$ again, but it will increase slower. For $\tau < \tau_c$, there will be three stationary points: a maximum at $\xi = 0$, and two minima on either side, at $\xi = \xi_0 \neq 0$.

If we add an applied field λ, take $F(\xi, \lambda) - \lambda\xi$ instead. Extrema occur when $\dfrac{\partial}{\partial \xi}[F(\xi, \lambda) - \lambda\xi] = 0$. Keeping just the quadratic and quartic terms, we get λ to be a cubic in ξ. Plotting ξ as a (multivalued) function of λ, we get the Maxwell construction, as before. Again, the mixed state will be favored. The free energy shifts, so one of the minima is below the other.

17.1 Landau Theory Critical Parameters

Let's write that $g_2(\tau) \approx \alpha(\tau - \tau_c)$, where $\alpha > 0$. Then $F(\xi, \tau) = g_0(\tau_c) + \frac{1}{2}\alpha(\tau - \tau_c)^2 + \frac{1}{4}g_4(\tau_c)\xi^4 + \cdots$. We only keep the constant order terms for g_0 and g_4 since they are nonzero and therefore dominant for $\tau \approx \tau_c$.

When $\lambda = 0$, $0 = \dfrac{\partial F}{\partial \xi} = \alpha(\tau - \tau_c)\xi + g_4\xi^3 + \ldots$. When $\tau > \tau_c$ there is one solution, $\xi_0 = 0$. When $\tau < \tau_c$, there are 3 solutions, $\xi_0 = 0$ and $\xi_0 = \pm\left(\frac{\alpha}{g_4}(\tau_c - \tau)\right)^{1/2}$. That's one of our predictions: $\xi_0 \sim (\tau_c - \tau)^\beta$, and $\beta = \frac{1}{2}$.

We can evaluate the susceptibility, which is $\chi = \left(\dfrac{\partial \xi}{\partial \lambda}\right)_\tau$. Since $\lambda = \left(\dfrac{\partial F}{\partial \xi}\right)_\tau$, we have $\chi^{-1} = \left(\frac{\partial^2 F}{\partial \xi^2}\right)_\tau$, evaluated at $\xi = \xi_0$ and $\lambda = 0$. We compute that $\left(\frac{\partial^2 F}{\partial \xi^2}\right)_\tau = \alpha(\tau - \tau_c) + 3g_4\xi_0^2$. When $\tau > \tau_c$, $\xi_0 = 0$ makes $\chi^{-1} = \alpha(\tau - \tau_c)$, so $\chi \sim \frac{1}{|\tau - \tau_c|^\gamma}$, and $\gamma = 1$. When $\tau < \tau_c$, $\chi^{-1} = \alpha(\tau - \tau_c) + 3g_4\frac{\alpha}{g_4}(\tau_c - \tau) = 2\alpha(\tau_c - \tau)$. That is, there are two linear approximations to χ^{-1} near $\tau = \tau_c$, approaching zero with slopes whose ratio is -2.

What about the heat capacity? Entropy $\sigma = -\left(\dfrac{\partial F}{\partial \tau}\right)_\xi$ is continuous at $\tau = \tau_c$, so there is no latent heat. The heat capacity is $C_\xi = \tau\left(\dfrac{\partial \sigma}{\partial \tau}\right)_\xi = -\tau\left(\frac{\partial^2 F}{\partial \tau^2}\right)_\xi$. Now $\dfrac{\partial^2 F}{\partial \tau^2} = g_0''(\tau) + g_2''(\tau)\frac{1}{2}\xi^2 + \frac{1}{4}g_4''(\tau)\xi^4 + \cdots$. When $\tau > \tau_c$, $\xi_0 = 0$, so $C_\xi = -\tau g_0''(\tau)$. When $\tau < \tau_c$, we can only write $C_\xi = -\tau(g_0''(\tau) + g_2''(\tau)\frac{1}{2}\frac{\alpha}{g_4}(\tau_c - \tau) + \cdots)$. That is, the heat capacity $C_\xi(\tau)$ is continuous at $\tau = \tau_c$, but $\dfrac{d}{d\tau}C_\xi(\tau)$ is discontinuous at $\tau = \tau_c$.

How are λ and ξ related at $\tau = \tau_c$? $\lambda = \left(\dfrac{\partial F}{\partial \xi}\right)_\tau = \alpha(\tau - \tau_c)\xi + g_4\xi^3 + \cdots \propto \xi^3$ when $\tau = \tau_c$. That is, in general $\lambda \sim \xi^\delta$, and $\delta = 3$. This is another prediction.

But as we know, these values do not match the experimental values. Therefore, our fundamental assumption is wrong: $F(\xi, \tau)$ is not analytic. Thus F must actually be analytic! In other words, there are singularities due to large fluctuations at long wavelengths. The order parameter will depend on the spatial position. There's a critical slowing-down due to long-wavelength fluctuations, which decay slowly.

There is a critical cloudiness where overdense and underdense regions due to fluctuations appear as $\tau \to \tau_c$. These will even scatter light when the droplet size is on the range of visible light wavelengths. These fluctuations have no characteristic length scale, i.e. occur at all length sclaes as $\tau \to \tau_c$.

Kadanoff-Wilson scaling theory takes averages of portions of a magnet, say, and redoing the problem for a larger length scale. The formulas for F and G will have similar functional forms.

