The Oxford Solid State Basics

Solutions to Exercises

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There are no exercises for chapter 1.

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(2.1) Einstein Solid

(a) *Classical Einstein (or "Boltzmann") Solid:*

Consider a three dimensional simple harmonic oscillator with mass m and spring constant k (i.e., the mass is attracted to the origin with the same spring constant in all three directions). The Hamiltonian is given in the usual way by

$$H = \frac{\mathbf{p}^2}{2m} + \frac{k}{2}\mathbf{x}^2$$

▷ Calculate the classical partition function

$$Z = \int \frac{\mathbf{dp}}{(2\pi\hbar)^3} \int \mathbf{dx}\, e^{-\beta H(\mathbf{p},\mathbf{x})}$$

Note: in this problem $\mathbf{p}$ and $\mathbf{x}$ are three dimensional vectors.

▷ Using the partition function, calculate the heat capacity $3k_B$.

▷ Conclude that if you can consider a solid to consist of N atoms all in harmonic wells, then the heat capacity should be $3Nk_B = 3R$, in agreement with the law of Dulong and Petit.

(b) *Quantum Einstein Solid:*

Now consider the same Hamiltonian quantum mechanically.

▷ Calculate the quantum partition function

$$Z = \sum_j e^{-\beta E_j}$$

where the sum over j is a sum over all eigenstates.

▷ Explain the relationship with Bose statistics.

▷ Find an expression for the heat capacity.

▷ Show that the high temperature limit agrees with the law of Dulong of Petit.

▷ Sketch the heat capacity as a function of temperature.

(See also exercise 2.7 for more on the same topic)

(a)

$$H = \frac{\mathbf{p}^2}{2m} + \frac{k}{2}\mathbf{x}^2$$

$$Z = \int \frac{\mathbf{dp}}{(2\pi\hbar)^3} \int \mathbf{dx}\, e^{-\beta H(\mathbf{p},\mathbf{x})}$$

Since,

$$\int_{-\infty}^{\infty} dy\, e^{-ay^2} = \sqrt{\pi/a}$$

in three dimensions, we get

$$Z = \left[1/(2\pi\hbar)\sqrt{\pi/(\beta/2m)}\sqrt{\pi/(\beta k/2))}\right]^3 = (\hbar\omega\beta)^{-3}$$

with $\omega = \sqrt{k/m}$. From the partition function

$$U = -(1/Z)\partial Z/\partial\beta = 3/\beta = 3k_B T$$

Thus the heat capacity $\partial U/\partial T$ is $3k_B$.

(b) Quantum mechanically, for a 1d harmonic oscillator, we have eigenenergies

$$E_n = \hbar\omega(n + 1/2)$$

with $\omega = \sqrt{k/m}$. The partition function is then

$$\begin{aligned} Z_{1d} &= \sum_{n\geq 0} e^{-\beta\hbar\omega(n+1/2)} \\ &= e^{-\beta\hbar\omega/2} 1/(1 - e^{-\beta\hbar\omega}) \\ &= 1/[2\sinh(\beta\hbar\omega/2)] \end{aligned}$$

The expectation of energy is then

$$\begin{aligned} \langle E \rangle &= -(1/Z)\partial Z/\partial\beta = (\hbar\omega/2)\coth(\beta\hbar\omega/2) \\ &= \hbar\omega(n_B(\beta\hbar\omega) + \frac{1}{2}) \end{aligned}$$

where n_B is the boson occupation factor

$$n_B(x) = 1/(e^x - 1)$$

(hence again the relationship with free bosons). The high temperature limit gives $n_B(x) \to 1/(x + x^2/2) = 1/x - 1/2$ so that $\langle E \rangle \to k_B T$. More generally, we obtain

$$C = k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

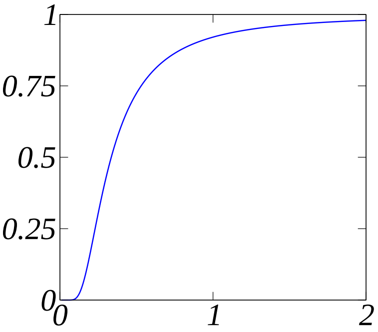


Fig. 2.1 Heat capacity in the Einstein model (per atom) in one dimension. Units are k_b on vertical axis and $k_b T/\omega$ on horizontal. In three dimensions, the heat capacity per atom is three times as large.

In 3D,

$$E_{n_1,n_2,n_3} = \hbar\omega[(n_1 + 1/2) + (n_2 + 1/2) + (n_3 + 1/2)]$$

and

$$Z_{3d} = \sum_{n1,n2,n3\geq 0} e^{-\beta E_{n_1,n_2,n_3}} = [Z_{1d}]^3$$

and correspondingly

$$\langle E \rangle = 3\hbar\omega(n_B(\beta\hbar\omega) + \frac{1}{2})$$

So the high temperature limit is $\langle E \rangle \to 3k_B T$ and the heat capacity $C = \partial\langle E \rangle/\partial T = 3k_B$. More generally we obtain

$$C = 3k_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

Plotted this looks like Fig. 2.1.

(2.2) Debye Theory I

(a)‡ State the assumptions of the Debye model of heat capacity of a solid.

▷ Derive the Debye heat capacity as a function of temperature (you will have to leave the final result in terms of an integral that cannot be done analytically).

▷ From the final result, obtain the high and low temperature limits of the heat capacity analytically.

You may find the following integral to be useful

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \sum_{n=1}^{\infty} \int_0^\infty x^3 e^{-nx} = 6 \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{15}$$

By integrating by parts this can also be written as

$$\int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{4\pi^4}{15} .$$

(b) The following table gives the heat capacity C for potassium iodide as a function of temperature.

T(K)	C(J K^{-1}mol^{-1})
0.1	8.5×10^{-7}
1.0	8.6×10^{-4}
5	.12
8	.59
10	1.1
15	2.8
20	6.3

▷ Discuss, with reference to the Debye theory, and make an estimate of the Debye temperature.

(a) The key assumption of Debye theory is that the dispersion curve is linear ($\omega = vk$) up to a cut-off frequency ω_{Debye} determined by the requirement that the total number of vibrational modes is correct.

For a crystal containing N atoms, the low temperature limiting form is

$$C = \frac{12 N k_B \pi^4}{5} \left(\frac{T}{T_D} \right)^3 \tag{2.1}$$

and the high temperature limit is $3Nk_B$. Here, $T_D = \hbar\omega_{Debye}/k_B$.

The full derivation goes as follows. For oscillators with frequency $\omega(\mathbf{k})$ a system has a full energy

$$E = L^3 \int d^3k (2\pi)^3 \hbar\omega(\mathbf{k}) [n_B(\beta\hbar\omega(\mathbf{k})) + 1/2]$$

One includes also a factor of 3 out front to account for the three different sound modes (two transverse and one longitudinal) and we cut off the integral at some cutoff frequency ω_{cutoff}. We use the assumption that $\omega = v|\mathbf{k}|$ although it is not much harder to consider three different velocities for the three different modes. We thus obtain

$$E \;\; = \;\; \int_0^{\omega_{cutoff}} d\omega g(\omega) [n_B(\beta\hbar\omega) + 1/2]\hbar\omega$$

where

$$g(\omega) = N \left[\frac{12\pi\omega^2}{(2\pi)^3 n v^3} \right] = N \frac{9\omega^2}{\omega_d^3}$$

and we have replaced $nL^3 = N$ where n is the density of atoms. Here $\omega_d^3 = 6\pi^2 n v^3$ is the Debye frequency, and $\hbar\omega_d = k_B T_{Debye}$ defines the Debye temperature. Note that there is no dependence of $g(\omega)$ on the density n (it cancels). This shows that until the cutoff is imposed, there is actually no knowledge of the underlying lattice — only the overall volume and sound velocity.

We should choose the cutoff frequency such that we have the right number of modes in the system, thus we have

$$3N = \int_0^{\omega_{cutoff}} d\omega g(\omega)$$

performing this integral, we find that the proper value of ω_{cutoff} is exactly the Debye frequency ω_d that we just defined.

The general heat Debye theory heat capacity will then be

$$C = d\langle E\rangle/dT = \frac{k_B}{(k_B T)^2}\int_0^{\omega_d} d\omega g(\omega)(\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

Defining $x = \hbar\omega/k_B T$ we obtain

$$C = d\langle E\rangle/dT = N k_B \left(\frac{T}{T_{Debye}}\right)^3 9\int_0^{\hbar\omega_d/k_B T} dx x^4 \frac{e^x}{(e^x-1)^2}$$

This integral is known as the Debye integral. In the low temperature limit, we can extend the integral out to infinity whereupon it just gives the constant $4\pi^4/15$ recovering the above claimed result Eq. 2.1.

In the high temperature limit, the exponents can be expanded such that the Debye integral becomes

$$\int_0^{\hbar\omega_d/k_B T} dx x^4 \frac{e^x}{(e^x-1)^2} = \int_0^{\hbar\omega_d/k_B T} dx x^2 = (1/3)(\hbar\omega_d/k_B T)^3$$

which then recovers the law of Dulong-Petit $C = 3Nk_B$

(b) Given the heat capacity and the temperature, in the low T limit we should have (from Eq. 2.1)

$$T_D = \left(\frac{12R\pi^4 T^3}{5C}\right)^{1/3}$$

The table of heat capacity looks like

T(K)	0.1	1.0	5	8	10	15	20
C (J K $^{-1}$ mol $^{-1}$)	8.5×10^{-7}	8.6×10^{-4}	1.2×10^{-1}	5.9×10^{-1}	1.1	2.8	6.3
$\left(\frac{12R\pi^4 T^3}{5C}\right)^{1/3}$ (K)	132	131	127	119	121	132	135

So T_{Debye} is about 130K. The fact that the T^3 fit is not perfect is a reflection of (a) that Debye theory is just an approximation (in particular that phonons have a nonlinear spectrum!) and (b) that one needs to be in the low T limit to obtain perfect T^3 scaling. (Note that at low enough T, the T^3 scaling does indeed work).

(2.3) Debye Theory II

Use the Debye approximation to determine the heat capacity of a two dimensional solid as a function of temperature.

▷ State your assumptions.

You will need to leave your answer in terms of an integral that one cannot do analytically.

▷ At high T, show the heat capacity goes to a constant and find that constant.

▷ At low T, show that $C_v = KT^n$ Find n. Find K in terms of a definite integral.

If you are brave you can try to evaluate the integral, but you will need to leave your result in terms of the Riemann zeta function.

In 2d there should be 2N modes. So high T heat capacity should be $C = 2k_b N$ (Law of Dulong-Petit).

Assume longitudinal and transverse sound velocities are equal.

$$2N = 2A \int_0^{|k|=k_{Debye}} \frac{d^2k}{(2\pi)^2} = \frac{2(\pi k_{Debye}^2}{(2\pi)^2}$$

with A the area. So

$$k_{Debye} = \sqrt{4\pi n}$$

with $n = N/A$ the density. So $\Theta_{Debye} = \hbar k_{Debye} c$ with c the sound velocity.

Since phonons obey bose statistics we have

$$\begin{aligned}
E &= 2A \int_0^{|k|=k_{Debye}} \frac{d^2k}{(2\pi)^2} \epsilon_k n_B(\beta\epsilon_k) \\
&= 2A \int_0^{|k|=k_{Debye}} \frac{d^2k}{(2\pi)^2} \hbar ck \frac{1}{e^{\beta\hbar ck}-1} \\
&= 2A \frac{2\pi}{(2\pi)^2} \int_0^{|k|=k_{Debye}} k\,dk\,\hbar ck \frac{1}{e^{\beta\hbar ck}-1} \\
&= \frac{A}{\pi} \int_0^{\Theta_{Debye}} \frac{d\epsilon}{\hbar c} \frac{\epsilon}{\hbar c} \epsilon \frac{1}{e^{\beta\epsilon}-1}
\end{aligned}$$

Let $z = \beta\epsilon = \epsilon/(k_b T)$ and we get

$$E = \frac{A(k_bT)^3}{\pi\hbar^2c^2} \int_0^{\Theta_{Debye}/(k_bT)} \frac{z^2dz}{e^z-1}$$

For large T, Θ/T is small so z is small, so

$$\frac{z^2dz}{e^z-1} = z$$

so we get

$$\int_0^{\Theta_{Debye}/(k_bT)} zdz = (\Theta_{Debye}/(k_bT))^2/2$$

so in this limit

$$E = \frac{A(k_bT)\Theta_{Debye}^2}{2\pi\hbar^2c^2} = \frac{Ak_{Debye}^2 k_bT}{2\pi} = A\frac{(4\pi N/A)k_bT}{2\pi} = 2Nk_bT$$

which gives

$$C = dE/dT = 2Nk_b$$

as expected.

For small T, the upper limit of the integral goes to infinity and we have

$$E = \frac{A(k_bT)^3}{\pi\hbar^2c^2}\int_0^\infty \frac{z^2dz}{e^z-1}$$

So

$$C_v = KT^2$$

where

$$K = \frac{3Ak_b^3}{\pi\hbar^2c^2}\int_0^\infty \frac{z^2dz}{e^z-1}$$

To evaluate the integral we have

$$\begin{aligned}\int_0^\infty \frac{z^2dz}{e^z-1} &= \int_0^\infty \frac{z^2dz}{e}^{-z}\sum_{n=0}^\infty e^{-nz} \\ &= \sum_{n=1}^\infty \int_0^\infty dzz^2e^{-nz} = \sum_{n=1}^\infty 2/n^3 = 2\zeta(3)\end{aligned}$$

Thus we obtain

$$K = \frac{6Ak_b^3\zeta(3)}{\pi\hbar^2c^2}$$

(2.4) Debye Theory III

Physicists should be good at making educated guesses: Guess the element with the highest Debye temperature. The lowest? You might not guess the ones with the absolutely highest or lowest temperatures, but you should be able to get close.

Largest Debye temperature should be the one with the highest speed of sound which is probably the hardest element (ie., highest spring constant) and/or smallest mass. Diamond is the obvious guess (and indeed it does have the highest Debye temperature). $\Theta_{Debye} = 2230K$. The lowest is harder to guess. One presumably wants a soft material of some sort – also possibly a heavy material.

Soft and heavy metals like mercury are good guesses. (in fact mercury is liquid at room temperature and one has to go to low T to measure a Debye temperature). Also good guesses are Noble gases where the spring constant is very low (weak interaction between the atoms). Also heavy soft group 1 metals are good guesses. Many of these are gas or liquid at room T and a Debye temeperature can only be measured at low T.

Material	Θ_{Debye}
Neon	75 K
Argon	92 K
Krypton	64 K
Xenon	64 K
Radon	64 K
Mercury	69 K
Potassium	91 K
Rubidium	56 K
Cesium	32 K

Some Low Debye Temperatures

(2.5) Debye Theory IV
From Fig. 2.3 (main text) estimate the Debye temperature of diamond. Why does it not quite match the result listed in Table 2.2 (main text)?

Extracting the slope from the figure gives $C/T^3 \approx 1.9{\times}10^{-7}\mathrm{J/(mol-K^4)}$ Then using the formula

$$C = \frac{12Nk_B\pi^4}{5}\left(\frac{T}{T_D}\right)^3$$

We obtain

$$T_D \approx 2200K$$

The reason that it does not match the Debye temperature given in the figure caption has to do with the comment in the caption. Debye theory predicts the heat capacity at all possible temperatures. The Debye temperature quoted in the text is chosen so as to give a good fit over the full temperature range. The Debye temperature measured here is chosen to give a good fit at the lowest temperatures (where Debye theory can actually be exact).

(2.6) Debye Theory V*
In the text we derived the low temperature Debye heat capacity assuming that the longitudinal and transverse sound velocities are the same and also that the sound velocity is independent of the direction the sound wave is propagating.

(a) Suppose the transverse velocity is v_t and the longitudinal velocity is v_l. How does this change the Debye result? State any assumptions you make.

(b) Instead suppose the velocity is anisotropic. For example, suppose in the $\hat{x}, \hat{y}$ and $\hat{z}$ direction, the sound velocity is v_x, v_y and v_z respectively. How does this change the Debye result?

(a) This is actually quite simple. The derivation of the heat capacity follows the text (or exercise 2.1). The only difference is in the density of states. In the isotropic calculation we use

$$g(\omega) = N\left[\frac{12\pi\omega^2}{(2\pi)^3 n v^3}\right]$$

Recall the origin of these factors. Really we had (See Eq. 2.3 of the main text)

$$g(\omega) = 3L^3\frac{4\pi\omega^2}{(2\pi)^3 v^3}$$

where the factor of 3 out front is for the three polarizations of the sound waves. One could just as well have written it as

$$g(\omega) = L^3\frac{4\pi\omega^2}{(2\pi)^3}\left(\frac{1}{v^3}+\frac{1}{v^3}+\frac{1}{v^3}\right)$$

separating out the three different polarizations. Now, if the three polarizations have three different velocities, we have

$$g(\omega) = L^3 \frac{4\pi\omega^2}{(2\pi)^3}\left(\frac{1}{v_1^3} + \frac{1}{v_2^3} + \frac{1}{v_3^3}\right)$$

this is true since the density of states of the three different excitation modes simply add. In an isotropic solid, the two transverse mode have the same velocity v_t and the one longitudinal mode has velocity v_l and we would have

$$g(\omega) = L^3 \frac{4\pi\omega^2}{(2\pi)^3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)$$

The remainder of the derivation is unchanged. Thus, defining $\bar{v}$ such that

$$\frac{3}{\bar{v}^3} = \frac{2}{v_t^3} + \frac{1}{v_l^3}$$

we obtain the low temperature capacity in the usual form

$$C = \frac{12 N k_B \pi^4}{5}\left(\frac{T}{T_D}\right)^3$$

where now

$$(k_B T_D)^3 = 6\pi^2 n \hbar^3 \bar{v}^3.$$

Note that the high frequency cutoff is different for the two types of modes (but the k cutoff is the same for both modes).

(b) If instead we have three different sound velocities in three different directions, the situation is more complicated (and here we neglect the differences between longitudinal and transverse modes). Here we must make some assumption about the sound velocity in some arbitrary direction. A reasonable guess would be as follows. If you consider a sound wave in direction $\hat{k}$ (with $\hat{k} = \mathbf{k}/|\mathbf{k}|$ a unit vector), we would have

$$v(\hat{k}) = \sqrt{v_x^2 \hat{k}_x^2 + v_y^2 \hat{k}_y^2 + v_z^2 \hat{k}_z^2}$$

Now, following the usual derivation of Debye theory, we start with

$$\langle E \rangle \;=\; 3\frac{L^3}{(2\pi)^3}\int dk_x dk_y dk_z \; \hbar\omega(\mathbf{k}) \left(n_B(\beta\hbar\omega(\mathbf{k})) + \frac{1}{2}\right).$$

And now

$$\omega(\mathbf{k}) = v(\hat{k})|\mathbf{k}| = \sqrt{v_x^2 k_x^2 + v_y^2 k_y^2 + v_z^2 k_z^2}$$

Since the system is now not isotropic, we cannot do the usual thing and convert to spherical polar coordinates directly. Instead, we rescale the axes first writing (with $j = x, y, z$)

$$\mathbf{K}_j = k_j v_j$$

So that

$$\omega(\mathbf{K}) = v(\hat{k})|\mathbf{k}| = \sqrt{K_x^2 + K_y^2 + K_z^2}$$

and

$$\langle E \rangle \;=\; 3\frac{L^3}{(2\pi)^3 v_x v_y v_z} \int dK_x dK_y dK_z \, \hbar\omega(\mathbf{K}) \left(n_B(\beta\hbar\omega(\mathbf{K})) + \frac{1}{2} \right).$$

We can now use spherical symmetry to obtain

$$\langle E \rangle = 3\frac{4\pi L^3}{(2\pi)^3 v_x v_y v_z} \int_0^\infty \omega^2 d\omega (\hbar\omega) \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right). \qquad (2.2)$$

The rest of the derivation follows as usual to give the usual expression for heat capacity

$$C = \frac{12 N k_B \pi^4}{5} \left(\frac{T}{T_D} \right)^3$$

where now

$$(k_B T_D)^3 = 6\pi^2 n \hbar^3 v_x v_y v_z \;.$$

(2.7) Diatomic Einstein Solid*

Having studied exercise 2.1, consider now a solid made up of diatomic molecules. We can (very crudely) model this as a two particles in three dimensions, connected to each other with a spring, both in the bottom of a harmonic well.

$$H = \frac{\mathbf{p_1}^2}{2m_1} + \frac{\mathbf{p_2}^2}{2m_2} + \frac{k}{2}\mathbf{x_1}^2 + \frac{k}{2}\mathbf{x_2}^2 + \frac{K}{2}(\mathbf{x_1} - \mathbf{x_2})^2$$

Here k is the spring constant holding both particles in the bottom of the well, and K is the spring constant holding the two particles together. Assume that the two particles are distinguishable atoms.

(For this problem you may find it useful to transform to relative and center-of-mass coordinates. If you find this difficult, for simplicity you may assume that $m_1 = m_2$.)

(a) Analogous to exercise 2.1 above, calculate the classical partition function and show that the heat capacity is again $3k_B$ per particle (i.e., $6k_B$ total).

(b) Analogous to exercise 2.1 above, calculate the quantum partition function and find an expression for the heat capacity. Sketch the heat capacity as a function of temperature if $K \gg k$.

(c)** How does the result change if the atoms are indistinguishable?

(a) We can write the partition function as

$$Z = \int \frac{\mathbf{dp_1}}{(2\pi\hbar)^3} \frac{\mathbf{dp_2}}{(2\pi\hbar)^3} \int \mathbf{dx_1 dx_2} e^{-\beta H}$$

Considering the momentum integrals first, we have

$$\int \mathbf{dp} e^{-\beta \mathbf{p}^2/(2m)} = \left(\frac{2\pi m}{\beta} \right)^{3/2}$$

Then the spatial integrals are made simple by transforming

$$\begin{aligned} \mathbf{Y} &= \mathbf{x_1} - \mathbf{x_2} \\ \mathbf{y} &= (\mathbf{x_1} + \mathbf{x_2})/2 \end{aligned}$$

So the spatial integrals are

$$\int \mathbf{dY dy} e^{-\beta\left(-k\mathbf{y}^2 - (k/4 + K/2)\mathbf{Y}^2\right)} = \left(\frac{\pi}{k\beta} \right)^{3/2} \left(\frac{\pi}{\beta(k/4 + K/2)} \right)^{3/2}$$

Putting these together we get a partition function

$$Z = \left(\frac{\pi}{k\beta}\right)^{3/2} \left(\frac{\pi}{\beta(k/4+K/2)}\right)^{3/2} \left(\frac{2\pi m_1}{\beta}\right)^{3/2} \left(\frac{2\pi m_2}{\beta}\right)^{3/2} \sim \beta^{-6}$$

The energy is

$$\langle E\rangle = -\partial \ln Z/\partial\beta = 6/\beta$$

So the heat capacity for the two particles is

$$C = \partial\langle E\rangle/\partial T = 6k_B$$

(b) The case where the two masses are identical is fairly simple. Again, we construct

$$\begin{aligned} \mathbf{Y} &= \mathbf{x_1} - \mathbf{x_2} \\ \mathbf{y} &= (\mathbf{x_1} + \mathbf{x_2})/2 \end{aligned}$$

and correspondingly

$$\begin{aligned} \mathbf{Q} &= (\mathbf{p_1} - \mathbf{p_2})/2 \\ \mathbf{q} &= (\mathbf{p_1} + \mathbf{p_2}) \end{aligned}$$

Note that these two variables are constructed so that $[Q_j, Y_k] = i\hbar\delta_{jk}$ and $[q_j, y_k] = i\hbar\delta_{jk}$ and all other commutators are zero (in other words, these are canonical conjugates). The Hamiltonian is now written as

$$H = \frac{\mathbf{Q}^2}{2(m/2)} + \frac{\mathbf{q}^2}{2(2m)} + k\mathbf{Y}^2 + \left(\frac{k}{4} + \frac{K}{2}\right)\mathbf{y}^2$$

which comprises two independent three-dimensional harmonic oscillators with frequencies

$$\begin{aligned} \omega_1 &= \sqrt{4k/m} \\ \omega_2 &= \sqrt{(k/2+K)/(2m)} \end{aligned}$$

The heat capacity is then (analogous to 2,1)

$$C = 3k_B(\beta\hbar\omega_1)^2 \frac{e^{\beta\hbar\omega_1}}{(e^{\beta\hbar\omega_1}-1)^2} + 3k_B(\beta\hbar\omega_2)^2 \frac{e^{\beta\hbar\omega_2}}{(e^{\beta\hbar\omega_2}-1)^2} \tag{2.3}$$

The case of unequal masses is more tricky. The general method is similar to the discussion outlined in problem *** below. First, rescale $\mathbf{r}_i = \mathbf{p}_i\sqrt{m_i}$ and $\mathbf{x}_i = \mathbf{z}_i/\sqrt{m_i}$ so that the Hamiltonian reads

$$H = \frac{\mathbf{r_1}^2}{2} + \frac{\mathbf{r_2}^2}{2} + \frac{k}{2m_1}\mathbf{z_1}^2 + \frac{k}{2m_2}\mathbf{z_2}^2 + \frac{K}{2}\left(\mathbf{z_1}/\sqrt{m_1} - \mathbf{z_2}/\sqrt{m_2}\right)^2 \tag{2.4}$$

Note that $\mathbf{r}$ and $\mathbf{z}$ are canonically conjugate just like $\mathbf{p}$ and $\mathbf{x}$. The potential can be viewed as a matrix which we can write as

$$\begin{pmatrix} (k+K)/m_1 & -K/\sqrt{m_1 m_2} \\ -K/\sqrt{m_1 m_2} & (k+K)/m_2 \end{pmatrix}$$

We can diagonalize this matrix to define two new decoupled degrees of freedom representing two independent harmonic oscillators. The frequencies of these oscillaltors squared are the eigenvalues of the above matrix.

$$
\begin{aligned}
\omega_1 &= \frac{(k+K)(m_1+m_2)+\sqrt{(k+K)^2(m_1-m_2)^2+4K^2m_1m_2}}{2m_1m_2} \\
\omega_2 &= \frac{(k+K)(m_1+m_2)-\sqrt{(k+K)^2(m_1-m_2)^2+4K^2m_1m_2}}{2m_1m_2}
\end{aligned}
$$

And the heat capacity is given by formula 2.3 using these two oscillator frequencies. A plot is given in Fig. 2.2.

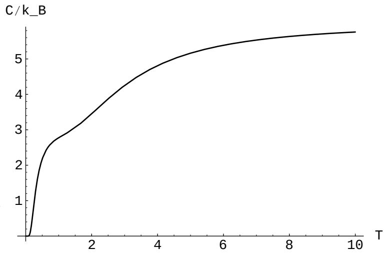


Fig. 2.2 Heat capacity of two einstein oscillators. Here $\omega_1 = 1$ and $\omega_2 = 10$

(d) If the two atoms are indistinguishable then they must obey either Bose or Fermi statistics depending on the atom type. The center of mass degree of freedom ($\mathbf{y}$ above) has the same Einstein heat capacity as calculated before. However, the relative degree of freedom does not. Due to the statistics, the *relative* wavefunction must obey $\Psi(\mathbf{Y}) = \pm\Psi(-\mathbf{Y})$ with the ± depending on whether we have bosons or fermions. Since the three dimesional harmonic motion wavefunction can be decomposed into three one-dimensional wavefunctions $\Psi(\mathbf{r}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$, and ψ_n is symmetric or antisymmetric depending on whether n is even or odd, we must have that

$$
n_x + n_y + n_z = \text{even for bosons, odd for fermions}
$$

So when we write the partition function for this oscillator, instead of

$$
\sum_{n_x,n_y,n_z\geq 0} e^{-\beta\hbar\omega(n_x+n_y+n_z+3/2)}
$$

as usual, we instead only include the terms of sum respecting the even/odd symmetry. This restriction can be handled by writing

$$
\sum_{n_x+n_y+n_z=\text{even/odd}} \to \frac{1}{2} \sum_{n_x,n_y,n_z\geq 0} (1 \pm (-1)^{n_x+n_y+n_z})
$$

The sum can then be evaluated to give a partition function

$$
Z_{\text{bose/fermi}} = e^{-\frac{3}{2}\beta\hbar\omega} 2\left[\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)^2 \pm \left(\frac{1}{1+e^{-\beta\hbar\omega}}\right)^3\right]
$$

which then can be differentiated to get the heat capacity. I obtained

$$
C = k_b \frac{24e^{2\omega/k_bT}\left(1+2e^{2\omega/k_bT}+5e^{4\omega/k_bT}\right)}{\left(1+2e^{2\omega/k_bT}-3e^{4\omega/k_bT}\right)^2 (k_bT)^2}
$$

for the fermi case and

$$
C = k_b \frac{24e^{2\omega/k_bT}\left(5+2e^{2\omega/k_bT}+e^{4\omega/k_bT}\right)}{\left(-3+2e^{2\omega/k_bT}+e^{4/k_bT}\right)^2 (k_bT)^2}
$$

for the bose case. Note that both of these have the correct Dulong-Petit high temperature limit of $3k_b$.

(2.8) Einstein Versus Debye*

In both the Einstein model and the Debye model the high temperature heat capacity is of the form

$$C = Nk_B(1 - \kappa/T^2 + \ldots)$$

▷ For the Einstein model calculate κ in terms of the Einstein temperature.

▷ For the Debye model calculate κ in terms of the Debye temperature.

From your results give an approximate ratio $T_{Einstein}/T_{Debye}$. Compare your result to the values for silver given in Fig. 2.4 (main text). (The ratio you calculate should be close to the ratio stated in the caption of the Figure. It is not exactly the same though. Why might it not be?).

Expanding the heat capacity of a single Einstein oscillator

$$\begin{aligned}
C &= k_b(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \\
&\sim k_b(\beta\hbar\omega^2)\frac{1+\beta\hbar\omega+(\beta\hbar\omega)^2/2}{[\beta\hbar\omega+(\beta\hbar\omega)^2/2+(\beta\hbar\omega)^3/6]^2} \\
&\sim k_b\frac{1+\beta\hbar\omega+(\beta\hbar\omega)^2/2}{[1+(\beta\hbar\omega)/2+(\beta\hbar\omega)^2/6]^2} \\
&\sim k_b\frac{1+\beta\hbar\omega+(\beta\hbar\omega)^2/2}{[1+(\beta\hbar\omega)/2+(7/12)(\beta\hbar\omega)^2]} \\
&\sim k_b\left(1+\beta\hbar\omega+(\beta\hbar\omega)^2/2\right)[1-(\beta\hbar\omega)/2+(5/12)(\beta\hbar\omega)^2] \\
&\sim k_b\left(1-(\beta\hbar\omega)^2/12+\ldots\right)
\end{aligned}$$

So $\kappa = T^2_{Einstein}/12$.

We can handle the Debye case by realizing that the heat capacity is just an integration over Einstein oscillators. So

$$\begin{aligned}
C &= \int_0^{\omega_D} d\omega g(\omega) k_b(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \\
&\sim k_b\int_0^{\omega_D} d\omega g(\omega)\left(1-(\beta\hbar\omega)^2/12+\ldots\right)
\end{aligned}$$

where $g(\omega) = N9\omega^2/\omega_D^3$. Note that the integration is cut off so that the integral over 1 gives precisely $3Nk_b$ as it should. Thus we obtain

$$C \sim 3k_BN\left(1-(\beta\hbar\omega_D)^2/20+\ldots\right)$$

So $\kappa = T^2_{Debye}/20$. Setting $T^2_{Einstein}/12 = T^2_{Debye}/20$ we would predict

$$T_{Debye} = \sqrt{5/3}\; T_{Einstein} \approx 1.29 T_{Einstein}$$

In the data from Fig 2.4 the ratio is $215/151 \approx 1.42$. The reason this does not match perfectly with our prediction is mainly because T_{Debye} and $T_{Einstein}$ are likely fit over the full range of the heat capacities measured, not just in the high temperature limit. If they were fit parameters for only the high temperature limit, the ratio would come out as we predicted here.

Electrons in Metals: Drude Theory

3

(3.1) Drude Theory of Transport in Metals

(a)‡ Assume a scattering time τ and use Drude theory to derive an expression for the conductivity of a metal.

(b) Define the resistivity matrix $\underset{\sim}{\varrho}$ as $\mathbf{E} = \underset{\sim}{\varrho}\mathbf{j}$. Use Drude theory to derive an expression for the matrix $\underset{\sim}{\varrho}$ for a metal in a magnetic field. (You may assume $\mathbf{B}$ parallel to the $\hat{z}$ axis. The under-tilde means that the quantity $\underset{\sim}{\varrho}$ is a matrix.) Invert this matrix to obtain an expression for the conductivity matrix $\underset{\sim}{\sigma}$.

(c) Define the Hall coefficient.

▷ Estimate the magnitude of the Hall voltage for a specimen of sodium in the form of a rod of rectangular cross-section 5mm by 5mm carrying a current of 1A down its long axis in a magnetic field of 1T perpendicular to the long axis. The density of sodium atoms is roughly 1 gram/cm^3, and sodium has atomic mass of roughly 23. You may assume that there is one free electron per sodium atom (sodium has *valence* 1).

▷ What practical difficulties would there be in measuring the Hall voltage and resistivity of such a specimen. How might these difficulties be addressed).

(d) What properties of metals does Drude theory not explain well?

(e)* Consider now an applied AC field $\mathbf{E} \sim e^{i\omega t}$ which induces an AC current $\mathbf{j} \sim e^{i\omega t}$. Modify the above calculation (in the presence of a magnetic field) to obtain an expression for the complex AC conductivity matrix $\underset{\sim}{\sigma}(\omega)$. For simplicity in this case you may assume that the metal is very clean, meaning that $\tau \to \infty$, and you may assume that $\mathbf{E} \perp \mathbf{B}$. You might again find it convenient to assume $\mathbf{B}$ parallel to the $\hat{z}$ axis. (This exercise might look hard, but if you think about it for a bit, it isn't really much harder than what you did above!)

▷ At what frequency is there a divergence in the conductivity? What does this divergence mean? (When τ is finite, the divergence is cut off.)

▷ Explain how could one use this divergence (known as the cyclotron resonance) to measure the mass of the electron. (In fact, in real metals, the measured mass of the electron is generally not equal to the well-known value $m_e = 9.1095 \times 10^{-31}$ kg. This is a result of *band structure* in metals, which we will explain in Part VI.)

(a) We consider an electron with momentum $\mathbf{p}$ at time t and we ask what momentum it will have at time $t + dt$. There is a probability dt/τ that it will scatter to momentum zero. If it does not scatter to momentum zero (with probability $1 - dt/\tau$) it simply accelerates as dictated by its usual equations of motion $d\mathbf{p}/dt = \mathbf{F}$ Thus

$$\langle \mathbf{p}(t+dt) \rangle = \left(1 - \frac{dt}{\tau}\right)(\mathbf{p}(t) + \mathbf{F}dt)$$

or

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} - \frac{\mathbf{p}}{\tau} \tag{3.1}$$

where here the force $\mathbf{F}$ on the electron is just the Lorentz force

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

In absence of magnetic field

$$\frac{d\mathbf{p}}{dt} = -e\mathbf{E} - \frac{\mathbf{p}}{\tau}$$

In steady state, $d\mathbf{p}/dt = 0$ so we have

$$m\mathbf{v} = \mathbf{p} = -e\tau\mathbf{E}$$

with m the mass of the electron and $\mathbf{v}$ its velocity. If there is a density n of electrons in the metal, and they are all moving at velocity $\mathbf{v}$ then the electrical current is given by

$$\mathbf{j} = -en\mathbf{v} = \frac{e^2\tau n}{m}\mathbf{E}$$

or in other words, the conductivity of the metal is

$$\sigma = \frac{e^2\tau n}{m} \tag{3.2}$$

(b) In both an electric and a magnetic field

$$\frac{d\mathbf{p}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \mathbf{p}/\tau$$

Again setting this to zero in steady state, and using $\mathbf{p} = m\mathbf{v}$ and $\mathbf{j} = -ne\mathbf{v}$, we obtain an equation for the steady state current

$$0 = -e\mathbf{E} + \frac{\mathbf{j} \times \mathbf{B}}{n} + \frac{m}{ne\tau}\mathbf{j}$$

or

$$\mathbf{E} = \left(\frac{1}{ne}\mathbf{j} \times \mathbf{B} + \frac{m}{ne^2\tau}\mathbf{j}\right)$$

We now define the 3 by 3 resistivity matrix $\underset{\sim}{\rho}$ which relates the current vector to the electric field vector

$$\mathbf{E} = \underset{\sim}{\rho}\mathbf{j}$$

We then obtain components of this matrix

$$\rho_{xx} = \rho_{yy} = \rho_{zz} = \frac{m}{ne^2\tau}$$

and if we imagine $\mathbf{B}$ oriented in the $\hat{z}$ direction, then

$$\rho_{xy} = -\rho_{yx} = \frac{B}{ne}$$

Inverting this equation we obtain a conductivity matrix

$$\begin{aligned} \sigma_{zz} &= ne^2\tau/m \\ \sigma_{xx} = \sigma_{yy} &= \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2) = \sigma_{zz}/[1 + (eB\tau/m)^2] \\ \sigma_{yx} = -\sigma_{xy} &= \rho_{xy}/(\rho_{xx}^2 + \rho_{xy}^2) = \sigma_{zz}(eB\tau/m)/[1 + (eB\tau/m)^2] \end{aligned}$$

with all other entries in the σ matrix being zero.

