Chapter 9
Statistical Mechanics

9.1 Statistical Distributions

This first section is just an overview.

Statistical mechanics deals with the behavior of systems of a large number of particles.

> It does this by calculating the most probable behavior of the system as a whole, rather than by being concerned with the behavior of individual particles.

> In statistical mechanics, we assume that the more ways there are to arrange the particles to give a particular distribution of energies, the more probable is that distribution.

> Seems reasonable, but it nevertheless is an assumption.

Beiser mentions W, which is the number of ways to arrange particles to give a particular distribution of energies. The idea is to calculate W, and find when W is maximized. That gives us the most probable state of the system.

> W doesn't appear anywhere else in this chapter. In previous editions, it was calculated in an appendix, where Beiser derived all the distribution functions we will use.

Here, in words, is the equation we will be working with:

> (# of particles in a state of energy E)=(# of states having energy E)*(probability that a particle occupies the state of energy E).

> If we know the distribution (the probability that a particle occupies a state of energy E), we can make a number of useful calculations.

> Mathematically, the equation is written

$$n(\varepsilon) \; = \; g(\varepsilon)f(\varepsilon).$$

> It is common to use epsilon to represent energy; I will call it "E" when I say it.

> In systems such as atoms, only discrete energy levels are occupied, and the distribution of energies is not continuous.

> On the other hand, it may be that the distribution of energies is continuous, or at least can be approximated as being continuous.. In that case, we replace $g(\epsilon)$ by $g(\epsilon)d\epsilon$, the number of states between ϵ and $\epsilon+d\epsilon$.

We will find that there are several possible distributions f(ϵ) which depend on whether particles are distinguishable, and what their spins are.

> Beiser mentions them (Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac) in this section, but I will save that for later, when we treat the distributions in separate sections, beginning with the next section.

9.2 Maxwell-Boltzmann Statistics

Classical particles which are identical but far enough apart to distinguish obey Maxwell-Boltzmann statistics.

> Example: ideal gas molecules.

The Maxwell-Boltzmann distribution function is

$$f(\epsilon) = A\,e^{-\epsilon/kT}.$$

The number of particles having energy ϵ at temperature T is

$$n(\epsilon) = Ag(\epsilon)\,e^{-\epsilon/kT}.$$

A is like a normalization constant; we integrate n(ϵ) over all energies to get N, the total number of particles. A is fixed to give the "right" answer for the number of particles. For some calculations, we may not care exactly what the value of A is.

ϵ is the particle energy, k is Boltzmann's constant (1.38×10^{-23} J/K), and T is the temperature in Kelvins.

> When k and T appear together, you can be sure that k is Boltzmann's constant.

> Beiser justifies this distribution in Chapter 9, and but doesn't derive it in the current text. I won't go through all this justification. You can read it for yourself.

Important example, page 300.

> A cubic meter of atomic H at 0°C and atmospheric pressure contains about 2.7×10^{27} H atoms. Find how many are in their first excited state, n=2.

> For an atom in the ground state

$$n(\epsilon_1) = Ag(\epsilon_1)\,e^{-\epsilon_1/kT},$$

> and for an atom in the first excited state

$$n(\epsilon_2) = Ag(\epsilon_2)\,e^{-\epsilon_2/kT},$$

We can divide the equation for n(ϵ_1) by the equation for n(ϵ_2) to get

$$\frac{n(\varepsilon_2)}{n(\varepsilon_1)} = \frac{g(\varepsilon_2)}{g(\varepsilon_1)} e^{-(\varepsilon_2-\varepsilon_1)/kT}.$$

Now, we know ϵ_1, ϵ_2, and T. We need to calculate the $g(\epsilon)$'s, which are the number of states of energy ϵ.

We can do this for hydrogen by counting up the number of allowed electron states corresponding to each ϵ, or we can simply recall that there are $2n^2$ states corresponding to each n, so that $g(\epsilon_1)=2(1)^2$ and $g(\epsilon_2)=2(2)^2$.

Plugging all of our numbers into the equation for $n(\epsilon_2)/n(\epsilon_1)$ gives $n(\epsilon_2)/n(\epsilon_1)=1.3x10^{-188}$. In other words, none of the atoms are in the n=2 state.

You can ignore example 9.2; you won't be tested on it.