The scaling hypothesis for Gibbs free energy: Let $L_{\text{big cell}} = \tilde{\Omega} L_{\text{small cell}}$. Then with $\epsilon = \frac{\tau - \tau_c}{\tau_c}$, $\xi \to \tilde{\Omega}^{\text{power}}\xi$ and $\epsilon \to \tilde{\Omega}^{\text{power}}\epsilon$. The correlation length, the size of the fluctuation droplets diverges as $\tau \to \tau - c$. We'll get $G(\Omega^p\epsilon, \Omega^q\lambda) = \Omega G(\epsilon, \tau)$, where Ω is a dimensionless number.

Differentiating this and evaluating at $\tau = \tau_c$, $\Omega^{2q}\chi(\Omega^p\epsilon) = \Omega\chi(\epsilon)$, or $\chi(\epsilon) = \Omega^{2g-1}\chi(\Omega^p)$, a constant. Therefore, choose $\Omega(\epsilon)$ so that $\Omega^p\epsilon$ is constant, and $\Omega \sim \epsilon^{-1/p}$. Therefore, $\chi(\epsilon) \sim (\epsilon^{-1/p})^{2q-1} = \frac{1}{\epsilon^\gamma}$, where $\gamma = \frac{2q-1}{p}$. On the homework, we'll derive a similar result for $\lambda \sim \xi^\delta$ and $c_\lambda \sim \frac{1}{|\epsilon|^\alpha}$. Since the values are consistent across different systems, this scaling theory is more effective than Landau theory, but it doesn't give us p and q directly.

18 Thursday, May 27, 2010

18.1 Second Order Phase Transitions and Scaling

The function $F(\xi, \tau)$ is even in ξ. We had four predictions:

- The minimum at $\tau < \tau_c$ occurs at $\xi \sim (\tau_c - \tau)^\beta$.
- $\chi = \left(\dfrac{\partial\xi}{\partial\lambda}\right)_\tau \sim \frac{1}{|\tau-\tau_c|^\gamma}$.
- At $\tau = \tau_c$, $\lambda \sim \xi^\delta$.
- $C_\xi \sim \tau\left(\dfrac{\partial\sigma}{\partial\tau}\right)_\xi \sim \frac{1}{|\tau-\tau_c|^\alpha}$.

Actually, the experimental values of F and G are singular at the critical point. Landau assumed that fluctuations were negligible, but in fact, there are large fluctuations at a large range of length scales.

To make some new predictions, we consider scale invariants. They are properties that look the same at all length scales. The assumption that the change in length scale is equivalent to rescaling of $\epsilon = \frac{\tau-\tau_c}{\tau_c}$ and the external field λ. That is, the scaling hypothesis assumes $G(\Omega^p\epsilon, \Omega^q\lambda) = \Omega G(\epsilon, \lambda)$, where p and q are arbitrary constants. Let's calculate what this predicts about these singularities. For $\chi = -\left(\frac{\partial^2 G}{\partial\lambda^2}\right)_\tau$, as $\lambda \to 0$, $\chi(\epsilon) = \Omega^{2q-1}\chi(\Omega^p\epsilon)$. Letting $\Omega = |\epsilon|^{-1/p}$, the $\chi(\Omega^p\epsilon)$ is constant, so $\chi(\epsilon) \sim \frac{1}{|\epsilon|^{(2q-1)/p}}$. This gives $\gamma = \frac{2q-1}{p}$. We can use similar adjustments to make predictions on α, β, and δ. This gives us two relations among these parameters, and these *do* agree with experiment.

We can think of Landau theory as a sort of "mean-field theory" because it assumes that the average field over all particles is the field felt at a particular point. Taking the magnet as an example, this is not true because the nearest neighbors have a greater effect.

How can we study this? How can we change the number of neighbors? We can change the number of dimensions in our problem. With larger dimensions d, each spin has more neighbors, so it's a better approximation to ignore fluctuations. There's some "upper-critical dimension" d_c, where if $d > d_c$, fluctuations are suppressed, and Landau theory works, but if $d < d_c$, there are large fluctuations and Landau theory fails. It turns out that $d_c = 4$, so Landau was slightly unlucky that we live in 3 dimensions. At $d = d_c = 4$, this is the "marginal dimension," and Landau theory almost works.

There's also a lower critical dimension d_{lower} such that the system is disordered at every $\tau > 0$. For example, for a uniaxial magnet (spins must be up or down), $d_{\text{lower}} = 1$. Think of a series of spins which will want to align, but every once in a while will have a kink. Since the next spin will want to align with the kink, it will continue in the opposite orientation until another kink occurs. These kinks will add an approximately constant energy to the system, and will be Boltzmann-depressed, but as long as there is at least one, the overall spin will be small and nonoriented.

By contrast, in two dimensions, kinks will have to occur along surfaces of droplets, and the energy of a droplet is proportional to its perimeter.

Wilson had a crazy idea: Since Landau theory works in 4 dimensions, we instead assume we have $4 - \epsilon$ dimensions, expand in a power series in ϵ, and then take $\epsilon = 1$. This actually works.

We can also talk about universality classes. For example, a rotationally invariant magnet, where spins can point in any direction, has $d_{\text{lower}} = 2$. This is different because it has a different symmetry.