(c) The Hall coefficient is $R_H = \rho_{yx}/B$ which is $-1/ne$ in Drude theory. If sodium n= 1 gm /cm^3 with atomic mass $M = 23$, this is then a density of atoms of

$$n = N_A \times n/M = 2.6 \times 10^{28}\text{m}^{-3}$$

hence the same density of electrons assuming one free electron per atom. The cross section of the rod is L by L with $L = 5mm$, so the current density is $j = I/L^2$. The Hall resistivity is $\rho_{xy} = B/(ne)$ so the Hall voltage is $j\rho_{xy}L$. So the total Hall voltage is

$$V = \frac{IB}{Lne} = 4.8 \times 10^{-8}\text{Volts}$$

Some of the problems with making this measurement might be:

- This is a very small voltage: One needs a sensitive voltmeter
- There may be contact resistance: Use a high impedance voltmeter
- Contacts may not be perfectly aligned: Try varying (reversing) the magnetic field to pick out only the B dependent part (I.e., measure $(V(B) - V(-B))/2$).
- Could have heating

Tutors might also use this problem as an opportunity to discuss how useful lock-in amplifiers are (which most students do not appear to know).

(d) Drude theory fails to explain why the electrons do not carry heat capacity of $3/2k_B$ per electron as a classical gas would. This results in incorrect predictions of, ex, thermoelectric coefficients. Drude theory also fails to explain why the sign of the Hall effect can be different in different samples. Drude theory does not explain why we should only count valence electrons.

(e) Drude theory at finite frequency. We start with the equation of motion simplified by setting $\tau \to \infty$

$$\frac{d\mathbf{p}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

setting $\mathbf{E} = \hat{x}E_x^0 e^{i\omega t}$ and $\mathbf{B} = B\hat{z}$,

$$\begin{aligned} m\dot{v}_x &= -eE_x^0 e^{i\omega t} - ev_y B \\ m\dot{v}_y &= ev_x B \end{aligned}$$

We can differentiate the first equation to give

$$m\ddot{v}_x = -i\omega e E_x^0 e^{i\omega t} - e\dot{v}_y B$$

then plug in the second equation to give

$$\ddot{v}_x = -i\omega e(E_x^0/m)e^{i\omega t} - (eB/m)^2 v_x$$

which is the equation of a driven harmonic oscillator. We use the ansatz solution $v_x = v_x^0 e^{i\omega t}$ so we obtain

$$-\omega^2 v_x^0 = -i\omega(eE_x^0/m) - (eB/m)^2 v_x^0$$

which we solve

$$v_x^0 = \frac{-i\omega(eE_x/m)}{(eB/m)^2 - \omega^2}$$

and similarly

$$v_y^0 = \frac{-(eB/m)(eE_x/m)}{(eB/m)^2 - \omega^2}$$

with the current being $j = -env$ we obtain

$$\begin{aligned} \sigma_{xx} &= i\omega(ne^2/m)/[(eB/m)^2 - \omega^2] \\ \sigma_{yx} &= (eB/m)(ne^2/m)/[(eB/m)^2 - \omega^2] \end{aligned}$$

The cyclotron frequency eB/m is the natural oscillation frequency of a particle of charge $-e$ of mass m in magnetic field B. This divergent response is easy to detect experimentally as a strong absorbtion of the ac electric field at a particular frequency. (Then this obviously can be converted into a measurement of the mass).

The motion in the z-direction is unaffected by the magnetic field in the z direction so that we have

$$\sigma_{zz} = ne^2/(i\omega m)$$

and off-diagonal terms including z are zero.

Note, the calculation may look a bit nicer if you set $\mathbf{v}$ or equivalently $\mathbf{j}$, and solve for $\mathbf{E}$ to obtain the finite frequency resistance matrix, and then invert last. Lets try doing it that way also. Starting with

$$\frac{d\mathbf{p}}{dt} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

Writing $\mathbf{E} = \mathbf{E}_0 e^{i\omega t}$ and $\mathbf{j} = \mathbf{j}_0 e^{i\omega t}$ and also $\mathbf{j} = n(-e)\mathbf{v} = n(-e)\mathbf{p}/m$ we then have

$$i\omega m \mathbf{j}_0/(n(-e)) = -e[\mathbf{E}_0 + \mathbf{j}_0 \times \mathbf{B}/(n(-e))]$$

or

$$\mathbf{E}_0 = \left(\frac{i\omega m}{ne^2}\right)\mathbf{j}_0 - \mathbf{B} \times \mathbf{j}_0/(n(-e))$$

So assuming $\mathbf{B}$ in the $\hat{z}$ direction, we have a resistivity matrix

$$\underset{\sim}{\rho} = \begin{pmatrix} \frac{i\omega m}{ne^2} & B/(-ne) & 0 \\ B/(ne) & \frac{i\omega m}{ne^2} & 0 \\ 0 & 0 & \frac{i\omega m}{ne^2} \end{pmatrix}$$

which we invert to get the same result as above.

(3.2) Scattering Times

The following table gives electrical resistivities ρ, densities n, and atomic weights w for the metals silver and lithium:

	ρ (Ωm)	n (g/cm^3)	w
Ag	1.59×10^8	10.5	107.8
Li	9.28×10^8	0.53	6.94

▷ Given that both Ag and Li are monovalent (i.e., have one free electron per atom), calculate the Drude scattering times for electrons in these two metals.

In the kinetic theory of gas, one can estimate the scattering time using the equation

$$\tau = \frac{1}{n\langle v \rangle \sigma}$$

where n is the gas density, $\langle v \rangle$ is the average velocity (see Eq. 3.4 main text), and σ is the cross-section of the gas molecule—which is roughly πd^2 with d the molecule diameter. For a nitrogen molecule at room temperature, we can use $d = .37$nm.

▷ Calculate the scattering time for nitrogen gas at room temperature and compare your result to the Drude scattering times for electrons in Ag and Li metals.

Note: the table should read 10^{-8} not 10^8 !

We use $\sigma = \rho^{-1} = Ne^2\tau/m$ with m the free electron mass and where N here is the electron density which we calculate by

$$N = n \frac{\text{Avagadro Number}}{\text{mol-weight in grams/cm}^3} 10^6$$

Solving for τ we get

$$\begin{aligned} \tau_{Ag} &= 3.8 \times 10^{-14}\text{sec} \\ \tau_{Li} &= 8.3 \times 10^{-15}\text{sec} \end{aligned}$$

The second part should say room temperature and pressure. The weight of a Nitrogen molecule is about 28 times that of a proton (two nitrogen atoms of atomic weight 14). So the velocity at 300 K is

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi 28 m_p}} \approx 475\text{m/sec}$$

uncoincidentally being close to the speed of sound in air. The density is given by $n = P/RT$ with R the gas constant. At $P = 10^5$ pascals and $T = 300$ K, this gives .025 mol/m^3. (This should be the usual 22.4 moles per liter that people remember, but we used 300 K instead of 273 and we approximated the pressure). Multiplying by Avagadro's number give the density that we should use in the equation

$$\tau = \frac{1}{n\langle v \rangle \sigma} \approx 2 \times 10^{-10}\text{sec}$$

So electrons scatter much much much more often — this is not surprising considering how much higher their density is than that of the nitrogen gas.

(3.3) Ionic Conduction and Two Carrier Types
In certain materials, particularly at higher temperature, positive ions can move throughout the sample in response to applied electric fields, resulting in what is known as ionic conduction. Since this conduction is typically poor, it is mainly observable in materials where there are no free electrons that would transport current. However, occasionally it can occur that a material has both electrical conduction and ionic conduction of roughly the same magnitude—such materials are known as mixed ion–electron conductors.

Suppose free electrons have density n_e and scattering time τ_e (and have the usual electron mass m_e and charge $-e$). Suppose that the free ions have density n_i, scattering time τ_i, mass m_i and charge $+e$. Using Drude theory,

(a) Calculate the electrical resistivity.
(b) Calculate the thermal conductivity.
(c)* Calculate the Hall resistivity.

If we fix the electric field, both species respond to the electric field independently. So the total conductivity is the sum of the two independent conductivities

$$\sigma = \sigma_e + \sigma_i = e^2 \left(\frac{n_e \tau_e}{m_e} + \frac{n_i \tau_i}{m_i} \right)$$

And thus

$$\rho = \frac{1}{e^2 \left(\frac{n_e \tau_e}{m_e} + \frac{n_i \tau_i}{m_i} \right)}$$

The thermal conductivity is similar – both pieces add

$$\kappa = \kappa_e + \kappa_i = \frac{4 k_B^2 T}{\pi} \left(\frac{n_e \tau_e}{m_e} + \frac{n_i \tau_i}{m_i} \right)$$

Note that the Weidemann-Franz law continues to hold here in the ratio of σ to κ.

The Hall resistivity is more complicated. To simplify, if we apply magentic field in the z direction, we need only keep track of conductivity in the x, y plane (i.e., we can think of this as a two dimensional problem).

For a single species, we have (See exercise 3.1)

$$\rho = \begin{pmatrix} r & BR \\ -BR & r \end{pmatrix}$$

where $r = m/(nq^2\tau)$ and $R = q/n$ with q the charge on the charge carrier. We define tensors ρ_e and ρ_i for the two separate species in terms of $r_j = m_j/(n_j q_j^2 \tau_j)$ and $R_j = q_j/n_j$ with $j = e$ or i. The conductivity tensors are $\sigma_j = \rho_j^{-1}$ and then the total conductivity tensor is $\sigma = \sigma_e + \sigma_i$. Finally this is inverted to give the tensor $\rho_{total} = \sigma^{-1}$. There is a lot of algebra involved in this. I obtained

$$\begin{aligned} \rho_{xx} &= \frac{B^2(r_e R_i^2 + r_i R_e^2) + r_i r_e (r_e + r_i)}{B^2(R_e + R_i)^2 + (r_e + r_i)^2} \\ \rho_{xy} &= \frac{B \left(B^2 R_e R_i (R_e + R_i) + R_i r_e^2 + R_e r_i^2 \right)}{B^2(R_e + R_i)^2 + (r_e + r_i)^2} \end{aligned}$$

More Electrons in Metals: Sommerfeld (Free Electron) Theory

4

(4.1) Fermi Surface in the Free Electron (Sommerfeld) Theory of Metals

(a)‡ Explain what is meant by the Fermi energy, Fermi temperature and the Fermi surface of a metal.

(b)‡ Obtain an expression for the Fermi wavevector and the Fermi energy for a gas of electrons (in 3D).

▷ Show that the density of states at the Fermi surface, dN/dE_F can be written as $3N/2E_F$.

(c) Estimate the value of E_F for sodium [The density of sodium atoms is roughly 1 gram/cm^3, and sodium has atomic mass of roughly 23. You may assume that there is one free electron per sodium atom (sodium has *valence* one)]

(d) Now consider a two-dimensional Fermi gas. Obtain an expression for the density of states at the Fermi surface.

(a.i) Fermi Energy E_F is chemical potential at $T = 0$. Note, if there is a filled band the chemical potential is mid-gap, and this differs from the conventional intuition that it is the highest filled state at zero temperature. Note that some books define fermi energy to be chemical potential as a function of temperature. This is annoying — why define a new quantity if it is just another name for the old quantity?!

(a.ii) Fermi temperature $T_F = E_F/k_b$ with k_b being Boltzmann's constant.

(a.iii) Fermi surface is the surface in momentum space separating the filled and unfilled states at zero temperature. (This is ill-defined for the case of a filled band – but we don't do band theory until later in the course). Or the manifold of states having energy E_F. Note that it need not be a sphere, for example, if the effective mass (defined later!) is anisotropic you get an ellipsoid instead.

(b)

$$N = 2V \int_{k<k_F} \frac{d\mathbf{k}}{(2\pi)^3} = \frac{2V}{(2\pi)^3} \frac{4\pi k_F^3}{3}$$

Note the factor of 2 out front is for two species of spins. This result implies

$$k_F = (3\pi^2 N/V)^{1/3}$$

which gives us the Fermi energy

$$E_F = \frac{\hbar^2 (3\pi^2 N/V)^{2/3}}{2m} \tag{4.1}$$

with m the (effective) electron mass.

Here is a short way to show that the density of states at the Fermi surface is $3N/2E_F$. We write the density as

$$E_F = C(N)^{2/3}$$

where C is a bunch of constants (given in Eq. 4.1, although we actually don't care about its actual value). We then have

$$dE_F/dN = (2/3)CN^{-1/3} = (2/3)E_F/N$$

which immediately gives us

$$dN/dE_F = (3/2)N/E_F$$

(c) Sodium had density of 1gm/cc and atomic mass 23. Thus we have

$$\begin{aligned}&(1gm/cm^3)(10^2 cm/m)^3(mole/23gm)(6.02 \times 10^{23} atoms/mole)\\ &= 2.6 \times 10^{28} atom/m^3.\end{aligned}$$

(See also part (c) of problem 3.1.) With 1 free electron per atom, this gives us the density N/V and we can plug this into Eq. 4.1 yielding

$$E_F = 5 \times 10^{-19} J = 3.2eV$$

dividing by Boltzmann's constant this gives about 37,000 Kelvin.

(d) For a 2d Fermi gas we have

$$N = 2A \int_{k<k_F} \frac{d\mathbf{k}}{(2\pi)^2} = \frac{2A}{(2\pi)^2}\pi k_F^2$$

where A is the (2d) area of the system. Thus we obtain

$$k_F = (2\pi N/A)^{1/2}$$

The Fermi energy is then

$$E_F = \frac{\hbar^2(2\pi N/A)}{2m} = \frac{\hbar^2 \pi N/A}{m}$$

The density of states is then independent of energy and is given by

$$dN/dE = Am/(\hbar^2 \pi) = N/E_F$$

One can ask the same question in d dimensions and use a similar scheme to do the calculation.

(4.2) Velocities in the Free Electron Theory

(a) Assuming that the free electron theory is applicable: show that the speed v_F of an electron at the Fermi surface of a metal is $v_F = \frac{\hbar}{m}(3\pi^2 n)^{1/3}$ where n is the density of electrons.

(b) Show that the mean drift speed v_d of an electron in an applied electric field E is $v_d = |\sigma E/(ne)|$, where σ is the electrical conductivity, and show that σ is given in terms of the mean free path λ of the electrons by $\sigma = ne^2\lambda/(mv_F)$.

(c) Assuming that the free electron theory is applicable to copper:

(i) calculate the values of both v_d and v_F for copper at 300K in an electric field of 1 V m^{-1} and comment on their relative magnitudes.
(ii) estimate λ for copper at 300K and comment upon its value compared to the mean spacing between the copper atoms.

You will need the following information: copper is monovalent, meaning there is one free electron per atom. The density of atoms in copper is $n = 8.45 \times 10^{28}$ m^{-3}. The conductivity of copper is $\sigma = 5.9 \times 10^7 \Omega^{-1}\mathrm{m}^{-1}$ at 300K.

(a) As in the previous problem, in 3D, $k_F = (3\pi^2 n)^{1/3}$ with $n = N/V$. Thus $p_F = \hbar k_F$ and the fermi velocity is $v_F = \hbar k_F/m$.

(b) If an electric field $\mathbf{E}$ is applied, a current density $\mathbf{j} = \sigma\mathbf{E}$ flows, with σ the conductivity. The electrical current is then given by $\mathbf{j} = -en\mathbf{v}_d$ where $-e$ is the electron charge, n is the density of the electrons, and $\mathbf{v}_d$ is the average drift velocity. Thus we obtain

$$|v_d| = |\sigma E/(ne)|$$

Deriving the conductivity from the mean free path is an exercise in Drude theory. As in problem 3.1, we have the Drude theory expression

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} - \frac{\mathbf{p}}{\tau}$$

With $\mathbf{F} = -e\mathbf{E}$ we then have the steady state momentum $\mathbf{p} = -e\mathbf{E}/\tau$ corresponding to the steady state drift velocity $\mathbf{v}_d = -e\mathbf{E}/(\tau m)$. The current density is then $\mathbf{j} = ne^2/(\tau m)\mathbf{E}$ yielding the usual expression for the Drude conductivity

$$\sigma = \frac{ne^2\tau}{m}$$

Now if the *typical* velocity of an electron is on the order of the Fermi velocity v_F, then in the scattering time τ the distance traveled, i.e., the mean free path is $\lambda = \tau v_F$. Thus we can rewrite the Drude conductivity as

$$\sigma = \frac{ne^2\lambda}{mv_F}$$

(c.i) On the scale of the Fermi temperature, 300K is close to zero kelvin so we can ignore this temperature.

$$v_F = \hbar(3\pi^2 n)^{1/3}$$

we obtain $v_F \approx 1.6 \times 10^6 m/sec$. This is about 0.5% of the speed of light. Very fast.

The drift velocity is

$$v_d = \sigma E/(ne)$$

which gives $v_d \approx 4.4 \times 10^{-3} m/sec$. I.e., very slow.

(c.ii) Use here

$$\lambda = v_F \sigma m/(ne^2)$$

plugging in numbers this gives $\lambda \approx 3.9 \times 10^{-8} m$, or about 400 angstoms – roughly 100 lattice spacings.

(4.3) Physical Properties of the Free Electron Gas

In both (a) and (b) you may always assume that the temperature is much less than the Fermi temperature.

(a)‡ Give a simple but approximate derivation of the Fermi gas prediction for heat capacity of the conduction electron in metals.

(b)‡ Give a simple (not approximate) derivation of the Fermi gas prediction for magnetic susceptibility of the conduction electron in metals. Here susceptibility is $\chi = dM/dH = \mu_0 dM/dB$ at small H and is meant to consider the magnetization of the electron spins only.

(c) How are the results of (a) and (b) different from that of a classical gas of electrons?

▷ What other properties of metals may be different from the classical prediction?

(d) The experimental specific heat of potassium metal at low temperatures has the form:

$$C = \gamma T + \alpha T^3$$

where $\gamma = 2.08\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $\alpha = 2.6\,\mathrm{mJ\,mol^{-1}\,K^{-4}}$.

▷ Explain the origin of each of the two terms in this expression.

▷ Make an estimate of the Fermi energy for potassium metal.

(a) Let the density of states at the Fermi surface be given by $D(E_F)$ (and assume this is a nonzero quantity). At temperature T, electrons within an energy k_bT of the Fermi surface can be excited above the Fermi energy. Typically if an electron is excited, it will gain an energy of order k_bT. Thus, the electron energy (above the ground state) is roughly $(k_bT)^2 D(E_F)$. Thus the heat capacity is approximately

$$C = dE/dT \approx 2k_b(k_bT)D(E_F)$$

In a slightly more careful (but still not exact) treatment, one approximates the smooth fermi function as a simple function as shown here in Fig. 4.1.

In this picture, the approximation to the fermi function is given by

$$n(E) = \begin{cases} 1 & (E-\mu)/k_bT < -2 \\ 0 & (E-\mu)/k_bT > 2 \\ 1/2 - (E-\mu)/(4k_bT) & \text{otherwise} \end{cases}$$

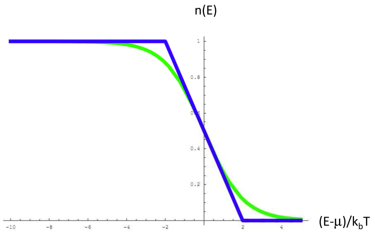


Fig. 4.1 The Fermi function (green) and a simple approximation to the fermi function (blue).

In this approximation, one can calculate that the energy is given by

$$\begin{aligned} E(T) &= \text{Constant} + D\int_{-2/k_bT}^{2/k_bT} dE E(1/2 - E/(4k_bT)) \\ &= \text{Constant} + D(k_bT)^2(4/3) \end{aligned}$$

which results in $C = (8/3)k_b(k_bT)D(E_F)$.

An exact calculation (See Ashcroft+Mermin, or exercise 4.9.b below) of this result is

$$C = (\pi^2/3)k_b(k_bT)D(E_F) = N(\pi^2/2)k_b(k_bT)/E_F \tag{4.2}$$

This calculation is an exercise given as an additional problem.

Note that as discussed above, for a free fermi gas $D(E_F) = 3N/2E_F$. Thus up to constants of order one we have

$$C \sim k_bN(k_bT/E_F)$$

which is very small since $T \ll T_F$.

(b) There are several ways that the electrons can respond to the magnetic field. First, we assume that the magnetic field couples only to the spins of the electron (we ignore orbital effects). The Hamiltonian (neglecting the Lorentz force of the magnetic field) becomes

$$H = \frac{\mathbf{p}^2}{2m} + \mathfrak{g}\mu_B \mathbf{B}\cdot\boldsymbol{\sigma}$$

where $\mathfrak{g} = 2$ is the g-factor of the electron $\mathbf{B}$ is the externally applied magnetic field and $\boldsymbol{\sigma}$ is the spin of the electron which takes eigenvalues $\pm 1/2$. Here $\mu_B \approx .67(K/T)/k_B$ the conventional Bohr magneton. Thus in the magnetic field the energy of an electron with spin up or down

(with up meaning it points the same way as the applied field)

$$\begin{aligned}\epsilon(\mathbf{k},\uparrow) &= \frac{\hbar^2|\mathbf{k}|^2}{2m} + \mu_b|B| \\ \epsilon(\mathbf{k},\downarrow) &= \frac{\hbar^2|\mathbf{k}|^2}{2m} - \mu_b|B|\end{aligned}$$

The spin magnetization of the system in the direction of the applied magnetic field will then be

$$M = -\frac{1}{V}\frac{dE}{dB} = -([\#\text{ up spins}] - [\#\text{ down spins}])\,\mu_B/V \tag{4.3}$$

So when the magnetic field is applied, it is lower energy for the spins to be pointing down, so more of them will point down.

Let us now calculate the Pauli paramagnetism of the free electron gas at $T = 0$. With zero magnetic field applied, both the spin up and spin down states are filled up to the Fermi energy (i.e, to the Fermi wavevector). Near the Fermi level the density of states per unit volume for spin up electrons is $g(E_F)/2$ and similarly the density of states per unit volume for spin down electrons is $g(E_F)/2$. When B is applied, the spin ups will be more costly by an energy $\mu_B B$. Thus, (assuming that the chemical potential does not change) we will have $(g(E_F)/2)\mu_B B$ fewer spin ups electrons per unit volume. Similarly, the spin downs will be less costly by the same amount, so we will have $(g(E_F)/2)\mu_B B$ more spin downs per unit volume. Note that the total number of electrons in the system did not change, so our assumption that the chemical potential did not change is correct. (Recall that chemical potential is always adjusted so it gives the right total number of electrons in the system). Thus, using Eq. 4.3 the moment per unit volume is given by

$$M = g(E_F)\mu_B^2 B$$

and hence the magnetic susceptibility $\chi = \partial M/\partial H$ is given (at $T = 0$ by)

$$\chi_{Pauli} = \mu_0 \mu_B^2 g(E_F)$$

(c) For a classical monatomic gas, the specific heat is given by the equipartition law $C = 3k_B N$ which is larger than the result above by roughly a factor of $E_F/k_b T$ which could be a factor of 100 or more.

Similarly, for a single isolated spin 1/2 we can calculate the partition function (this calculation was done in stat mech class last year).

$$Z = e^{\beta g \mu_B B/2} + e^{-\beta g \mu_B B/2}$$

The expectation of the moment (per spin) is then

$$m = -d\log Z/d(B\beta) = (g\mu_B/2)\tanh(\beta g \mu_B B/2)$$

For small B this is

$$m = (g\mu_B/2)^2(B/k_b T)$$

thus the total susceptibility for N spins (recall susceptibility is measured per unit volume) is

$$dM/dH = \mu_0 dM/dB = N\mu_0 (g\mu_B/2)^2 (1/k_b T)$$

which, for any $T \ll T_F$ is much larger than the Pauli susceptibility calculated above (by a factor of approximately T_F/T).

Other properties that differ from the classical prediction include: Thermopower, Peltier Coefficinent, Average Electron Velocity, Compressibility, ...

(d) The T^3 term is clearly from Debye phonon specific heat. The T-linear term is the specific heat of free electrons. Using the above formula Eq. 4.2 yields

$$E_F = (\pi^2/2)R(T/C_{linear}) =\approx 2 \times 10^4 K k_B \approx 1.7\text{eV}$$

The real value is roughly 2.1 eV.

Another method would be to use the density of potassium and assume the valence is 1. If you do this, you get something much closer to the right answer.

(4.4) Another Review of Free Electron Theory

▷ What is the *free electron model* of a metal.

▷ Define *Fermi energy* and *Fermi temperature*.

▷ Why do metals held at room temperature feel cold to the touch even though their Fermi temperatures are much higher than room temperature?

(a) A d-dimensional sample with volume L^d contains N electrons and can be described as a free electron model. Show that the Fermi energy is given by

$$E_F = \frac{\hbar^2}{2mL^2}(Na_d)^{2/d}$$

Find the numerical values of a_d for $d = 1, 2$, and 3.

(b) Show also that the density of states at the Fermi energy is given by

$$g(E_F) = \frac{Nd}{2L^d E_F}$$

▷ Assuming the free electron model is applicable, estimate the Fermi energy and Fermi temperature of a one-dimensional organic conductor which has unit cell of length 0.8 nm, where each unit cell contributes one mobile electron.

(c) Consider relativistic electrons where $E = c|\mathbf{p}|$. Calculate the Fermi energy as a function of the density for electrons in $d = 1, 2, 3$ and calculate the density of states at the Fermi energy in each case.

The free electron model of a metal describes electrons in a metal as a noninteracting gas of fermions at some fixed density (usually chosen to be v electrons per unit cell of the metal where v is the valence).

Fermi Energy E_F is chemical potential at $T = 0$. Note, if there is a filled band the chemical potential is mid-gap, and this differs from the conventional intuition that it is the highest filled state at zero temperature. Note that some books define fermi energy to be chemical potential as a function of temperature. This is annoying — why define a new quantity if it is just another name for the old quantity?!

Fermi temperature $T_F = E_F/k_b$ with k_b being Boltzmann's constant.

Due to Pauli exclusion, a metal can have a very high Fermi temperature (high chemical potential) even if the material is at zero temperature — i.e., if the material is in its ground state. When you touch a material and it feels hot, this is because heat has flowed from the material to you. If the material is in its ground state (despite having a high fermi temperature) it cannot lower its own energy and therefore cannot transfer heat to you. Note: Having a high chemical potential DOES mean that the material might have a tendency to transfer electrons to another body with fewer electrons (although this might create a charge imbalance that then prevents further flow of electrons). We discuss physics of this type in Chapter 18.

(a) In any number of dimensions we can write

$$N = 2L^d \int_{|k|<k_F} \frac{d^d k}{(2\pi)^d}$$

with the 2 accounting for spin. The integration is over a d-dimensional ball. In 1,2, 3d we obtain

$$N/L^d = \begin{cases} 2k_F/\pi & 1d \\ k_F^2/(2\pi) & 2d \\ k_F^3/(3\pi^2) & 3d \end{cases}$$

So that

$$k_F = \begin{cases} (N/L)(\pi/2) & 1d \\ (N^{1/2}/L)(2\pi)^{1/2} & 2d \\ (N^{1/3}/L)(3\pi^2)^{1/3} & 3d \end{cases}$$

And in any dimension $E_F = \hbar^2 k_F^2/(2m)$, so that $a_1 = \pi/2$ and $a_2 = 2\pi$ and $a_3 = 3\pi^2$.

(b) We have

$$E_F = C_d/L^2 N^{2/d}$$

for some constant C_d. Then

$$dE_F/dN = (2/d)(E_F/N)$$

and

$$g(E_F) = (1/V)(dN/dE_F) = (N/L^d)(d/(2E_F)).$$

For a one dimensional system, as noted above $E_F = (\hbar^2/(2m))(\pi/2)^2(N/L)^2$ where here $N/L = 1/(.8nm)$ This gives me $E_F = 2.4 \times 10^{-20} J$ or $T_F = E_F/k_b = 1700K$.

(c) Our above expression for k_F still holds. So

$$E_F = c\hbar|k_F| = c\hbar(N^{1/d}/L)a_d$$

So here we have

$$dE_F/dN = (1/d)(E_F/N)$$

and

$$g(E_F) = (1/V)(dN/dE_F) = (N/V)(d/E_F)$$

(4.5) Chemical Potential of 2D Electrons
Show that for free electron gas in two dimensions, the chemical potential μ is independent of the temperature so long as $T \ll \mu$. Hint: first examine the density of states in two dimensions.

The key here is to realize that the density of states is independent of energy. From the previous problem, in 2d, we have $E_F \sim N$, and $g(E_F) \sim N/E_F$ so that the density of states is a constant independent of temperature. Now, given a fixed density of electrons, the chemical potential is set by

$$n = \int_0^\infty dE g(E) \frac{1}{e^{\beta(E-\mu)} + 1}$$

where g here is now constant. The point here is that except for corrections exponentially small in $\beta\mu$ the value of the integral is independent of β. Therefore the dependence of n on μ is to a very good approximation independent of temperature.

To see this in more detail rewrite as

$$\begin{aligned} n/g &= \int_{-\mu}^\infty dx \frac{1}{e^{\beta x} + 1} = \int_{-\mu}^\infty dx \frac{e^{-\beta x}}{e^{-\beta x} + 1} \\ &= \frac{1}{\beta} \ln(e^{\beta\mu} + 1) \end{aligned}$$

Now for large $\beta\mu$ we can expand to get

$$n/g = \mu + \mathcal{O}(e^{-\beta\mu})$$

so, as claimed, the relationship of n to μ is to a good approximation independent of T so long as $\mu \gg k_b T$.

(4.6) Chemical Potential at $T = 0$
Consider a system of N non-interacting electrons. At $T = 0$ the N lowest-energy eigenstates will be filled and all the higher energy eigenstates will be empty. Show that at $T = 0$ the energy of the chemical potential is precisely half way between the highest energy filled eigenstate and the lowest-energy unfilled eigenstate.

This is a bit more difficult than it appears as most generally one should consider the possibility that the highest filled state at energy E_1 or lowest unfilled state at energy E_2 are degenerate – i.e, there is more than one eigenstate at the given energy. Let us call the degeneracies of these levels g_1 and g_2 respectively. Let us focus on these two energies only and assume for now (to be justified in retrospect) that we can ignore any other states in the system with the intuition that any state with energy below E_1 is completely filled and can be ignored any any state with energy above E_2 is completely empty and can be ignored.

We take our system (E_1 with degeneracy g_1 and E_2 with degeneracy g_2) and will fill it with exactly g_1 electrons. (Were we to choose fewer, the lowest unfilled would move down to E_1 were we to choose more the highest filled would move up to E_2). Fermi occupation then gives us

$$N = g_1 = \frac{g_1}{e^{\beta(E_1-\mu)}+1} + \frac{g_2}{e^{\beta(E_2-\mu)}+1}$$

Defining $x = e^{\beta(E_1-\mu)}$ and $z = e^{-\beta(E_2-E_1)}$ this then becomes

$$g_1 = \frac{g_1}{x+1} + \frac{g_2}{x/z+1}$$

Solving for x (and taking the positive root only) gives

$$x = \frac{(g_2-g_1)z + \sqrt{(g_2-g_1)^2 z^2 + 4 g_1 g_2 z}}{2g_1}$$

Since temperature is small, z becomes very small, so we can expand this expression to give

$$x = \sqrt{g_1 g_2 z}$$

Or equivalently taking log of both sides

$$\beta(E_1-\mu) = \frac{1}{2}\left(\ln(g_1 g_2) - \beta(E_2-E_1)\right)$$

Taking the limit of small temperature or large β, this becomes

$$\mu = (E_1+E_2)/2 + \ldots$$

(4.7) More Thermodynamics of Free Electrons

(a) Show that the kinetic energy of a free electron gas in three dimensions is $E = \frac{3}{5}E_F N$.

(b) Calculate the pressure $P = -\partial E/\partial V$, and then the bulk modulus $B = -V\partial P/\partial V$.

(c) Given that the density of atoms in sodium is $2.53\times10^{22}\text{cm}^{-3}$ and that of potassium is $1.33\times10^{22}\text{cm}^{-3}$, and given that both of these metals are monovalent (i.e., have one free electron per atom), calculate the bulk modulus associated with the electrons in these materials. Compare your results to the measured values of 6.3 GPa and 3.1 GPa respectively.

(a) We begin with the fact that the density of state $g(\epsilon) \sim \epsilon^{1/2}$. To see this note that $\epsilon \sim k^2$ so $d\epsilon \sim kdk$ and $dN \sim \mathbf{dk} \sim k^2 dk$, so we have $dN/d\epsilon \sim k \sim \epsilon^{1/2}$. We can thus write $g(\epsilon) = C\epsilon^{1/2}$ for some constant C and

$$\begin{aligned} N &= V\int_0^{E_F} d\epsilon g(\epsilon) = CV(2/3)E_F^{3/2} \\ E &= V\int_0^{E_F} \epsilon d\epsilon g(\epsilon) = CV(2/5)E_F^{5/2} \end{aligned}$$

Thus dividing one by the other we get

$$E/N = (3/5)E_F$$

(b) From exercise 4.4.a or on dimensional grounds $E_F \sim V^{-2/3}$, so $E \sim V^{-2/3}$ so the pressure is

$$P = -\frac{\partial E}{\partial V_N} = \frac{2}{3}\frac{E}{V} = \frac{2}{5}\frac{NE_F}{V}$$

Since $P \sim V^{-5/3}$ we then have the bulk modulus

$$B = -V\frac{\partial P}{\partial V} = \frac{5}{3}P = \frac{10}{9}\frac{E}{V} = \frac{2E_F}{3}\frac{N}{V}$$

(c) From exercise 4.1 or 4.4 we calculate the fermi energy $E_F = 5.0 \times 10^{-19} J$ and $E_F = 3.3 \times 10^{-19}$ for sodium and potassium respectively. Thus we obtain $B = 8.5$ GPa and $B = 2.9$ GPa respectively. Not too shabby!!

(4.8) Heat Capacity of a Free Electron Gas*

In Exercise 4.3.a we approximated the heat capacity of a free electron gas

(a*) Calculate an exact expression for the heat capacity of a 2d metal at low temperature.

(b**) Calculate an exact expression for the heat capacity of a 3d metal at low temperature.

The following integral may be useful for these calculations:

$$\int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x+1)^2} = \frac{\pi^2}{3} = \zeta(2)/2$$

Note that for the 3d case you have to worry about the fact that the chemical potential will shift as a function of temperature. Why does this not happen (at least for low T) in the 2d case?