9.3 Molecular Energies in an Ideal Gas

In this section, we use the Maxwell-Boltzmann distribution to learn about the energies and speeds of molecules in an ideal gas.

First, we need to calculate $n(\epsilon)$.

We begin by writing

$$n(\varepsilon)d\varepsilon = Ag(\varepsilon)e^{-\varepsilon/kT}d\varepsilon.$$

In other words, we suppose a continuous distribution of particle energies.

Is this a reasonable thing to do? If so, why?

Now, we need $g(\epsilon)$. The example on page 300 of section 9.2 was a specific quantum mechanical calculation, applicable to hydrogen. Here we will do the calculation of $g(\epsilon)$ classically. This calculation is valid where the number of particles is small compared to the available states.

In three dimensions a classical particle's momentum is

$$p = \sqrt{2m\varepsilon} = \sqrt{p_x^2 + p_y^2 + p_z^2}.$$

The number of momentum states in a spherical shell from p to p+dp is proportional to $4\pi p^2 dp$ (the volume of the shell).

Thus, we can write the number of states having momentum between p and p+dp as

$$g(p)dp = Bp^2 dp.$$

Since each p corresponds to a single ϵ,

$$g(\varepsilon)d\varepsilon = g(p)dp = B\,p^2\,dp,$$

where B is the proportionality constant, which we will evaluate later.

Now,

$$p^2 = 2m\varepsilon, \qquad p = \sqrt{2m\varepsilon}, \qquad dp = \sqrt{2m}\,\frac{1}{2}\varepsilon^{-1/2}\,d\varepsilon,$$

so that

$$p^2\,dp \propto \varepsilon\,\varepsilon^{-1/2}\,d\varepsilon,$$

and

$$n(\varepsilon)d\varepsilon = C\sqrt{\varepsilon}\,e^{-\varepsilon/kT}\,d\varepsilon.$$

To find the constant C, we evaluate

$$N = \int_0^\infty n(\varepsilon)d\varepsilon = C\int_0^\infty \sqrt{\varepsilon}\,e^{-\varepsilon/kT}\,d\varepsilon.$$

Could you do the integral? Could you look it up? The result is

$$N = \frac{C}{2}\sqrt{\pi}(kT)^{3/2},$$

so that

$$n(\varepsilon)d\varepsilon = \frac{2\pi N}{(\pi kT)^{3/2}}\sqrt{\varepsilon}\,e^{-\varepsilon/kT}\,d\varepsilon.$$

This is the number of molecules having energy between ϵ and $\epsilon+d\epsilon$ in a sample containing N molecules at temperature T.

Plot:

This plot was a bit of a pain to do with Quattro Pro, which I used to generate the numbers to input into a plotting package, but is trivial to create with Mathcad. The disadvantage with Mathcad (non-windows) is that you can't export a graph into Wordperfect.
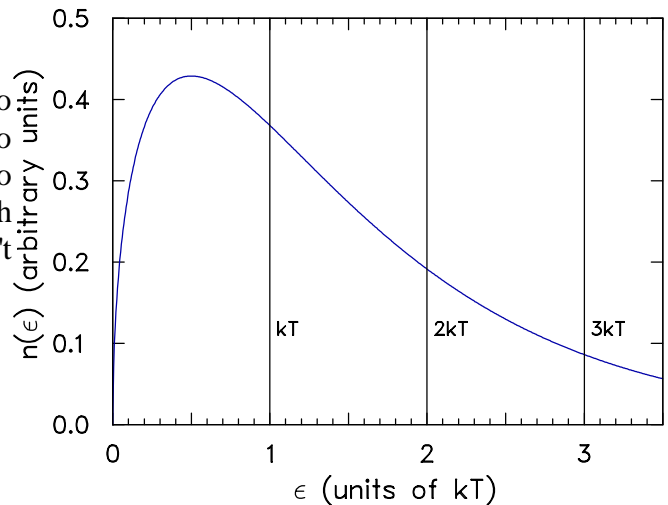
The total energy of the system is

$$E \;=\; \int_0^\infty \varepsilon n(\varepsilon)d\varepsilon \;=\; \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty \varepsilon^{3/2} e^{-\varepsilon/kT} d\varepsilon.$$

Evaluation of the integral gives E=3NkT/2.

The average energy <u>per molecule</u> is just

$$\bar{\varepsilon} \;=\; \frac{3}{2}kT,$$

which is exactly the result you get from elementary kinetic theory of gases.