18.2 Kinetic Theory (Chapter 14)

The rest of the book is full of fun applications. We'll focus on kinetic theory, which is a "microscopic view of macroscopic phenomena."

For example, we have already looked at non-ideal gases. We can also consider diffusion, the essentially random movement of particles in a gas. This is relevant to diffusive transport, which has a lot of applications. Charge transport relates to electrical conductivity; energy transport relates to heat conduction; and momentum transport relates to viscosity. There's a fundamental time scale for mixing in each of these cases.

We won't get to diffusion until next time, though. A lot of what we'll be looking at today is considered classical statistical physics; we won't need quantum that much.

18.2.1 Principle of equipartition of energy

One theorem the masters of statistical physics arrived at is the *principle of equipartition of energy.* If we consider a free particle in 3D, we've already discussed how we count states. We convert a sum to an integral, getting $\frac{V}{(2\pi\hbar)^3}\int d^3p$ or $\int \frac{d^3x d^3p}{(2\pi\hbar)^3}$. That is, $(2\pi\hbar)^3 = h^3$ is the "phase-space volume per orbital" (in 3 dimensions). Now, Boltzmann and other classical physicists didn't know about h, but they didn't need to; they just assumed that the volume taken up per orbital would be some finite constant.

Considering an ideal gas of N particles, in classical physics, we can predict the system given the positions $\vec{x}_1, \dots, \vec{x}_N$ and momenta $\vec{p}_1, \dots, \vec{p}_N$. State counting would simply correspond to integrating $\int d^3x_1 d^3x_2 \cdots d^3x_N d^3p_1 \cdots d^3p_N$. Then the kinetic energy is just $E = \frac{1}{2M}(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2})$. If we wanted to calculate the average energy, we lose our normalization constant, getting $\frac{\int e^{-E/\tau}\left(\frac{\vec{p}_1^{\,2}}{2M}\right)}{\int e^{-E/\tau}}$, where this integral is really $\int d^3x_1 d^3x_2 \cdots d^3x_N d^3p_1 \cdots d^3p_N$. Now the exponential of energy is the product of the exponentials of the energies of the particles, so we can separate out each of the particles, and consider it for just one particle: $\langle E \rangle = N \langle E_i \rangle$. Moreover, $\vec{p}^{\,2} = p_x^2 + p_y^2 + p_z^2$, and these three dimensions are going to come out the same. Then we get

$$\langle E_i \rangle = \frac{3\tau \int_{-\infty}^{\infty} dp\, \frac{p^2}{2m\tau} e^{-p^2/2m\tau}}{\int_{-\infty}^{\infty} dp\, e^{-p^2/2m\tau}} = 3\tau \frac{\int_{-\infty}^{\infty} x^2 e^{-x^2}\, dx}{\int_{-\infty}^{\infty} e^{-x^2}\, dx} = \frac{3}{2}\tau.$$

Then the total energy is $U = \langle E \rangle = \frac{3}{2}N\tau$.

Notice that this generalizes: For *any* degree of freedom entering the energy E quadratically, the average energy contribution is $\frac{1}{2}\tau$. This is the statement of equipartition of energy. For example, with a harmonic oscillator with Hamiltonian $H = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2}m_i w_i x_i^2$, e.g. N atoms in 3D space in an elastic solid, then there are $3N$ momentum coordinates and $3N$ position coordinates, all entering the energy quadratically, so $U = 3N\tau$.

This means that $C_V = 3N$, which we derived earlier as the classical limit of a more general setup, as Dulong and Petit found.

We've been assuming that $\tau \gg \hbar\omega$ in order to be able to replace the sum over occupation number by an integral. For bosons, recall that $\langle E \rangle = \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}$, which is τ for $\tau \gg \hbar\omega$ and $\hbar\omega e^{-\hbar\omega/\tau}$. That is, it is exponentially suppressed when τ is small. We say that that degree of freedom "freezes out" at low temperatures.

To understand the equipartition of energy, let's consider more complicated molecules, like diatomic molecules. What other degrees of freedom do we have?

There will be two rotational degrees of freedom and one vibrational degree of freedom in addition to the three momentum degrees of freedom. For the vibrational degree of freedom, we'll get out τ, that is, $\frac{1}{2}\tau$ for the momentum and position of the vibration.

For the angular momentum, we won't consider the full quantum theory of angular momentum, but suffice it to say that the Hamiltonian is $H = \frac{1}{2I}(L_1^2 + L_2^2)$, where θ is angular position and $L = -i\hbar\dfrac{\partial}{\partial\theta}$. The eigenfunctions are going to be $\psi(\theta) = e^{im\theta}$ for $m \in \mathbb{Z}$. Then $L = m\hbar$, and we can write $E = \frac{1}{2I}\hbar^2(m_1^2 + m_2^2)$.