(a) As pointed out in exercise 4.6, in two dimensions μ is indepdendent of temperature — a result of the fact that the density of states is a constant (the answer to the last part of this question). First we need to evaluate the value of the density of states. Using the result of 4.4, we obtain at the fermi energy (and therefore at all energies)

$$g = \frac{m}{\hbar^2 \pi}$$

We thus have

$$\mu = E_F = n/g$$

We can then write the total energy as

$$E = V\int_0^{\infty} d\epsilon\, \epsilon\, \frac{g}{e^{\beta(\epsilon-\mu)}+1} = Vg\int_{-\mu}^{\infty} dx \frac{x}{e^{\beta x}+1} + Vg\int_{-\mu}^{\infty} dx \frac{\mu}{e^{\beta x}+1}$$

where we have defined $x = \epsilon - \mu$. We recognize the second term here as simply being μN, and as discussed in 4.6, this is independent of temperature. To evaluate the first term, we integrate by parts to get

$$E - N\mu = \left.\frac{gVx^2/2}{e^{\beta x}+1}\right|_{-\mu}^{\infty} - gV\int_{-\mu}^{\infty} dx\, \frac{x^2}{2}\, \frac{-\beta e^{\beta x}}{(e^{\beta x}+1)^2}$$

Assuming $\beta\mu$ is large, to within corrections that are of order of $e^{-\beta\mu}$ we can throw away the first term and we can extend the integral in the second term all the way to $-\infty$ (since the argument is peaked near $x = 0$ wiht only exponentially small tails). Scaling out the factor of β and using the integral given we obtain

$$E - N\mu = Vg(k_bT)^2\frac{\pi^2}{6} + \mathcal{O}(e^{-\beta\mu})$$

Differentiating to obtan the heat capacity we obtain

$$C/V = gk_b(k_bT)\pi^2/3$$

which is precisely the result claimed above in exercise 4.3 (see Eq. 4.2). However, here note that up to exponentially small corrections, this is exact – in other words, there is no subleading T^n with $n > 1$ term at all!

(b) In the more general case where $g(E)$ is not a constant, one must use the so-called Sommerfeld expansion. This is quite a bit more complex. First we will quote the key formula and use it to derive our result for the heat capacity, then we will go back to derive Sommerfeld's formula.

Defining the Fermi function

$$n_F(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$

The Sommerfeld formula is

$$\int_{\infty}^{\infty} H(\epsilon)n_F(\epsilon)d\epsilon = \int_{\infty}^{\mu} H(\epsilon)d\epsilon + \frac{\pi}{6}(k_bT)^2H'(\mu) + \mathcal{O}(T^4) \qquad (4.4)$$

The intuition behind this formula is that at low temperature the fermi function is a step function (given by the first term). The finite slope of the fermi function where it is almost a step creates the small correction term which is determined by H'. Note that as we determinmed in 4.6 and above, if the argument H is constant, then up to exponentially small terms, there is no correction term at any order in T. One could carry this expansion to higher order and pick up terms related to H'' etc as well.

Expecting that the chemical potential will remain very close to the Fermi energy at low temperatures, we can conclude

$$\int_{\infty}^{\infty} H(\epsilon)n_F(\epsilon)d\epsilon = \int_{\infty}^{E_F} H(\epsilon)d\epsilon + (\mu - E_F)H(E_F) + \frac{\pi}{6}(k_bT)^2H'(E_F) + \ldots$$

Using this equation to write an expression for the density

$$\begin{aligned} \frac{N}{V} &= \int_0^{\infty} g(\epsilon)n_F(\epsilon)d\epsilon && (4.5)\\ &= \int_{\infty}^{E_F} d\epsilon g(\epsilon) + (\mu - E_F)g(E_F) + \frac{\pi}{6}(k_bT)^2g'(\mu) + \ldots \\ &= \frac{N(T=0)}{V} + \left\{(\mu - E_F)g(E_F) + \frac{\pi}{6}(k_bT)^2g'(E_F)\right\} && (4.6) \end{aligned}$$

Since we are fixing the density N, the term in brackets must remain zero for all temperatures (accurate to order T^2). This confirms that $\mu = E_F + \mathcal{O}(T^2)$ and confirms our suspicion that it should be very close to E_F at low temperature. Note also that for $g' = 0$, such as in 2d, $\mu = E_F$ independent of temperature.

We can then write a similar expression for the energy density

$$\begin{aligned}
\frac{E}{V} &= \int_0^\infty \epsilon g(\epsilon) n_F(\epsilon) d\epsilon \\
&= \int_\infty^{E_F} \epsilon g(\epsilon) d\epsilon + E_F(\mu - E_F) g(E_F) + \frac{\pi}{6}(k_b T)^2 (\epsilon g(\epsilon))'_{\epsilon = E_F} + \ldots \\
&= \frac{E(T=0)}{V} + E_F \left\{ (\mu - E_F) g(E_F) + \frac{\pi}{6}(k_b T)^2 g'(E_F) \right\} \\
&\quad + \frac{\pi^2}{6}(k_b T)^2 g(E_F) + \ldots \qquad (4.7)
\end{aligned}$$

Note that in the final equation the term in brackets is the same as the term in brackets from Eq. 4.6 which we have set to zero in order to keep the density constant as a function of temperature. Thus we obtain

$$\frac{E}{V} = \frac{E(T=0)}{V} + \frac{\pi^2}{6}(k_b T)^2 g(E_F) + \ldots$$

Which we differentiate to obtain the heat capacity

$$C/V = \frac{\pi^2}{3} k_b (k_b T) g(E_F)$$

as claimed.

Finally we return to prove the Sommerfeld formula 4.4. The quantity we would like to evaluate is

$$I = \int_\infty^\infty H(\epsilon) n_F(\epsilon) d\epsilon$$

Let us define a function

$$K(\epsilon) = \int_{-\infty}^{\epsilon} d\epsilon' H(\epsilon')$$

So that, integrating by parts, we have

$$I = \int_\infty^\infty K(\epsilon) \frac{-\partial n_F(\epsilon)}{\partial \epsilon} d\epsilon$$

there are no boundary terms (to accuracy of $\mathcal{O}(e^{-\beta\mu})$ because $\partial n_F / \partial \epsilon$ decays very rapidly away from the chemical potential. Note now that the function $\partial n_F / \partial \epsilon$ is a symmetric (even) function around the chemical potential. Thus let if expand K in a taylor series around the chemical potential only the even terms will have a nonzero contribution, thus we have

$$I = \int_\infty^\infty \left[K(\mu) + \frac{1}{2}(\epsilon - \mu)^2 K''(\mu) + \ldots \right] \frac{-\partial n_F(\epsilon)}{\partial \epsilon} d\epsilon \qquad (4.8)$$

$$\int_{\infty}^{\infty} \frac{-\partial n_F(\epsilon)}{\partial \epsilon} = 1$$

the first term in the expansion of Eq. 4.8 is just

$$K(\mu) = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon$$

as required. The next term gives a prefactor of $K''(\mu) = H'(\mu)$ and requires that we evaluate the integral

$$\int_{\infty}^{\infty} \frac{1}{2}(\epsilon - \mu)^2 \frac{-\partial n_F(\epsilon)}{\partial \epsilon} d\epsilon = \frac{1}{2} \int_{\infty}^{\infty} \frac{x^2 e^{\beta x}}{(e^{\beta x} + 1)^2} = (k_b T)^2 \pi^2 / 6$$

using the given integral. Thus we have obtained the first two terms of Eq. 4.8. By followin a similar procedure one can evaluate higher terms in the expansion and in particular we will find that the next term in the expansion must be proportional to T^4.

The Periodic Table

5

(5.1) Madelung's Rule

▷ Use Madelung's rule to deduce the atomic shell filling configuration of the element tungsten (symbol W) which has atomic number 74.

▷ Element 118 has recently been discovered, and is expected to be a noble gas, i.e., is in group VIII. (No real chemistry tests have been performed on the element yet, as the nucleus decays very quickly.) Assuming that Madelung's rule continues to hold, what should the atomic number be for the next noble gas after this one?

Angular momentum l orbitals ($l = 0$ is called s, $l = 1$ is called p, etc) contain up to $2(2l+1)$ electrons. Madulung's rule fills orbitals according to the diagram Fig. 5.1: from lowest $n + l$ to highest, and for cases of the same $n + l$, fill the lower n first. So we have

Tungsten atomic number 74:

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^1$0 $4p^6$ $5s^2$ $4d^{10}$ $5p^6$ $6s^2$ $4f^{14}$ $5d^4$.

Note that the "exponents" add to 74. Or equivalently we write

[Xe] $4f^{14}$ $5d^4$.

Note that the noble gases occur whenever a p-shell has just filled. Element 118 has a filled 7p shell. Madelung's rule tells us that we then have to fill 8s, 5g, 6f, 7d and finally 8p. This brings us to element 168. For entertainment sake (and you can try to prove this) note that the sequence of nobel gas element numbers 2, 10, 18, 36, 54, 86, 118, 168 has successive differences which are twice the perfect squares each occurring twice. (10-2)/2 = 4 , (18-10)/2 = 4, (36-18)/2 = 9, (54-36)/2 = 9, (86-54)/2 = 16, (118-86)/2=16, (168-118)/2 = 25, and so forth.

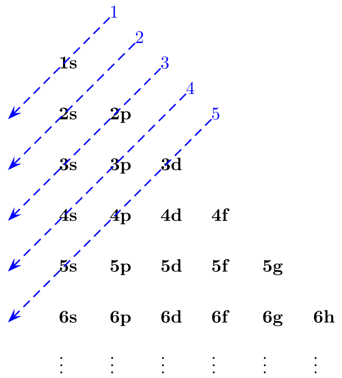


Fig. 5.1 Ordering of filling orbitals in atoms (Madelung's rule).

(5.2) Effective Nuclear Charge and Ionization Energy

(a) Let us approximate an electron in the n^{th} shell (i.e., principal quantum number n) of an atom as being like an electron in the n^{th} shell of a hydrogen atom with an effective nuclear charge Z. Use your knowledge of the hydrogen atom to calculate the ionization energy of this electron (i.e., the energy required to pull the electron away from the atom) as a function of Z and n.

(b) Consider the two approximations discussed in the text for estimating the effective nuclear charge:

- (Approximation a)

$$Z = Z_{nuc} - N_{inside}$$

- (Approximation b)

$$Z = Z_{nuc} - N_{inside} - (N_{same} - 1)/2$$

where Z_{nuc} is the actual nuclear charge (or atomic number), N_{inside} is the number of electrons in shells inside of n (i.e., electrons with principal quantum numbers $n' < n$), and N_{same} is the total number of electrons in the n^{th} principal shell (including the electron we are trying to remove from the atom, hence the -1).

▷ Explain the reasoning behind these two approximations.

▷ Use these approximations to calculate the ionization energies for the atoms with atomic number 1 through 21. Make a plot of your results and compare them to the actual ionization energies (you will have to look these up on a table).

Your results should be qualitatively quite good. If you try this for higher atomic numbers, the simple approximations begin to break down. Why is this?

Neglecting fine structure, the energy of an electron in the n^{th} shell of hydrogen is

$$E_n = \frac{-\mathrm{Ry}}{n^2}$$

where Ry=13.6 eV is the Rydberg constant. For a hydrogenic atom with nuclear charge Z, the Coulomb interaction is Z times as strong as in hydrogen, resulting in binding energy which is Z^2 as strong. To see this in detail, one can solve the Schroedinger equation in detail. However, without doing this one can get it by a scaling argument as well. The bound state is a balancing of the kinetic with the potential energy. So roughly one should be able to estimate the binding energy by setting these equal to each other. Setting the the length scale to a, (i.e, define a to be the effective Bohr radius) we have

$$KE = \frac{\hbar^2}{ma^2} = PE = \frac{Ze^2}{4\pi\epsilon_0 a}$$

solving for a obtains $a \sim 1/Z$ and plugging back into PE or KE we determine that the kinetic energy should scale as Z^2.

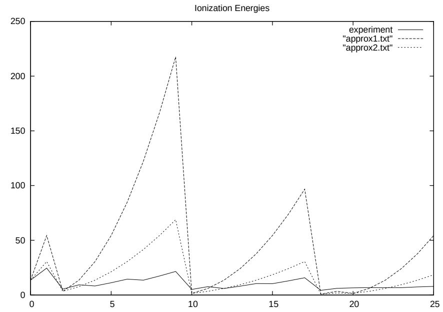


Fig. 5.2 Ionization Energy (eV) as a function of atomic number. Exact compared to the two proposed approximations

The two approximations are plotted here with the exact ionization energies. Qualitatively they are OK, but quantitatively not so good I guess.

One can do a bit better (See Fig. 5.3) by assuming that p-shells are "outside" of s-shells. In other words, a single electron in a p-shell sees a charge of $Z = 1$ since the entire s-shell is inside of it. In this case one gets the following figure (in the two apperoximations discussed above). In fact, this is getting to be pretty decent. Notice with this second approximation one obtains a dip in the ionization energy for filled s-shells (such as atomic numbers 4 and 12) which is seen in the experiment, although is weaker in reality.

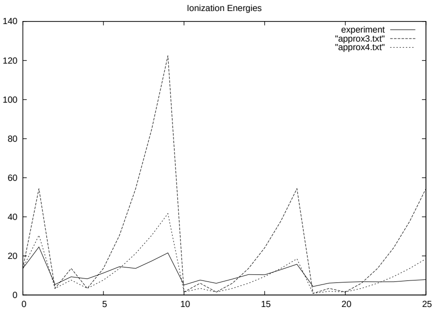


Fig. 5.3 Ionization Energy (eV) as a function of atomic number. Exact compared to the two proposed approximations with the modification that p-shells are declared to be outside of s-shells.

Once you get to the transition metals, the d-shells really are not very easily described as being inside or outside of anything. And often when transition metals ionize, they lose their s-electrons.

(5.3) Exceptions to Madelung's Rule

Although Madelung's rule for the filling of electronic shells holds extremely well, there are a number of exceptions to the rule. Here are a few of them:

$\mathrm{Cu} = [\mathrm{Ar}]\, 4s^1 3d^{10}$
$\mathrm{Pd} = [\mathrm{Kr}]\, 5s^0 4d^{10}$
$\mathrm{Ag} = [\mathrm{Kr}]\, 5s^1 4d^{10}$
$\mathrm{Au} = [\mathrm{Xe}]\, 6s^1 4f^{14} 5d^{10}$

▷ What should the electron configurations be if these elements followed Madelung's rule and the Aufbau principle?

▷ Explain how the statement "3d is inside of 4s" might help justify this exception in copper.

Madelung's rule incorrectly predicts:

$\mathrm{Cu} = [\mathrm{Ar}]\, 4s^2 3d^9$
$\mathrm{Pd} = [\mathrm{Kr}]\, 5s^2 4d^8$
$\mathrm{Ag} = [\mathrm{Kr}]\, 5s^2 4d^9$
$\mathrm{Au} = [\mathrm{Xe}]\, 6s^2 4f^{14} 5d^9$

For copper, the fact that 3d is inside 4s makes the 4s electron less well bound than you might otherwise expect. Thus the d electrons can fill preferentially over the s in some cases.

(5.4) Mendeleev's Nobel Prize

Imagine writing a letter to the Nobel committee nominating Mendeleev, the creator of the periodic table, for a Nobel Prize. Explain why the periodic table is so important. Remember that the periodic table (1869) was devised many years before the structure of the hydrogen atom was understood. (If you do not already have some background in chemistry, you may want to read the next chapter before attempting this exercise.)

Dear Nobel Committee,

Do I have to smack you upside the head? Do the right thing and give the prize to Mendeleev for God sake!

Sincerely,

Professor Steven H. Simon

What Holds Solids Together: Chemical Bonding

6

(6.1) Chemical Bonding

(a) Qualitatively describe five different types of chemical bonds and why they occur.

▷ Describe which combinations of what types of atoms are expected to form which types of bonds (make reference to location on the periodic table).

▷ Describe some of the qualitative properties of materials that have these types of bonds.

(Yes, you can just copy the table out of the chapter summary, but the point of this exercise is to learn the information in the table!)

(b) Describe qualitatively the phenomenon of van der Waals forces. Explain why the force is attractive and proportional to $1/R^7$ where R is the distance between two atoms.

(a) Just look at the table in the Chapter Summary of chapter 6.

(b) van der Waals forces are from correlated dipole flucuations. If the electron is a given fixed position, there is a dipole moment $\mathbf{p} = e\mathbf{r}$ where $\mathbf{r}$ is the vector from the electron to the proton. With the electron "orbiting" (i.e, in an eigenstate), the average dipole moment is zero. However, if an electric field is applied to the atom, the atom will develop a polarization (i.e., it will be more likely for the electron to be found on one side of the nucleus than on the other). We write

$$\mathbf{p} = \chi \mathbf{E}$$

with χ the polarizability. .

Now, let us suppose we have two such atoms, separated a distance r in the $\hat{x}$ direction. Suppose one atom momentarily has a dipole moment $\mathbf{p}_1$ (for definiteness, suppose this dipole moment is in the $\hat{z}$ direction). Then the second atom will feel an electric field

$$E = \frac{p_1}{4\pi\epsilon_0 r^3}$$

in the negative $\hat{z}$ direction. The second atom then, due to its polarizability, develops a dipole moment $p_2 = \chi E$ whi ch in turn is attracted to the first atom. The potential energy between these two dipoles is

$$U = \frac{-|p_1||p_2|}{4\pi\epsilon_0 r^3} = \frac{-p_1 \chi E}{(4\pi\epsilon_0) r^3} = \frac{-|p_1|^2 \chi}{(4\pi\epsilon_0 r^3)^2}$$

corresponding to a force which is attractive and proportional to $1/r^7$. Note that while for a single isolated atom $\langle \mathbf{p} \rangle = 0$ the result is proportional instead to $\langle |\mathbf{p}|^2 \rangle \sim \langle |\mathbf{r}|^2 \rangle \sim$ with $\mathbf{r}$ the position of an electron, is nonzero. This calculation is done more carefully in problem 6.6 below.

(6.2) Covalent Bonding in Detail*

(a) *Linear Combination of Atomic Orbitals:*

In Section 6.2.2 we considered two atoms each with a single atomic orbital. We called the orbital $|1\rangle$ around nucleus 1 and $|2\rangle$ around nucleus 2. More generally we may consider any set of wavefunctions $|n\rangle$ for $n = 1, \ldots, N$. For simplicity, let us assume this basis is orthonormal $\langle n|m\rangle = \delta_{n,m}$ (More generally, one cannot assume that the basis set of orbitals is orthonormal. In Exercise 6.5 we properly consider a non-orthonormal basis.)

Let us write a trial wavefunction for our ground state as

$$|\Psi\rangle = \sum_n \phi_n |n\rangle.$$

This is known as a linear combination of atomic orbitals, LCAO, or tight binding (it is used heavily in numerical simulation of molecules).

We would like to find the lowest-energy wavefunction we can construct in this form, i.e., the best approximation to the actual ground-state wavefunction. (The more states we use in our basis, generally, the more accurate our results will be.) We claim that the ground state is given by the solution of the effective Schroedinger equation

$$\mathcal{H}\,\boldsymbol{\phi} = E\,\boldsymbol{\phi} \qquad (6.1)$$

where $\boldsymbol{\phi}$ is the vector of N coefficients ϕ_n, and $\mathcal{H}$ is the N by N matrix

$$\mathcal{H}_{n,m} = \langle n|H|m\rangle$$

with H the Hamiltonian of the full system we are considering. To prove this, let us construct the energy

$$E = \frac{\langle \psi|H|\psi\rangle}{\langle \psi|\psi\rangle}$$

▷ Show that minimizing this energy with respect to each ϕ_n gives the same eigenvalue equation, Eq. 6.1. (Caution: ϕ_n is generally complex! If you are not comfortable with complex differentiation, write everything in terms of real and imaginary parts of each ϕ_n.) Similarly, the second eigenvalue of the effective Schroedinger equation will be an approximation to the first excited state of the system.

(b) *Two-orbital covalent bond*

Let us return to the case where there are only two orbitals in our basis. This pertains to a case where we have two identical nuclei and a single electron which will be shared between them to form a covalent bond. We write the full Hamiltonian as

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r} - \mathbf{R_1}) + V(\mathbf{r} - \mathbf{R_2}) = K + V_1 + V_2$$

where V is the Coulomb interaction between the electron and the nucleus, R_1 is the position of the first nucleus and R_2 is the position of the second nucleus. Let ϵ be the energy of the atomic orbital around one nucleus in the absence of the other. In other words

$$\begin{aligned} (K + V_1)|1\rangle &= \epsilon|1\rangle \\ (K + V_2)|2\rangle &= \epsilon|2\rangle \end{aligned}$$

Define also the cross-energy element

$$V_{cross} = \langle 1|V_2|1\rangle = \langle 2|V_1|2\rangle$$

and the hopping matrix element

$$t = -\langle 1|V_2|2\rangle = -\langle 1|V_1|2\rangle$$

These are not typos!

▷ Why can we write V_{cross} and t equivalently using either one of the expressions given on the right-hand side?

▷ Show that the eigenvalues of our Schroedinger equation Eq. 6.1 are given by

$$E = \epsilon + V_{cross} \pm |t|$$

▷ Argue (perhaps using Gauss's law) that V_{cross} should roughly cancel the repulsion between nuclei, so that, in the lower eigenstate the total energy is indeed lower when the atoms are closer together.

▷ This approximation must fail when the atoms get sufficiently close. Why?

(a) writing

$$|\psi\rangle = \sum_n \phi_n |n\rangle$$

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{n,m}\phi_n^* \mathcal{H}_{nm}\phi_m}{\sum_n |\phi_n|^2} \tag{6.2}$$

We can extremize by differentiating with respect to ϕ_n^*. Note: When working with complex quantities we can simplify life by treating ϕ_n and ϕ_n^* as independent variables. We thus have

$$\begin{aligned} 0 &= \frac{\partial E}{\partial \phi_n^*} = \frac{\sum_m \mathcal{H}_{nm}\phi_m}{\sum_p |\phi_p|^2} - \left(\frac{\sum_{n,m}\phi_n^* \mathcal{H}_{nm}\phi_m}{\sum_n |\phi_n|^2}\right)\frac{\phi_n}{\sum_p |\phi_p|^2} \\ 0 &= \sum_m \mathcal{H}_{nm}\phi_m - E\phi_n \end{aligned}$$

where we have used Eq. 6.2 to identify E.

(b) The 2 by 2 matrix given by $\mathcal{H}$ in this basis is

$$\begin{pmatrix} \epsilon + V_{cross} & t \\ t^* & \epsilon + V_{cross} \end{pmatrix}$$

which has eigenvalues $E = \epsilon + V_{cross} \pm |t|$. Note that t can always be taken as real by simply making a gauge transform on the single particle wavefunction (i.e., redefining the phase of one of the wavefunctions to absorb the phase of t).

Here V_{cross} is the potential felt by the electron on atom 2 due to the nucleus of atom 1. Since the charge distribution of the electron on atom 2 is roughly spherical we can use Gauss's law to calculate its interaction energy with the nucleus of atom 1. If the nucleus of atom 1 is outside of this spherical distribution of charge of the electron, Gauss's law tells us that we can treat the entire spherical distribution of charge as if it is all at the center of the sphere. In this way, the charge of the electron on atom 2 exactly cancels the charge of the nucleus of atom 2.

When the two nuclei get close, this argument no longer works, as the nucleus is then inside much of the distribution of the electron charge. If the electron charge distribution remains spherical, the nucleus of atom 2 will only see electron charge that is at smaller distances (inside) to the center of this spherical distribution. When the nuclei are very close together, the nucleus does not see the electron charge at all, and only sees the other nucleus. Also, when the atoms get close together, the assumption of orthogonality of grounds tate orbitals on different sites breaks down. (One has to choose whether you want orthogonal orbitals or orbitals that are eigenstates of the single atom Hamiltonian.)

(6.3) LCAO and the Ionic–Covalent Crossover For Exercise 6.2.b consider now the case where the atomic orbitals $|1\rangle$ and $|2\rangle$ have unequal energies $\epsilon_{0,1}$ and $\epsilon_{0,2}$. As the difference in these two energies increases show that the bonding orbital becomes more localized on the lower-energy atom. For simplicity you may use the orthogonality assumption $\langle 1|2\rangle = 0$. Explain how this calculation can be used to describe a crossover between covalent and ionic bonding.

Here we have instead, the two by two hamiltonian matrix

$$\begin{pmatrix} \epsilon_1 & t \\ t^* & \epsilon_2 \end{pmatrix}$$

where we have now absorbed V_{cross} into the values of ϵ_i. The lower energy eigenstate is

$$E_{ground} = \frac{1}{2}\left\{(\epsilon_1 + \epsilon_2) + \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4t^2}\right\}$$

with normalized eigenvector

$$\psi = \frac{(X, 2t)}{\sqrt{4t^2 + X^2}}$$

with

$$X = E_2 - E_1 + \sqrt{(E_2 - E_1)^2 + 4t^2}$$

When $E_2 - E_1 \gg t$ then $X \gg t$ and all of the wavefunction ends up on the first atom (i.e., the one with the lower energy). Similarly, if $E_1 - E_2 \gg t$ then conversely all of the weight of the wavefunction ends up on the second atom. In Fig. 6.1 it is shown how the weight of the wavefunction moves from towards the lower energy atom as a function of energy.

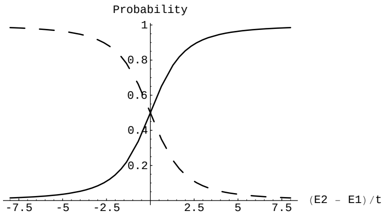


Fig. 6.1 Probability (squared amplitude) of ground state wavefunction being on site 1 (solid) or site 2 (dashed) as a function of $E_2 - E_1$.

When the energies on the two sites are equal, one has an equal sharing of the wavefunction in the ground state (as in the prior problem). However, as the energy difference is increased, the ground state moves more towards the lower energy site, until the bond is completely "ionic" meaning that the electron is completely transferred from one atom to the other.

(6.4) Ionic Bond Energy Budget The ionization energy of a sodium atom is about 5.14 eV. The electron affinity of a chlorine atom is about 3.62 eV. When a single sodium atom bonds with a single chlorine atom, the bond length is roughly 0.236 nm. Assuming that the cohesive energy is purely Coulomb energy, calculate the total energy released when a sodium atom and a chlorine atom come together to form a NaCl molecule. Compare your result to the experimental value of 4.26 eV. Qualitatively account for the sign of your error.

(c) The cohesive energy is (with d the bond distance)

$$E_{coh} = \frac{e^2}{4\pi\epsilon_0 d} = 6.10eV$$

Thus the total bonding energy is

$$E = -5.14eV + 3.62eV + 6.10eV = 4.58eV$$

which is slightly larger than the experimentally measured bonding energy. The reason for the discrepancy is that there must be a repulsive force in addition to the coulomb attractive force which reduces the magnitude of the cohesive (binding) energy.

In the Fig. 6.2 the lower curve is the pure Coulomb energy. The upper curve includes a short range repulsion. The repulsion *must* be there, or there would be no minimum in the curve!

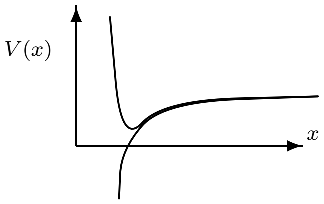


Fig. 6.2 Probability (squared amplitude) of ground state wavefunction being on site 1 (solid) or site 2 (dashed) as a function of $E_2 - E_1$.

(6.5) LCAO Done Right*

(a)* In Exercise 6.2 we introduced the method of linear combination of atomic orbitals. In that exercise we assumed that our basis of orbitals is orthonormal. In this exercise we will relax this assumption.

Consider now many orbitals on each atom (and potentially many atoms). Let us write

$$|\psi\rangle = \sum_{i=1}^{N} \phi_i |i\rangle$$

for an arbitrary number N of orbitals. Let us write the N by N overlap matrix $\mathcal{S}$ whose elements are

$$\mathcal{S}_{i,j} = \langle i|j\rangle$$

In this case do *not* assume that $\mathcal{S}$ is diagonal.

Using a similar method as in Exercise 6.2, derive the new "Schroedinger equation"

$$\mathcal{H}\boldsymbol{\phi} = E\mathcal{S}\boldsymbol{\phi} \tag{6.3}$$

with the same notation for $\mathcal{H}$ and ϕ as in Exercise 6.2. This equation is known as a "generalized eigenvalue problem" because of the $\mathcal{S}$ on the right-hand side.

(b)** Let us now return to the situation with only two atoms and only one orbital on each atom but such that $\langle 1|2\rangle = \mathcal{S}_{1,2} \neq 0$. Without loss of generality we may assume $\langle i|i\rangle = 1$ and $S_{1,2}$ is real. If the atomic orbitals are s-orbitals then we may assume also that t is real and positive (why?).

Use Eq. 6.3 to derive the eigenenergies of the system.

(a) This is very similar to 6.2.

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{n,m}\phi_n^*\mathcal{H}_{nm}\phi_m}{\sum_{n,m}\phi_n^* S_{nm}\phi_m} \tag{6.4}$$

We can extremize by differentiating with respect to ϕ_n^* to give

$$\begin{aligned} 0 &= \frac{\partial E}{\partial \phi_n^*} = \frac{\sum_m \mathcal{H}_{nm}\phi_m}{\sum_{n,m}\phi_n^* S_{nm}\phi_m} - \left(\frac{\sum_{n,m}\phi_n^*\mathcal{H}_{nm}\phi_m}{\sum_{n,m}\phi_n^* S_{nm}\phi_m}\right)\frac{\sum_{n,m} S_{nm}\phi_m}{\sum_{n,m}\phi_n^* S_{nm}\phi_m} \\ 0 &= \sum_m \mathcal{H}_{nm}\phi_m - E\sum_m S_{nm}\phi_m \end{aligned}$$

where we have used Eq. 6.4 to identify E.

(b) An s-orbital can be taken to be manifestly postive everywhere (no nodes), so overlaps S_{ij} must be real and positive. Here the easiest thing to do is to just apply $\mathcal{S}^{-1}$ to both sides of the equation to give the eigenvalue problem

$$\mathcal{S}\mathcal{H}\phi = E\phi$$

Here, let us write the Hamiltonian as

$$\mathcal{H} = \begin{pmatrix} \epsilon & t \\ t^* & \epsilon \end{pmatrix}$$

where we have absorbed V_{cross} into ϵ, and

$$\mathcal{S} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}$$

with $S = \mathcal{S}_{12}$. The matrix we want to diagonalize is then

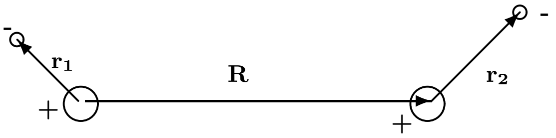
$$\mathcal{S}^{-1}\mathcal{H} = \frac{1}{1-S^2}\begin{pmatrix} \epsilon - St & t - \epsilon S \\ t - \epsilon S & \epsilon - St \end{pmatrix}$$

The eigenvalues are easily seen to be

$$E = \frac{1}{1-S^2}\left([\epsilon - St] \pm |t - \epsilon S|\right)$$

(6.6) Van der Waals Bonding in Detail*

(a) Here we will do a much more precise calculation of the van der Waals force between two hydrogen atoms. First, let the positions of the two nuclei be separated by a vector $\mathbf{R}$, and let the vector from nucleus 1 to electron 1 be $\mathbf{r}_1$ and let the vector from nucleus 2 to electron 2 be $\mathbf{r}_2$ as shown in the following figure.



Let us now write the Hamiltonian for both atoms (assuming fixed positions of nuclei, i.e., using Born–Oppenheimer approximation) as

$$\begin{aligned} H &= H_0 + H_1 \\ H_0 &= \frac{\mathbf{p_1}^2}{2m} + \frac{\mathbf{p_2}^2}{2m} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r_2}|} \\ H_1 &= \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|} + \frac{e^2}{4\pi\epsilon_0|\mathbf{R} - \mathbf{r_1} + \mathbf{r_2}|} \\ &- \frac{e^2}{4\pi\epsilon_0|\mathbf{R} - \mathbf{r_1}|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{R} + \mathbf{r_2}|} \end{aligned}$$

Here H_0 is the Hamiltonian for two non-interacting hydrogen atoms, and H_1 is the interaction between the atoms.

Without loss of generality, let us assume that $\mathbf{R}$ is in the $\hat{x}$ direction. Show that for large $\mathbf{R}$ and small $\mathbf{r}_i$, the interaction Hamiltonian can be written as

$$H_1 = \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|^3}(z_1z_2 + y_1y_2 - 2x_1x_2) + \mathcal{O}(1/R^4)$$

where x_i, y_i, z_i are the components of $\mathbf{r_i}$. Show that this is just the interaction between two dipoles.

(b) *Perturbation Theory:*

The eigenvalues of H_0 can be given as the eigenvalues of the two atoms separately. Recall that the eigenstates of hydrogen are written in the usual notation as $|n, l, m\rangle$ and have energies $E_n = -\text{Ry}/n^2$ with $\text{Ry} = me^4/(32\pi^2\epsilon_0^2\hbar^2) = e^2/(8\pi\epsilon_0 a_0)$ the Rydberg (here $l \geq 0$, $|m| \leq l$ and $n \geq l + 1$). Thus the eigenstates of H_0 are written as $|n_1, l_l, m_1; n_2, l_2, m_2\rangle$ with energies $E_{n_1,n_2} = -\text{Ry}(1/n_1^2 + 1/n_2^2)$. The ground state of H_0 is $|1, 0, 0; 1, 0, 0\rangle$.

▷ Perturbing H_0 with the interaction H_1, show that to first order in H_1 there is no change in the ground-state energy. Thus conclude that the leading correction to the ground-state energy is proportional to $1/R^6$ (and hence the force is proportional to $1/R^7$).

▷ Recalling second-order perturbation theory show that we have a correction to the total energy given by

$$\delta E = \sum_{\substack{n_1,n_2\\ l_1,l_2\\ m_1,m_2}} \frac{|<1,0,0;1,0,0|\ H_1\ |n_1,l_l,m_1;n_2,l_2,m_2\rangle|^2}{E_{0,0}-E_{n_1,n_2}}$$

▷ Show that the force must be attractive.

(c)**Bounding the binding energy:*

First, show that the numerator in this expression is zero if either $n_1 = 1$ or $n_2 = 1$. Thus the smallest E_{n_1,n_2} that appears in the denominator is $E_{2,2}$. If we replace E_{n_1,n_2} in the denominator with $E_{2,2}$ then the $|\delta E|$ we calculate will be greater than than the $|\delta E|$ in the exact calculation. On the other hand, if we replace E_{n_1,n_2} by 0, then the $|\delta E|$ will always be less than the δE of the exact calculation.

▷ Make these replacements, and perform the remaining sum by identifying a complete set. Derive the bound

$$\frac{6e^2a_0^5}{4\pi\epsilon_0 R^6} \le |\delta E| \le \frac{8e^2a_0^5}{4\pi\epsilon_0 R^6}$$

You will need the matrix element for a hydrogen atom

$$\langle 1,0,0|x^2|1,0,0\rangle = a_0^2$$

where $a_0 = 4\pi\epsilon_0\hbar^2/(me^2)$ is the Bohr radius. (This last identity is easy to derive if you remember that the ground-state wavefunction of a hydrogen atom is proportional to $e^{-r/2a_0}$.)

(a) In fact, this is more or less the definition of dipole interaction! Let us start by deriving

$$\begin{aligned}\frac{1}{|\mathbf{R}-\mathbf{a}|} &= \frac{1}{R\sqrt{1+\frac{2\mathbf{a}\cdot\mathbf{R}}{R^2}+\frac{a^2}{R^2}}}\\ &= \frac{1}{R}\left\{1-\frac{\mathbf{a}\cdot\mathbf{R}}{R^2}+\left[-\frac{1}{2}\frac{a^2}{R^2}+\frac{3}{2}\frac{(\mathbf{a}\cdot\mathbf{R})^2}{R^4}\right]+\ldots\right\} \quad (6.5)\end{aligned}$$

Applying this to all the terms in

$$\begin{aligned}H_1 &= \frac{e^2}{4\pi\epsilon_0|\mathbf{R}|}+\frac{e^2}{4\pi\epsilon_0|\mathbf{R}-\mathbf{r_1}+\mathbf{r_2}|}\\ &- \frac{e^2}{4\pi\epsilon_0|\mathbf{R}-\mathbf{r_1}|}-\frac{e^2}{4\pi\epsilon_0|\mathbf{R}+\mathbf{r_2}|}\end{aligned}$$

We discover that the first two leading orders completely cancel, thus leaving us with only the contribution of the terms coming from the square bracketed terms of Eq. 6.5. We then obtain

$$H_1 = \frac{e^2}{4\pi\epsilon_0 R}\left(\frac{r_1^2+r_2^2-|\mathbf{r_1}-\mathbf{r_2}|^2}{2R^2}+\frac{3(\mathbf{R}\cdot(\mathbf{r_2}-\mathbf{r_1}))^2-(\mathbf{R}\cdot\mathbf{r_1})^2-(\mathbf{R}\cdot\mathbf{r_2})^2)}{R^4}\right)$$

with $\mathbf{R}$ in the $\hat{x}$ direction, this simplifies to

$$H_1 = \frac{e^2}{4\pi\epsilon_0 R^3}\left(\mathbf{r_1}\cdot\mathbf{r_2}+3\left[(x_1-x_2)^2-x_1^2-x_2^2\right]\right)$$

which then simplifies to the desired answer.