Things to note about our result for ideal gas energy:

The energy is independent of the molecular mass.

Which gas molecules will move faster at a given temperature: lighter or heavier ones? Why?

$\bar{\varepsilon}$ at room temperature is about 40 meV, or (1/25) eV. This is not a large amount of energy.

kT/2 of energy "goes with" each degree of freedom.

Since ε=mv^2/2, we can also calculate the number of molecules having speeds between v and v+dv.

The result is

$$n(v)dv \;=\; \frac{\sqrt{2}\pi N\, m^{3/2}}{(\pi kT)^{3/2}} v^2 e^{-mv^2/2kT} dv.$$

The speed of a molecule having the average energy comes from $\bar{\varepsilon}$=mv^2/2=3kT/2.

The result is just

$$v_{RMS} \;=\; \sqrt{\overline{vbar}^2} \;=\; \sqrt{\frac{3kT}{m}}.$$

This is an RMS speed because mv^2/2 is an average of the energy, so it gives an average of the square of the speed.

The average speed $\bar{v}$ can be calculated from

$$\bar{v} \;=\; \frac{\int_0^\infty vn(v)dv}{\int_0^\infty n(v)dv}.$$

It turns out that v_{RMS}=1.09$\bar{v}$.

You can also set dn(v)/dv=0 to find the most probable speed

$$v_p = \sqrt{\frac{2kT}{m}}.$$

Now we've gone through a lot of math without thinking much about the physics of our system of gas molecules. We should step back and consider what we've done.

A statistical approach has let us calculate the properties of an ideal gas. We've looked at a few of these properties (energies and speeds).

This is "modern" physics, but not quantum physics.

9.4 Quantum Statistics

Here we deal with ideal particles whose wave functions overlap. We introduce quantum physics because of this overlap.

The function $f(\epsilon)$ depends on whether or not the particles obey the Pauli exclusion principle.

Recall that electrons and other particles with half-integral spin (1/2, 3/2, 5/2, etc.) are *fermions* and obey the Pauli exclusion principle. The wave function of a system of fermions is *antisymmetric* because it changes sign upon the exchange of any pair of fermions. We will find that fermions follow *Fermi-Dirac* statistics.

Recall also that photons and other particles with integral spin (0, 1, 2, etc.) are *bosons* and are not subject to the Pauli exclusion principle. The wave function of a system of bosons is *symmetric* because it sign remains unchanged upon the exchange of any pair of bosons. We will find that bosons follow *Bose-Einstein* statistics.

Let's explore symmetric and antisymmetric wave functions in a little more detail.

Consider a system of two particles, 1 and 2, having two states, a and b. If the particles are distinguishable and we put one particle in each state, there are two possible wave functions:

$$\Psi_I = \Psi_a(1)\Psi_b(2) \quad \text{and} \quad \Psi_{II} = \Psi_a(2)\Psi_b(1).$$

If the particles are indistinguishable, then we cannot tell whether the system is in state ψ_I or ψ_{II}, and, because both states are equally likely, we write the system wave function as a linear combination of ψ_I and ψ_{II}.
If the particles are bosons, the system wave function is symmetric:

$$\Psi_B = \frac{1}{\sqrt{2}}\left[\Psi_a(1)\Psi_b(2) + \Psi_a(2)\Psi_b(1)\right] = \Psi_S$$

If the particles are fermions, the wave function is antisymmetric:

$$\Psi_F \;=\; \frac{1}{\sqrt{2}}\Big[\psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1)\Big] \;=\; \Psi_A$$

What happens if we try to put both particles 1 and 2 in the same state?

If the particles are distinguishable,

$$\Psi_M \;=\; \psi_a(1)\,\psi_a(2),$$

and the probability density for distinguishable particles is

$$\Psi_M^{*}\Psi_M \;=\; \psi_a^{*}(1)\,\psi_a^{*}(2)\,\psi_a(1)\,\psi_a(2).$$

Recall that distinguishable particles were described in the previous section by Maxwell-Boltzmann statistics.

If the particles are bosons, we get

$$\Psi_B \;=\; \sqrt{2}\,\psi_a(1)\,\psi_a(2),$$

with a probability density

$$\Psi_B^{*}\Psi_B \;=\; 2\,\psi_a^{*}(1)\,\psi_a^{*}(2)\,\psi_a(1)\,\psi_a(2) \;=\; 2\,\Psi_M^{*}\Psi_M.$$

In other words, if the particles are bosons, they are twice as likely to be in the same state as distinguishable particles.