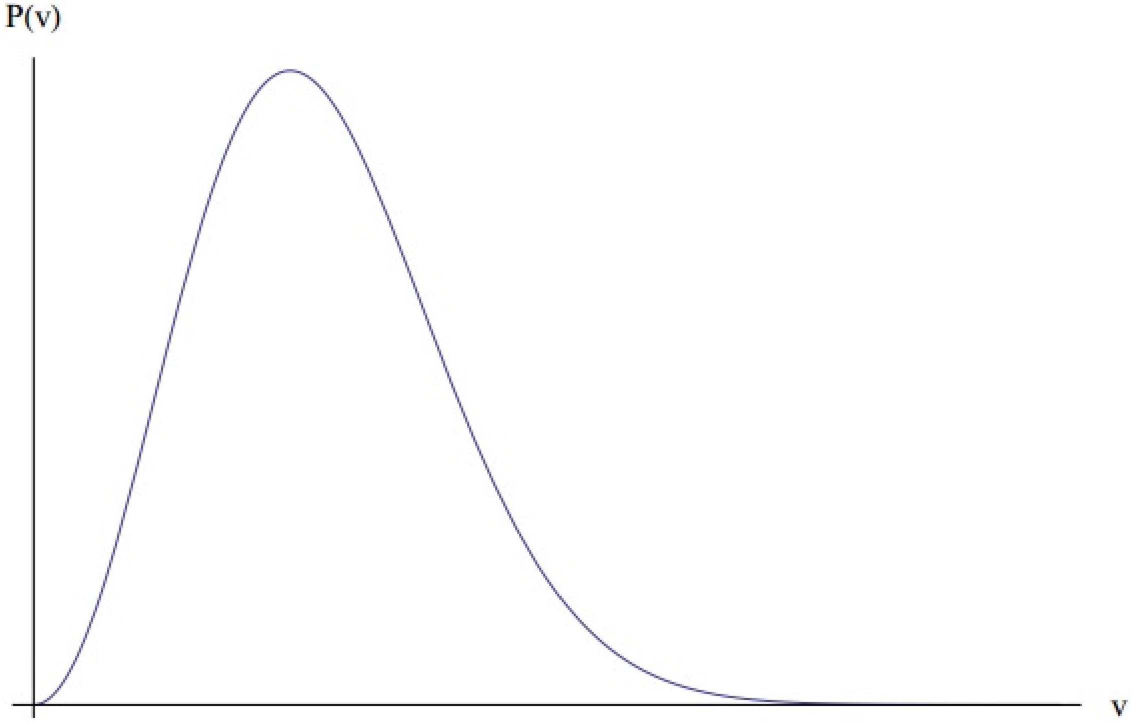
For classical physics, all we're concerned about is that this enters the energy quadratically. But we can also consider the freeze-out of this degree of freedom. This occurs when the temperature is small compared to the energy, or $\tau \ll \hbar^2/2I$.

At $T = 300\mathrm{K}$, rotation is accessible, but vibration is frozen out. If we vary the temperature from $\tau \approx 0$ upwards, first the heat capacity is $C_V = \frac{3}{2}N$, the same as a monatomic gas. Then once rotation becomes accessible, the heat capacity increases to $C_V = \left(\frac{3}{2}+1\right)N$. Increase temperature some more, and vibration will become accessible, making the heat capacity $\left(\frac{3}{2}+1+1\right)N$.

18.2.2 Maxwell distribution of velocity

Let's calculate the distribution of speeds in an ideal gas. A sum over states is replaced with $CV\int d^3p = CV4\pi\int_0^\infty p^2dp = C'\int_0^\infty v^2dv$, where we absorb all those constants, including the masses, in the constant C'. Then kinetic energy is $\frac{1}{2}mv^2$, which will Boltzmann mute the velocity, and the probability distribution will be given by $P(v)dv = \frac{dv\,v^2e^{-Mv^2/2\tau}}{\int dv\,v^2e^{-Mv^2/2\tau}}$. The denominator is equal to $(\tau/M)^{3/2}\int_0^\infty dx\,x^2e^{-x^2/2} = (\tau/M)^{3/2}\frac{1}{4}\sqrt{2\pi}$, so

$$P(v)dv = \left(\frac{M}{\tau}\right)^{3/2}\frac{4}{\sqrt{2\pi}}dv\,v^2e^{-\frac{1}{2}Mv^2/\tau}.$$



Note that if you open a hole in the side of the box and measure the distribution of velocities, the higher velocities are overrepresented, since they will reach the hole from farther away, making the distribution $\propto v^3e^{-\frac{1}{2}Mv^2/\tau}$.

18.2.3 Mean Free Path

The atoms do collide, so let's give them a nonzero radius d. As a particle travels a distance L, it sweeps out a volume πd^2L. Therefore, the number of collisions accrued over this time should be πd^2Ln. So the mean free path will be $\frac{1}{\pi d^2n}$.

If the gas is particularly dilute, the mean free path will be large compared with the size of the particles. That is, the fraction $\frac{L}{d} = \frac{1}{\pi n d^3} \gg 1$ for dilute gases. We can also compare the mean free path to the typical distance between particles: $nL^3 = \frac{1}{n^2\pi^2 d^6}$, so $n^{1/3}L \sim \frac{1}{(nd^3)^{2/3}}$. Therefore, the mean free path is large compared with the distance between particles, for a dilute gas.

We'll talk about diffusion and transport on Tuesday.

19 Tuesday, June 1, 2010

Recall that we were discussing the equipartition of energy. This computation showed that the average energy due to a quadratic degree of freedom (meaning, a phasespace variable, which appears quadratically in the Hamiltonian) is $\frac{1}{2}\tau$. This applies if the variable is "accessible," or classical, generally when $\tau \gg \hbar\omega$.