(b) The expectation of x or y or z in the ground state of the hydrogen atom $|100\rangle$ is zero due to the fact that the state is spherically symmetric. As a result taking the expectation of H_1 in the ground state gives zero. Thus the leading correction to the energy occurs at second order in H_1

and is proportional to $1/R^6$ (assuming it does not vanish, which we will show next).

Given then the form of the 2nd order perturbation theory, note that every term has an overall *negative* sign (numerator is positive, denominator is negative). Thus the interaction is of the form $-C/R^6$ for some positive constant C (to be calculated), and hence the force is attractive.

(c) As just above, since x or y or z has zero expectation in the ground state, this means H_1 has zero matrix element unless $n_1 > 1$ and $n_2 > 1$ (for $n = 1$ we must have $l = m = 0$).

First let us consider the quantity

$$
\begin{aligned}
I = & \sum_{\substack{n_1,n_2\\ l_1,l_2\\ m_1,m_2}} |<1,0,0;1,0,0|\; H_1\; |n_1,l_l,m_1;n_2,l_2,m_2\rangle|^2 && (6.6)\\
= & \sum_{\substack{n_1,n_2\\ l_1,l_2\\ m_1,m_2}} \langle 1,0,0;1,0,0|\; H_1\; |n_1,l_l,m_1;n_2,l_2,m_2\rangle && (6.7)\\
& \times \langle n_1,l_l,m_1;n_2,l_2,m_2|\; H_1\; |1,0,0;1,0,0\rangle && (6.8)
\end{aligned}
$$

We notice the complete set in the middle here, so we do the sum over the set to obtain

$$
\begin{aligned}
I &= \langle 1,0,0;1,0,0|\; H_1^2\; |1,0,0;1,0,0\rangle\\
&= \left(\frac{e^2}{4\pi\epsilon_0 R}\right)^2 \left(\langle y_1^2\rangle\langle y_2^2\rangle + \langle z_1^2\rangle\langle z_2^2\rangle + 4\langle x_1^2\rangle\langle x_2^2\rangle\right)
\end{aligned}
$$

with all expectations being in the ground state of the respective hydrogen atom (each bracket gives a_0^2). Thus we obtain

$$
I = \left(\frac{e^2}{4\pi\epsilon_0 R^3}\right)^2 6a_0^4
$$

Now, the upper bound is defined by setting $E_{n_1,n_2} = E_{2,2}$ whereas the lower bound is defined by setting $E_{n_1,n_2} = 0$ so we obtain

$$
\frac{I}{E_{0,0}} < |\delta E| < \frac{I}{E_{0,0} - E_{2,2}}
$$

Here using the excitation spectrum of the hydrogen atom, we have $E_{0,0}$ =-2Ry and $E_{2,2} = -\mathrm{Ry}/2$ so $E_{0,0} - E_{2,2} = -(3/2)\mathrm{Ry}$, and using the fact that the Rydberg is $e^2/(8\pi\epsilon_0 a_0)$ we have

$$
W = I/\mathrm{Ry} = \frac{12\mathrm{e}^2\mathrm{a}_0^5}{4\pi\epsilon 0\mathrm{R}^6}
$$

so our inequality is

$$
\frac{W}{2} < |\delta E| < \frac{2W}{3}
$$

which is the required result.

Types of Matter

7

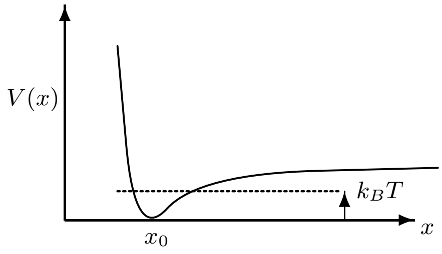
There are no exercises for chapter 7.

One-Dimensional Model of Compressibility, Sound, and Thermal Expansion

8

(8.1) Potentials Between Atoms

As a model of thermal expansion, we study the distance between two nearest-neighbor atoms in an anharmonic potential that looks roughly like this



where x is the distance between the two neighboring atoms. This potential can be expanded around its minimum as

$$V(x) = \frac{\kappa}{2}(x - x_0)^2 - \frac{\kappa_3}{3!}(x - x_0)^3 + \ldots \qquad (8.1)$$

where the minimum is at position x_0 and $\kappa_3 > 0$. For small energies, we can truncate the series at the cubic term. (Note that we are defining the energy at the bottom of the well to be zero here.)

A very accurate approximate form for interatomic potentials (particularly for inert atoms such as helium or argon) is given by the so-called Lennard-Jones potential

$$V(x) = 4\epsilon\left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^{6}\right] + \epsilon \qquad (8.2)$$

where ϵ and σ are constants that depend on the particular atoms we are considering.

▷ What is the meaning of the exponent 6 in the second term of this expression (i.e., why is the exponent necessarily chosen to be 6).

▷ By expanding Eq. 8.2 around its minimum, and comparing to Eq. 8.1, calculate the values of the coefficients x_0, κ, and κ_3 for the Lennard-Jones potential in terms of the constants ϵ and σ. We will need these results in Exercise 8.3.

The exponent 6 determines the long range behavior of the potential and is fixed by the form of the Van der Waals interaction.

By setting $dV/dx = 0$ we find the minimum at $x_0 = 2^{1/6}\sigma$.

Taking second and third derivatives at this position

$$\left.\frac{d^2V}{dx^2}\right|_{x=x_0} = 36 \times 2^{2/3}\epsilon/\sigma^2 = \kappa \approx 57\epsilon/\sigma^2 \qquad (8.3)$$

and

$$\left.\frac{d^3V}{dx^3}\right|_{x=x_0} = -756\sqrt{2}\,\epsilon/\sigma^3 = -\kappa_3 \approx 1069\epsilon/\sigma^3 \qquad (8.4)$$

(8.2) Classical Model of Thermal Expansion

(i) In classical statistical mechanics, we write the expectation of x as

$$\langle x \rangle_\beta = \frac{\int dx\, x\, e^{-\beta V(x)}}{\int dx\, e^{-\beta V(x)}}$$

Although one cannot generally do such integrals for arbitrary potential $V(x)$ as in Eq. 8.1, one can expand the exponentials as

$$e^{-\beta V(x)} = e^{-\frac{\beta \kappa}{2}(x-x_0)^2}\left[1 + \frac{\beta \kappa_3}{6}(x-x_0)^3 + \ldots\right]$$

and let limits of integration go to $\pm\infty$.

▷ Why is this expansion of the exponent and the extension of the limits of integration allowed?

▷ Use this expansion to derive $\langle x \rangle_\beta$ to lowest order in κ_3, and hence show that the coefficient of thermal expansion is

$$\alpha = \frac{1}{L}\frac{dL}{dT} \approx \frac{1}{x_0}\frac{d\langle x \rangle_\beta}{dT} = \frac{1}{x_0}\frac{k_B\, \kappa_3}{2\kappa^2}$$

with k_B Boltzmann's constant.

▷ In what temperature range is the above expansion valid?

▷ While this model of thermal expansion in a solid is valid if there are only two atoms, why is it invalid for the case of a many-atom chain? (Although actually it is not so bad as an approximation!)

$$\langle x \rangle_\beta = \frac{\int dx\, x\, e^{-\beta V(x)}}{\int dx\, e^{-\beta V(x)}}$$

with

$$e^{-\beta V(x)} = e^{-\frac{\beta \kappa}{2}(x-x_0)^2}\left[1 + \frac{\beta \kappa_3}{6}(x-x_0)^3 + \ldots\right]$$

Redefine $y = (x - x_0)$ so we have

$$\begin{aligned}\langle x \rangle_\beta &= \frac{\int dy\,(y+x_0)\, e^{-\frac{\beta\kappa}{2}y^2}\left[1 + \frac{\beta\kappa_3}{6}y^3 + \ldots\right]}{\int dy e^{-\frac{\beta\kappa}{2}y^2}\left[1 + \frac{\beta\kappa_3}{6}y^3 + \ldots\right]} \\ &= x_0 + \frac{\frac{\beta\kappa_3}{6}\int dy\, y^4\, e^{-\frac{\beta\kappa}{2}y^2}}{\int dy\, e^{-\frac{\beta\kappa}{2}y^2}} + \ldots\end{aligned}$$

Using

$$\int dx e^{-ax^2} = \sqrt{\pi/a}$$

as a generating function, we have

$$\int dx x^4 e^{-ax^2} = (d/da)^2 \int dx e^{-ax^2} = (d/da)^2 \sqrt{\pi/a} = (3/4)\sqrt{\pi/a^5}$$

gives

$$\langle x \rangle_T = x_0 + \frac{\kappa_3 (k_b T)}{2\kappa^2} + \ldots$$

Thus

$$\frac{1}{x_0}\frac{d\langle x \rangle_T}{dT} = \frac{1}{x_0}\frac{\kappa_3 k_b}{2\kappa^2}$$

In order for this calculation to be valid, since we have treated the cubic term perturbatively, this term actually must be small compared to the leading term.

Roughly, if the leading term is most important, we have $\kappa(x-x_0)^2 \sim k_bT$ which means that the typical deviation is $|x-x_0| \sim \sqrt{k_bT/\kappa}$. Then in order to have the leading term be larger than the cubic term, we have

$$\kappa|x-x_0|^2 \gg \kappa_3|x-x_0|^3$$

or

$$k_bT \gg \kappa_3(k_bT/\kappa)^{3/2}$$

or equivalently

$$k_bT \ll \kappa^3/\kappa_3^2$$

For a many atom chain, one must solve for the normal modes of the chain. Then at finite temperature one should "occupy" the phonons thermally and then calculate the effect of the nonlinear terms in this state. What we have done in this problem is more or less the thermal expansion of an Boltzmann model of a solid.

(8.3) Properties of Solid Argon

For argon, the Lennard-Jones constants ϵ and σ from Eq. 8.2 are given by $\epsilon = 10$meV and $\sigma = .34$nm. You will need to use some of the results from Exercise 8.1.

(a) *Sound*

Given that the atomic weight of argon is 39.9, estimate the sound wave velocity in solid argon. The actual value of the longitudinal velocity is about 1600 m/sec.

(b) *Thermal Expansion*

Using the results of Exercise 8.2, estimate the thermal expansion coefficient α of argon. Note: *You can do this part even if you couldn't completely figure out Exercise 8.2!*

The actual thermal expansion coefficient of argon is approximately $\alpha = 2 \times 10^{-3}$/K at about 80K. However, at lower temperature α drops quickly. In the next exercise will use a more sophisticated quantum model to understand why this is so.

Sound: From the text in one dimension we have

$$v = \sqrt{\kappa x_0^2/m}$$

where x_0 is the neighbor distance. From our above problem on Lennard-Jones, we have

$$\kappa x_0^2 = 72\epsilon$$

and the mass $m = .0399\text{kg}/\text{N}_\text{A}$. Which gives

$$v = 1320\text{m/s}$$

Thermal expansion. Plugging in our above expression for x_0, κ and κ_3 for the Lennard Jones case, we obtain

$$\alpha = \frac{1}{x_0}\frac{\kappa_3 k_b}{2\kappa^2} = \frac{7k_b}{48\epsilon} \approx .0012/K$$

(8.4) Quantum Model of Thermal Expansion

(a) In quantum mechanics we write a Hamiltonian

$$H = H_0 + \delta V$$

where

$$H_0 = \frac{p^2}{2m} + \frac{\kappa}{2}(x - x_0)^2 \tag{8.5}$$

is the Hamiltonian for the free Harmonic oscillator, and δV is the perturbation (see Eq. 8.1)

$$\delta V = -\frac{\kappa_3}{6}(x - x_0)^3 + \ldots$$

where we will throw out quartic and higher terms.

▷ What value of m should be used in Eq. 8.5?

Using perturbation theory it can be shown that, to lowest order in κ_3 the following equation holds

$$\langle n|x|n\rangle = x_0 + E_n\kappa_3/(2\kappa^2) \tag{8.6}$$

where $|n\rangle$ is the eigenstate of the Harmonic oscillator whose energy is

$$E_n = \hbar\omega(n + \frac{1}{2}) + \mathcal{O}(\kappa_3) \qquad n \geq 0$$

with $\omega = \sqrt{\kappa/m}$. In (c) we will prove Eq. 8.6. For now, take it as given.

▷ Note that even when the oscillator is in its ground state, the expectation of x deviates from x_0. Physically why is this?

(b)* Use Eq. 8.6 to calculate the quantum expectation of x at any temperature. We write

$$\langle x\rangle_\beta = \frac{\sum_n \langle n|x|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

▷ Derive the coefficient of thermal expansion.

▷ Examine the high temperature limit and show that it matches that of Exercise 8.2.

▷ In what range of temperatures is our perturbation expansion valid?

▷ In light of the current quantum calculation, when is the classical calculation from Exercise 8.2 valid?

▷ Why does the thermal expansion coefficient drop at low temperature?

(c)** Prove Eq. 8.6 by using lowest-order perturbation theory.

Hint: It is easiest to perform this calculation by using raising and lowering (ladder) operators. Recall that one can define operators a and $a^\dagger$ such that $[a, a^\dagger] = 1$ and

$$\begin{aligned} a^\dagger|n\rangle_0 &= \sqrt{n+1}|n+1\rangle_0 \\ a|n\rangle_0 &= \sqrt{n}|n-1\rangle_0 \ . \end{aligned}$$

Note that these are kets and operators for the unperturbed Hamiltonian H_0. In terms of these operators, we have the operator $x - x_0$ given by

$$x - x_0 = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger).$$

(a) For a system of two atoms, one should use the "reduced" mass $\mu = m_1 m_2/(m_1 + m_2)$ which for two identical atoms is $m/2$.

Quantum mechanically the oscillator does not sit in its exact minimum, rather it has “quantum fluctuations” around this minimum . Since the well is asymmetric around the minimum, the expectation value of the position is slightly greater than x_0 even in the ground state.

(b)

$$\begin{aligned} \langle x\rangle_\beta &= \frac{\sum_n \langle n|x|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{\sum_n \langle n|(x_0 + E_n\kappa_3/(2\kappa^2))|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \\ &= x_0 + \frac{\langle E\rangle_\beta \kappa_3}{2\kappa^2} \end{aligned}$$

where $\langle E\rangle_\beta$ is the energy expectation of a harmonic oscillator of frequency ω at temperature $\beta = 1/(k_b T)$. As derived above when we discussed Einstein model, this expectation is

$$\langle E\rangle_\beta = (n_B(\beta\hbar\omega) + \frac{1}{2})\hbar\omega = \frac{\hbar\omega}{2}\coth(\beta\hbar\omega/2)$$

with n_B the boson occupation factor. Thus we obtain

$$\langle x\rangle_\beta = x_0 + (\kappa_3\hbar\omega/(4\kappa^2))\coth(\beta\hbar\omega/2)$$

The coefficient of thermal expansion is then

$$\alpha = \frac{1}{x_0}\frac{d\langle x\rangle_\beta}{dT} = \frac{\kappa_3}{2x_0\kappa^2}\frac{d\langle E\rangle}{dT}$$

where $C = d\langle E\rangle/dT$ is exactly the specific heat of a harmonic oscillator (recall einstein model). Thus we obtain

$$\alpha = \frac{\kappa_3 C}{2x_0\kappa^2} = \frac{\kappa_3}{2x_0\kappa^2}k_b(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

We can see that the thermal expansion drops as modes "freeze" out, entirely analogous to the specific heat dropping at low temperature.

In the high T limit, the specific heat C goes to k_b, so we obtain

$$\alpha = (\kappa_3 k_b/(2x_0\kappa^2))$$

in agreement with the classical result.

For the classical calculation to be valid, we must have $k_bT \gg \hbar\omega$ so that quantum mechanics can be replaced by classical mechanics.

(c) First let us consider the unperturbed harmonic oscillator. Recall the raising and lowering operators

$$\begin{aligned} a &= \sqrt{\frac{m\omega}{2\hbar}}[(x-x_0)+(i/m\omega)p] \\ a^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}[(x-x_0)-(i/m\omega)p] \end{aligned} \tag{8.7}$$

So that the position is given by

$$x - x_0 = \sqrt{\hbar/(2m\omega)}(a+a^\dagger)$$

Write the eigenstates $|n\rangle_0$ to mean the eigenstates of the unperturbed oscillator with energy $E_n = \hbar\omega(n+1/2)$. In lowest order perturbation theory, the perturbed eigenket is given by

$$|n\rangle = |n\rangle_0 + \frac{-\kappa_3}{6}\left(\frac{\hbar}{2m\omega}\right)^{3/2}\sum_m |m\rangle_0 \frac{{}_0\langle m|(a+a^\dagger)^3|n\rangle_0}{E_n - E_m}$$

So that we have

$$\langle n|x-x_0|n\rangle = \frac{-2\kappa_3}{6}\left(\frac{\hbar}{2m\omega}\right)^2\sum_m \frac{{}_0\langle n|a+a^\dagger|m\rangle_0 \;\; {}_0\langle m|(a+a^\dagger)^3|n\rangle_0}{E_n-E_m}$$

There are two nonzero terms of the sum, the one where $n = m+1$ which gives us a denominator $\hbar\omega$ and a numerator

$$\begin{aligned} & {}_0\langle n|a^\dagger|n-1\rangle_0 \;\; {}_0\langle n-1|a^\dagger aa + aa^\dagger a + aaa^\dagger|n\rangle_0 \\ = \;& \sqrt{n}\left(\sqrt{n}(n-1) + n\sqrt{n} + (n+1)\sqrt{n}\right) = 3n^2 \end{aligned}$$

and also the term with $n = m - 1$ which gives a denominator $-\hbar\omega$ and a numerator

$$\begin{aligned} & {}_0\langle n|a|n+1\rangle_0 \;\; {}_0\langle n+1|a^\dagger a^\dagger a + a^\dagger a a^\dagger + a a^\dagger a^\dagger|n\rangle_0 \\ = \;& \sqrt{n+1}\left(n\sqrt{n+1} + (n+1)\sqrt{n+1} + (n+2)\sqrt{n+1}\right) = 3(n+1)^2 \end{aligned}$$

Thus we get

$$\langle n|x - x_0|n\rangle = \frac{2\kappa_3}{6}\left(\frac{\hbar}{2m\omega}\right)^2 \frac{1}{\hbar\omega}(6n+3) = E_n\kappa_3/(2\kappa^2)$$

Vibrations of a One-Dimensional Monatomic Chain

9

(9.1) Classical Normal Modes to Quantum Eigenstates

In Section 9.3 we stated without proof that a classical normal mode becomes a quantum eigenstate. Here we prove this fact for a simple diatomic molecule in a potential well (see Exercise 2.7 for a more difficult case, and see also Exercise 9.7 where this principle is proven in more generally).

Consider two particles, each of mass m in one dimension, connected by a spring (K), at the bottom of a potential well (with spring constant k). We write the potential energy as

$$U = \frac{k}{2}(x_1^2 + x_2^2) + \frac{K}{2}(x_1 - x_2)^2$$

▷ Write the classical equations of motion.

▷ Transform into relative $x_{rel} = (x_1 - x_2)$ and center of mass $x_{cm} = (x_1 + x_2)/2$ coordinates.

(a) Show that in these transformed coordinates, the system decouples, thus showing that the two normal modes have frequencies

$$\begin{aligned} \omega_{cm} &= \sqrt{k/m} \\ \omega_{rel} &= \sqrt{(k + 2K)/m}. \end{aligned}$$

Note that since there are two initial degrees of freedom, there are two normal modes.

Now consider the quantum-mechanical version of the same problem. The Hamiltonian is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(x_1, x_2)$$

▷ Again transform into relative and center of mass coordinates.

Define the corresponding momenta $p_{rel} = (p_1 - p_2)/2$ and $p_{cm} = (p_1 + p_2)$.

(b) Show that $[p_\alpha, x_\gamma] = -i\hbar\delta_{\alpha,\gamma}$ where α and γ take the values *cm* or *rel*.

(c) In terms of these new coordinates show that the Hamiltonian decouples into two independent harmonic oscillators with the same eigenfrequencies ω_{cm} and ω_{rel}. Conclude that the spectrum of this system is

$$E_{n_{rel},n_{cm}} = \hbar\omega_{rel}(n_{rel} + \frac{1}{2}) + \hbar\omega_{cm}(n_{cm} + \frac{1}{2})$$

where n_{cm} and n_{rel} are non-negative integers.

(d) At temperature T what is the expectation of the energy of this system?

(a) The equations of motion are

$$\begin{aligned} m\ddot{x}_1 &= -kx_1 - K(x_1 - x_2) \\ m\ddot{x}_2 &= -kx_2 - K(x_2 - x_1) \end{aligned}$$

Taking the sum and difference of these two equations gives

$$\begin{aligned} m\ddot{x}_{cm} &= -kx_{cm} \\ m\ddot{x}_{rel} &= -(k + 2K)x_{rel} \end{aligned}$$

which we identify as harmonic oscillators of frequencies

$$\begin{aligned}\omega_{cm} &= \sqrt{k/m} \\ \omega_{rel} &= \sqrt{(k+2K)/m}\end{aligned}$$

(b) We have $[p_i, x_j] = -i\hbar\delta_{ij}$. Defining $p_{rel} = (p_1 - p_2)/2$ and $p_{cm} = p_1 + p_2$ and $x_{rel} = x_1 - x_2$ and $x_{cm} = (x_1 + x_2)/2$ we obtain

$$\begin{aligned}
[p_{rel}, x_{rel}] &= \frac{1}{2}([p_1, x_1] - [p_1, x_2] - [p_2, x_1] + [p_2, x_2]) \\
&= \frac{1}{2}(-i\hbar)(1 - 0 - 0 + 1) = -i\hbar \\
[p_{rel}, x_{cm}] &= \frac{1}{4}([p_1, x_1] + [p_1, x_2] - [p_2, x_1] - [p_2, x_2]) \\
&= \frac{1}{4}(-i\hbar)(1 + 0 - 0 - 1) = 0 \\
[p_{cm}, x_{rel}] &= ([p_1, x_1] - [p_1, x_2] + [p_2, x_1] - [p_2, x_2]) \\
&= (-i\hbar)(1 + 0 - 0 - 1) = 0 \\
[p_{cm}, x_{cm}] &= \frac{1}{2}([p_1, x_1] + [p_1, x_2] + [p_2, x_1] + [p_2, x_2]) \\
&= \frac{1}{2}(-i\hbar)(1 + 0 + 0 + 1) = -i\hbar
\end{aligned}$$

One could alternately dmonstrate that $p_{rel} = -i\hbar\partial/\partial x_{rel}$ etc using jacobians to confirm these commutations.

(c) We have

$$\begin{aligned}
p_1 &= p_{cm}/2 + p_{rel} \\
p_2 &= p_{cm}/2 - p_{rel} \\
x_1 &= x_{cm} + x_{rel}/2 \\
x_2 &= x_{cm} - x_{rel}/2
\end{aligned}$$

So the Hamiltonian becomes

$$\begin{aligned}
H &= \frac{1}{2m}(p_1^2 + p_2^2) + \frac{k}{2}(x_1^2 + x_2^2) + \frac{K}{2}(x_1 - x_2)^2 \\
&= \frac{1}{2m}(p_{cm}^2/2 + 2p_{rel}^2) + \frac{k}{2}(2x_{cm}^2 + x_{rel}^2/2) + \frac{K}{2}x_{rel}^2
\end{aligned}$$

which decouples into (note the total mass is $2m$ and the reduced mass is $m/2$)

$$\begin{aligned}
H_1 &= \frac{p_{cm}^2}{2(2m)} + \frac{2k}{2}x_{cm}^2 \\
H_2 &= \frac{p_{rel}^2}{2(m/2)} + \frac{(k/2 + K)}{2}x_{rel}^2
\end{aligned}$$

which are two independent harmonic oscilators with frequencies

$$\begin{aligned}\omega_{cm} &= \sqrt{k/m} \\ \omega_{rel} &= \sqrt{(k+2K)/m}\end{aligned}$$

such that the spectrum can be written as

$$E_{n_{rel},n_{cm}} = \hbar\omega_{rel}(n_{rel} + \frac{1}{2}) + \hbar\omega_{cm}(n_{cm} + \frac{1}{2})$$

At temperature T, the expectation of the energy of this system will correspondingly be

$$\langle E \rangle = \hbar\omega_{rel}(n_B(\beta\hbar\omega_{rel}) + 1/2) + \hbar\omega_{cm}(n_B(\beta\hbar\omega_{cm}) + 1/2)$$

where $n_B(x) = 1/(e^x - 1)$ is the usual Bose factor.

The purpose of this exercise is not just to do another quantum mechanics problem. It is here to point out that coupled deg rees of freedom act just like a single simple harmonic oscillator once the degrees of freedom are "rediagonalized". This is important motivation for treating phonons (coupled modes of springs) as individual harmonic oscillators.

(9.2) Normal Modes of a One-Dimensional Monatomic Chain

(a)‡ Explain what is meant by "normal mode" and by "phonon".

▷ Explain briefly why phonons obey Bose statistics.

(b)‡ Derive the dispersion relation for the longitudinal oscillations of a one-dimensional mass-and-spring crystal with N identical atoms of mass m, lattice spacing a, and spring constant κ (motion of the masses is restricted to be in one dimension).

(c)‡ Show that the mode with wavevector k has the same pattern of mass displacements as the mode with wavevector $k + 2\pi/a$. Hence show that the dispersion relation is periodic in reciprocal space (k-space).

▷ How many *different* normal modes are there.

(d)‡ Derive the phase and group velocities and sketch them as a function of k.

▷ What is the sound velocity?

▷ Show that the sound velocity is also given by $v_s = 1/\sqrt{\beta\rho}$ where ρ is the chain density and β is the compressibility.

(e) Find the expression for $g(\omega)$, the density of states of modes per angular frequency.

▷ Sketch $g(\omega)$.

(f) Write an expression for the heat capacity of this one-dimensional chain. You will inevitably have an integral that you cannot do analytically.

(g)* However, you can expand exponentials for high temperature to obtain a high-temperature approximation. It should be obvious that the high-temperature limit should give heat capacity $C/N = k_B$ (the law of Dulong–Petit in one dimension). By expanding to next non-trivial order, show that

$$C/N = k_B(1 - A/T^2 + \ldots)$$

where

$$A = \frac{\hbar^2\kappa}{6mk_B^2}.$$

(a) A *normal mode* is a periodic collective motion where all particles move at the same frequency. A *phonon* is a quantum of vibration.

[I do not like the definition "a quantum of vibrational energy". The vibration does carry energy, but it carries momentum as well, so why specify energy only?]

Each classical normal mode of vibration corresponds to a quantum mode of vibration which can be excited multiple times. A single mode may be occupied by a single phonon, or it may be occupied with multiple phonons corresponding to a larger amplitude oscillation. The fact that the same state may be multiply occupied by phonons means that phonons must be bosons.

(b) The equation of motion for the n^{th} particle along the chain is given by

$$m\ddot{x}_n = \kappa(x_{n+1} - x_n) + \kappa(x_{n-1} - x_n) = \kappa(x_{n+1} + x_{n-1} - 2x_n)$$

note that na is the equilibrium position of the n^{th} particle. Using the ansatz

$$x_n = Ae^{i\omega t - ikna}$$

we obtain

$$\begin{array}{rcl} -\omega^2 m e^{i\omega t - ikna} & = & \kappa e^{i\omega t}(e^{ik(n+1)a} + e^{ik(n-1)a} - 2e^{ikn}) \\ \omega^2 m = & = & 2\kappa(\cos(ka) - 1) \end{array}$$

or

$$\omega = \sqrt{(2\kappa/m)(\cos(ka) - 1)} = 2\sqrt{\kappa/m}\,|\sin(ka/2)|$$

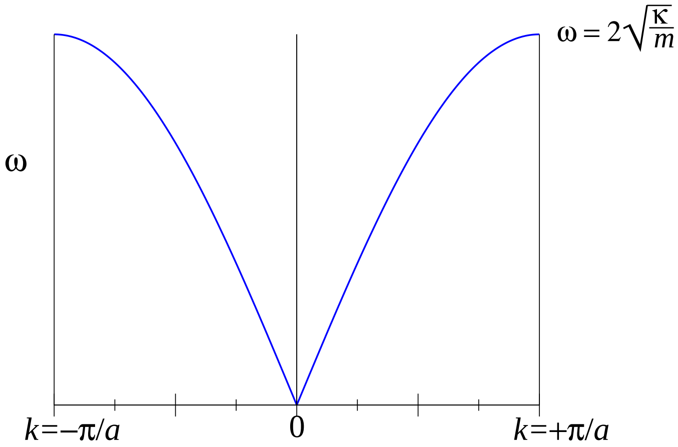


Fig. 9.1 Dispersion relation for vibrations of the one-dimensional monatomic harmonic chain. The dispersion is periodic in $k \to k + 2\pi/a$.

(c)

$$e^{-i(k+2\pi/a)na} = e^{-i(k+2\pi/a)na} = e^{-ikna}$$

If you assume periodic boundary conditions, then $k = 2\pi m/L$ but k is identified with $k + 2\pi/a$ so that there are therefore exactly $N = L/a$ different normal modes.

(d)

$$v_{phase} = \omega(k)/k = 2\sqrt{\kappa/m}\,|\sin(ka/2)|/k$$

and

$$v_{group} = d\omega(k)/dk = \sqrt{\kappa/m}\,a\cos(|k|a/2) = (a/2)\omega_0\sqrt{1 - \omega^2/\omega_0^2}$$

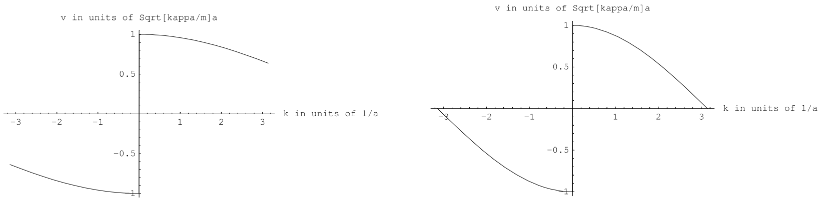


Fig. 9.2 The monatomic harmonic chain. Right: Phase velocity. Left: Group velocity. Note velocities are signed quantities, to the left of the origin, the velocity should have negative sign.

where $\omega_0 = 2\sqrt{\kappa/m}$. Note that the phase velocity is not periodic in the Brillouin zone! One can understand this if you think carefully about aliasing of waves. The phase velocity is the velocity at which the peaks of waves move. However, the waves are only defined at the position of the masses along the chain. We write $\cos(kna)$ for the positions of the masses at some time, but this only defines the value of the wave for integer n. For integer n, we have k is the same as $k + 2\pi/a$. However, the "peak" of this function may be between the integer values of n. However, when we make n non-integer, then k is no longer the same as $k + 2\pi/n$.

For sketches see figure 9.2

The sound velocity is the velocity at small k. This is

$$v = a\sqrt{\kappa/m}$$

. The density of the chain is $\rho = m/a$ and the compressibility is $\beta = -(1/L)dL/dF = 1/(\kappa a)$. Thus we obtain $v^{-2} = \rho\beta$

(e) Note first that

$$(\omega(k)/2)^2 + (v_{group}(k)/a)^2 = \kappa/m \tag{9.1}$$

Density of states is uniform in k. If there are N sites in the system, there are N modes total. The density of states in k is therefore $dN/dk = Na/(2\pi) = L/(2\pi)$ where L is the length of the system.

Thus we have

$$\begin{aligned} g(\omega) &= dN/d\omega = (dN/dk)(dk/d\omega) = \frac{Na}{2\pi v_{group}} \\ &= \frac{N}{2\pi\sqrt{\kappa/m}\cos(|k|a/2)} \\ &= \frac{2N}{2\pi\sqrt{(\kappa/m) - (\omega(k)/2)^2}} \end{aligned} \tag{9.2}$$

where we have used Eq. 9.1.

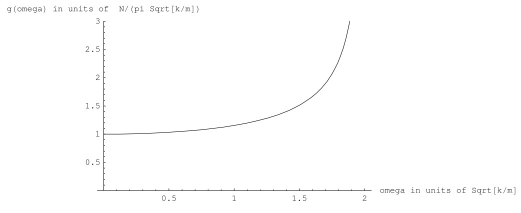


Fig. 9.3 The one dimensional harmonic chain. Density of states $g(\omega)$. Note that the DOS diverges at $\omega = 2\sqrt{k/m}$ where the group velocity goes to zero.

The additional factor of 2 that appears up top is to account for the fact that for each value of $\omega > 0$ there are actually two values of k with that ω. (Note if you integrate over frequency you correctly get back N degrees of freedom).

(f) The energy stored in the chain is given by

$$U = \int d\omega g(\omega) \hbar\omega (n_B(\omega) + 1/2)$$

so the heat capacity is $C = \partial U/\partial T$. Note that we can drop the $+1/2$ since it has no derivative.

(g) To recover the law of Dulong-Petit, one takes the high temperature limit of $n_B(\omega) = k_B T/\hbar\omega$ so th at we have

$$C = \frac{\partial}{\partial T} \int d\omega g(\omega)(k_B T) = k_B \int d\omega g(\omega) = k_B N$$

To go further, we use the high temperature expansion (expanding $1/(e^x - 1)$ for small x)

$$n_B(\omega) + 1/2 = \frac{k_B T}{\hbar\omega} + \frac{1}{12}\frac{\hbar\omega}{k_B T} + \ldots$$

So that we now have

$$C = \frac{\partial U}{\partial T} = k_B N - \frac{1}{T^2} \int d\omega \hbar\omega g(\omega) \left[\frac{1}{12}\frac{\hbar\omega}{k_B}\right]$$

So that the coefficient A defined in the problem has the values

$$A = \frac{\hbar^2}{12 N k_B^2} \int d\omega \omega^2 g(\omega)$$

Inserting our expression for $g(\omega)$ we obtain

$$A = \frac{\hbar^2}{12\pi k_B^2} \int_0^{\omega_{max}} d\omega \frac{\omega^2}{\sqrt{(\kappa/m) - (\omega/2)^2}}$$

Defining $x = (\omega/2)\sqrt{m/\kappa}$ we obtain

$$A = \frac{\hbar^2}{12\pi k_B^2}\frac{8\kappa}{m}\int_0^1 dx \frac{x^2}{\sqrt{1-x^2}}$$

The integral is evaluated to give $\pi/4$ (make the substitution $x = \sin\theta$). Thus we obtain

$$A = \frac{\hbar^2}{6k_B^2}\frac{\kappa}{m}$$

as required.

(9.3) More Vibrations

Consider a one-dimensional spring and mass model of a crystal. Generalize this model to include springs not only between neighbors but also between second nearest neighbors. Let the spring constant between neighbors be called κ_1 and the spring constant between second neighbors be called κ_2. Let the mass of each atom be m.

(a) Calculate the dispersion curve $\omega(k)$ for this model.

(b) Determine the sound wave velocity. Show the group velocity vanishes at the Brillouin zone boundary.