On the other hand, if the particles are fermions,

$$\Psi_F \;=\; \frac{1}{\sqrt{2}}\Big[\psi_a(1)\,\psi_a(2) - \psi_a(1)\,\psi_a(2)\Big] \;=\; 0,$$

with a probability density

$$\Psi_F^{*}\Psi_F \;=\; 0.$$

If the particles are fermions, it is impossible for both particles to be found in the same state.

In general, the presence of a boson in a particular quantum state ***increases*** the probability that other bosons will be found in the same state, but the presence of a fermion in a particular quantum state ***prevents*** other fermions from being in that state.

We are now ready to write down the distribution functions for bosons and fermions.

For bosons, the distribution function is

$$f_{BE}(\varepsilon) \;=\; \frac{1}{e^{\alpha}\,e^{\varepsilon/kT} - 1}.$$

For fermions, the distribution function is

$$f_{FD}(\varepsilon) = \frac{1}{e^{\alpha}e^{\varepsilon/kT}+1}.$$

These were derived in an appendix in the previous edition of Beiser, but are just given as truth here.

Remember, bosons are particles with integral spins. There is no limit on the number of bosons which may occupy any particular state (typically the ground state). Examples are photons in a cavity, phonons, and liquid ^{4}He.

Also remember, fermions are particles with half integral spin, with only one particle per state n, l, m_l, m_s. The +1 in the denominator of $f(\epsilon)$ means that the $f(\epsilon)$ is never greater than 1. Examples are free electrons in metals and nuclei in collapsed stars.

The Fermi energy is the energy at which $f_{FD}=1/2$. From this we see that $\epsilon_F=-\alpha kT$, and we can write f_{FD} as

$$f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon-\varepsilon_F/kT)}+1}.$$

Here's a plot of the Fermi-Dirac distribution function at T=0, 150, 300, and 1000K.

Fermi–Dirac Distribution Function for ϵ_F=1 eV

109
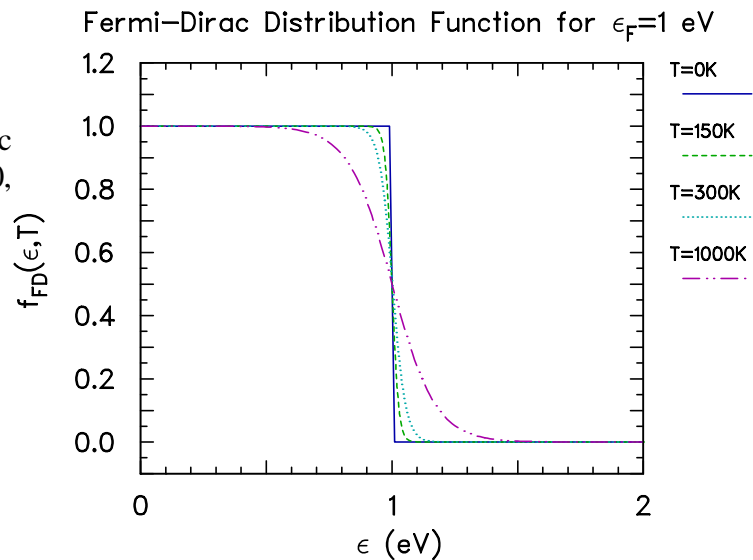
Here's a comparison of the Fermi-Dirac and Bose-Einstein distribution functions at T=300K.