An example: Pressure. We imagine pressure microscopically with particles impinging on the boundary. They come in with a momentum of mv_z in the perpendicular direction and bounce elastically, imparting an impulse of $2mv_z$ on the surface. The concentration will be $\frac{1}{2}nv_z$ to account for the faster particle hitting the wall more often. Therefore, $p = \frac{F}{A} = \left\langle (\frac{1}{2}nv_z)(2mv_z) \right\rangle = n\left\langle mv_z^2 \right\rangle = n\tau$ by the equipartition of energy. This is exactly what the ideal gas law says: $p = \frac{N}{V}\tau$.

19.1 Diffusion and mean free path

Now let's use our examination of mean free path to understand diffusion. We consider the particles as billiard balls with radius d. If a particle travels a distance L, it sweeps out an area of $L\pi d^2$, so the number of collisions in that time will be $L\pi d^2 n$. This gave us a mean free path of $\frac{\text{distance}}{\text{\# of collisions}} = \frac{1}{\pi d^2 n} = l_{MFP}$.

We noted that since $\frac{1}{n} \sim l_{sep}^3$ (the typical separation between neighbors), so $l_{MFP} \sim \frac{l_{sep}^3}{d^2}$, or $\frac{l_{MFP}}{l_{sep}} \sim \frac{l_{sep}^2}{d^2} \gg 1$ for a dilute gas.

To think about diffusion, imagine a blog of ink placed in a large container of water. Eventually, due to the thermal random motion of the ink, the blob will spread out.

Diffusion can be expressed as a linear PDE: Start with $\vec{J} = D(-\vec{\nabla}n)$, where J is the flux, D is a diffusivity constant, and n is the concentration. The minus sign says that particles move from high concentration to low concentration.

Consider a small cube and how quickly the (ink) particles will escape from this cell. By the divergence theorem, this is $\int d\vec{a}\cdot J = \int d^3x\, \vec{\nabla}\cdot\vec{J}$, a volume integral over the cell. Thus we have $-\int d^3x \,\frac{\partial n}{\partial t} = -\frac{d}{dt}\int d^3x\, n = \int d^3x\, \vec{\nabla}\cdot\vec{J}$, so $\frac{\partial n}{\partial t} = -\vec{\nabla}\cdot\vec{J} = D\nabla^2 n$. This is known as the Diffusion Equation:

$$\boxed{\frac{\partial}{\partial t} n = D\nabla^2 n}.$$

We can also think of the concentration $n(\vec{x},t)$ as a probability distribution of the positions of the particles $P(\vec{x},t)$, which evolves over time. Supposing this distribution is sharply peaked initially (the ink blob), there are more particles at the top of the peak than nearby, so the peak will diffuse outwards.

Let's model this with a discrete system in one-dimensional space and time. We have a line of sites with separation Δ, and we update the probability distribution in each time interval of duration ϵ. At each time interval, individual particles can move one space to the left or the right with probability 1/2.

This rewrites $P(x,t)$ as $P(s,n)$ where $x = \Delta s$ and $t = \epsilon n$ and s and n are integers. Suppose we know for certain that a particle is at $s = 0$ at time $n = 0$. After n updates, $n = n_L + n_R$ and $s = n_R - n_L$ where n_L is the number of steps to the left and n_R is the number of steps to the right.

This is exactly the mathematical problem we considered at the beginning of the year with spins in a magnet. We approximate the binomials as a Gaussian, yielding $P(s,n) = \frac{1}{\sqrt{2\pi n}}e^{-s^2/2n}$ for $n \gg 1$ and $s \ll n$.

To relate this back to x and t, we must consider a probability distribution where for a small interval Δx, the probability a particle is in this interval is $P(x,t)\Delta x$. This probability distribution is then just

$$P(x,t) = \frac{1}{\Delta}\frac{1}{\sqrt{2\pi n}}e^{-s^2/2n} = \frac{1}{\sqrt{2\pi\frac{\Delta^2}{\epsilon}t}}e^{-\left(\frac{\epsilon}{2\Delta^2}\frac{x^2}{t}\right)}.$$

With $D = \frac{\Delta^2}{2\epsilon}$ (as we'll find, this matches our diffusion constant in the PDE), this becomes $P(x,t) = \frac{1}{\sqrt{4\pi Dt}}e^{-x^2/4Dt}$.

Let's rederive our PDE from the discrete model. We do this by deriving a difference equation. The probability of being at site s at time n is $P(s,n) = \frac{1}{2}P(s-1,n-1)+\frac{1}{2}P(s+1,n-1) = P(s,n-1)+\frac{1}{2}[P(s-1,n-1)-2P(s,n-1)+P(s+1,n-1)]$. The quantity in brackets looks like a discrete approximation to a second derivative. We can rewrite it all as

$$\begin{aligned}
P(s,n)-P(s,n-1) &= \frac{1}{2}[P(s+1,n-1)-P(s,n-1)] - \frac{1}{2}[P(s,n-1)-P(s-1,n-1)]\\
\epsilon\left.\frac{\partial P}{\partial t}\right|_{(s,n-1/2)} &\approx \frac{1}{2}\Delta\left.\frac{\partial P}{\partial x}\right|_{(s+1/2,n-1)} - \frac{1}{2}\Delta\left.\frac{\partial P}{\partial x}\right|_{(s-1/2,n-1)} \approx \frac{1}{2}\Delta^2\left.\frac{\partial^2 P}{\partial x^2}\right|_{(s,n-1)}\\
\frac{\partial P}{\partial t} &= \frac{\Delta^2}{2\epsilon}\frac{\partial^2 P}{\partial x^2}.
\end{aligned}$$

Therefore, $D = \frac{\Delta^2}{2\epsilon}$ is the diffusion constant in one dimension.