(a) Use the same approach

$$\begin{aligned} m\ddot{x}_n &= \kappa_1(x_{n+1}-x_n) + \kappa_1(x_{n-1}-x_n) + \kappa_2(x_{n+2}-x_n) + \kappa_1(x_{n-2}-x_n) \\ &= \kappa_1(x_{n+1}+x_{n-1}-2x_n) + \kappa_2(x_{n+2}+x_{n-2}-2x_n) \end{aligned}$$

Using the same ansatz

$$x_n = Ae^{i\omega t - ikna}$$

we obtain

$$-m\omega^2 = 2\kappa_1(\cos(ka)-1) + 2\kappa_2(\cos(2ka)-1) \qquad (9.3)$$

so

$$\omega = \sqrt{\frac{2\kappa_1}{m}(\cos(ka)-1) + \frac{2\kappa_2}{m}(\cos(2ka)-1)}$$

(b) To obtain the sound velocity, expand for small k to obtain

$$\omega = \sqrt{\frac{2\kappa_1}{m}\frac{(ka)^2}{2} + \frac{2\kappa_2}{m}\frac{(2ka)^2}{2}} = \left(a\sqrt{\frac{\kappa_1+4\kappa_2}{m}}\right)k$$

Thus the sound velocity is

$$v_s = a\sqrt{\frac{\kappa_1+4\kappa_2}{m}}$$

The easiest way to examine $\partial\omega/\partial k$ at the zone boundary is to differentiate Eq. 9.3 to given

$$m\omega\partial\omega/\partial k = -2a\kappa_1\sin(ka) - 4a\kappa_2\sin(2ka)$$

At the zone boundary $k = \pi/2$ both terms on the right hand side are zero, hence we have zero group velocity.

(9.4) Decaying Waves
In the dispersion curve of the harmonic chain (Eq. 9.3), there is a maximum possible frequency of oscillation ω_{max}. If a vibration with frequency $\omega > \omega_{max}$ is forced upon the chain (say by a driving force) the "wave" will not propagate along the chain, but rather will decay as one moves away from the point where the oscillation is imposed (this is sometimes known as an "evanescent" wave). With $\omega > \omega_{max}$ solve Eq. 9.3 for a complex k to determine the decay length of this evanescent wave. What happens to this length as $\omega \to \omega_{max}$?

The usual form is

$$\Omega = \omega/\omega_{max} = \pm\sin(ka/2)$$

with ± chosen so Ω is positive. Thus

$$ka = \pm 2\sin^{-1}\Omega$$

When $\Omega = 1$ then $ka = \pi$. When $\Omega > 1$ then ka becomes complex with a real part of π. The complex part gets smaller and vanishes as Ω approaches 1 from above. The complex part of k gives the inverse length scale of the wave's decay (and it can decay left-going or right-going depending on the ± sign). So as Ω approachs 1 from above, the length scale of decay grows longer and longer until at 1 it extends over the entire system and is a nondecaying wave.

See also the solution of 9.6 below, which is quite similar.

To check these properties of the arcsin, consider

$$y = \sin(x) = \frac{z - z^{-1}}{2i}$$

where $z = e^{ix}$. Multiplying by z we obtain the quadratic

$$z^2 - 2izy - 1 = 0$$

Solving this equation gives

$$z = iy \pm \sqrt{1 - y^2}$$

Note that for $y > 1$ we have $z = e^{ix}$ along the positive imaginary axis, which means $x = \pi/2 + \text{real}$. For $y = 1$ we have $x = \pi/2$ whereas for $y < 1$ we obtain a complex valued z with unti magnitude, thus a real x.

If one is concerned that this solution might not work, one can always go back to the equations of motion

$$m\ddot{x}_n = \kappa(x_{n+1} - x_n) + \kappa(x_{n-1} - x_n) = \kappa(x_{n+1} + x_{n-1} - 2x_n)$$

Using the ansatz

$$x_n = Ae^{i\omega t - ikna}$$

we obtain

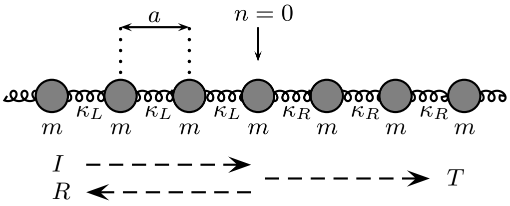
$$\begin{array}{rcl} -\omega^2 m e^{i\omega t - ikna} & = & \kappa e^{i\omega t}(e^{ik(n+1)a} + e^{ik(n-1)a} - 2e^{ikn}) \\ \omega^2 m = & = & 2\kappa(\cos(ka) - 1) \end{array}$$

Note that nowhere did we specify that k is real (!) so we can happily extend into the complex plane. Using double angle formula

$$\omega^2 = \frac{4\kappa}{m}\sin^2(ka/2)$$

The only thing we would need to be careful about is choosing the sign of the square root.

(9.5) Reflection at an Interface*
Consider a harmonic chain of equally spaced identical masses of mass m where left of the $n = 0$ mass the spring constant is κ_L but right of the $n = 0$ mass, the spring constant is κ_R, as shown in this figure.



A wave with amplitude I is incident on this interface from the left, where it can be either transmitted with amplitude T or reflected with amplitude R. Using the following ansatz form

$$\delta x_n = \begin{cases} Te^{i\omega t - ik_L na} & n \geq 0 \\ Ie^{i\omega t - ik_R na} + Re^{i\omega t + ik_R na} & n < 0 \end{cases}$$

derive T/I and R/I given ω, κ_L, κ_R and m.

Oops sorry about the typo, it should read

$$\delta x_n = \begin{cases} Te^{i\omega t - ik_R na} & n \geq 0 \\ Ie^{i\omega t - ik_L na} + Re^{i\omega t + ik_L na} & n < 0 \end{cases}$$

On both the left and the right, we must have the usual relations between $k_{L,R}$ and ω

$$\omega = 2\sqrt{\kappa_{L,R}/m}|\sin(k_{L,R}a/2)|$$

or

$$k_{L,R} = \frac{2}{a}\sin^{-1}\left(\frac{\omega}{2}\sqrt{m/\kappa_{L,R}}\right)$$

with these values of k, the ansatz form will then satisfy the equations of motion except near the boundary.

Near the boundary, we have equations of motion for δx_{-1} and δx_0 which involve δx coordinates on both sides of the junction. We write

$$\begin{aligned} m\,\ddot{\delta x}_{-1} &= \kappa_L(\delta x_{-2} + \delta x_0 - 2\delta x_{-1}) \\ m\,\ddot{\delta x}_0 &= \kappa_L(\delta x_{-1} - \delta x_0) + \kappa_R(\delta x_1 - \delta x_0) \end{aligned}$$

Plugging in the ansatz form of the wavefunction and doing a bit of algebra gives us

$$\begin{aligned}(-m\omega^2 + 2\kappa_L)\left(Ie^{ik_La} + Re^{-ik_La}\right) &= \kappa_L\left(Ie^{ik_L2a} + Re^{-ik_L2a} + T\right)\\ (-m\omega^2 + \kappa_L + \kappa_R)T &= \kappa_L\left(Ie^{ik_La} + Re^{-ik_La}\right) + \kappa_R T e^{-ik_Ra}\end{aligned} \tag{9.4}$$

The first equation simplifies quite a bit by rewriting the dispersion relation as

$$-m\omega^2 = 2\kappa_L(\cos(k_La) - 1)$$

So that

$$-m\omega^2 + 2\kappa_L = \kappa_L\left(e^{ik_La} + e^{-ik_La}\right) \tag{9.5}$$

and the first equation becomes simply

$$I + R = T$$

which is just extending the wavefunction from the left hand side until it hits position zero and matching it to the value of the wave from the right at this position.

Plugging this into the second equation of Eq. 9.4 and solving to obtain

$$T/I = \frac{\kappa_L 2i\sin(k_La)}{-m\omega^2 + \kappa_L(1 - e^{-ik_La}) + \kappa_R(1 - e^{-ik_Ra})}$$

In the denominator we can simplify further applying 9.5 to give us

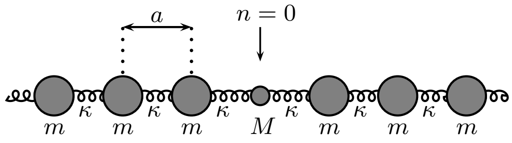
$$-m\omega^2/2 + \kappa_L(1 - e^{-ik_La}) = i\kappa_L\sin(k_La)$$

and similarly for the right hand wave so that we get

$$T/I = \frac{2}{1 + \frac{\kappa_R\sin(k_Ra)}{\kappa_L\sin(k_La)}}$$

(9.6) Impurity Phonon Mode*

Consider a harmonic chain where all spring constants have the same value κ and masses have value m, except for the mass at position $n = 0$ which instead has value $M < m$ as shown in this figure:



Along with traveling wave solutions, there can be a standing wave normal mode localized near the impurity. Use an ansatz of the form

$$\delta x_n = Ae^{i\omega t - q|n|a}$$

with q real to solve for the frequency of this impurity mode. Consider your result in the context of Exercise 9.4.

Another error here: q needs to have both real and imaginary parts.

This problem is fairly easy once you have solved 9.4. For $0 < \omega < \omega_{max}$ the only solution to our equations of motion (except at the impurity site) is for the usual waves

$$-m\omega^2 = 2\kappa(\cos(ka) - 1) \tag{9.6}$$

or equivalently

$$\omega = \omega_{max}|\sin(ka/2)|$$

or

$$ka = 2\sin^{-1}(\omega/\omega_{max})$$

with $\omega > \omega_{max} = 2\sqrt{\kappa/m}$ we have decaying solutions of the form given by the usual where (as shown in Exercise 9.4)

$$ka = \pi \pm iqa$$

with q here real. Then on the left we choose + and on the right we choose − so that the wave decays away from the impurity. So we have

$$\delta x_n = \left\{ \begin{array}{ll} Ae^{i\omega t + i\pi n + qan} & n \leq 0 \\ Ae^{i\omega t - i\pi n - qan} & n \geq 0 \end{array} \right.$$

with $q > 0$ this solves all of the equations of motion except for the one at $n = 0$

$$M\,\ddot{\delta x}_0 \quad = \quad \kappa(\delta x_{-1} + \delta x_1 - 2\delta x_0)$$

Plugging in our ansatz, we obtain the three equations

$$-M\,\omega^2 \quad = \quad \kappa(-e^{-qa} - e^{-qa} - 2)$$

Taking this equation with to Eq. 9.6 and eliminating ω^2 we obtain

$$M(\cosh(qa) + 1) = m(e^{-qa} + 1)$$

Now, if $M = m$ the only place the two sides are equal is at $q = 0$, which means there is no bound state. Further, since the left hand side grows with increasing q and the right shrinks with q it is clear that there can be no solution for $M > m$. However, for $M < m$ there is one crossing of the two curves, which finds the q appropriate for the bound state. In fact, one can go a bit further analytically, writing $z = e^{qa}$ we have

$$(M/m)((z + z^{-1})/2 + 1) = z^{-1} + 1$$

which is a quadratic equation in z, which we can solve to given

$$z = e^{qa} = \frac{2m}{M} - 1$$

Or

$$qa = \log\left(\frac{2m}{M} - 1\right)$$

which, since we require $q > 0$ has a solution only for $M < m$. Finally to obtain the frequency, one just has to plub back into our dispersion relation to give

$$-m\omega^2 = 2\kappa(\cos(\pi + iqa) - 1)$$

which gives a real frequency greater than ω_{max}

(9.7) General Proof That Normal Modes Become Quantum Eigenstates*

This proof generalizes the argument given in Exercise 9.1. Consider a set of N particles $a = 1, \ldots N$ with masses m_a interacting via a potential

$$U = \frac{1}{2}\sum_{a,b} x_a\, V_{a,b}\, x_b$$

where x_a is the deviation of the position of particle a from its equilibrium position and V can be taken (without loss of generality) to be a symmetric matrix. (Here we consider a situation in 1d, however, we will see that to go to 3d we just need to keep track of three times as many coordinates.)

(i) Defining $y_a = \sqrt{m_a}\, x_a$, show that the classical equations of motion may be written as

$$\ddot{y}_a = -\sum_b S_{a,b}\, y_b$$

where

$$S_{a,b} = \frac{1}{\sqrt{m_a}} V_{a,b} \frac{1}{\sqrt{m_b}}$$

Thus show that the solutions are

$$y_a^{(m)} = e^{-i\omega_m t} s_a^{(m)}$$

where ω_m is the m^{th} eigenvalue of the matrix S with corresponding eigenvector $s_a^{(m)}$. These are the N normal modes of the system.

(ii) Recall the orthogonality relations for eigenvectors of hermitian matrices

$$\sum_a [s_a^{(m)}]^*[s_a^{(n)}] = \delta_{m,n} \qquad (9.7)$$

$$\sum_m [s_a^{(m)}]^*[s_b^{(m)}] = \delta_{a,b}. \qquad (9.8)$$

Since S is symmetric as well as hermitian, the eigenvectors can be taken to be real. Construct the transformed coordinates

$$Y^{(m)} = \sum_a s_a^{(m)} x_a \sqrt{m_a} \qquad (9.9)$$

$$P^{(m)} = \sum_a s_a^{(m)} p_a / \sqrt{m_a} \qquad (9.10)$$

show that these coordinates have canonical commutations

$$[P^{(m)}, Y^{(n)}] = -i\hbar\delta_{n,m} \qquad (9.11)$$

and show that in terms of these new coordinates the Hamiltonian is rewritten as

$$H = \sum_m \left[\frac{1}{2}[P^{(m)}]^2 + \frac{1}{2}\omega_m^2 [Y^{(m)}]^2\right]. \qquad (9.12)$$

Conclude that the quantum eigenfrequencies of the system are also ω_m. (Can you derive this result from the prior two equations?)

Yet another typo, in part (i) it should say $-\omega_m^2$ is the mth eigenvaluer.

(i) First given the expression for U, differentiate with resepect to x_a to obtain the force on particle a

$$F_a = -\frac{\partial U}{\partial x_a} = -\sum_b V_{a,b} x_b$$

The equation of motion is then

$$m_a \ddot{x}_a = -\sum_b V_{a,b} x_b$$

Now defining $x_a = y_a/\sqrt{m_a}$ we obtain

$$\ddot{y_a} = -\sum_b \frac{1}{\sqrt{m_a}} V_{a,b} \frac{1}{\sqrt{m_a}} y_b = -\sum_b S_{a,b} y_b$$

as required. Using the ansatz $y_a = e^{-i\omega t} s_a$ we have

$$\omega^2 s_a = \sum_b S_{a,b} s_a \tag{9.13}$$

which is solved by s_a being the eigenvector of S and ω^2 its eigenvalue.

(ii) Given

$$\begin{aligned} Y^{(m)} &= \sum_a s_a^{(m)} x_a \sqrt{m_a} \\ P^{(n)} &= \sum_b s_b^{(n)} p_b / \sqrt{m_b} \end{aligned}$$

we calculate

$$[P^{(n)}, Y^{(m)}] = \sum_{a,b} s_b^{(n)} s_a^{(m)} [p_b, x_a] \sqrt{m_a/m_b}$$

Using the canonical commutations

$$[p_b, x_a] = -i\hbar \delta_{ab}$$

we have

$$[P^{(n)}, Y^{(m)}] = -i\hbar \sum_a s_a^{(m)} s_a^{(n)} = -i\hbar \delta_{nm}$$

where we have used the orthogonality of eigenstates.

Next let us look at the terms of the proposed Hamiltonian

$$\begin{aligned} \sum_m \frac{1}{2} [P^{(m)}]^2 &= \sum_m \sum_{a,b} \frac{1}{2} s_a^{(m)} s_b^{(m)} p_a p_b / \sqrt{m_a m_b} \\ &= \sum_a \frac{1}{2m_a} p_a^2 \end{aligned}$$

where we have used the orthogonality of s to collapse the m sum and generate δ_{ab}.

Now examining the second term of the proposed Hamiltonian

$$\sum_m \frac{1}{2} \omega_m^2 [Y^{(m)}]^2 = \sum_m \sum_{a,b} \frac{1}{2} s_a^{(m)} \omega_m^2 s_b^{(m)} x_a x_b \sqrt{m_a m_b}$$

But here we can use Eq. 9.13 to replace ω^2 with the matrix S giving us

$$\begin{aligned} \sum_m \frac{1}{2} \omega_m^2 [Y^{(m)}]^2 &= \sum_m \sum_{a,b,c} \frac{1}{2} s_a^{(m)} S_{b,c} s_c^{(m)} x_a x_b \sqrt{m_a m_b} \\ &= \sum_{a,b} \frac{1}{2} S_{b,a} x_a x_b \sqrt{m_a m_b} = \sum_{a,b} \frac{1}{2} x_a V_{a,b} x_b \end{aligned}$$

where we have used the orthogonality of s and taken the sum over m to give a δ_{ac}.

Thus the given Hamiltonian is equivalent to the original Hamitlonian

$$H = \sum_a \frac{1}{2m_a} p_a^2 + \sum_{a,b} \frac{1}{2} x_a V_{a,b} x_b$$

The new form of the Hamiltonian in terms of P and Y has each m coordinate completely decoupled. Further the P and Y satisfy canonical commutations for momenta and positon so each m is simply a harmonic oscillator with frequency ω_m.

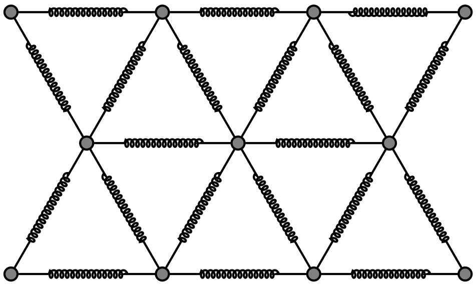
If one wanted to derive the spectrum from the Hamiltonian, one could follow the usual procedure of writing

$$a^\dagger = \frac{1}{\sqrt{2\hbar}} \left(P/\sqrt{\omega} + i\sqrt{\omega} Y \right)$$

to rewrite the Hamiltonian for each decoupled mode as

$$H = \hbar\omega(a^\dagger a + 1/2)$$

(9.8) Phonons in 2d*



Consider a mass and spring model of a two-dimensional triangular lattice as shown in the figure (assume the lattice is extended infinitely in all directions). Assume that identical masses m are attached to each of their six neighbors by equal springs of equal length and spring constant κ. Calculate the dispersion curve $\omega(\mathbf{k})$. The two-dimensional structure is more difficult to handle than the one-dimensional examples given in this chapter. In Chapters 12 and 13 we study crystals in two and three dimensions, and it might be useful to read those chapters first and then return to try this exercise again.

Ok, this one is pretty hard if you have never seen such a thing before. Probably it should have two stars.

First of all, one assumes that the crystal starts in equilibrium with the springs unstretched. Forces on the springs will be proportional to the amount of stretching. Note however, that if one of the masses is displaced in a direction perpendicular to one of its attaching springs, to linear order, the spring is not stretched at all (it is only rotated)! So in other words, we need only keep track of the stretching in the direction parallel to the spring.

Let us let the edge have unit length for simplicity of notation. If we let the position of a sites in equilibrium be called $\mathbf{r_n}$ and let the displacements from this equilibrium be called $\mathbf{u}_{\mathbf{r_n}}$. Now let us define three unit vectors $\mathbf{a_i}$ pointing in the three directions of the lattice edges $\mathbf{a_1} = (1,0)$, $\mathbf{a_2} = (1/2, \sqrt{3}/2)$, $\mathbf{a_2} = (-1/2, \sqrt{3}/2)$. The total potential energy of the system can then be written as

$$U = \frac{\kappa}{2} \sum_{\mathbf{r_n}} \sum_{j=1}^{3} \left(\left[\mathbf{u_{r_n}} - \mathbf{u_{r_n + a_j}} \right] \cdot \mathbf{a_j} \right)^2$$

where here we have included each spring once in the sum and we have dotted the displacement with its direction so as to only count stretching of the spring and not rotation. The force on a mass, and hence using newton's law we have

$$m\ddot{u}^{\alpha}_{\mathbf{r_n}} = F^{\alpha}_{\mathbf{r_n}} = \frac{-\partial U}{\partial u^{\alpha}_{\mathbf{r_n}}}$$

where α is a basis direction (say, x or y). Carefully taking the derivative we get

$$m\ddot{u}^{\alpha}_{\mathbf{r_n}} = -\kappa \left(\sum_{j=1}^{3} a^{\alpha}_{j} \left(\sum_{\beta} [u^{\beta}_{\mathbf{r_n + a_j}} + u^{\beta}_{\mathbf{r_n - a_p}} - 2u^{\beta}_{\mathbf{r_n}}] a^{\beta}_{j} \right) \right)$$

Using a wave ansatz

$$u^{\alpha}_{\mathbf{r_n}} = U^{\alpha} e^{i\omega t - i\mathbf{k}\cdot\mathbf{r_n}}$$

We obtain the two by two eigenvalue problem

$$\omega^2 U^{\alpha} = \sum_{\beta} D_{\alpha\beta}(\mathbf{k}) U^{\beta}$$

where the so-called dynamical matrix is given by

$$D_{\alpha\beta}(\mathbf{k}) = \frac{\kappa}{m} \sum_{j=1}^{3} a^{\alpha}_{j} a^{\beta}_{j} (e^{i\mathbf{k}\cdot\mathbf{a_j}} + e^{-i\mathbf{k}\cdot\mathbf{a_j}} - 2)$$

Note that this matrix is symmetric in α and β. Plugging in the values of a_j and using some trig identities we gets

$$D = \frac{\kappa}{m} \left\{ \begin{pmatrix} 4 & 0 \\ 0 & 0 \end{pmatrix} \sin^2(\frac{\mathbf{k}\cdot\mathbf{a_1}}{2}) + \begin{pmatrix} 1 & \sqrt{3} \\ \sqrt{3} & 3 \end{pmatrix} \sin^2(\frac{\mathbf{k}\cdot\mathbf{a_2}}{2}) + \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & 3 \end{pmatrix} \sin^2(\frac{\mathbf{k}\cdot\mathbf{a_3}}{2}) \right\}$$

For each $\mathbf{k}$ there will be two eigenvalues which correspond to the longitudinal and transverse phonon modes. The eigenvalues of this becomes

$$\omega^2 = \frac{2\kappa}{m} \left(S_1 + S_2 + S_3 \pm \sqrt{S_1^2 + S_2^2 + S_3^2 - S_1 S_2 - S_1 S_3 - S_2 S_3} \right)$$

where

$$S_i = \sin^2(\frac{\mathbf{k}\cdot\mathbf{a_i}}{2})$$

These spectra are shown in figures 9.4 - 9.6. Note that the spectrum is periodic in the Brillouin zone – which has the shape of a hexagon.

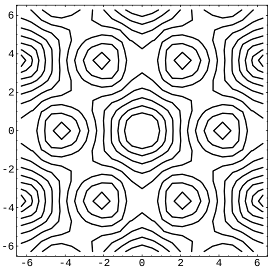


Fig. 9.4 Contour plot of the transverse mode frequency of the triangular lattice phonons in k_x, k_y space.

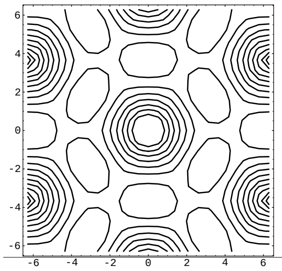


Fig. 9.5 Contour plot of the longitudinal mode frequency of the triangular lattice phonons in k_x, k_y space.

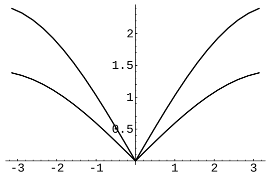


Fig. 9.6 Cut along $\mathbf{k} = (kx, 0)$ of the spectrum of the triangular lattice phonons.

Vibrations of a One-Dimensional Diatomic Chain

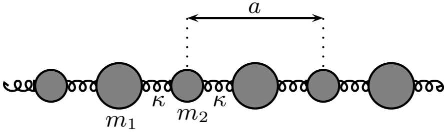
10

(10.1) Normal modes of a One-Dimensional Diatomic Chain

(a) What is the difference between an acoustic mode and an optical mode.

▷ Describe how particles move in each case.

(b) Derive the dispersion relation for the longitudinal oscillations of a one-dimensional diatomic mass-and-spring crystal where the unit cell is of length a and each unit cell contains one atom of mass m_1 and one atom of mass m_2 connected together by springs with spring constant κ, as shown in the figure (all springs are the same, and motion of particles is in one dimension only).



(c) Determine the frequencies of the acoustic and optical modes at $k = 0$ as well as at the Brillouin zone boundary.

▷ Describe the motion of the masses in each case (see margin note 4 of this chapter!).

▷ Determine the sound velocity and show that the group velocity is zero at the zone boundary.

▷ Show that the sound velocity is also given by $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

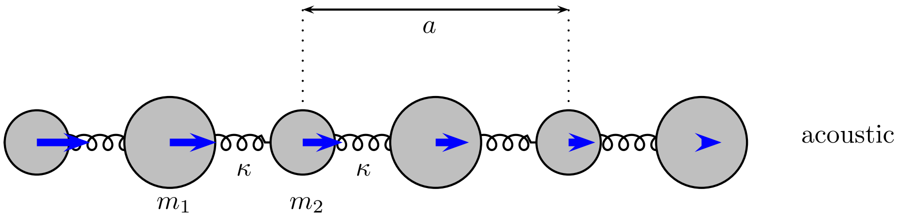
(d) Sketch the dispersion in both reduced and extended zone scheme.

▷ If there are N unit cells, how many different normal modes are there?

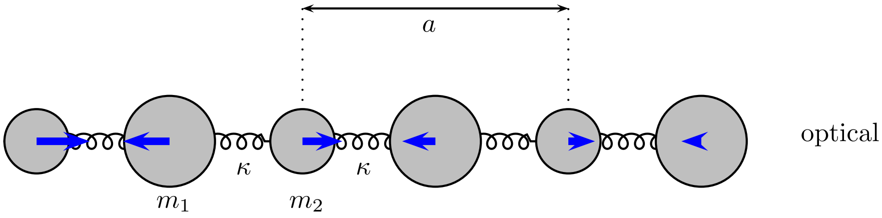
▷ How many *branches* of excitations are there? I.e., in reduced zone scheme, how many modes are there there at each k?

(e) What happens when $m_1 = m_2$?

The following figure depicts a long wavelength acoustic wave: All atoms in the unit cell move in-phase with a slow spatial modulation. Acoustic waves $\omega \sim k$ for small k.



The following depicts a long wavelength optical wave: The two different types of atoms move out of phase, with a slow spatial modulation. (In general a long wavelength optical mode is any long wavelength mode where not all atoms in the unit cell are moving in phase). Note that the amplitude of motion of the different atoms in the cells is generally not the same. Optical modes have ω nonzero as $k \to 0$.



(b) Let x_n be the position of the n^{th} particle of mass m_1 and y_n be the position of the n^{th} particle of mass m_2. We can assume that the equilibrium position of x_n is given by na and the equilibrium position of y_n is given by $na + d$.

We write the equations of motion for the *deviations* from these equilibrium positions δx_n and δy_n.

$$\begin{aligned} m_1 \ddot{\delta x}_n &= -\kappa(\delta x_n - \delta y_{n-1}) - \kappa(\delta x_n - \delta y_n) \\ m_2 \ddot{\delta y}_n &= -\kappa(\delta y_n - \delta x_n) - \kappa(\delta y_n - \delta x_{n+1}) \end{aligned}$$

Writing the ansätze

$$\begin{aligned} \delta x_n &= A_x e^{ikan - i\omega t} \\ \delta y_n &= A_y e^{ikan - i\omega t} \end{aligned}$$

we obtain the equations

$$\begin{aligned} -m_1 \omega^2 A_x e^{ikna} &= -2\kappa A_x e^{ikna} + \kappa A_y (e^{ikna} + e^{ik(n-1)a}) \\ -m_2 \omega^2 A_y e^{ikna} &= -2\kappa A_y e^{ikna} + \kappa A_x (e^{ikna} + e^{ik(n+1)a}) \end{aligned}$$

or

$$\begin{aligned} \omega^2 A_x &= 2(\kappa/m_1) A_x - (\kappa/m_1)(1 + e^{-ika}) A_y & (10.1) \\ \omega^2 A_y &= 2(\kappa/m_2) A_y - (\kappa/m_2)(1 + e^{ika}) A_x & (10.2) \end{aligned}$$

which is an eigenvalue problem from ω^2. Thus we need to find the roots of the determinant

$$\left| \begin{array}{cc} 2(\kappa/m_1) - \omega^2 & -(\kappa/m_1)(1 + e^{-ika}) \\ -(\kappa/m_2)(1 + e^{ika}) & 2(\kappa/m_2) - \omega^2 \end{array} \right|$$

which gives the equation

$$
\begin{aligned}
0 &= \omega^4 - \omega^2\left(2\kappa(1/m_1 + 1/m_2)\right) + \frac{\kappa^2}{m_1 m_2}\left(4 - (1+e^{ika})(1+e^{-ika})\right) \\
0 &= \omega^4 - \omega^2\left(\frac{2(m_1+m_2)\kappa}{m_1 m_2}\right) + \frac{\kappa^2}{m_1 m_2}\left(2 - 2\cos(ka)\right)
\end{aligned}
$$

with the solution (skipping a few steps)

$$
\begin{aligned}
\omega^2 &= \frac{\kappa}{m_1 m_2}\left(m_1 + m_2 \pm \sqrt{m_1^2 + m_2^2 + 2m_1 m_2 \cos(ka)}\right) \\
&= \frac{\kappa}{m_1 m_2}\left(m_1 + m_2 \pm \sqrt{(m_1+m_2)^2 - 4m_1 m_2 \sin^2(ka/2)}\right)
\end{aligned}
$$

(c) At $k = 0$, $\cos(ka) = 1$, the acoustic mode has zero energy, whereas the optical mode has energy

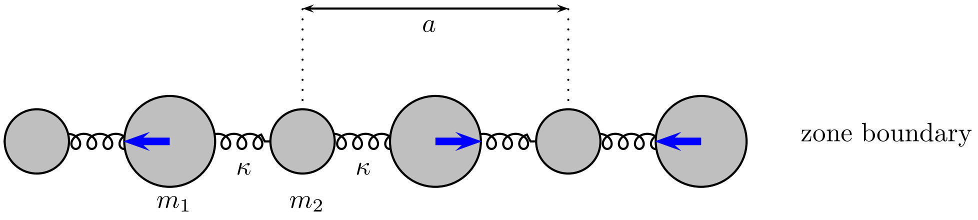
$$\omega = \sqrt{\frac{2\kappa(m_1+m_2)}{m_1 m_2}}$$

At the zone boundary $\cos(ka) = -1$, so the two modes have energy

$$\omega = \sqrt{\frac{2\kappa m_1}{m_1 m_2}} \quad \text{and} \quad \sqrt{\frac{2\kappa m_2}{m_1 m_2}}$$

the greater of which is the optical mode, the lesser being the acoustic mode.

To find the motions corresponding to these modes we need to plug our frequencies back into Eqs. 10.1 and 10.2 to find the relation between A_x and A_y. For the acoustic mode at $k = 0$ we obtain $A_x = A_y$ which means the two masses move in phae with the same amplitude. For the optical mode at $k = 0$ we have $A_x = -(m_2/m_1)A_y$ meaning that the two different masses move in opposite directions with the heavier mass moving with lower amplitude. At the zone boundary the two modes correspond to one of the masses staying still and the other mass moving. For example, for the lower frequency mode, the higher mass particles move and the lower mass particle stays fixed. Since we are at the zone boundary, every other higher mass particle moves in the opposite direction (thus compressing symmetrically around the fixed particle. An example of a zone boundary mode is shown in the following figure



To find the sound velocity, expand the cos around $k = 0$, one obtains the acoustic mode velocity $\omega = vk$ with

$$v = a\sqrt{\frac{\kappa}{2(m_1 + m_2)}}$$

We check that $v^{-2} = \rho\beta$. The density of the chain is $\rho = (m_1 + m_2)/a$, the compressibility of two springs in series is $\kappa/2$ so the compressibility of the chain is $\beta = -(1/L)dL/dF = 2/(\kappa a)$.

Near the zone boundary, since the group velocity is $d\omega/dk$ and since $d\omega/d\cos(ka)$ is nonsingular, the group velocity must be zero by using the chain rule since $d\cos(ka)/dk = a\sin(ka) = 0$ at the zone boundary $(k = \pi/a)$.

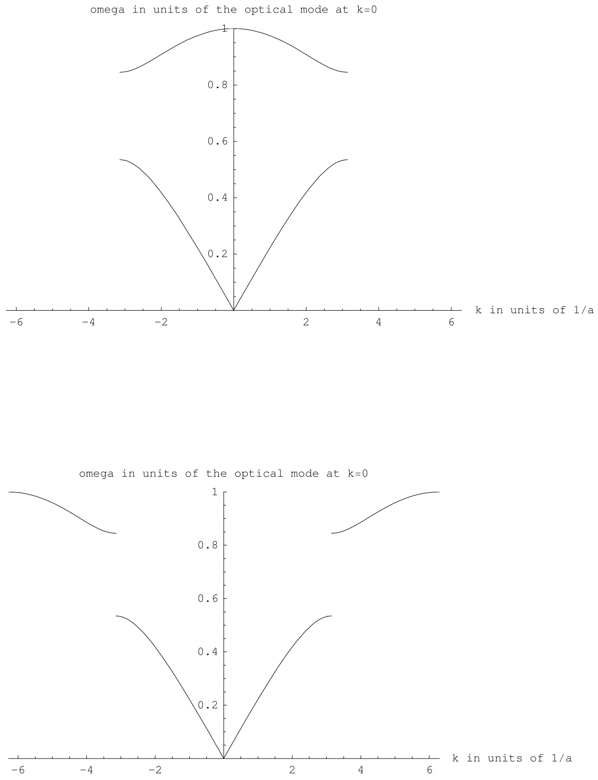


Fig. 10.1 Diatomic Chain. Top Reduced Zone Scheme. Bottom Extended Zone Scheme. Both pictures use $m_1/m_2 = .4$.

If there are N unit cells, therefore $2N$ atoms, there are 2N modes. There are 2 modes per k in the reduced zone scheme, therefore two branches.

(e) When $m_1 = m_2$ the unit cell is now of size $a/2$ so the Brillouin zone is doubled in size. In this limit, the gap at the Brillouin zone boundary vanishes and the two branches become the single branch of the monatomic chain (this is most easily described in extended zone scheme).

(10.2) Decaying Waves
Consider the alternating diatomic chain dispersion as discussed in the text Eq. 10.6 and shown in Fig. 10.6. For frequencies above $\omega_+(k=0)$ there are no propagating wave modes, and similarly for frequencies between $\omega_-(k=\pi/a)$ and $\omega_+(k=\pi/a)$ there are no propagating wave modes. As in Exercise 9.4, if this chain is driven at a frequency ω for which there are no propagating wave modes, then there will be a decaying, or evanescent, wave instead. By solving 10.6 for a complex k, find the length scale of this decaying wave.

As in problem 9.4, we simply want to analytically extend k to complex numbers. From the text Eq. 10.6 we can rearrange to obtain

$$ka = \cos^{-1}\left\{\frac{1}{2\kappa_1\kappa_2}\left[(m\omega^2 - \kappa_1 - \kappa_2)^2 - \kappa_1^2 - \kappa_2^2\right]\right\}$$

The argument on the right hand size is greater than 1 for ω larger than the $q = 0$ optical mode freuquency, whereas for ω between the zone boundary acoustic and optical model frequencies, the right hand side is less than -1. The arccos of a number greater than one is pure imaginary and grows from 0 as the argument increases from unity. Whereas the arcos of a number less than -1 is $\pi +$ imaginary with the imaginary part growing from zero as the argument decreases from -1. The length scale of decay is always given by $L = a/q$ with q the imaginary part of k.

(10.3) General Diatomic Chain*
Consider a general diatomic chain as shown in Fig. 10.1 with two different masses m_1 and m_2 as well as two different spring constants κ_1 and κ_2 and lattice constant a.

(a) Calculate the dispersion relation for this system.

(b) Calculate the acoustic mode velocity and compare it to $v_s = \sqrt{\beta^{-1}/\rho}$ where ρ is the chain density and β is the compressibility.