If you notice anything "funny" about the scaling of this plot (how can we have a probability greater than 1?), it's because we really should set the parameter α (which is related to the Fermi Energy in the Fermi-Dirac distribution) equal to zero for the Bose-Einstein distribution. I didn't do that here, and generated a figure like figure 9.5 in Beiser.
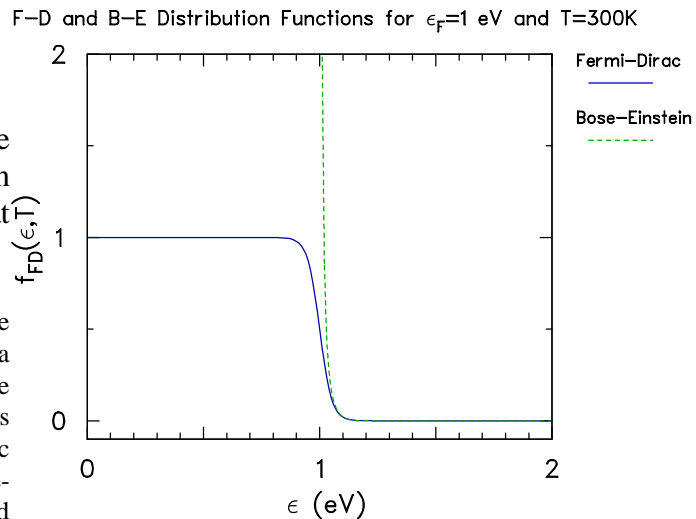
Note how the plot shows the following:

> The presence of a boson in a particular quantum state ***increases*** the probability that other bosons will be found in the same state.

> The presence of a fermion in a particular quantum state ***prevents*** other fermions from occupying the same state.

Table 9.1 on page 311--study this table for the quizzes and exams!

9.5 Rayleigh-Jeans Formula

A blackbody is the best possible absorber/emitter of radiation.

> We already covered this in chapter 2. Review your class notes, or my WordPerfect notes, for details.

The spectrum of blackbody radiation depends only on the temperature of the blackbody.

> This is nice because you don't need to worry about the details of the composition of the blackbody.

> We can make a surprisingly good blackbody out of a box with a hole. The radiation coming out of the hole is typical of blackbody radiation.

Here are a couple of blackbody spectra. Rayleigh and Jeans tried to calculate this classically.
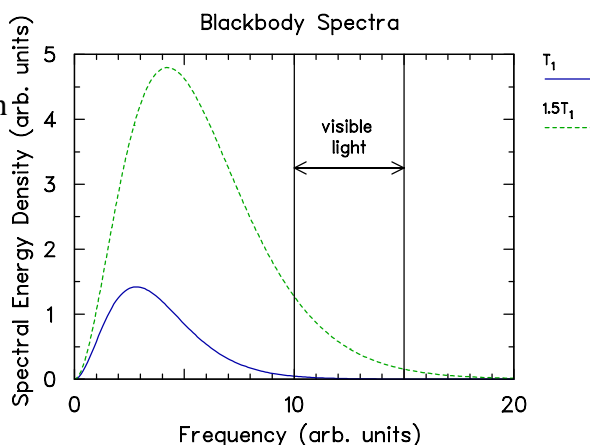
Blackbody Spectra

Here's the basic idea behind the calculation: to calculate the spectrum of radiation from a blackbody, consider a box with a hole in it.

Radiation can get in the hole. It then reflects back and forth inside the cavity.

We've discussed this problem before in several different contexts. If the radiation interferes destructively, it will never get out. We only see radiation (waves) getting out that were able to set up standing waves inside the cavity.

Our job is thus to determine what kinds of standing waves can exist in the cavity, and what their energies are.

It is not difficult, but it is somewhat tedious, to calculate the number of standing waves allowed for any particular frequency interval. This is the result:

$$g(f)df = \frac{8\pi L^3}{c^3} f^2 df,$$

where g(f)df is the number of standing waves ("modes") between f and f+df, and L^3 is the cavity volume. Note that the number of modes is proportional to f^2.

The details of this derivation are worthwhile if you are going to study solid state physics at a more advanced level. I won't test you on the details here, but you should understand the results.

You can calculate the density of standing waves by dividing the above result by the volume, L^3.

To get the energy density (energy per unit volume), simply multiply by the energy of an oscillator of frequency f (we assume the waves originate in oscillators in the cavity walls).

Remember, kT/2 goes with each degree of freedom, and an oscillator has two degrees of freedom, so multiply by kT.

The spectral energy density is thus

$$u(f)df = \frac{8\pi f^2 kT}{c^3} df.$$

The plot below shows a blackbody spectrum and the Rayleigh-Jeans result.