Our probability distribution satisfies some additional properties: $P \geq 0$, $\int P dx = 1$, and $P(x,t=0) = \delta(x)$. Thus (you can check) the solution is $P(x,t) = \frac{1}{\sqrt{4\pi Dt}}e^{-x^2/4Dt}$, as we found earlier.

Note in this model that particles move at a speed $\frac{\Delta}{\epsilon}\bar{c}$, and the particle "forgets" its direction of motion in time ϵ. Thus, we can express this in terms of the mean free path as $D = \frac{1}{2}\bar{c}l_{MFP}$.

Things don't actually change much in higher dimensions. In d spatial dimensions, let's consider a (hyper)cubic lattice. There are $2d$ neighbors for each site. The particle has a $\frac{1}{2d}$ probability of hopping to each neighbor. The last calculation is entirely identical, except we have a $\frac{1}{2d}$ where we had $\frac{1}{2}$, so $\frac{\partial P}{\partial t} = \frac{1}{2d}\frac{\Delta^2}{\epsilon}\nabla^2 P$, or $D = \frac{\Delta^2}{2d\epsilon}$. In 3D, this is $\frac{1}{6}\frac{\Delta^2}{\epsilon} = \frac{1}{6}\bar{c}l_{MFP}$. If you read Kittel and Kroemer's analysis, they come out with a $\frac{1}{3}$ in front, but that's okay; it's a crude model we should only expect to give us order of magnitude estimates. What goes wrong is that we've chosen six special directions, while if you relax that, the constant changes.

Another way to consider n dimensions is that the particle is diffusing independently in each of the dimensions. $1/d$ of its moves are in a given dimension, and this yields the desired result immediately.

For three dimensions, the overall probability distribution is $\frac{1}{(4\pi Dt)^{3/2}}e^{-\vec{x}^2/4Dt}$. Then $\left\langle \vec{x}^2\right\rangle = 3(2Dt) = \frac{\Delta^2}{\epsilon}t$. Alternatively, $\left\langle x_1^2\right\rangle = \left\langle x_2^2\right\rangle = \left\langle x_3^2\right\rangle = \frac{\Delta^2}{\epsilon}\frac{t}{3}$

This discussion is mathematically very similar to our calculations of the spreading of wave packets in Ph12b, except there are no is and no phase factors. The Schrödinger equation and diffusion equation are similar.

The distribution varies with $\frac{\vec{x}^2}{t^2} = 6D/t \to \infty$ as $t \to 0$. Therefore, the trajectory of a particle is continuous but not differentiable.

19.2 The Einstein Relation

Who figured out that diffusion could be explained microscopically? Einstein, of course. What year? 1905, of course. Another important thing Einstein explained in this paper is this: Consider a force on a particle in a viscous fluid, so it will reach some velocity v, and these will be proportional: $\vec{v} = b\vec{F}$ where b is the mobility. The Einstein relation says that $D = b\tau$. We'll derive this in a couple different ways.

Consider layers of different concentrations of our particle. At equilibrium, the flux is zero, so $-D\vec{\nabla}n+n\vec{v} = -D\vec{\nabla}n + nb\vec{F}$.

We also know that at equilibrium, concentration is going to proportional to the Boltzmann factor: $n = Ae^{-U(\vec{x})/\tau}$ where $\vec{F} = -\vec{\nabla}U$ and A is a constant. Therefore, $\vec{\nabla}n = -\frac{1}{\tau}\vec{\nabla}Un = \frac{1}{\tau}\vec{F}n$, and substituting in, $0 = \vec{F}n(-D/\tau + b)$, so $D = b\tau$ as desired.

Another derivation: Suppose we have particles with speed $V = \Delta/\epsilon$ whose direction is reset in time ϵ. Then $D = \frac{1}{2d}\frac{\Delta^2}{\epsilon} = \frac{1}{2d}V^2\epsilon$. The force applied to the particles accelerates them with $\vec{a} = \vec{F}/M$. But since the particles have their velocities reset every ϵ, this acceleration only produces an average drift speed of $v = \frac{1}{2}\vec{a}\epsilon = \frac{F\epsilon}{2M}$. Thus the mobility is $b = \frac{\epsilon}{2M}$. We can also solve for $\epsilon = \frac{2dD}{V^2}$, so $b = \frac{dD}{MV^2}$. By equipartition of energy, $\left\langle \frac{1}{2}MV^2 \right\rangle = \frac{1}{2}\tau d$. Then the average mobility $b = \frac{dD}{\langle MV^2 \rangle} = \frac{D}{\tau}$, which is Einstein's relation.

Feynman always said that if you have to give two derivations, they must be lousy derivations. Well, in this case, the first derivation was a good one and the second was instructive. It explained how the temperature entered the equation through the equipartition theorem. Similar arguments may be applied to many systems, producing "fluctuation-dissipation relations." The diffusion constant D is the fluctuation and the mobility b is the dissipation. Note that we can write the Einstein relation as $\frac{\langle x^2 \rangle}{b} = 6\tau t$.