(a) This is the same approach as the prior cases, just a bit more algebra to keep track of

$$\begin{aligned} m_1\ddot{\delta x}_n &= -\kappa_1(\delta x_n - \delta y_{n-1}) - \kappa_2(\delta x_n - \delta y_n) \\ m_2\ddot{\delta y}_n &= -\kappa_2(\delta y_n - \delta x_n) - \kappa_1(\delta y_n - \delta x_{n+1}) \end{aligned}$$

Writing the ansätze

$$\begin{aligned} \delta x_n &= A_x e^{ikan - i\omega t} \\ \delta y_n &= A_y e^{ikan - i\omega t} \end{aligned}$$

we obtain the equations

$$\begin{aligned}-m_1\omega^2 A_x e^{ikna} &= -(\kappa_1+\kappa_2)e^{ikna}A_x + (\kappa_2 e^{ikna} + \kappa_1 e^{ik(n-1)a})A_y \\ -m_2\omega^2 A_y e^{ikna} &= -(\kappa_1+\kappa_2)e^{ikna}A_y + (\kappa_2 e^{ikna} + \kappa_1 e^{ik(n+1)a})A_x\end{aligned}$$

or

$$\begin{aligned}\omega^2 A_x &= \left(\frac{\kappa_1+\kappa_2}{m_1}\right)A_x + \left(\frac{\kappa_2}{m_1} + e^{-ika}\frac{\kappa_1}{m_1}\right)A_y \\ \omega^2 A_y &= \left(\frac{\kappa_1+\kappa_2}{m_2}\right)A_y + \left(\frac{\kappa_2}{m_2} + e^{ika}\frac{\kappa_1}{m_2}\right)A_x\end{aligned}$$

which is an eigenvalue equation for ω^2. The secular equation is then

$$0 = (\kappa_1+\kappa_2 - m_1\omega^2)(\kappa_1+\kappa_2 - m_2\omega^2) - \kappa_1^2 - \kappa_2^2 - 2\kappa_1\kappa_2\cos(ka)$$

or

$$\omega^4 - \frac{(\kappa_1+\kappa_2)(m_1+m_2)}{m_1 m_2}\omega^2 - \frac{4\kappa_1\kappa_2}{m_1 m_2}\sin^2(ka/2) = 0$$

with the solution (skipping a few steps)

$$\begin{aligned}\omega^2 &= \frac{(\kappa_1+\kappa_2)(m_1+m_2)}{2m_1 m_2} \\ &\quad \pm\frac{1}{2}\sqrt{\frac{(\kappa_1+\kappa_2)^2(m_1+m_2)^2}{(m_1 m_2)^2} - \frac{16\kappa_1\kappa_2}{m_1 m_2}\sin^2(ka/2)}\end{aligned}$$

(b) Simply taylor expanding the dispersion gives us

$$\omega = \sqrt{\frac{\kappa_1\kappa_2}{(\kappa_1+\kappa_2)(m_1+m_2)}}ak$$

or

$$v_s = \sqrt{\frac{a^2\kappa_1\kappa_2}{(\kappa_1+\kappa_2)(m_1+m_2)}}$$

Now the hydrodynamic approach. The density of the chain is $\rho = (m_1+m_2)/a$, the spring constant of the two springs in series is $\kappa_1\kappa_2/(\kappa_1\kappa_2)$ so the compressibility of the chain is $\beta = -(1/L)dL/dF = (\kappa_1\kappa_2)/(\kappa_1 + \kappa_2)/$. Plugging this into $v_s = \sqrt{\beta^{-1}/\rho}$ gives the same result.

(10.4) Second Neighbor Diatomic Chain* Consider the diatomic chain from Exercise 10.1. In addition to the spring constant κ between neighboring masses, suppose that there is also a next nearest-neighbor coupling with spring constant κ' connecting equivalent masses in adjacent unit cells. Determine the dispersion relation for this system. What happens if $\kappa' \gg \kappa$?

We write the equations of motion

$$\begin{aligned}
m_1 \delta\ddot{x}_n &= -\kappa(\delta x_n - \delta y_{n-1}) - \kappa(\delta x_n - \delta y_n) - \kappa'(\delta x_n - \delta x_{n-1}) - \kappa'(\delta x_n - \delta x_{n+1}) \\
m_2 \delta\ddot{y}_n &= -\kappa(\delta y_n - \delta x_n) - \kappa(\delta y_n - \delta x_{n+1}) - \kappa'(\delta y_n - \delta y_{n-1}) - \kappa'(\delta y_n - \delta y_{n+1})
\end{aligned}$$

Writing the usual ansätze

$$\begin{aligned}
\delta x_n &= A_x e^{ikan - i\omega t} \\
\delta y_n &= A_y e^{ikan - i\omega t}
\end{aligned}$$

we obtain the equations

$$\begin{aligned}
-m_1\omega^2 A_x e^{ikna} &= -2(\kappa+\kappa')A_x e^{ikna} + \kappa A_y(e^{ikna} + e^{ik(n-1)a}) + \kappa' A_x(e^{ik(n+1)a} + e^{ik(n-1)a}) \\
-m_2\omega^2 A_y e^{ikna} &= -2(\kappa+\kappa')A_y e^{ikna} + \kappa A_x(e^{ikna} + e^{ik(n+1)a}) + \kappa' A_y(e^{ik(n+1)a} + e^{ik(n-1)a})
\end{aligned}$$

or

$$\begin{aligned}
m_1\omega^2 A_x &= 2\left[(\kappa+\kappa') - \kappa'\cos(ka)\right] A_x - \kappa(1 + e^{-ika})A_y \\
m_2\omega^2 A_y &= 2\left[(\kappa+\kappa') - \kappa'\cos(ka)\right] A_y - \kappa(1 + e^{ika})A_x
\end{aligned}$$

which is an eigenvalue problem for ω^2. Using some trig identies and some algebra the secular equation can be reduced to

$$0 = m_1 m_2\,\omega^4 - (m_1+m_2)\left(2\kappa + 4\kappa'\sin^2(ka/2)\right)\omega^2 + \left([4\kappa^2 + 16\kappa\kappa']\sin^2(ka/2) + 16\kappa'^2\sin^4(ka/2)\right)$$

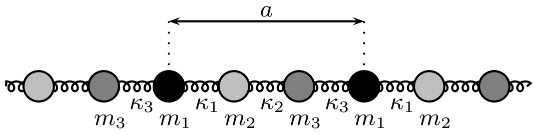
with the solution

$$\begin{aligned}
\omega^2 &= \frac{1}{2m_1m_2}\Big\{(m_1+m_2)(2\kappa + 4\kappa'\sin^2(ka/2)) \\
&\quad \pm\sqrt{(m_1+m_2)^2(2\kappa+4\kappa'\sin^2(ka/2))^2 - 4m_1m_2([4\kappa^2+16\kappa\kappa']\sin^2(ka/2) + 16\kappa'^2\sin^4(ka/2))}\Big\} \\
&= \frac{1}{m_1m_2}\Big\{(m_1+m_2)(\kappa + 2\kappa'\sin^2(ka/2)) \\
&\quad \pm\sqrt{4m_1m_2\kappa^2\cos^2(ka/2) + 4(m_1-m_2)^2\left(\kappa'^2\sin^4(ka/2) + \kappa\kappa'\sin^2(ka/2)\right)}\Big\}
\end{aligned}$$

Note that when $\kappa_2 = 0$ we recover the diatomic chain from Exercise 10.1. When $\kappa' \gg \kappa$ we get two decoupled monatomic chains (as should be expected!).

(10.5) Triatomic Chain*

Consider a mass-and-spring model with three different masses and three different springs per unit cell as shown in this diagram.



As usual, assume that the masses move only in one dimension.

(a) At $k = 0$ how many optical modes are there? Calculate the energies of these modes. Hint: You will get a cubic equation. However, you already know one of the roots since it is the energy of the acoustic mode at $k = 0$

(b)* If all the masses are the same and $\kappa_1 = \kappa_2$ determine the frequencies of all three modes at the zone boundary $k = \pi/a$. You will have a cubic equation, but you should be able to guess one root which corresponds to a particularly simple normal mode.

(c)* If all three spring constants are the same, and $m_1 = m_2$ determine the frequencies of all three modes at the zone boundary $k = \pi/a$. Again you should be able to guess one of the roots.

With three particles in the unit cell, in one dimesion there is one acoustic mode and two optical modes.

Declaring the unit cell to be one set of m_1, m_2, m_3 with positions x, y, z our equations of motion are

$$\begin{aligned} m_1 \delta\ddot{x}_n &= -\kappa_3(\delta x_n - \delta z_{n-1}) - \kappa_1(\delta x_n - \delta y_n) \\ m_2 \delta\ddot{y}_n &= -\kappa_1(\delta y_n - \delta x_n) - \kappa_2(\delta y_n - \delta z_n) \\ m_3 \delta\ddot{z}_n &= -\kappa_2(\delta z_n - \delta y_n) - \kappa_3(\delta z_n - \delta x_{n+1}) \end{aligned}$$

Plugging in the usual wave ansatz gives us the secular determinant

$$0 = \begin{vmatrix} \kappa_3 + \kappa_1 - m_1\omega^2 & \kappa_1 & \kappa_3 e^{-ika} \\ \kappa_1 & \kappa_1 + \kappa_2 - m_2\omega^2 & \kappa_2 \\ \kappa_3 e^{ika} & \kappa_2 & \kappa_2 + \kappa_3 - m_3\omega^2 \end{vmatrix}$$

which multiplied out gives the secular polynomial

$$\begin{aligned} 0 \;=\; & m_1 m_2 m_3\, \omega^6 \\ & - \left[\kappa_1(m_1 + m_2)m_3 + \kappa_3 m_2(m_1 + m_3) + \kappa_2 m_1(m_2 + m_3)\right]\omega^4 \\ & + \left[(\kappa_2\kappa_3 + \kappa_1\kappa_2 + \kappa_3\kappa_1)(m_1 + m_2 + m_3)\right]\omega^2 \\ & - \left[\kappa_1\kappa_2\kappa_3(2 - 2\cos(ka))\right] \end{aligned} \qquad (10.3)$$

At $k = 0$, the final term vanishes and the secular polynomial clearly has $\omega = 0$ a root. This we could have guessed in advance since we know the acoustic mode should come down to zero frequency at $k = 0$. Once we remove the obvious factor of ω^2 the remaining polynomial is just quadratic and we can obtain the two roots in the obvious way.

(b) Setting all the masses the same and $\kappa_1 = \kappa_2$, and setting $ka = \pi$ we obtain

$$\begin{aligned} 0 \;=\; & m^3\omega^6 - \left[2m^2(2\kappa_1 + \kappa_3)\right]\omega^4 \\ & + \left[(2\kappa_1\kappa_3 + \kappa_1^2)(3m)\right]\omega^2 - \left[\kappa_1^2\kappa_3(4)\right] \end{aligned} \qquad (10.4)$$

Here we have a difficult cubic. However, with some intuition we realize that there should be a mode at the zone boundary where the κ_3 spring does not compress at all – the two masses connected to κ_3 moving in unison, but since we are at the zone boundary every other κ_3 spring moves in the opposite direction. The two masses moving in unison have mass $2m$ and have a restoring force of $2\kappa_1$ from the two springs on the two sides. Thus we expect a frequency of $\omega^2 = \kappa_1/m$. Indeed, this frequncy solves Eq. 10.4. We can thus factor out this root to obtain a quadratic which we then solve to get the two other roots at the zone boundary

$$\omega^2 = \frac{3\kappa_1 + 2\kappa_3 \pm \sqrt{9\kappa_1^2 - 4\kappa_1\kappa_3 + 4\kappa_3^2}}{2m}$$

(c) Setting all of the spring constants the same and $m_1 = m_2$ and setting $ka = \pi$ we obtain

$$\begin{aligned} 0 &= m_1^2 m_3\,\omega^6 - [2\kappa m_1(2m_3 + m_1)]\,\omega^4 \\ &\quad + \left[(2m_1 + m_3)(3\kappa^2)\right]\,\omega^2 - 4\kappa^3 \end{aligned} \qquad (10.5)$$

Very similar reasoning suggests a mode at this wavevector with frequency $\omega^2 = \kappa/m_1$ (which is indeed a solution) which we can then factor out to give the two additional zone boundary modes

$$\omega^2 = \kappa\left(\frac{3m_3 + 2m_1 \pm \sqrt{9m_3^2 - 4m_1m_3 + 4m_1^2}}{2m_1m_3}\right)$$

Tight Binding Chain (Interlude and Preview)

11

(11.1) Monatomic Tight Binding Chain

Consider a one-dimensional tight binding model of electrons hopping between atoms. Let the distance between atoms be called a, and here let us label the atomic orbital on atom n as $|n\rangle$ for $n = 1 \ldots N$ (you may assume periodic boundary conditions, and you may assume orthonormality of orbitals, i.e., $\langle n|m\rangle = \delta_{nm}$). Suppose there is an on-site energy ϵ and a hopping matrix element $-t$. In other words, suppose $\langle n|H|m\rangle = \epsilon$ for $n = m$ and $\langle n|H|m\rangle = -t$ for $n = m \pm 1$.

▷ Derive and sketch the dispersion curve for electrons. (Hint: Use the effective Schroedinger equations of Exercise 6.2a. The resulting equation should look very similar to that of Exercise 9.2.)

▷ How many different eigenstates are there in this system?

▷ What is the effective mass of the electron near the bottom of this band?

▷ What is the density of states?

▷ If each atom is monovalent (it donates a single electron) what is the density of states at the Fermi surface?

▷ Give an approximation of the heat capacity of the system (see Exercise 4.3).

▷ What is the heat capacity if each atom is divalent?

Write a general wavefunction as

$$\Psi = \sum_n \phi_n |n\rangle$$

The schroedinger equation (See problem 6.2a) is

$$E\phi_n = \epsilon\phi_n - t(\phi_{n+1} + \phi_{n-1})$$

write the ansatz

$$\phi_n = e^{ikna}$$

and we obtain

$$E(k) = \epsilon - 2t\cos(ka)$$

(I won't sketch this because it is rather trivial). Note however, for $t > 0$ the minimum occurs at $k = 0$ whereas for $t < 0$ the minimum is at the zone boundary.

If there are N sites in the system, the total length of the system (assumed periodic) is Na. Thus k must be quantized $k = 2\pi m/(Na)$. Thus there are exactly N different values of k within the Brillouin zone. This is to be expected. If we started with a Hilbert space of N dimensions (described by states $|n\rangle$), then we expect that there should be exactly

N eigenstates. (And one gets twice as many eigenstates if you include spin).

Expanding around the minimum one obtains

$$E = \text{const} + |t|a^2k^2$$

which we set equal to a free particle dispersion

$$\hbar^2k^2/(2m^*) = |t|a^2k^2$$

yielding an effective mass

$$m^* = \hbar^2/(2|t|a^2)$$

The density of states in k space is uniform as usual $dN/dk = L/(2\pi) = Na/(2\pi)$ (I have not included spin here yet) so the density of states in energy

$$dN/dE = (dN/dk)(dk/dE)$$

Now using

$$dE/dk = 2ta\sin(ka) = 2|t|a\sqrt{1 - ((E-\epsilon)/(2t))^2}$$

we obtain

$$dN/dE = \frac{N}{2\pi}\frac{2*2}{2|t|\sqrt{1 - ((E-\epsilon)/(2t))^2}}$$

and, as in exercise 9.2 there is an extra factor of 2 being that one has two possible k states for each energy E and still another factor of 2 to include the 2 spin states. (Note if you integrate over frequency you correctly get back $2N$ degrees of freedom, now with the factor of 2 for spin included).

If each atom is monovalent, the band is exactly half filled (since two electrons can go into each orbital). Thus the density of states is

$$dN/dE = \frac{N}{\pi}\frac{1}{|t|}$$

The heat capacity is given in terms of the density of states as

$$C_V = \tilde{\gamma}k_B^2 g(E_F)VT$$

with $\tilde{\gamma} = \pi^2/6$ (the exact number is from a more complicated calculation that the students are not responsible for). Here $g(E_F)V = \frac{N}{\pi}\frac{1}{|t|}$.

If there were two electrons per atom, then the band would be completely full, and there would be no freedom in the system at all. The heat capacity would be zero. The spin susceptibility would be zero too.

(11.2) Diatomic Tight Binding Chain

We now generalize the calculation of the previous exercise to a one-dimensional diatomic solid which might look as follows:

$$-A-B-A-B-A-B-$$

Suppose that the onsite energy of type A is different from the onsite energy of type B. I.e, $\langle n|H|n\rangle$ is ϵ_A for n being on a site of type A and is ϵ_B for n being on a site of type B. (All hopping matrix elements $-t$ are still identical to each other.)

▷ Calculate the new dispersion relation. (This is extremely similar to Exercise 10.1. If you are stuck, try studying that exercise again.)

▷ Sketch this dispersion relation in both the reduced and extended zone schemes.

▷ What happens if $\epsilon_A = \epsilon_B$?

▷ What happens in the "atomic" limit when t becomes very small.

▷ What is the effective mass of an electron near the bottom of the lower band?

▷ If each atom (of either type) is monovalent, is the system a metal or an insulator?

▷ *Given the results of this exercise, explain why LiF (which has very ionic bonds) is an extremely good insulator.

The unit cell a is now the distance from an A atom to the next A atom. Let ϕ_n^A be the amplitude of the wavefunction on the n^{th} site of type A and ϕ_n^B be the amplitude on the n^{th} site of type B.

The Schroedinger equation becomes

$$\begin{aligned} E\phi_n^A &= \epsilon_A\phi_n^A - t(\phi_n^B + \phi_{n-1}^B) \\ E\phi_n^B &= \epsilon_B\phi_n^B - t(\phi_n^A + \phi_{n+1}^A) \end{aligned}$$

Using the ansätz

$$\begin{aligned} \phi_n^A &= Ae^{ikna} \\ \phi_n^B &= Be^{ikna} \end{aligned}$$

gives

$$\begin{aligned} EA &= \epsilon_A A - t(1+e^{-ika})B \\ EB &= \epsilon_B B - t(1+e^{ika})A \end{aligned}$$

again giving a two by two eigenvalue problem, where we solve for the roots of the determinant

$$\left| \begin{array}{cc} \epsilon_A - E & -t(1+e^{-ika}) \\ -t(1+e^{ika}) & \epsilon_B - E \end{array} \right|$$

yielding the secular equation

$$0 = E^2 - E(\epsilon_A + \epsilon_B) + (\epsilon_A\epsilon_B - t^2(2+2\cos(ka)))$$

with the solutions

$$E_\pm(k) = \frac{1}{2}\left(\epsilon_A + \epsilon_B \pm \sqrt{(\epsilon_A - \epsilon_B)^2 + 4t^2(2+2\cos(ka))}\right)$$

Note that in the limit that $\epsilon_A = \epsilon_B$ we recover

$$E = \epsilon \pm 2|t|\cos(ka/2)$$

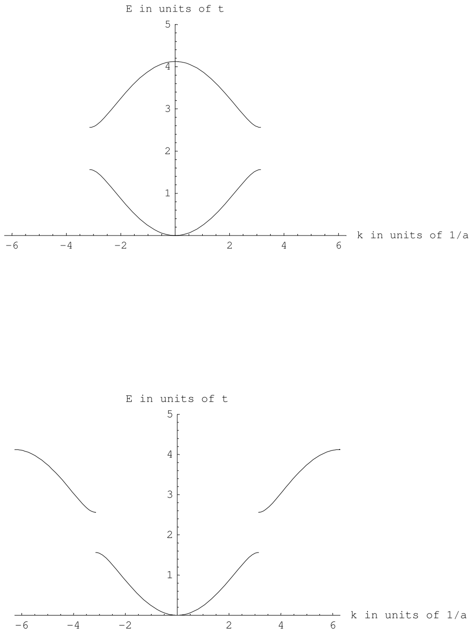


Fig. 11.1 Diatomic Tight Binding Problem in 1D. Left: Reduced Zone scheme. Right: Extended Zone scheme. In both pictures we have chosen $\epsilon_A = 2.56$ and $\epsilon_B = 1.56$

which matches the solution of part (a) above, but for the change in the definition of the size of the unit cell. (See the figure for sketches of the dispersion)

In the limit of small t the bands become very flat at energies ϵ_A and ϵ_B.

Expanding around the minimum gives

$$E = \text{constant} + \frac{2t^2(ka)^2}{\sqrt{(\epsilon_A - \epsilon_B)^2 + 16t^2}}$$

which we set equal to $\hbar^2 k^2/(2m^*)$ to yield

$$m^* = \frac{\hbar^2 \sqrt{(\epsilon_A - \epsilon_B)^2 + 16t^2}}{4t^2 a^2}$$

If each atom is monovalent, there are now two electrons per unit cell, and this fills exactly the lower band (leaving the upper band empty). The system is therefore an insulator.

If $\epsilon_A = \epsilon_B$ this becomes a monotonic chain, the gap closes and it becomes a metal.

For LiF we can expect a much lower energy for electrons on F than on Li (F high high electron affinity, Li has low ionization energy). So we can set $\epsilon_A \ll \epsilon_B$. What happens in this limit is that the band are extremely far apart – thus a very good insulator. Further, if we look a the eigenvectors in the lower band, we will find that they are almost completely on the lower energy atoms. Thus the free electron is transferred almost completely from the higher to the lower energy atom.

(11.3) Tight Binding Chain Done Right

Let us reconsider the one-dimensional tight binding model as in Exercise 11.1. Again we assume an on-site energy ϵ and a hopping matrix element $-t$. In other words, suppose $\langle n|H|m\rangle = \epsilon$ for $n = m$ and $\langle n|H|m\rangle = -t$ for $n = m \pm 1$. However, now, let us no longer assume that orbitals are orthonormal. Instead, let us assume $\langle n|m\rangle = A$ for $n = m$ and $\langle n|m\rangle = B$ for $n = m + 1$ with $\langle n|m\rangle = 0$ for $|n - m| > 1$.

▷ Why is this last assumption (the $|n - m| > 1$ case) reasonable?

Treating the possible non-orthogonality of orbitals here is very similar to what we did in Exercise 6.5. Go back and look at that exercise.

▷ Use the effective Schroedinger equation from Exercise 6.5 to derive the dispersion relation for this one-dimensional tight binding chain.

One can assume that orbitals far apart have no overlap since the tails of wavefunctions decay exponentially.

The generalized Schoedinger equation is

$$\sum_m H_{nm}\phi_m = E\sum_m S_{nm}\phi_m$$

where here

$$\begin{aligned} H_{nm} &= \epsilon_0\delta_{nm} - t(\delta_{n,m+1} + \delta_{n,m-1}) \\ S_{nm} &= A\delta_{nm} + B\delta_{n,m+1} + B^*\delta_{n,m-1} \end{aligned}$$

(note we did not promise that B is real!). Plugging in our wave ansatz $\phi_m = e^{imka}$ into the Schroedinger equation, we obtain

$$E(A + Be^{ik} + B^*e^{-ik}) = \epsilon_0 - 2t\cos(ka)$$

or

$$E = \frac{\epsilon_0 - 2t\cos(ka)}{A + Be^{ik} + B^*e^{-ik}}$$

(11.4) Two Orbitals per Atom

(a) Consider an atom with two orbitals, A and B having eigenenergies ϵ^A_{atomic} and ϵ^B_{atomic}. Now suppose we make a one-dimensional chain of such atoms and let us assume that these orbitals remain orthogonal. We imagine hopping amplitudes t_{AA} which allows an electron on orbital A of a given atom to hop to orbital A on the neighboring atom. Similarly we imagine a hopping amplitude t_{BB} that allows an electron on orbital B of a given atom to hop to orbital B on the neighboring atom. (We assume that V_0, the energy shift of the atomic orbital due to neighboring atoms, is zero).

▷ Calculate and sketch the dispersion of the two resulting bands.

▷ If the atom is diatomic, derive a condition on the quantities $\epsilon^A_{atomic} - \epsilon^B_{atomic}$, as well as t_{AA} and t_{BB} which determines whether the system is a metal or an insulator.

(b)* Now suppose that there is in addition a hopping term t_{AB} which allows an electron on one atom in orbital A to hop to orbital B on the neighboring atom (and vice versa). What is the dispersion relation now?

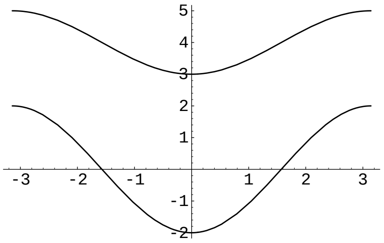


Fig. 11.2 Dispersion in the two orbital tight binding model (Eqs. 11.1 and 11.2). Here, $t_{AA} = 1$, $t_{BB} = 2$, $\epsilon_A = 0$, $\epsilon_B = 4$. Horizontal axis is ka.

(a) The two orbitals are completely decoupled from each other. So we get two independent dispersions (we assume t's real here)

$$E = \epsilon_A - 2t_{AA}\cos(ka) \tag{11.1}$$

and

$$E = \epsilon_B - 2t_{BB}\cos(ka) \tag{11.2}$$

A sketch is given in Fig. 11.2.

It should say ”’if the atom is divalent” not diatomic (doh!). If the atom is divalent, then it will be a metal if the bands overlap and an insulator (or semiconductor) if the bands do not overlap. A band with the dispersion as in Eqs. 11.1 has a band which extends from $\epsilon_A - 2|t_{AA}|$ to $\epsilon_A + 2|t_A A|$ (and similar for the other band – this holds even if t's are complex). In order for the bands to not overlap we must have either

$$\epsilon_A + 2|t_{AA}| < \epsilon_B - 2|t_{BB}|$$

or

$$\epsilon_B + 2|t_{BB}| < \epsilon_A - 2|t_{AA}|$$

If neither of these is satisfied the bands must overlap and we have a metal. Note if we are tricky we can summarize the two above conditions as one condition which, if satisfied, tells us we have an insulator

$$|\epsilon_A - \epsilon_B| > 2\left(|t_{AA}| - |t_{BB}|\right)$$

(b) When there is hopping t_{AB} between an A orbital on one site and a B orbital on a neighboring site, we have a matrix schroedinger equation

$$\begin{aligned} E\phi_n^A &= \epsilon_A\phi_n^A - t_{AA}\phi_{n+1}^A - t_{AA}^*\phi_{n-1}^A - t_{AB}\phi_{n+1}^B - t_{AB}^*\phi_{n-1}^B \\ E\phi_n^B &= \epsilon_B\phi_n^B - t_{BB}\phi_{n+1}^B - t_{BB}^*\phi_{n-1}^B - t_{AB}\phi_{n+1}^A - t_{AB}^*\phi_{n-1}^A \end{aligned}$$

Using the usual ansätz

$$\begin{aligned} \phi_n^A &= Ae^{ikna} \\ \phi_n^B &= Be^{ikna} \end{aligned}$$

we obtain

$$\begin{aligned} EA &= \left(\epsilon_A - t_{AA}e^{ika} - t_{AA}^*e^{-ika}\right)A + \left(-t_{AB}e^{ika} - t_{AB}^*e^{-ika}\right)B \\ EB &= \left(\epsilon_B - t_{BB}e^{ika} - t_{BB}^*e^{-ika}\right)B + \left(-t_{AB}e^{ika} - t_{AB}^*e^{-ika}\right)A \end{aligned}$$

which is an eigenvalue equation for E. Defining

$$T_{AA} = t_{AA}e^{ika} + t_{AA}^*e^{-ika} = 2\mathrm{Re}[t_{AA}e^{ika}] \tag{11.3}$$

$$T_{BB} = t_{BB}e^{ika} + t_{BB}^*e^{-ika} = 2\mathrm{Re}[t_{BB}e^{ika}] \tag{11.4}$$

$$T_{AB} = t_{AB}e^{ika} + t_{AB}^*e^{-ika} = 2\mathrm{Re}[t_{AB}e^{ika}] \tag{11.5}$$

We can write the secular equation as

$$
\begin{aligned}
0 \;=\;& E^2 + E\left(T_{AA} + T_{BB} - \epsilon_A - \epsilon_B\right) \\
& + \left(\epsilon_A - T_{AA}\right)\left(\epsilon_B - T_{BB}\right) - T_{AB}^2
\end{aligned}
\qquad (11.6)
$$

which we solve as a quadratic equation to give

$$
E = \frac{1}{2}\left(\epsilon_A + \epsilon_B - T_{AA} - T_{BB} \pm \sqrt{(\epsilon_A - \epsilon_B - T_{AA} + T_{BB})^2 - 4T_{AB}^2}\right)
$$

(11.5) Electronic Impurity State*

Consider the one-dimensional tight binding Hamiltonian given in Eq. 11.4. Now consider the situation where one of the atoms in the chain (atom $n = 0$) is an impurity such that it has an atomic orbital energy which differs by Δ from all the other atomic orbital energies. In this case the Hamiltonian becomes

$$
H_{n,m} = \epsilon_0 \delta_{n,m} - t(\delta_{n+1,m} + \delta_{n-1,m}) + \Delta \delta_{n,m}\delta_{n,0}.
$$

(a) Using an ansatz

$$
\phi_n = A e^{-qa|n|}
$$

with q real, and a the lattice constant, show that there is a localized eigenstate for any negative Δ, and find the eigenstate energy. This exercise is very similar to Exercise 9.6.

(b) Consider instead a continuum one-dimensional Hamiltonian with a delta-function potential

$$
H = -\frac{\hbar^2}{2m^*}\partial_x^2 + (a\Delta)\delta(x).
$$

Similarly show that there is a localized eigenstate for any negative Δ and find its energy. Compare your result to that of part (a).

(a) Consider first without the impurity. Propose exponentially decaying or growing solutions

$$
\phi_n = A e^{\pm qa|n|}
$$

plugging these in we obtain

$$
E = \epsilon_0 - 2t\cosh(qa) \qquad (11.7)
$$

these give solutions with q real for $(\epsilon_0 - E)/2t > 1$, or in other words, for energies below the bottom of the band. These are analogous to the evanescent waves discussed in Exercises 9.4 and 10.2.

Now, we can patch together two of these evanescent waves at the impurity. Examining the schroedinger equation at position zero, we have

$$
E\phi_0 = (\epsilon_0 + \Delta)\phi_0 - t(\phi_1 + \phi_{-1})
$$

which gives us

$$
E - \epsilon_0 - \Delta = 2te^{-qa}
$$

Then plugging in the value of E in terms of q from Eq. 11.7, we obtain

$$
-\Delta = 2\sinh(qa)
$$

recalling that Δ was negative we have a solution for any value of $\Delta < 0$ with

$$
qa = \sinh^{-1}(|\Delta|/(2t))
$$

Plugging back into Eq. 11.7 we obtain the bound state energy

$$E = \epsilon_0 - 2t\sqrt{[\Delta/(2t)]^2 + 1}$$

and note that for $\Delta = 0$ this gives us the energy at the bottom of the band.

(b) For the continuum problem we have similarly a decaying waves of the form e^{-qx} with energies

$$E = \frac{-\hbar^2 q^2}{2m^*}$$

Then we need to patch together solutions at zero, we have

$$\partial\psi_- - \partial\psi_+ = 2q = (a|\Delta|)(2m^*)/\hbar^2$$

or

$$q = (a|\Delta|m^*)/\hbar^2$$

with energy

$$E = -a^2 m^* \Delta^2/(2\hbar^2)$$

To compare to the above tight binding problem, we use the value of the effective mass $m^* = \hbar^2/(2ta^2)$ to obtain

$$q = |\Delta|/(2t)$$

which matches our above result for small Δ. Correspondingly the energy is

$$E = -\Delta^2/(4t)$$

which also matches the above result for small Δ so long as we choose the bottom of the band to be called zero energy.

(11.6) Reflection from an Impurity*
Consider the tight binding Hamiltonian from the previous exercise representing a single impurity in a chain. Here the intent is to see how this impurity scatters a plane wave incoming from the left with unit amplitude (this is somewhat similar to Exercise 9.5). Use an ansatz wavefunction

$$\phi_n = \begin{cases} Te^{-ikna} & n \geq 0 \\ e^{-ikna} + Re^{+ikna} & n < 0 \end{cases}$$

to determine the transmission T and reflection R as a function of k.

Use the schroedinger equation at position $n = -1$

$$E\phi_{-1} = \epsilon_0\phi_{-1} - t(\phi_0 + \phi_{-2})$$

and at position zero

$$E\phi_0 = (\epsilon_0 + \Delta)\phi_0 - t(\phi_1 + \phi_{-1})$$

and we plug in the ansatz form. The former equation simply tells us that we must have $1 + R = T$ (To see this recall that the relationship between E and k is fixed by the plane wave away from positon zero. So this first equation tells us that position ϕ_0 must just be the usual continuation of this wave-front with no changes.) The second equation then gives us

$$ET = (\epsilon_0 + \Delta)T - t(Te^{ika} + e^{ika} + Re^{-ika})$$

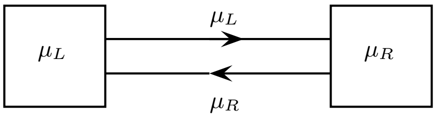
Using $1 + R = T$ as well as using $E = \epsilon_0 + 2t\cos(ka)$ this becomes

$$T = \frac{1}{\frac{\Delta}{2it\sin(ka)} + 1}$$

Note that when $\Delta = 0$, we have complete transmission $T = 1$ and $R = 0$. With $R = T - 1$, we have $|R|^2 + |T|^2 = 1$ which indicates current conservation.

(11.7) Transport in One Dimension*

(a) Consider the one-dimensional tight binding chain discussed in this chapter at (or near) zero temperature. Suppose the right end of this chain is attached to a reservoir at chemical potential μ_R and the left end of the chain is attached to a reservoir at chemical potential μ_L and let us assume $\mu_L > \mu_R$. The particles moving towards the left will be filled up to chemical potential μ_R, whereas the particles moving towards the right will be filled up to chemical potential μ_L, as shown in the bottom of Fig. 11.4, and also diagrammed schematically in the following figure



(i) Argue that the total current of all the particles moving to the right is

$$j_R = \int_0^\infty \frac{dk}{\pi} v(k) n_F(\beta(E(k) - \mu_L))$$

with $v(k) = (1/\hbar)d\epsilon(k)/dk$ the group velocity and n_F the Fermi occupation factor; and an analogous equation holds for left moving current.

(ii) Calculate the conductance G of this wire, defined as

$$J_{total} = GV$$

where $J_{total} = j_L - j_R$ and $eV = \mu_L - \mu_R$, and show $G = 2e^2/h$ with h Planck's constant. This "quantum" of conductance is routinely measured in disorder free one-dimensional electronic systems.

(iii) In the context of Exercise 11.2, imagine that an impurity is placed in this chain between the two reservoirs to create some backscattering. Argue that the conductance is reduced to $G = 2e^2|T|^2/h$. This is known as the Landauer formula and is a pillar of nano-scale electronics.

(b) Now suppose that the chemical potentials at both reservoirs are the same, but the temperatures are T_L and T_R respectively.

(i) Argue that the heat current j^q of all the particles moving to the right is

$$j^q_R = \int_0^\infty \frac{dk}{\pi} v(k)\ (E(k) - \mu)\ n_F(\beta_L(E(k) - \mu))$$

and a similar equation holds for left-moving heat current.

(ii) Define the *thermal* conductance K to be

$$J^q = K(T_L - T_R)$$

where $J^q = j^q_L - j^q_R$ and $T_L - T_R$ is assumed to be small. Derive that the thermal conductance can be rewritten as

$$K = \frac{-2}{hT} \int_{-\infty}^{\infty} dE(E - \mu)^2 \frac{\partial}{\partial E} n_F(\beta(E - \mu)).$$

Evaluating this expression, confirm the Wiedemann–Franz ratio for clean one-dimensional systems

$$\frac{K}{TG} = \frac{\pi^2 k_B^2}{3e^2}$$

(Note that this is a relationship between conductance and thermal conductance rather than between conductivity and thermal conductivity.) In evaluating the above integral you will want to use

$$\int_{-\infty}^{\infty} dx\, x^2 \, \frac{\partial}{\partial x} \frac{1}{e^x + 1} = -\frac{\pi^2}{3}\,.$$

If you are very adventurous, you can prove this nasty identity using the techniques analogous to those mentioned in footnote 20 of Chapter 2, as well as the fact that the Riemann zeta function takes the value $\zeta(2) = \pi^2/6$ which you can prove analogous to the appendix of that chapter.