The Rayleigh Jeans equation above is the origin of the "ultraviolet catastrophe." It predicts increasing energy density with increasing f. It doesn't match experiment at all. It doesn't even come close. Something is seriously wrong.
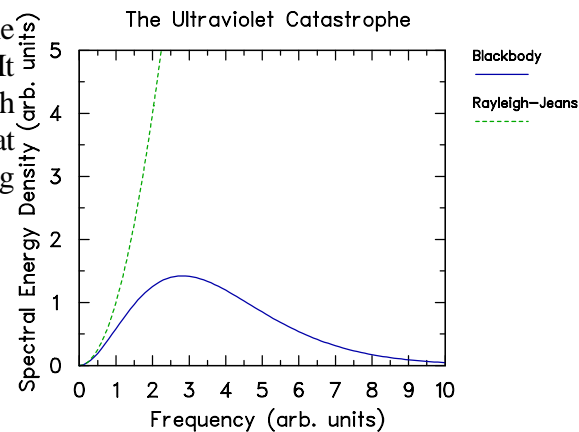
9.6 Planck Radiation Law

In the last section we derived the Rayleigh-Jeans formula for the spectral energy density for blackbody radiation. We found that it failed miserably.

What's wrong with the Rayleigh-Jeans formula?

We divided up the energy into kT/2 for each degree of freedom. This is fine for a continuous energy distribution. It doesn't work when energy is quantized in units of hf. Therefore, our energy density was wrong.

Our density of standing wave modes,

$$G(f) = \frac{8\pi f^2}{c^3} df$$

as calculated above is OK.

To get the energy density of photons in the cavity, we multiply our density of modes by the energy of each mode and the probability as a function of T that a mode is occupied. This gives us the real energy density.

So, we simply multiply G(f)df by hf (energy of a photon) and the f_{BE} of the Bose-Einstein distribution (note two different f's here, which is why it might be better to use ν for frequency):

$$u(f)df = hf\, G(f)df\; f_{BE}(f) = \frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT}-1} df.$$

This is called the Planck radiation formula, and it works very well. Plug it into Mathcad and

try it some time.

Note that $\alpha=0$ in Bose-Einstein distribution function, which you use in the equation above. α is a constant which appears in an equation which says that the number of particles is conserved. If we don't require conservation of particles, we set $\alpha=0$.

Wien's displacement law

You can calculate the wavelength at the peak of the energy density by expressing u as a function of wavelength and taking the derivative.

The result is $\lambda_{max}T=2.898 \times 10^{-3}$ m·K, Wien's displacement law, which tells which way the peak in the spectrum shifts as the temperature changes.

The Stefan-Boltzmann law

The total energy density inside the cavity is found by integrating the energy density over all frequencies.

The result is proportional to T^4.

The Stefan-Boltzmann law says $R=e\sigma T^4$, where R is the radiated energy per second per unit area, and e is the emissivity of the radiating surface, and σ is a constant (see Beiser for the value of σ).

Consider designing a cryostat or furnace. What things would you worry about? What would you do to make the cryostat or furnace work well? Are there important design differences? Explain.

9.7 Specific Heats of Solids

You ought to read this section for ideas. I won't give you test problems on it.

The specific heat of a solid is the amount of energy that needs to be added in order to raise its temperature by some amount.

We calculate specific heats by calculating a material's internal energy as a function of temperature. The specific heat is the derivative of the energy with respect to T.

Classically, if we think of atoms as 3-dimensional harmonic oscillators, each with 2 degrees of freedom, then the energy of a solid should be equal to N*3*2*kT/2=3kT, where N is the number of atoms in the solid.

Taking $\partial/\partial T$ gives a specific heat per mole at constant volume of 3R, where R is the universal gas constant.

How well does this work? Not bad at room temperature for many solids, but miserably at low

temperatures.

Why? We just did the same thing Rayleigh and Jeans did (remember the ultraviolet catastrophe?). We assumed kT is the average energy per oscillator in a solid.

If we do like we did in the last section, and use

$$f_{BE}(f) = \frac{1}{e^{hf/kT} - 1}$$

for the probability that an oscillator has the frequency f, we obtain the Einstein formula for the specific heat of a solid.

The Einstein formula works "pretty well," although the shape at low T is wrong.

Einstein's derivation of heat capacity, and Debye's model for the heat capacity (which gives the right T-dependence) are each worth about a day's lecture in an elementary solid state physics course.

9.8 Free Electrons in a Metal

What's your idea of an atomic-level scale picture of a metal?

In metals, each atom contributes one or more electron to a common "electron gas."

That's a lot of electrons. Classically, these electrons should constitute a major contribution to metallic heat capacity. But they don't.

Why not?