We saw a similar relation when we examined Johnson-Nyquist noise. Our equation there was $\frac{\langle v^2 \rangle}{R} = 4\tau(\Delta f)$.

Einstein's relation was relevant because there was still legitimate debate over the existence of atoms, so it was relevant to try to nail down Avogadro's number and give the sizes of atoms. Stokes had previously derived the mobility $b = \frac{1}{6\pi\eta r}$ for a particle of radius r in a fluid of viscosity η. Einstein's relation gives us $\frac{\langle x^2 \rangle}{t} = 6D = 6(k_BT)b = \frac{k_BT}{\pi\eta r}$. While he might not have known about Brown's work on Brownian motion, Einstein predicted that this equation could be used to calculate Boltzmann's constant, which you can use to calculate Avogadro's constant: $pV = \bar{N}RT = k_BNT$, where $\bar{N}$ is the number of moles of particles, so $\frac{N}{\bar{N}} = N_A = R/k_B$ and R (the gas constant) was known. The experiment was done, and for particles of a radius of a micron,

Einstein also came up with other methods for determining Boltzmann's constant (or equivalently Avogadro's constant), such as the Rayleigh-Jeans law he discovered earlier. Using these calculations, he got $N_A = 6.17 \times 10^{23}$, a pretty good approximation.

We'll also say a few words about viscosity. In a pipe, a fluid will have velocity zero near the edges and a maximum velocity in the middle, so there is a velocity gradient. There is going to be transverse diffusion, and this will lead to a momentum diffusion from the center of the pipe to the edges, where it is transferred to the pipe. Equivalently, this shows that one must do work to push the fluid through the pipe. By a derivation we don't have time for, the viscosity is related to the diffusion by $\eta = D\rho$, where ρ is the (mass) density.

20 Thursday, June 3, 2010

The website says that the final is due on the 9th, but since the official exam period ends the 11th, it will be due then instead. The final will be posted by tomorrow. Format is like previous exams: 4 hours, 4 questions, focuses on second half topics.

20.1 Diffusion

Diffusion describes processes on scales where the width of the system is large compared with the mean free path. The prototypical example is a blob of ink spreading in water. The movement is described by a flux $\vec{J} = -D\nabla\vec{n}$, and satisfies the PDE $\frac{\partial n}{\partial t} = D\nabla^2 n$.

We modeled this setup with a discrete system, starting in one dimension. Sites are separated by a distance Δ and a particle moves left or right with probability $1/2$, a random walk. In d dimensions, we derived that $D = \frac{\Delta^2}{2d\epsilon}$. The $2d$ enters in because there are $2d$ directions to hop. In particular, for $d = 3$, $D = \frac{1}{6}\frac{\Delta}{\epsilon}\Delta$. We can think of $\frac{\Delta}{\epsilon}$ as the speed of the particles, and Δ as the mean free path. There is a similar relation with speed and mean free path, but with a factor of $1/3$ due to the crudeness of our model.

We can solve the PDE if we assume initial conditions of a δ-function at the origin. This yields $P(x,t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-\vec{x}^2/4Dt}$. The variance of this Gaussian is given by $\left\langle \vec{x}^2 \right\rangle = (2d)Dt = \frac{\Delta^2}{\epsilon} t$.

We also derived a "fluctuation-dissipation relation," $D = b\tau$, where b is the *mobility.* The mobility is the constant of proportionality of the terminal velocity and the applied force on the particles. This can be used to determine Boltzmann's constant and Avogadro's number, as Einstein did in 1905.

20.2 Maxwell's demon

Can we exploit these fluctuations to do something useful? Can we use knowledge of the microscopic state to attack the limitations of the second law? The answer is no, but for quite subtle reasons. This was uncovered by Maxwell, and in 1871 wrote about this in "Limitations of the Second Law."

Suppose we have a box divided into two halves A and B. The box is isolated and begins at temperature τ. We want to decrease the temperature of the A half and increase that of the B half. We introduce a passage between the halves with a small shutter separating them. Our demon (or we can think of him as a good guy) opens the shutter if a fast particle is moving toward it from side A or if a slow particle is moving toward it from side B, but closes it otherwise.

After operating in this fashion for a while, the A side should cool and the B side heat up. But the second law says that we cannot transfer heat from a cold system to a hot system without work. And it seems that by only opening the shutter slightly, the demon could use arbitrarily small amounts of work. Maxwell was puzzled by this.

The next person to work on this was Leo Szilard (1929). Szilard was convinced that the demon might be doing something irreversible. He tried to address the questions but not quite successfully. He asked whether the demon generates a compensating entropy (i.e. dissipate heat) so the total entropy does not actually decrease.

Szilard's paper was important because he was hte first to try to explicity set up an equivalence between entropy and information. Shannon in 1948 carried this forward, inventing modern communication theory. He claimed that acquiring one bit of information would generate entropy $S \geq k_B \ln 2$. Often when we talk about information, we work in logarithms base 2 as a result.

Szilard was rather vague with what he wrote about this. He talked of measurement, memory and didn't really discuss erasure of memory. Later interpretations understood him to be saying that measurement is irreversible. However, this is wrong; there's a different resolution.