(a)(i) Genereally the velocity of a wavepacket is the group velocity $v = d\omega/dk$. Here, $\omega = E_k/\hbar$ To find the total right going current, one integrates over all possible k, the occupancy of that k times the group velocity, to obtain the current. There should be an additional factor of $-e$ out front to turn this into an electrical current. The integral over k usually has 2π downstairs, but the 2 is cancelled by a factor of 2 out front for two spins. The integral over k also usually comes with a factor of volume (or length in this case) out front. To see why this is missing we have to think carefully about the definition of current – which counts the number of particles crossing a given point in some unit of time. If one has a particle in a k eigenstate, it is delocalized over the entire system. Thus the "probability" that with velocity v it crosses that given point in a unit of time is given by v/L.

(ii) We can write the total current as

$$\begin{aligned} J &= -\frac{e}{\pi}\left[\int_0^{\infty} \frac{dE(k)}{dk} n_F(\beta(E_k - \mu_R))dk - \int_0^{-\infty} \frac{dE(k)}{dk} n_F(\beta(E_k - \mu_L))dk\right] \\ &= -\frac{e}{\hbar\pi}\left[\int_0^{\infty} dE n_F(\beta(E - \mu_R)) - \int_0^{\infty} dE n_F(\beta(E - \mu_L))\right] \\ &= -\frac{e}{\hbar\pi}\left[\mu_L - \mu_R\right] \end{aligned}$$

where in the last step we have assumed that $\mu \gg k_B T$ so that the occupancy at $E = 0$ is unity — in which case the integral of the Fermi function simply gives the chemical potential (one can see this by starting at $T = 0$ where the Fermi function is just a step function. As we raise the temperature, the change in the fermi function is symmetric around the chemical potential, so even though the fermi function gets smaller below μ and larger above μ the integral is unchanged).

Plugging in the expression for voltage

$$J = -\frac{e^2}{\pi\hbar} V$$

or $G = 2e^2/h$.

(iii) If the amplitude of transmission through the impurity is T then the probability of transmission is $|T|^2$. The resulting current is then reduced by the probability that each particle is transmitted. Thus we obtain

$$G = 2e^2|T|^2/h$$

Note that as we discovered in exercise 11.6, T is a function of wavevector and hence energy. Once should use k near k_F to calculate T. The reason for this is that all of the net current is coming from near the Fermi surface. Well below the fermi surface the currents of left and right movers exactly cancel.

(b) (i) The argument here is quite similar. Here each electron is moving with velocity v, but is carrying energy $E - \mu$. Here energy is measured with respect to the chemical potential – this is an appropriate definition since even at $T = 0$ the addition of an electron carries the chemical potential worth of energy. The difference from this $T = 0$ energy is the excess heat added.

(ii) We take the difference of right moving and left moving energy currents (the sign gives current moving from left to right)

$$\begin{aligned} J^q &= \frac{-1}{\pi}\left[\int_0^{\infty}\frac{dE(k)}{dk}(E_k-\mu)n_F(\beta_R(E_k-\mu))dk - \int_0^{-\infty}\frac{dE(k)}{dk}(E_k-\mu)n_F(\beta_L(E_k-\mu_L))dk\right] \\ &= \frac{-1}{\hbar\pi}\left[\int_0^{\infty} dE(E-\mu)n_F(\beta_R(E-\mu)) - \int_0^{\infty} dE(E-\mu)n_F(\beta_L(E-\mu))\right] \\ &= \frac{-1}{\hbar\pi}(\beta_R-\beta_L)\int_0^{\infty} dE(E-\mu)\frac{dn_F(\beta(E-\mu))}{d\beta} \end{aligned} \tag{11.8}$$

where we have made the approximation that $\beta_R - \beta_L$ is small to replace the finite difference with a derivative with respect to β. This then becomes.

$$J^q = \frac{-1}{\hbar\pi\beta}(\beta_R-\beta_L)\int_0^{\infty} dE(E-\mu)^2\frac{dn_F(\beta(E-\mu))}{dE}$$

then using

$$\beta_R - \beta_L \approx \frac{T_L - T_R}{k_B T^2}$$

gives the desired result. Note that the formula also extends the lower limit of integration to $-\infty$. This is allowed since dn_F/dE is strongly peaked around μ.

Finally scaling out some factors of β we obtain

$$K = \frac{-2T}{h}\int_{-\infty}^{\infty} dx x^2 \frac{d}{dx}\frac{1}{e^x+1} = \frac{2\pi^2 k_B^2 T}{3h}$$

Thus dividing by the expresion for G we obtain

$$\frac{K}{GT} = \frac{\pi^2 k_B^2 T}{3he^2}$$

which is the Weideman-Franz law.

For completeness, we evaluate the integral. First, note that the integrand is symmetric around zero so we can write

$$\begin{aligned}
I &= \int_{-\infty}^{\infty} dx x^2 \frac{d}{dx}\frac{1}{e^x+1} = 2\int_0^{\infty} dx x^2 \frac{d}{dx}\frac{1}{e^x+1} = -4\int_0^{\infty} dx x \frac{e^{-x}}{1+e^{-x}} \\
&= 4\int_0^{\infty} dx x \sum_{n=1}^{\infty}(-e^x)^n = 4\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \\
&= -4\left[\sum_{n=1}^{\infty}\frac{1}{n^2} - 2\sum_{n=1,\text{evens}}^{\infty}\frac{1}{n^2}\right] = 4(1-\frac{2}{4})\zeta(2) = 2\zeta(2)
\end{aligned}$$

The method of calculating $\zeta(2)$ proceeds similar to the appendix of Chapter 1. First, consider the function x in the range $[-\pi,\pi]$ as a fourier series. It can be writen as

$$x = \sum_{n=1}^{\infty} a_n \sin(nx)$$

with

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} x\sin(nx) = -2(-1)^n/n$$

The calculate

$$\int_{-\pi}^{\pi} dx\, x^2 = 2\pi^3/3$$

but also caculate the same quantity in terms of its fourier transforms (using percival's theorem)

$$\int_{-\pi}^{\pi} dx\, x^2 = \int_{-\pi}^{\pi} dx = \sum_{n=1}^{\infty} |a_n|^2 \sin^2(nx) = \sum_{n=1}^{\infty}\frac{4}{n^2}\pi$$

setting these two expressions equal to each other gives

$$\sum_{n=1}^{\infty}\frac{1}{n^2} = \frac{\pi^2}{6}$$

(11.8) Peierls Distortion*

Consider a chain made up of all the same type of atom, but in such a way that the spacing between atoms alternates as long-short-long-short as follows

$$-A = A - A = A - A = A-$$

In a tight binding model, the shorter bonds (marked with =) will have hopping matrix element $t_{short} = t(1+\epsilon)$ whereas the longer bonds (marked with $-$) have hopping matrix element $t_{long} = t(1-\epsilon)$. Calculate the tight-binding energy spectrum of this chain. (The onsite energy ϵ is the same on every atom). Expand your result to linear order in ϵ. Suppose the lower band is filled and the upper band is empty (what is the valence of each atom in this case?). Calculate the total ground-state energy of the filled lower band, and show it decreases linearly with increasing ϵ.

Now consider a chain of equally spaced identical A atoms connected together with identical springs with spring constant κ. Show that making a distortion whereby alternating springs are shorter/longer by δx costs energy proportional to $(\delta x)^2$. Conclude that for a chain with the valence as in the first part of this problem, a distortion of this sort will occur spontaneously. This is known as a Peierls distortion.

OK, I messed up this problem a bit, so bear with me.

First we need to evalulate the spectrum. Consider the unit cell to be a single unit like this $A = A-$. Call the left side the A site and the right site the B site. Set the onsite energy $epsilon_0$ to zero for simplicity and assume t is real (without loss of generality). We then have the tight-binding schroedinger equation

$$\begin{aligned} E\phi_n^A &= -t(1+\epsilon)\phi_n^B - t(1-\epsilon)\phi_{n-1}^B \\ E\phi_n^B &= -t(1+\epsilon)\phi_n^A - t(1-\epsilon)\phi_{n+1}^A \end{aligned}$$

Using the usual ansatz this gives us

$$\begin{aligned} EA &= -t(1+\epsilon)B - t(1-\epsilon)Be^{-ika} \\ EB &= -t(1+\epsilon)A - t(1-\epsilon)Ae^{ika} \end{aligned}$$

which is an eigenvalue problem with solutions

$$E(k) = \pm\,|2t[\cos(ka/2) + i\epsilon\sin(ka/2)]| = \pm|2t|\sqrt{\epsilon^2 + (1-\epsilon^2)\cos^2(ka/2)}$$

To find the total energy of a filled lower band, we need

$$E_{tot} = 2L\int \frac{dk}{2\pi}E(k)$$

which is some horrid ellipic integral. Ideally, we just evaluate this horrid integral and we are done, but this is very difficult analytically (we could do it numerically though!).

However, all we need to do is to make an estimate of how this changes to lowest order in ϵ. Near the zone boundary, since the cosine term is small the effect of epsilon is most pronounced where the energy reduction in the lower band is $-|2t\epsilon|$. As we move away from the zone boundary the cosine term becomes more important. Define $\kappa a = \pi - ka$ to be the distance to the zone boundary (focusing for now on the zone boundary at $ka = \pi$).

For small κ we see that the two term in the square root become roughly equal when

$$\kappa a \approx \epsilon$$

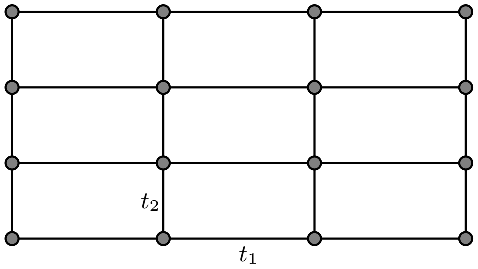
And when $\kappa a \gg \epsilon$ the cosine term dominates. Let us then split the integration roughly at this intermediate point $\kappa a \approx \epsilon$. For smaller κ, the energy reduction can be approximated as $-|2t\epsilon|$ for each value of κ and integrating then a range of κ that is ϵ large we get an energy reduction of $\sim L|t|\epsilon^2$, which we are not interested in. For the region further from the zone boundary, we have roughly

$$\begin{aligned} \delta E &\approx |2tL|\int_{\kappa a=\epsilon}^{\text{cutoff}} d\kappa\left[\sqrt{\epsilon^2 + (\kappa a)^2/4} - \kappa a/2\right] \\ &\approx |2tL|\int_{\kappa a=\epsilon}^{\text{cutoff}} d\kappa\frac{\epsilon^2}{\kappa} \approx |2tL|\epsilon^2\log(\epsilon/\text{cutoff}) \end{aligned}$$

here the cutoff is some arbitrary momentum much further from the zone boundary (it will not matter where we choose the cutoff!). Thus we see that the energy saving is proportional to $\epsilon^2 \log \epsilon$.

(ii) The energy of stretching springs is always quadratic in the stretching (hookes' law), hence proportional to ϵ^2. For small ϵ the electronic energy saving $\epsilon^2 \log \epsilon$ always wins, so the system always distorts spontaneously!

(11.9) Tight Binding in 2d*
Consider a rectangular lattice in two dimensions as shown in the figure. Now imagine a tight binding model where there is one orbital at each lattice site, and where the hopping matrix element is $\langle n|H|m\rangle = t_1$ if sites n and m are neighbors in the horizontal direction and is $= t_2$ if n and m are neighbors in the vertical direction. Calculate the dispersion relation for this tight binding model. What does the dispersion relation look like near the bottom of the band? (The two-dimensional structure is more difficult to handle than the one-dimensional examples given in this chapter. In Chapters 12 and 13 we study crystals in two and three dimensions, and it might be useful to read those chapters first and then return to try this exercise again.)



This is a lot easier than it looks! Let us label the sites (m,n). Let the wavefunctions on the sites be $\phi_{n,m}$ accordingly. The Schroedinger equation is then

$$E\phi_{n,m} = \epsilon_0\phi_{n,m} - t_1(\phi_{n+1,m} + \phi_{n-1,m}) - t_2(\phi_{n,m+1} + \phi_{n,m-1})$$

Using an ansatz

$$\phi_{n,m} = e^{ik_x n a_x + k_y m a_y}$$

where a_x and a_y are the lattice distances in the two directions.

and assuming both t_1 and t_2 real

$$E = \epsilon_0 - 2t_1\cos(k_x a_x) - 2t_2\cos(k_y a_y)$$

Assuming both t_1 and t_2 positive, the minimum occurs at $k_x = k_y = 0$. Near this minimum, we can expand to gets

$$E \approx (\epsilon_0 - 2t_1 - 2t_2) + \frac{1}{2}\left(t_1(k_x a_x)^2 + t_2(k_y a_y)^2\right)$$

which has equal-E contours which are ellipses. Thus near the bottom of the band we have an ellipsoidal bowl.

Crystal Structure

12

(12.1) Crystal Structure of NaCl Consider the NaCl crystal structure shown in Fig. 12.21. If the lattice constant is $a = 0.563$ nm, what is the distance from a sodium atom to the nearest chlorine? What is the distance from a sodium atom to the nearest other sodium atom?

Super easy: The Na-Cl distance is $a/2 = .2815$ nm whereas the Na-Na distance is $a\sqrt{2}/2 = .398$ nm.

(12.2) Neighbors in the Face-Centered Lattice.
(a) Show that each lattice point in an fcc lattice has twelve nearest neighbors, each the same distance from the initial point. What is this distance if the conventional unit cell has lattice constant a?
(b)* Now stretch the side lengths of the fcc lattice such that you obtain a face-centered *orthorhombic* lattice where the conventional unit cell has sides of length a, b, and c which are all different. What are the distances to these twelve neighboring points now? How many nearest neighbors are there?

(a) Given the primitive lattice vectors, one can define the fcc lattice as being vectors of the form $\frac{a}{2}(n, m, l)$ where n, m, l are either all even or two odd and one even. Among this sets of possible lattice points, the closest ones to $[0, 0, 0]$ are of the form $\frac{a}{2}[1, 1, 0]$. Here the two entries that are 1 could be either ± 1 which gives four possibilities. Further the 0 can be in one of three places. Thus we have 12 possibilities. The distance from $[0, 0, 0]$ to any of these points is $a\sqrt{2}/2$ (analogous to previous problem).

(b) In units of the three different (unequal) conventional unit cell lattice constants, the 12 points are still of the form $\frac{1}{2}[1, 1, 0]$ and permutations. The distances to these 12 points are then

$$
\begin{aligned}
[\pm 1, \pm 1, 0] \quad &\rightarrow \quad d = \frac{1}{2}\sqrt{a^2 + b^2} \\
[\pm 1, 0, \pm 1] \quad &\rightarrow \quad d = \frac{1}{2}\sqrt{a^2 + c^2} \\
[0, \pm 1, \pm 1] \quad &\rightarrow \quad d = \frac{1}{2}\sqrt{b^2 + c^2}
\end{aligned}
$$

There are four nearest neighbors corresponding to the smaller two of a, b, c.

(12.3) Crystal Structure

The diagram of Fig. 12.22 shows a plan view of a structure of cubic ZnS (zincblende) looking down the z axis. The numbers attached to some atoms represent the heights of the atoms above the $z = 0$ plane expressed as a fraction of the cube edge a. Unlabeled atoms are at $z = 0$ and $z = a$.

(a) What is the Bravais lattice type?

(b) Describe the basis.

(c) Given that $a = 0.541$ nm, calculate the nearest-neighbor Zn–Zn, Zn–S, and S–S distances.

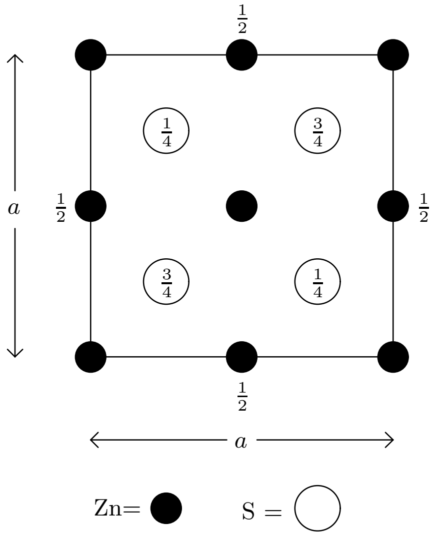


Fig. 12.23 Plan view of conventional unit cell of zincblende.

(a) The lattice is FCC (otherwise known as ”cubic F”)

(b) The basis can be described as Zn at position [0,0,0] and S at position $[\frac{1}{4}, \frac{1}{4}, \frac{3}{4}]$ (or equivalently, but less standard notation $[\frac{1}{4}, \frac{1}{4}, \frac{-1}{4}]$ all in units of the lattice constant.

(c) (just a bit of geometry:) nearest neighbor Zn-Zn is $a/\sqrt{2} = 0.383$ nm; nearest neighbor Zn-S is $a\sqrt{1/4^2 + 1/4^2 + 1/4^2} = 0.234$ nm; nearest neighbor S-S is $a/\sqrt{2} = 0.383$ nm;

(12.4) Packing Fractions

Consider a lattice with a sphere at each lattice point. Choose the radius of the spheres to be such that neighboring spheres just touch (see for example, Fig. 12.8. The packing fraction is the fraction of the volume of all of space which is enclosed by the union of all the spheres (i.e., the ratio of the volume of the spheres to the total volume).

(a) Calculate the packing fraction for a simple cubic lattice.

(b) Calculate the packing fraction for a bcc lattice.

(c) Calculate the packing fraction for an fcc lattice.

(a) The volume of a conventional unit cell is $V_{cell} = a^3$. Each cell corresponds to a single sphere. The radius of this sphere is $a/2$ so its volume is $V_{sphere} = 4\pi/3(a/2)^3$. Thus the packing fraction is $V_{sphere}/V_{cell} = \pi/6 \approx .52$.

(b) The volume of a conventional unit cell is $V_{cell} = a^3$. Each conventional unit cell contains two lattice points which are a distance $a\sqrt{3}/2$

apart from each other. Thus the radius of the each sphere is $a\sqrt{3}/4$ so has volume $V_{sphere} = 4\pi(a\sqrt{3}/4)^3/3$. Thus we have a packing fraction $2V_{sphere}/V_{cell} = \pi\sqrt{3}/8 \approx .68$

(c) The volume of a conventional unit cell is $V_{cell} = a^3$. Each conventional unit cell contains four lattice points which are a distance $a\sqrt{2}/2$ apart from each other. Thus the radius of the each sphere is $a\sqrt{2}/4$ so has volume $V_{sphere} = 4\pi(a\sqrt{2}/4)^3/3$. Thus we have a packing fraction $4V_{sphere}/V_{cell} = \pi/(3\sqrt{2}) \approx .74$

(12.5) Fluorine Beta Phase

Fluorine can crystalize into a so-called beta-phase at temperatures between 45 and 55 Kelvin. Fig. 12.24 shows the cubic conventional unit cell for beta phase fluorine in three-dimensional form along with a plan view.

- ▷ How many atoms are in this conventional unit cell?
- ▷ What is the lattice and the basis for this crystal?

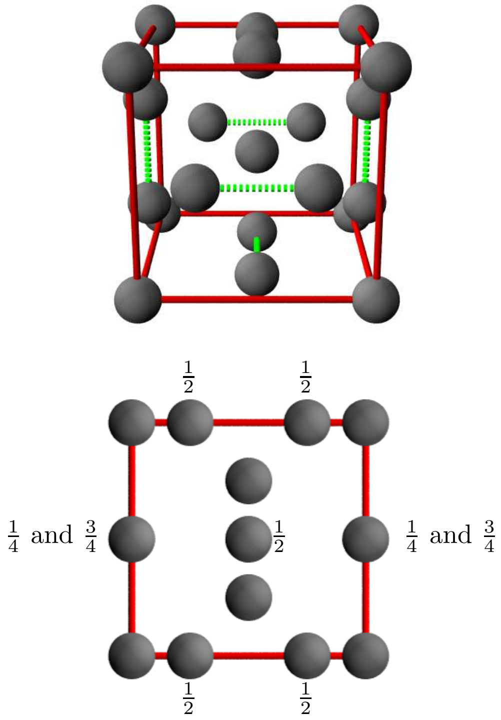


Fig. 12.23 A conventional unit cell for fluorine beta phase. All atoms in the picture are fluorine. Lines are drawn for clarity **Top:** Three-dimensional view. **Bottom:** Plan view. Unlabeled atoms are at height 0 and 1 in units of the lattice constant.

There are 8 atoms in the conventional unit cell. 1 in the corner (8 times 1/8). Each atom on the face counts 1/2. Then there is one in the center.

The lattice is simple cubic. The basis is

$$[0,0,0],\ [0,1/2,1/4],\ [0,1/2,3/4],\ [1/4,0,1/2],\ [3/4,0,1/2],\ [1/2,1/4,0],\ [1/2,3/4,0],\ [1/2,1/2,1/2]$$

Reciprocal Lattice, Brillouin Zone, Waves in Crystals

13

(13.1) Reciprocal Lattice

Show that the reciprocal lattice of a fcc (face-centered cubic) lattice is a bcc (body-centered cubic) lattice. Correspondingly, show that the reciprocal lattice of a bcc lattice is an fcc lattice. If an fcc lattice has conventional unit cell with lattice constant a, what is the lattice constant for the conventional unit cell of the reciprocal bcc lattice?

Consider now an orthorhombic face-centered lattice with conventional lattice constants a_1, a_2, a_3. What it the reciprocal lattice now?

Brief Solution

Say we have an fcc lattice in real space. This can be written as cubic with a basis $R_1 = [0,0,0]$, and $R_2 = [1/2,1/2,0]$ and $R_3 = [1/2,0,1/2]$ and $R_4 = [0,1/2,1/2]$ in units of the lattice constant a. In reciprocal space, we propose a basis for the reciprocal lattice which is $S_1 = (0,0,0)$ and $S_2 = (1/2,1/2,1/2)$ in units of the reciprocal cubic lattice constant $4\pi/a$. For these to be reciprocal, we must therefore have

$$e^{i2\pi R_i \cdot S_j} = 1$$

for all i and j which is easy to check is true. Further, we can show that given the fcc basis there is no third point that can be added to the bcc basis which would still have the same property. Similarly, given the bcc basis there is no fifth point we can add to the fcc basis.

For the orthorhombic face centered system one would similarly obtain a reciprocal lattice which is an orthorhombic body centered systems with basis vectors $4\pi/a_i$.

Detailed Solution

The more straightforward way to find the reciprocal lattice of a direct lattice is by construction. Let us start with the direct lattice of the BCC lattice which has primitive lattice vectors

$$\begin{aligned}\mathbf{a_1} &= [1,0,0]a\\ \mathbf{a_2} &= [0,1,0]a\\ \mathbf{a_3} &= [1/2,1/2,1/2]a\end{aligned}$$

we then construct the primitive lattice vectors of the reciprocal lattice via

$$\mathbf{b_i} = \frac{2\pi bfa_j \times \mathbf{a_k}}{\mathbf{a_1}\cdot\mathbf{a_2}\times\mathbf{a_3}}$$

with i,j,k cyclic. This gives

$$\begin{aligned}\mathbf{b_1} &= (1/2,0,-1/2)\frac{4\pi}{a}\\ \mathbf{b_2} &= (0,1/2,-1/2)\frac{4\pi}{a}\\ \mathbf{b_3} &= (0,0,1)\frac{4\pi}{a}\end{aligned}$$

we can then reassemble these vectors to give the standard primitive lattice vectors for FCC

$$\begin{aligned}\mathbf{b_1'} &= \mathbf{b_1}+\mathbf{b_3} = & (1/2,0,1/2)\frac{4\pi}{a}\\ \mathbf{b_2'} &= \mathbf{b_2}+\mathbf{b_3} = & (0,1/2,1/2)\frac{4\pi}{a}\\ \mathbf{b_3'} &= \mathbf{b_1}+\mathbf{b_2}+\mathbf{b_3} = & (1/2,1/2,0)\frac{4\pi}{a}\end{aligned}$$

which shows us tht the fcc lattice has lattice constant $4\pi/a$. NOTE about making this transformation from $\mathbf{b}$ into $\mathbf{b}'$. We are guaranteed that that $\mathbf{b}$ are primitive lattice vectors. We assemble them together with integer coefficients to make $\mathbf{b}'$. However we must also be able to reassemble the $\mathbf{b}'$ with integer coefficients to get back the $\mathbf{b}$ in order for this to be an allowed transformation from one set of primitive lattice vectors to another.

Slick Solution

Once one has read chapter 14 on scattering and selection rules, we simply note that the selection rules on miller indices tell us the form of the reciprocal lattice. For example, if the direct lattice is BCC, the selection rule is that $h+k+l$ is even. This means that either all h,k,l are even or two are odd and one is even. Thus if we write

$$\mathbf{G}(hkl) = \frac{4\pi}{a}\left(\frac{h}{2}\hat{x} + \frac{k}{2}\hat{y} + \frac{l}{2}\hat{z}\right)$$

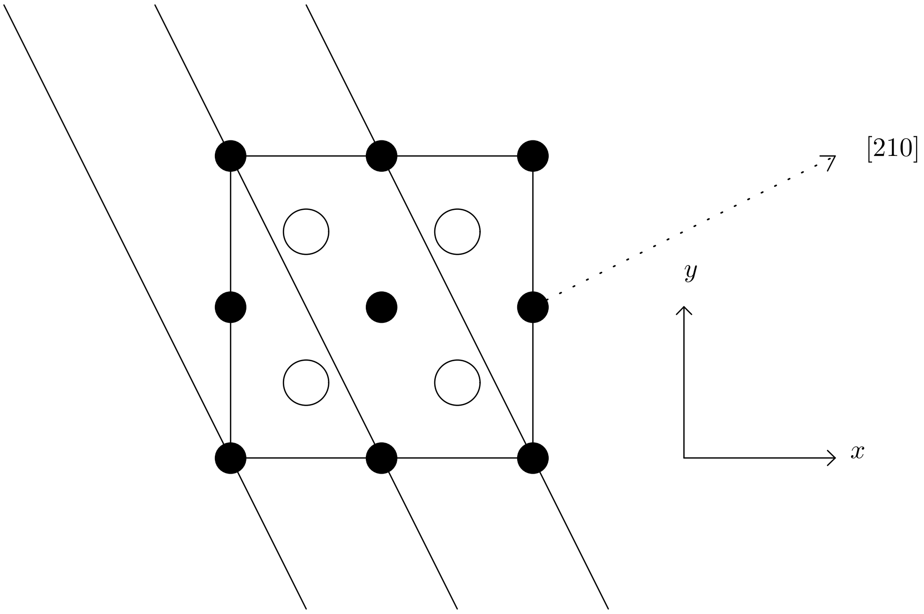
we must have either all $h/2, k/2, l/2$ integer or two half-odd integer and one integer. This is precisely the condition we would use to *define* an FCC lattice. The prefactor $4\pi/a$ then gives us the lattice constant.

Similarly in reverse, if the direct space lattice is FCC, the selection rule is h, k, l all even or all odd. This means $(h/2, k/2, l/2)$ all integer or all half-odd integer. This is precisely the condition for defining a BCC lattice.

The moral of this story is that scattering occurs when (h, k, l) represents a reciprocal lattice vector. The selection rules tell you when this is so.

(13.2) Lattice Planes

Consider the crystal shown in Exercise 12.3. Copy this figure and indicate the [210] direction and the (210) family of lattice planes.



(210) planes

NOTE: As drawn here this is a family of planes (it is a family of lattice planes for the corresponding simple cubic). For the FCC to be a family of lattice planes, it must have half the plane spacing so that it is called (420) and it cuts though every lattice point. So the question is not correctly written as it stands.

(13.3) Directions and Spacings of Crystal Planes

▷ ‡Explain briefly what is meant by the terms "crystal planes" and "Miller indices".

▷ Show that the general direction $[hkl]$ in a cubic crystal is normal to the planes with Miller indices (hkl).

▷ Is the same true in general for an orthorhombic crystal?

▷ Show that the spacing d of the (hkl) set of planes in a cubic crystal with lattice parameter a is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

▷ What is the generalization of this formula for an orthorhombic crystal?

A *crystal plane* is a plane which intersects at least three non-colinear (and therefore an infinite number of) points of the lattice.

Miller indices are a set of three integers which specify a set of parallel planes (or equivalently specify a vector in reciprocal space). If the axes of a lattice are mutually orthogonal , the Miller indices (hkl) specifies the reciprocal lattice vector $(2\pi)(h\hat{\mathbf{x}}/a_x+k\hat{\mathbf{y}}/a_y+l\hat{\mathbf{z}}/a_z$ where a_x, a_y and a_z are the length of the three basis vectors. In terms of lattice planes, one can determine the lattice vectors by picking any given plane from the family, and finding its intersection points with the three coordinate axes. These intersection points $(k_x, 0, 0)$ and $(0, k_y, 0)$ and $(0, 0, k_z)$ have the property that they are in the ratios

$$h : k : l = \frac{1}{k_x} : \frac{1}{k_y} : \frac{1}{k_z}$$

The actual values of $h : k : l$ are then the smallest integer values with these ratios. By convention note that negative numbers are denoted as an integer with a bar on top, ex $(1, 1, \bar{1})$ to denote $(1, 1, -1)$.

Let the basis vectors of the lattice be $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, assumed to be orthogonal. Let the lengths of these three lattice vectors be a, b, c respectively. The plane (hkl) can be defined as the plane connecting the points $\mathbf{a}/h$, $\mathbf{b}/k$ and $\mathbf{c}/l$. To construct a vector normal to this plane, take any two (noncolinear) vectors in this plane and take their cross product

$$\begin{aligned}\mathbf{n} &= (\mathbf{a}/h - \mathbf{b}/k) \times (\mathbf{a}/h - \mathbf{c}/l) \\ &= \frac{abc}{hkl}\left(\frac{h}{a^2}\mathbf{a} + \frac{k}{b^2}\mathbf{b} + \frac{l}{c^2}\mathbf{c}\right)\end{aligned}$$

This is only parallel to the vector [hkl] in the case of the cubic crystal $a = b = c$.

Much more succinctly one could also note that for orthogonal axes, $b_i = 2\pi/a_i$, and the family of lattice planes (hkl) is normal to the corresponding reciprocal lattice vector.

The unit normal in this direction is

$$\hat{\mathbf{n}} = \frac{1}{\sqrt{(h/a)^2 + (k/b)^2 + (l/c)^2}}\left(\frac{h}{a^2}\mathbf{a} + \frac{k}{b^2}\mathbf{b} + \frac{l}{c^2}\mathbf{c}\right)$$

To find the inter-planar spacing, take any vector that connects two adjacent planes and find the component in the direction of the normal to the plane. For example, the vector $\mathbf{a}/h$ connects two adjacent planes, and we can resolve it parallel to $\mathbf{n}$ by taking the dot product with the unit normal vector $\hat{\mathbf{n}}$. Thus we obtain

$$d_{hkl} = \hat{\mathbf{n}} \cdot \mathbf{a}/h = \frac{1}{\sqrt{(h/a)^2 + (k/b)^2 + (l/c)^2}} \tag{13.1}$$

with the case $a = b = c$ appropriate for cubic crystals.

Note: In cases where the axes are not orthogonal, this formula does not work.

(13.4) ‡Reciprocal Lattice

(a) Define the term Reciprocal Lattice.

(b) Show that if a lattice in 3d has primitive lattice vectors $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ then primitive lattice vectors for the reciprocal lattice can be taken as

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \tag{13.2}$$

$$\mathbf{b_2} = 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \tag{13.3}$$

$$\mathbf{b_3} = 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \tag{13.4}$$

What is the proper formula in 2d?

(c) Define tetragonal and orthorhombic lattices. For an orthorhombic lattice, show that $|\mathbf{b_j}| = 2\pi/|\mathbf{a_j}|$. Hence, show that the length of the reciprocal lattice vector $\mathbf{G} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$ is equal to $2\pi/d$, where d is the spacing of the (hkl) planes (see question 13)

(a) Given a lattice of points (in 3d it would look like $\mathbf{R}_{[uvw]} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$ with $[uvw]$ integers), the reciprocal lattice is defined by the set of points in $\mathbf{k}$ space such that

$$e^{i\mathbf{k}\cdot\mathbf{R}} = 1$$

for all points $\mathbf{R}$ in the lattice . Note that this set of points forms a lattice of values of $\mathbf{k}$.

(b) If we take

$$\begin{aligned} \mathbf{b_1} &= 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \\ \mathbf{b_2} &= 2\pi \frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \\ \mathbf{b_3} &= 2\pi \frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \end{aligned} \tag{13.5}$$

Then we can show the key formula

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}.$$

If these are our basis vectors for the reciprocal lattice, we then have a general reciprocal lattice point given by

$$\mathbf{G}_{hkl} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3} \tag{13.6}$$

with h, k, l integers. It is trivial to then see that

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1 \tag{13.7}$$

for any lattice vector $\mathbf{R}$ and any reciprocal lattice vector $\mathbf{K}$. However, this does not quite prove the desired statement. What it proves is that vector $\mathbf{K}$ of the form of Eq. 13.6 are in the reciprocal lattice. We need to show that there are no other vectors in the reciprocal lattice as well so that $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ can indeed be taken as the basis.

To show this, consider an arbitrary vector $\mathbf{K}$ of the form of Eq. 13.6 but do not require that h, k, l are integers. Given an arbitrary $\mathbf{R}_{uvw}$ of the real space lattice, in order that Eq. 13.7 is satisfied, we must have

$$uk + vh + wl = \text{integer}$$

for this to be true for *arbitrary* u, v, w which are integers, we can conclude that k, h, l are integers.

We can derive the 2d analogous formula by setting $\mathbf{a}_3 = \hat{\mathbf{z}}$ the unit vector normal to the plane, more conveniently written as

$$\begin{aligned} \mathbf{b_1} &= 2\pi \frac{\mathbf{a_2} \times \hat{\mathbf{z}}}{\hat{\mathbf{z}} \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} \\ \mathbf{b_2} &= 2\pi \frac{\hat{\mathbf{z}} \times \mathbf{a}_1}{\hat{\mathbf{z}} \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} \end{aligned}$$

(c) A tetragonal lattice is a lattice (in 3d) where all three basis vectors are normal to each other, and two of them are the same length but the third is a different length. An orthorhombic lattice is a lattice (in 3d) where all three basis vectors are normal to each other and all three have different lengths. (Note: crystals may have orthorhombic or tetragonal *symmetry* even if lattice constants in the three directions are all equal. The symmetry of a crystal has to do with whether it looks the same under various types of rotations. An orthorhombic crystal does not look the same under the three 90 degree rotations – this may be the case even if all three lattice constants are the same).

For an orthorhombic crystal, without loss of generality, let us write $\mathbf{a}_1 = a_1\hat{\mathbf{x}}$ and $\mathbf{a}_2 = a_2\hat{\mathbf{y}}$ and $\mathbf{a}_3 = a_3\hat{\mathbf{z}}$. We then just use the above formula Eq. 13.5 to obtain

$$\begin{aligned} \mathbf{b_1} &= 2\pi \frac{a_2 a_3}{a_1 a_2 a_3} \hat{\mathbf{y}} \times \hat{\mathbf{z}} = 2\pi\hat{\mathbf{x}}/a_1 \\ \mathbf{b_2} &= 2\pi \frac{a_2 a_3}{a_1 a_2 a_3} \hat{\mathbf{z}} \times \hat{\mathbf{x}} = 2\pi\hat{\mathbf{y}}/a_2 \\ \mathbf{b_3} &= 2\pi \frac{a_2 a_3}{a_1 a_2 a_3} \hat{\mathbf{x}} \times \hat{\mathbf{y}} = 2\pi\hat{\mathbf{z}}/a_3 \end{aligned}$$

So $|\mathbf{b_i}| = \mathbf{2}\pi/|\mathbf{a_i}|$. Thus the length of $\mathbf{G} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3}$ is given by

$$|G_{hkl}| = \sqrt{h^2|\mathbf{b}_1|^2 + k^2|\mathbf{b}_2|^2 + l^2|\mathbf{b}_3|^2} = \sqrt{(2\pi h/a_1)^2 + (2\pi k/a_2)^2 + (2\pi l/a_3)^2} = 2\pi/d_h$$

as given in Eq. 13.1.

(13.5) More Reciprocal Lattice

A two-dimensional rectangular crystal has a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm.

(a) Draw to scale a diagram of the reciprocal lattice.