In the discussions of heat capacity in the last section, we assumed atoms are harmonic oscillators, and used Bose-Einstein statistics.

But electrons are fermions, and obey Fermi-Dirac statistics.

$$f_{FD}(\varepsilon, T) = \frac{1}{e^{(\varepsilon - \varepsilon_f)/kT} + 1}.$$

Furthermore, only one electron in the electron gas of a metal can occupy a given quantum state.

Density of states

In our discussion of free electrons, we will need electronic densities of states. The density of states, in this case, is just how many electron states there are within some energy range.

Since electrons are represented by wavefunctions, we can determine densities of states by considering how electron waves can fit into some volume. Beiser has done this a couple of

times already. The result for electrons in a metal is

$$g(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi V\, m^{3/2}}{h^3}\sqrt{\varepsilon}\, d\varepsilon.$$

I won't derive this formula. Note that the density of states is proportional to the square root of the energy.

From this density of states, we can calculate the Fermi energy.

In metals, electrons fill energy levels beginning with the lowest empty level and proceeding to the highest.

No new ideas here.

In the ground state, there are no empty levels which have filled levels above them. Electrons stop filling energy levels when we run out of electrons.

Before, I defined ϵ_F as the energy at which $f(\epsilon)=1/2$. Actually, the Fermi level in the ground state is better defined as the highest filled energy level.

Defined this way, ϵ_F doesn't depend on temperature, and only depends on how many electrons are present in the given volume of metal. (If you take Solid State, you will find that ϵ_F has a weak temperature dependence.)

The total number of electrons in the volume V is given by

$$N = \int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon.$$

Carrying out the integral and solving for ϵ_F gives

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

The Fermi energy depends only on the density of free electrons.

Example: Calculate the Fermi energy of aluminum. See the Mathcad document aluminum.mcd.

9.9 Electron-Energy Distribution

Now that we know the density of states, $g(\epsilon)$, we can calculate the distribution of electron energies in a metal.

$n(\epsilon)d\epsilon=g(\epsilon)f(\epsilon)d\epsilon$, or

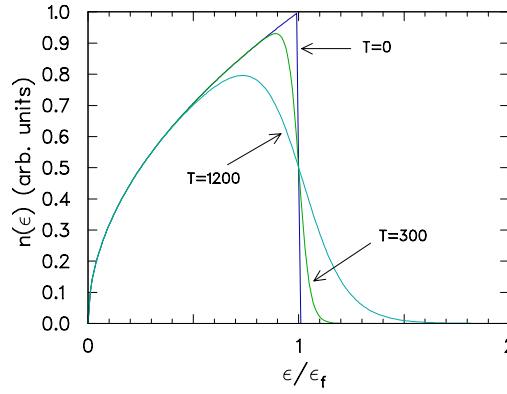$$n(\varepsilon)d\varepsilon \;=\; \frac{(8\sqrt{2}\pi V\, m^{3/2}/\, h^3)\sqrt{\varepsilon}\,d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}.$$

Note that $n(\varepsilon)$ is proportional to the square root of ε, divided by an exponential factor which is only important near ε_F for "normal temperatures.

Expressed in terms of ε_F,

$$n(\varepsilon)d\varepsilon \;=\; \frac{(3N/2)\,\varepsilon_F^{-3/2}\sqrt{\varepsilon}\,d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}.$$

Plot:

We can calculate the average electron energy at T=0.

The following is equivalent to Beiser's calculation: $f(\varepsilon)$ is 1 for $\varepsilon \le \varepsilon_F$ and 0 otherwise. The energy is

$$E_0 \;=\; \int_0^\infty \varepsilon g(\varepsilon) f(\varepsilon)\,d\varepsilon \;=\; \int_0^{\varepsilon_F} \varepsilon g(\varepsilon)\,d\varepsilon.$$

The integral is simple to do, and gives the result, after grouping constants and dividing by N, that $\varepsilon_{0,\,avg}=3\varepsilon_F/5$.

Does the result look reasonable?

This average electron energy is on the order of a few eV. An effective temperature calculated from $\varepsilon=kT$ is on the order of many thousands of degrees for typical metals.

The electronic heat capacity is proportional to kT/ε_F. This, plus the plot on the preceding page, shows why the electronic heat capacity is so low at ordinary temperatures.

9.10 Dying Stars

Read this section for fun and don't let me get in your way. I won't test you on it.