To get a firmer picture of what's going on, consider a 1-molecule gas. Usually statistical physics uses a bunch similar states, so if necessary use an ensemble of 1-molecule gases.

The steps look like this: (1) We place a partition between the sides. (2) We measure and record which side the particle is on, gaining 1 bit of information. (3) We then load a piston at the partition with a weight which can be drawn upwards (work can come out) when the 1-molecule gas expands isothermally. We already derived that the change in entropy in isothermal expansion is $\Delta S = Nk_B \ln(V_f/V_i) = 2Nk_B$ once the one-particle side fills the entire container. The work done is just $W = k_B T \ln Z$. This is repeatable, but we gain positive entropy of $k_B T \ln Z$.

Or is it? Charles Bennett in 1982 observed that this is not quite a closed cycle: We gain 1 bit of recorded information. In order to make this a closed cycle, we have to erase our memory. Previously, Landauer (1961) observed that erasure of a bit is irreversible. Erasure generates heat, which returns to the reservior. This is an adequate explanation, so let's examine the theory of recording and erasing of in format.

The demon's memory begins empty but later collects a list of states, say, $\uparrow$ corresponds to the particle being on the left. Initially, his memory is empty and there are two situations: particle on the left (denoted L) and particle on the right (R). After his measurement, the situation is $\uparrow L$ and $\downarrow R$. These are correlated, so if we looked at the subsystems of the memory and the molecule, each has 1 bit of information ($k_B \ln 2$) but the total system also has 1 bit, not 2. The entropy has not yet increased, so this measurement is reversible.

The next step is isothermal expansion, exploiting the demon's memory. This increases the entropy of the system by 1 bit because the correlation is destroyed and there are now four states: $\uparrow L, \uparrow R, \downarrow L, \downarrow R$. This entropy is gained from the thermal reservoir.

To reset the demon (erase his memory), we must remove one bit of entropy from the system, which returns to the reservoir. This erasure costs work $W \geq k_B T \ln 2$. If we don't reset his memory, it accumulates, and his memory behaves exactly as a zero temperature reservoir into which we have dumped "waste heat." If he had infinite memory, that's like an infinite zero temperature reservoir, which makes our conclusions not too surprising. If it is finite, he can continue for a while, but eventually has to dump the entropy to be able to continue.

Now we have a new version of the question: Why is erasure of information dissipative?

The first thing to notice is that erasure is "logically irreversible," in that it is not an invertible function. It takes a bit that is either 0 or 1 and maps both these values to 0, say. We want to argue that logical irreversibility implies thermodynamic irreversibility.

Let's pretend that the demon's memory is another molecule in another box, which can be on the left half or right half. We have a molecule on either side of the box, and we want it to end up always on the right side of the box. We have to do this without recording any information about its state. In other words, the operations we do have to work the same whether or not the molecule is on the left or right. How can we perform this?

First we remove the partition, then we isothermally compress. But this takes work, in fact, work of $W \geq k_B T \ln 2$, and dissipates an entropy of $k_B \ln 2$, as required.

Why is this irreversible? If we tried to undo our steps by expanding and then replacing the partition, the resulting bit would be uncorrelated with our original bit, so it's not reversible. Remember, we don't want to have a random bit in the memory afterwards, since we want to be able to perform some operation to correlate with the original gas particle.

This discussion can be extended further to ask the question: What is the thermodynamic cost of computation? For example, consider a NAND gate, which is logically universal; any gate can be constructed out of NAND gates. The NAND gate takes 00, 10, and 01 to 1 and 11 to 0. This is, of course, logically irreversible (many to one). Landauer was working for IBM and figured they would care about this, and concluded that computation thermodynamically requires $k_B T$ per logic gate.

But he was wrong. Measurement can be reversible. We can instead model NAND and other gates with 3 to 3 bit universal gates. An example is the Toffoli gate, which maps $(a, b, c) \mapsto (a, b, c \oplus ab)$. That is, it reverses the third bit if a and b are both 1. This is invertible (it is its own inverse). It is also universal, since $(a, b, 1) \mapsto (a, b, \neg(a \wedge b))$, which is the NAND gate. Essentially, you take a NAND gate but you keep the original bits as well.

Landauer, hearing this, might have complained that you have a bunch of junk information that you will have to erase at some point, which will generate entropy. But you can build a computer that does everything reversibly. Let me see if I can describe this. First we take our input and a bunch of zeros and produce our outputs and some junk. We then copy the output using some extra zeros (this is reversible), save one copy of the output, and then run the other copy and the junk backwards to get the input and zeros again. Overall we've just added a bunch of overhead (the extra zeros) to the system, and we can refine this, but the point is that we can do computation for free!

We want to end the term on a high note, but we should point out a couple caveats: (1) Today's processors use around $10^5 k_B T$ per operation, far from Landauer's limit anyways, for unrelated reasons. But at least there is no theoretical lower limit. (2) Reversible computation is error-prone, and suppressing errors requires cooling and hence dissipation. Information is stored in the position of electric charges, which we can think of being in a potential well. Like trying to place an air hockey puck on the air hockey table, we want to put the hockey puck in position without giving it enough energy to hop over to the other state.

More problems arise related to error correcting if you try to do quantum computing, because you additionally want to decohere the system from the entire surroundings, encrypt it, in other words.