▷ Label the reciprocal lattice points for indices in the range $0 \leq h \leq 3$ and $0 \leq k \leq 3$.

(b) Draw the first and second Brillouin zones using the Wigner–Seitz construction.

The reciprocal lattice vectors are $\mathbf{b}_1 = 2\pi\hat{\mathbf{x}}/|a_1|$, and $\mathbf{b}_2 = 2\pi\hat{\mathbf{y}}/|a_2|$. Their magnitudes are

$$|\mathbf{b}_1| = 13.4\text{nm}^{-1} \qquad |\mathbf{b}_2| = 18.4\text{nm}^{-1}$$

(a) A diagram of the reciprocal lattice is given in the figure.

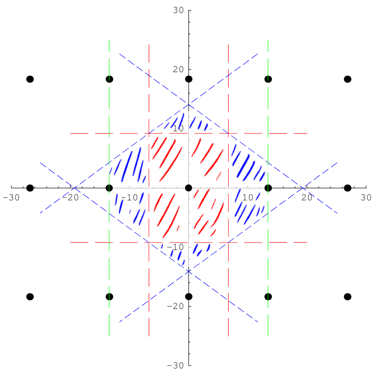


Fig. 13.1 Figures for problem 13. First Two Brillouin Zones. Red is the 1st Zone. Blue is the 2nd zone.

To find the Brillouin zones, one first constructs perpendicular bisectors between the origin and any given lattice point (shown as dotted lines on the plot). Then starting at the origin, the region one can get to without crossing a dotted line is the first zone. Crossing only one dotted line gets one to the second zone. etc.

(13.6) Brillouin Zones

(a) Consider a cubic lattice with lattice constant a. Describe the first Brillouin zone. Given an arbitrary wavevector $\mathbf{k}$, write an expression for an equivalent wavevector within the first Brillouin zone (there are several possible expressions you can write).

(b) Consider a triangular lattice in two dimensions (primitive lattice vectors given by Eqs. 12.3). Find the first Brillouin zone. Given an arbitrary wavevector $\mathbf{k}$ (in two dimensions), write an expression for an equivalent wavevector within the first Brillouin zone (again there are several possible expressions you can write).

(a) The reciprocal lattice of a cubic lattice with lattice constant a is a cubic lattice with lattice constant $2\pi/a$. The first Brillouin zone is a cube centered around the origin in reciprocal space (0,0,0), with side length $2\pi/a$. It spans $k_x, k_y, k_z \in [-\pi/a, \pi/a]$. Given an arbitrary $\mathbf{k} = (k_x, k_y, k_z)$ we can write the equivalent wavevector as $(k'_x, k'_y, k_z)'$ where

$$k'_j = k_j - [[(k_j + \pi/a)/(2\pi/a)]] * 2\pi/a \qquad (13.8)$$

with $j = x, y, z$ and [[ ]] is the floor function – meaning the greatest integer less than its argument. The point of Eq. 13.8 is that it takes k in units of the reciprocal lattice constant $(2\pi/a)$ and returns a number between -1/2 and +1/2 of the reciprocal lattice constant by appropriately adding or subtracting integer units of $2\pi/a$.

(b) Start with the primitive lattice vectors

$$\begin{aligned}\mathbf{a_1} &= a\hat{\mathbf{x}} \\ \mathbf{a_2} &= (a/2)\hat{\mathbf{x}} + (a\sqrt{3}/2)\hat{\mathbf{y}}\end{aligned}$$

We need to find vectors $\mathbf{b_1}, \mathbf{b_2}$ such that $\mathbf{a_i} \cdot \mathbf{b_j} = 2\pi\delta_{i,j}$. One way to do this is to use the usual 3d formula

$$\begin{aligned}\mathbf{b_1} &= 2\pi\frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \\ \mathbf{b_2} &= 2\pi\frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})} \\ \mathbf{b_3} &= 2\pi\frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}\end{aligned}$$

then assigning $\mathbf{a_3} = \hat{\mathbf{z}}$. The denominator is $a^2\sqrt{3}/2$. Thus we have

$$\begin{aligned}\mathbf{b_1} &= 2\pi[(a\sqrt{3}/2)\hat{\mathbf{x}} - (a/2)\hat{\mathbf{y}}]/(a^2\sqrt{3}/2) = (2\pi/a)[\hat{\mathbf{x}} - (\sqrt{3}/3)\hat{\mathbf{y}}] \\ \mathbf{b_2} &= 2\pi\hat{\mathbf{y}}a/(a^2\sqrt{3}/2) = (2\pi/a)\hat{\mathbf{y}}(2\sqrt{3}/3)\end{aligned}$$

These form the primitive lattice vectors of a triangular lattice in k-space. The first Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice — which is a hexagon centered around zero wavevector (see fig 12.6 of the book).

Two write a formula that translates any $\mathbf{k}$ into the first Brillouin zone, we first write any k point in terms of the primitive lattice vectors

$$\mathbf{k} = \alpha_1\mathbf{b_1} + \alpha_2\mathbf{b_2}$$

We are going to need to solve for α_i in terms of $\mathbf{k}$. To do this we write

$$\begin{aligned}\mathbf{k} \cdot \mathbf{b_1} &= \alpha_1|\mathbf{b_1}|^{\mathbf{2}} + \alpha_{\mathbf{2}}\mathbf{b_1} \cdot \mathbf{b_2} \\ \mathbf{k} \cdot \mathbf{b_2} &= \alpha_1\mathbf{b_1} \cdot \mathbf{b_2} + \alpha_2|\mathbf{b_2}|^{\mathbf{2}}\end{aligned}$$

and we will want to solve for the αs. In this particular case, things are quite easy since $|\mathbf{b_1}|^2 = |\mathbf{b_2}|^2 = -2\mathbf{b_1} \cdot \mathbf{b_2} = (2\pi/a)^2(4/3)$. So this becomes

$$\begin{aligned}\beta\mathbf{k} \cdot \mathbf{b_1} &= \alpha_1 - \alpha_2/2 \\ \beta\mathbf{k} \cdot \mathbf{b_2} &= -\alpha_1/2 + \alpha_2\end{aligned}$$

where we have defined

$$\beta = \frac{3}{4}\frac{a^2}{(2\pi)^2}$$

Solving this system of equations we obtain

$$\begin{aligned}\alpha_1 &= (\beta/3)(2\mathbf{k} \cdot \mathbf{b_1} + \mathbf{k} \cdot \mathbf{b_2}) \\ \alpha_2 &= (\beta/3)(\mathbf{k} \cdot \mathbf{b_1} + 2\mathbf{k} \cdot \mathbf{b_2})\end{aligned}$$

Now to obtain α within the first brillouin zone we need to shift both α's by integers until they lie in the range $[-1/2, 1/2]$. To do this we write

$$\alpha'_j = \alpha_j - [[\alpha_j + 1/2]]$$

again with [[ ]] being the floor function. Once we have α''s we construct

$$\mathbf{k}' = \alpha'_1 \mathbf{b_1} + \alpha'_2 \mathbf{b_2}$$

which is now within the first Brillouin zone.

(13.7) Number of States in the Brillouin Zone

A specimen in the form of a cube of side L has a primitive cubic lattice whose mutually orthogonal fundamental translation vectors (primitive lattice vectors) have length a. Show that the number of different allowed $\mathbf{k}$-states within the first Brillouin zone equals the number of primitive unit cells forming the specimen. (One may assume periodic boundary conditions, although it is worth thinking about whether this still holds for hard-wall boundary conditions as well.)

We are given a cubic lattice with lattice constant a and an overall size L on a size. The number of atoms in this sample are $N = (L/a)^3$. It is simplest to assume periodic boundary conditions. Since $e^{ik_x(x+L)} = e^{ik_x x}$ we must have $k_x = 2\pi n/L$ for n an integer. Thus (considering all three directions) there is one eigenstate per volume $(2\pi/L)^3$ in k-space.

The first Brillouin zone extends from $-\pi/a \le k_x, k_y, k_z \le \pi/a$. This has volume in k-space of $(2\pi/a)^3$. Dividing this by the volume occupied by one eigenstate gives a total of $(L/a)^3$ states in the first Brillouin zone.

This agreement is not coincidental. If one thinks in a tight-binding or atomic orbital picture, there should be exactly one orbital per atom per band when hopping is turned off. Once hopping is turned back on, each atomic orbital spreads into a band that fills the Brillouin zone, but the total number of states stays constant.

One can also consider the same problem with hard wall boundary conditions, although it is less convenient. In this case the eigenstates are not of the form e^{ikx} but are rather $\sin(kx)$ where $k > 0$, so one is not really talking about pure plane waves. In this case the analogue of the Brillouin zone goes from $0 \le k_x, k_y, k_z \le \pi/a$, but the density of k states is doubled, $k = \pi/L$ in each direction, so the total number of states remains the same as using periodic boundary conditions.

(13.8) Calculating Dispersions in $d > 1$*
(a) In Exercises 9.8 and 11.9 we discussed dispersion relations of systems in two dimensions (if you have not already solved those exercises, you should do so now).

▷ In Exercise 11.9 describe the Brillouin zone (you may assume perpendicular lattice vectors with length a_1 and a_2). Show that the tight-binding dispersion is periodic in the Brillouin zone. Show that the dispersion curve is always flat crossing a zone boundary.

▷ In Exercise 9.8, describe the Brillouin zone. Show that the phonon dispersion is periodic in the Brillouin zone. Show that the dispersion curve is always flat crossing a zone boundary.

(b) Consider a tight binding model on a three-dimensional fcc lattice where there are hopping matrix elements $-t$ from each site to each of the nearest-neighbor sites. Determine the energy spectrum $E(\mathbf{k})$ of this model. Show that near $\mathbf{k} = \mathbf{0}$ the dispersion is parabolic.

(a) [First see solutions for 9.8 and 11.9]

In Exercise 11.9, for a rectangular lattice with lattice vectors of length a_1 and a_2 the reciprocal lattice is rectangular with lattice vectors of length $b_1 = (2\pi)/a_1$ and $b_2 = (2\pi)/a_2$. The Brillouin zone is hence a rectangle extending between $k_x \in [-\pi/a_1, \pi/a_1]$ and $k_y \in [-\pi/a_2, \pi/a_2]$. Given the derived dispersion

$$E = \epsilon_0 - 2t_1 \cos(k_x a_1) - 2t_2 \cos(k_y a_2)$$

at the zone boundary, the cos is at its maximum, and its derivative is zero. Thus the dispersion is always flat approaching the zone boundary.

In Exercise 9.8 we have a triangular lattice, whose reciprocal lattice is also triangular and has a Wigner-Seitz cell which is hexagonal (see exercise 13.6.b also). Note also the figures shown in the solution of 9.8 which clearly show the hexagonal periodicity of the dispersion curve. Note that the dispersion must be symmetric as $\mathbf{k}$ approaches the zone boundary. Let the zone boundary wavevector be $\mathbf{b_i}/2 + \mathbf{k}_\perp$ where $\mathbf{k}_\perp \cdot \mathbf{b_i} = 0$. Imagine approaching the zone boundary via $\mathbf{k} = \alpha\mathbf{b_i}/2 + \mathbf{k}_\perp$ and taking α to one. Note that the dispersion must be symmetric around $\alpha = 1$ since (by reflection symmetry of the problem) the frequency at $\mathbf{k}$ is the same as the frequency at $\mathbf{k}' = -\alpha\mathbf{b_i}/2 + \mathbf{k}_\perp$. However, one can translate this by a reciprocal lattice vector to get $(2-\alpha)\mathbf{b_i}/2 + \mathbf{k}_\perp$ which is the same point reflected around the zone boundary. Thus, so long as the dispersion does not have a cusp at the zone boundary, it must have zero derivative.

Recall from Eq. 9.8 that the derived freuquency spectrum is

$$\omega^2 = \frac{2\kappa}{m}\left(S_1 + S_2 + S_3 \pm \sqrt{S_1^2 + S_2^2 + S_3^2 - S_1S_2 - S_1S_3 - S_2S_3}\right)$$

where

$$S_i = \sin^2(\frac{\mathbf{k}\cdot\mathbf{a_i}}{2})$$

where $\mathbf{a_i}$ are three independent vectors along the lattice. In terms of primitive lattice vectors here we can take $\mathbf{a_1}$ and $\mathbf{a_2}$ to be primitive lattice vector, and then $\mathbf{a_3} = \mathbf{a_2} - \mathbf{a_1}$.

The frequency is an analytic function in $\mathbf{k}$ so long as the argument of the square-root is nonzero. By rewriting the argument as

$$\frac{1}{2}\left[(S1-S2)^2+(S2-S3)^2+(S3-S1)^2\right]$$

it is clear the argument must be nonzero except at $\mathbf{k}=\mathbf{0}$. Thus we can conclude that the dispersion is analytic and symmetric around the zone boundary and therefore must have zero slope. This may seem like a bit of a cheat, but it is perfectly rigorous.

For those who would prefer to see this statment proven a bit more directly, we take the following approach. Let us start with the primitive lattice vectors

$$\begin{aligned}\mathbf{a_1} &= a\hat{\mathbf{x}} \\ \mathbf{a_2} &= (a/2)\hat{\mathbf{x}}+(a\sqrt{3}/2)\hat{\mathbf{y}}\end{aligned}$$

Recall that the reciprocal lattice vectors (see 13.6.b) are given by

$$\begin{aligned}\mathbf{b_1} &= 2\pi[(a\sqrt{3}/2)\hat{\mathbf{x}}-(a/2)\hat{\mathbf{y}}]/(a^2\sqrt{3}/2)=(2\pi/a)[\hat{\mathbf{x}}-(\sqrt{3}/3)\hat{\mathbf{y}}] \\ \mathbf{b_2} &= 2\pi\hat{\mathbf{y}}a/(a^2\sqrt{3}/2)=(2\pi/a)\hat{\mathbf{y}}(2\sqrt{3}/3)\end{aligned}$$

For simplicity let us imagine approachig the zone boundary

$$\mathbf{k}=\alpha\mathbf{b_2}/2+\mathbf{k}_\perp$$

(the other zone boundaries will be the same by symmetry). Here the direction orthogonal to $\mathbf{b_2}$ is $\mathbf{b_1}+\mathbf{b_2}/2$. So we can write $\mathbf{k}_\perp=\beta(\mathbf{b_1}+\mathbf{b_2}/2)$ for some value of β. We then have (using $\mathbf{a_i}\cdot\mathbf{b_j}=2\pi\delta_{ij}$ for $i,j\in 1,2$)

$$\begin{aligned}\mathbf{k}\cdot\mathbf{a_1} &= (\beta+\alpha)\pi \\ \mathbf{k}\cdot\mathbf{a_2} &= \beta 2\pi \\ \mathbf{k}\cdot\mathbf{a_3} &= (\beta-\alpha)\pi\end{aligned}$$

Now let us examine the terms in the dispersion. In particular we are concerned with the dependence of the dispersion on α near $\alpha=1$. Again all we need to do is to show that the dispersion is symmetric and analytic around $\alpha=1$. Here S_2 is independent of α so we are not concerned with that piece. Using $\sin^2(x/2)=(1-cos(x))/2$ we have that

$$\begin{aligned}S_1 &= [1-\cos((\beta+\alpha)\pi)]/2 \\ S_2 &= [1-\cos((\beta-\alpha)\pi)]/2\end{aligned}$$

The cos is periodic in $\alpha\to\alpha\pm 2$, and reflection of α around 1 (i.e., $\alpha\to 2-\alpha$) turns S_1 into S_2, hence leaves the freqeuncy unchanged. Thus we have the dispersion symmetric and analytic around the zone boundary, thus having zero slope.

(b) For an fcc lattice, if the conventional unit cell has lattice constant a, the vectors to the 12 nearest neighbors of a lattice point are given by

(see exercise 12.2)

$$\begin{aligned}&[\pm 1, \pm 1, 0]a/2\\&[\pm 1, 0, \pm 1]a/2\\&[0, \pm 1, \pm 1]a/2\end{aligned}$$

Thus we have the schroedinger equation (setting the onsite energy ϵ_0 to zero for simplicity)

$$E\psi(\mathbf{r}) = -t\sum_{\mathbf{u}} \psi(\mathbf{r}+\mathbf{u})$$

where the sum is over $\mathbf{u}$ being these 12 vectors. Using the usual ansatz $\psi(\mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$ we obtain

$$E = -t \sum_{\alpha=\pm 1, \beta=\pm 1} \left[e^{i\mathbf{k}\cdot[\alpha,\beta,0]a/2} + e^{i\mathbf{k}\cdot[\alpha,0,\beta]a/2} + e^{i\mathbf{k}\cdot[0,\alpha,\beta]a/2} \right]$$

or

$$E = -4t\left[\cos(k_x a/2)\cos(k_y a/2) + \cos(k_x a/2)\cos(k_z a/2) + \cos(k_y a/2)\cos(k_z a/2)\right]$$

Expanding around $\mathbf{k} = 0$ to second order we obtain

$$E = -12t + t\left[k_x^2 + k_y^2 + k_z^2\right](a^2) + \ldots$$

which is parabolic as claimed.

Wave Scattering by Crystals

14

(14.1) Reciprocal Lattice and X-ray Scattering Consider the lattice described in Exercise 13.5 (a two-dimensional rectangular crystal having a unit cell with sides $a_1 = 0.468$ nm and $a_2 = 0.342$ nm). A collimated beam of monochromatic X-rays with wavelength 0.166 nm is used to examine the crystal.

(a) Draw to scale a diagram of the reciprocal lattice.

(b) Calculate the magnitude of the wavevectors $\mathbf{k}$ and $\mathbf{k}'$ of the incident and reflected X-ray beams, and hence construct on your drawing the "scattering triangle" corresponding to the Laue condition $\Delta\mathbf{k} = \mathbf{G}$ for diffraction from the (210) planes (the scattering triangle includes $\mathbf{k}$, $\mathbf{k}'$ and $\Delta\mathbf{k}$).

A diagram of the reciprocal lattice is given in the figure. The scattering triangle is the triangle such that $|\mathbf{k}| = |\mathbf{k}'|$ and $\mathbf{k} + \mathbf{G} = |\mathbf{k}'|$ (Note for fixed $\mathbf{G}$ there are two such possible triangles).

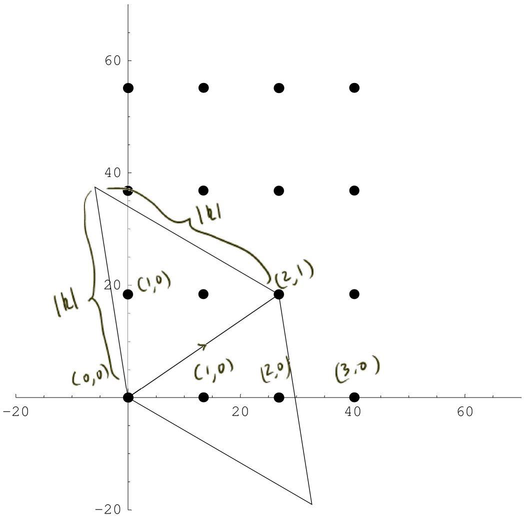


Fig. 14.1 A picture of the reciprocal Lattice with the scattering triangle for the (210) reciprocal wavevector.

(14.2) ‡ X-ray scattering II
$BaTiO_3$ has a primitive cubic lattice and a basis with atoms having fractional coordinates

Ba	$[0,0,0]$		
Ti	$[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$		
O	$[\frac{1}{2},\frac{1}{2},0]$,	$[\frac{1}{2},0,\frac{1}{2}]$,	$[0,\frac{1}{2},\frac{1}{2}]$

▷ Sketch the unit cell.
▷ Show that the X-ray structure factor for the $(00l)$ Bragg reflections is given by

$$S_{(hkl)} = f_{Ba} + (-1)^l f_{Ti} + \left[1 + 2(-1)^l\right] f_O$$

where f_{Ba} is the atomic form factor for Ba, etc.

▷ Calculate the ratio $I_{(002)}/I_{(001)}$, where $I_{(hkl)}$ is the intensity of the X-ray diffraction from the (hkl) planes. You may assume that the atomic form factor is proportional to atomic number (Z), and neglect its dependence on the scattering vector. $(Z_{\mathrm{Ba}} = 56,\ \ Z_{\mathrm{Ti}} = 22,\ \ Z_{\mathrm{O}} = 8.)$

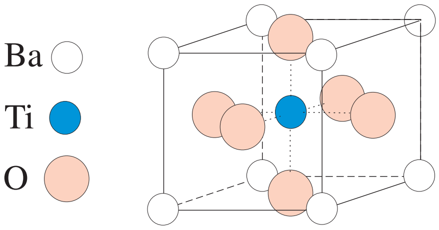


Fig. 14.2 Unit cell of $BaTiO_3$

The X-ray structure factor is given by

$$S_{(hkl)} = \sum_d f_d e^{i\mathbf{k}_{(hkl)}\cdot\mathbf{R}_d} = \sum_d f_d e^{2\pi i(hx_d + ky_d + lz_d)}$$

where $\mathbf{R}_d = (x_d, y_d, z_d)$ are the positions of atom d in the unit cell, and f_d it the corresponding form factor (which we take to be proportional to Z_d). If we are interested in $(00l)$ we set $h = k = 0$ and obtain

$$S_{(00l)} = f_{Ba} + (-1)^l f_{Ti} + [1 + 2(-1)^l] f_O$$

The Bragg peak intensity is proportional to the square of the structure factor (times a multiplicity factor, but the multiplicity for all (001) are the same!), thus we obtain

$$\frac{I_{002}}{I_{001}} = \frac{(f_{Ba} + f_{Ti} + 3f_O)^2}{(f_Ba - f_{Ti} - f_O)^2} \approx 15.4$$

In reality the form factor depends on the scattering vector, and the variation is different from each atom, so this is just an approximation.

(14.3) ‡ X-ray scattering and Systematic Absences

(a) Explain what is meant by "Lattice Constant" for a cubic crystal structure.

(b) Explain why X-ray diffraction may be observed in first order from the (110) planes of a crystal with a body-centered cubic lattice, but not from the (110) planes of a crystal with a face-centered cubic lattice.

▷ Derive the general selection rules for which planes are observed in bcc and fcc lattices.

(c) Show that these selection rules hold independent of what atoms are in the primitive unit cell, so long as the lattice is bcc or fcc respectively.

(d) A collimated beam of monochromatic X-rays of wavelength 0.162 nm is incident upon a powdered sample of the cubic metal palladium. Peaks in the scattered X-ray pattern are observed at angles of 42.3°, 49.2°, 72.2°, 87.4°, and 92.3° from the direction of the incident beam.

▷ Identify the lattice type.

▷ Calculate the lattice constant and the nearest-neighbor distance.

▷ If you assume there is only a single atom in the basis does this distance agree with the known data that the density of palladium is 12023 kg m^{-3}? (Atomic mass of palladium = 106.4.)

(e) How could you improve the precision with which the lattice constant is determined. (For one suggestion, see Exercise 14.10.)

(a) For a cubic lattice, the lattice constant is the distance between one lattice point and the nearest neighbor lattice point.

(b) The (110) planes of a body-centred cubic lattice contain all the lattice points, whereas the (110) planes of a crystal with a face-centred cubic lattice contain only half the lattice points. The remaining fcc lattice points lie on a set of planes half-way in between the (110) planes, and so X-rays reflected from these planes interfere destructively with X-rays reflected from the (110) planes.

Let us see this more analytically now:

We view both the bcc and fcc lattices as being a cubic lattice with a basis. For a cubic lattice, we must have $\mathbf{k}_{hkl} = (2\pi/a)(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}})$ (or in other words we consider reciprocal lattice vectors (h, k, l).)

Generally we sum over lattice points $\mathbf{R_i}$ in a unit cell to get the structure factor

$$S_{(hkl)} \sim \sum_{\mathbf{R}_i} e^{i\mathbf{R_i}\cdot\mathbf{k}_{(hkl)}}$$

The bcc lattice is a cubic lattice with a basis (0,0,0) and (1/2,1/2,1/2). So we obtain

$$S^{bcc}_{(hkl)} \sim 1 + e^{i\mathbf{k}_{(hkl)}\cdot[(1/2)\hat{\mathbf{x}}+(1/2)\hat{\mathbf{y}}+(1/2)\hat{\mathbf{z}}]} = 1 + (-1)^{h+k+l}$$

This is only nonzero when $h + k + l =$ even.

The fcc lattice is a cubic lattice with with basis (0,0,0) and (1/2,1/2,0) and (1/2,0,1/2) and (0,1/2,1/2). Analogously we obtain

$$S^{fcc}_{(hkl)} \sim 1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}$$

This is only nonzero when h, k, l are either all even or all odd.

Note that these selection rules hold for an orthorhombic lattice as well as for cubic (nowhere did we use the lattice constants in the three directions!).

(c) This is the general principle that you multiply a lattice by a basis. Suppose we have a Bravais lattice (either fcc or bcc) and then we have a basis of m atoms which are at positions $\mathbf{r}_j$ $(j = 1, \ldots m)$ with respect to the lattice points. These atoms may have scattering form factors f_j as well.

As above, we treat the Bravais lattice as a cubic lattice with a basis $\mathbf{R_i}$ (i=1,2 for bcc and $i = 1 \ldots 4$ for fcc). So positions of all of the atoms ($2m$ or $4m$ of them) in the full cubic unit cell can be written as

$$\mathbf{R}_{ij} = \mathbf{R}_i + \mathbf{r}_j$$

Writing the structure factor

$$S_{(hkl)} = \sum_{i,j} f_j e^{i\mathbf{k}_{(hkl)}\mathbf{R}_{ij}} = \sum_j f_j \left[\sum_i e^{i\mathbf{k}_{(hkl)}\mathbf{R}_i} \right] e^{i\mathbf{k}_{(hkl)}\mathbf{r}_j} \qquad (14.1)$$

The factor inside the brackets is exactly the structure factor for the Bravais lattice as calculated above. So if the fcc structure factor vanishes, then the structure will also vanish for any lattice having an fcc lattice with any basis.

(d) Note that the angle given is 2θ (the full deflection angle)! We are given 2θ then we use Bragg's law $\lambda = 2d\sin\theta$ to get the distance between lattice planes. We then examine the ratio's between these distances.

2θ	$d = \lambda/(2\sin\theta)$	$(d_{max}/d)^2$	$a_{estimate} = d\sqrt{h^2+k^2+l^2}$
42.3°	.224 nm	1	.389 nm
49.2°	.195 nm	1.33	.389 nm
72.2°	.137 nm	2.66	.389 nm
87.4°	.117 nm	3.67	.389 nm
92.3°	.112 nm	4.00	.389 nm

we see that the values of $1/d^2$ are in ratios 3:4:8:11:12. Recall (see problem 13.3) that for a cubic lattice $(a^2/d^2) = h^2 + k^2 + l^2$. So the observed peaks are of the types (1,1,1), (2,0,0), (2,2,0), (1,1,3), and (2,2,2). These are all even or all odd, which is characteristic of the fcc lattice. All measured scattering points give the same estimate of the lattice constant a to three digits (which is the same number of digits that the measurement contains... so no higher accuracy estimate can be made from this data).

$$\frac{m^3}{12023\,kg}\,\frac{.1064\,kg}{6.022\times10^{23}\,atoms} = 1.4682\times10^{-29}m^3/atom$$

Then for an fcc there are 4 atoms per unit cell, so the volume of the unit cell is $5.872 \times 10^{-29}m^3$. The cube root of this gives 3.887 nm which is in good agreement. An equivalent calculation is to calculate the density based on the lattice constant

$$\frac{4 * .1064\,kg}{6.022 \times 10^{23}\,atoms}\left(\frac{1}{.389 \times 10^{-9}m}\right)^3 = 12006\,kg/m^3$$

in good agreement.

(e) to improve the precision of the measurement one would need to obtain more "digits" of resolution in the measurement of the angle. There are several things that will help this. From Bragg's law $d \sim 1/\sin\theta$ so

$$\frac{1}{d}\frac{\partial d}{\partial \theta} = \cot\theta$$

So if there is an error in measurement of θ one ends up with a fractional error in d given by

$$\delta \log d = (\cot\theta)(\delta\theta)$$

As a result, error is minimized if one can work as close as possible to scattering angle of 90 degrees (See exercise 14.10).

In addition some experimental issues can be listed. A higher brightness source will frequently reduce the noise and make the signal easier to analyze. Better columnation will make measurements of angle more precise. At least as important is the calibration of the device that measures the angles! Defining the wavelength λ more precisely becomes necessary at some point. Temperature control is necessary since lattice constants do change as a function of temperature due to thermal expansion.

(14.4) ‡ Neutron Scattering

(a) X-ray diffraction from sodium hydride (NaH) established that the Na atoms are arranged on a face-centered cubic lattice.

▷ Why is it difficult to locate the positions of the H atoms using X-rays?

The H atoms were thought to be displaced from the Na atoms either by $[\frac{1}{4},\frac{1}{4},\frac{1}{4}]$ or by $[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$, to form the ZnS (zincblende) structure or NaCl (sodium chloride) structure, respectively. To distinguish these models a neutron powder diffraction measurement was performed. The intensity of the Bragg peak indexed as (111) was found to be much larger than the intensity of the peak indexed as (200).

▷ Write down expressions for the structure factors $S_{(hkl)}$ for neutron diffraction assuming NaH has

(i) the sodium chloride (NaCl) structure

(ii) the zinc blende (ZnS) structure.

▷ Hence, deduce which of the two structure models is correct for NaH. (Nuclear scattering length of Na $= 0.363 \times 10^5$nm; nuclear scattering length of H $= -0.374 \times 10^5$ nm.)

(b) How does one produce monochromatic neutrons for use in neutron diffraction experiments?

▷ What are the main differences between neutrons and X-rays?

▷ Explain why (inelastic) neutron scattering is well suited for observing phonons, but X-rays are not.

[This problem is based on a classic experiment by Shull et al, who later won a Nobel prize for his work on neutron scattering]

Note, the scattering length should be in units of 10^{-5} nm not 10^5 nm. It doesn't change the problem much though.

It is difficult to see H atoms with X-rays since the form factor (amplitude) of scattering is proportional to the charge of the nucleus (the atomic number), and the charge of H is very small.

From Eq. 14.1 above we have

$$S_{(hkl)} = \left(\sum_i e^{i\mathbf{k}_{(hkl)}\mathbf{R}_i} \right) \left(\sum_j b_j e^{i\mathbf{k}_{(hkl)}\mathbf{r}_j} \right)$$

where j are the elements of the basis and i are the 4-elements of the fcc lattice basis when fcc is viewed as a cubic lattice with a basis. Here I have replaced f_j by b_j which is the conventional notation for the scattering length (which is analogous to the form factor in X-rays) in neutron scattering. Note that the first factor in brackets is the scattering from the fcc lattice which always gives (See problem 14)

$$S^{fcc}_{hkl} = (1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)})$$

For the case of the NaCl structure, we have a basis of Na at [0,0,0] and H at [1/2,1/2,1/2]. So we obtain

$$S_{(hkl)} = (1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)})(b_{Na} + b_H e^{i\pi(h+k+l)})$$

For the case of the ZnS structure we have a basis of Na at [0,0,0] and H at [1/4,1/4,1/4] so we obtain

$$S_{(hkl)} = (1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)})(b_{Na} + b_H e^{i(\pi/2)(h+k+l)})$$

The powder scattering intensity is proportional to the structure factor squared times a multiplicity factor that counts how many symmetry related vectors give the same scattering pattern. The multiplicity of (111) is 8 (since each factor of 1 could have been $\bar{1}$), whereas the multiplicity of (200) is 6 since the 2 could be of either sign, and any one of the 3 entries could contain the 2.

Thus we obtain in the NaCl case a ratio of scattering intensities

$$\frac{I_{(111)}}{I_{(200)}} = \frac{(b_{Na} - b_H)^2}{(b_{Na} + b_H)^2} \frac{8}{6} = 6000$$

whereas in the ZnS case we have

$$\frac{I_{(111)}}{I_{(200)}} = \frac{(b_{Na}^2 + b_H^2)}{(b_{Na} - b_H)^2} \frac{8}{6} = 0.67$$

Thus we conclude that NaH has NaCl structure.

(b) Two typical schemes for producing monochromatic neutrons. (1) time of flight (a "chopper") can select a particular velocity (2) Bragg scattering of a given angle off of a crystal can select a particular wavelength.

The main things to know about the differences between X-rays and neutrons are:

X-rays are scattered by electrons. The electromagnetic interaction is relatively strong, and so X-rays typically penetrate only a few microns into a sample. The intensity of scattering varies with the atomic form factor $f(\Delta\mathbf{k})$, which approximately scales with the number of electrons in the atom.

Neutrons, on the other hand, are electrically neutral, and so interact weakly with matter. They penetrate typically a few cm into materials. Neutrons may scatter from nuclei (via the strong nuclear force) or unpaired electrons (via the magnetic dipole-dipole interaction). The diffraction theory is the same as for X-rays, except that for scattering from nuclei the atomic form factor $f(\Delta\mathbf{k})$ is replaced by the nuclear scattering length b, which is independent of $\Delta\mathbf{k}$. (Note, we typically make the approximation that f is independent of $\Delta\mathbf{k}$, to make calculations easier, but it is not really such a good approximation. In the neutron case, it really is a good approximation because the scattering is essentially off of a point nucleus). The scattering length b varies irregularly from nucleus to nucleus so that the scattering from light elements is similar in strength to that from heavy elements. Neutrons can thus easily see small atoms, and can easily distinguish atoms with similar atomic number.

Magnetic neutron diffraction can also be used to determine magnetic structures (in which case there is a form factor similar to that for X-rays).

The reason inelastic scattering of neutrons is more useful than X-rays for studying phonons is because the X-ray velocity (velocity of light) is huge. This makes it very difficult to conserve both momentum and energy in any inelastic process involving light since a very small momentum change corresponds to a huge energy change. Although with modern tools measurement of phonons using X-rays is now possible.

(14.5) And More X-ray Scattering

A sample of aluminum powder is put in an Debye–Scherrer X-ray diffraction device. The incident X-ray radiation is from Cu–Ka X-ray transition (this just means that the wavelength is $\lambda = .154$ nm). The following scattering angles were observed:

19.48° 22.64° 33.00° 39.68° 41.83° 50.35° 57.05° 59.42°

Given also that the atomic weight of Al is 27, and the density is 2.7 g/cm^3, use this information to calculate Avagadro′s number. How far off are you? What causes the error?

Note: The angles listed are θ not 2θ here. If you use 2θ by mistake you will discover that the ratios of d values do not make sense!

θ	$d = \lambda/(2\sin\theta)$	$(d_{max}/d)^2$	$a_{estimate} = d\sqrt{h^2+k^2+l^2}$
19.48°	.2309 nm	1	.3999 nm
22.64°	.2000 nm	1.33	.4001 nm
33.00°	.1414 nm	2.67	.3999 nm
39.68°	.1206 nm	3.66	.4000 nm
41.83°	.1155 nm	4.00	.4000 nm
50.35°	.1000 nm	5.33	.4000 nm
57.05°	.0918 nm	6.33	.4000 nm
59.42°	.0894 nm	6.66	.4000 nm

From the third column we see that we have an fcc lattice. From the final column we conclude the conventional lattice constant is about .4000 nm. There are four atoms per unit cell, so we would predict an atomic density of $4/(4\text{nm})^3 = 6.28 \times 10^{28}\text{m}^{-3}$. On the other hand, with atomic weight of 27 and density 2.7 g/cm^3 we predict an atomic density of $N_A \times 10^5\text{m}^{-3}$ with $N_A = 6.022 \times 10^{23}$ being Avagadro's number. (Or in other words, our slighly inaccurate prediction of Avagadro's number is 6.28×10^{23}). So we are off by abour 4%. Where does the error come from? There are a few possible places. First, the atomic mass is not quite 27, it is actually about 26.982 (depending a bit on isotopic abundances, but this is typical). But this is an error of much less than an percent. Probably the biggest possible error is that the density changes as a function of temperature. If the density is measured at one temperature, but the lattice constant is measured at another temperature, then there can be a substantial disagreement. In fact the linear thermal expansion coefficient of aluminum is about $(22 \times 10^{(} - 6))\text{K}^{-1}$ which would give a density different between $T = 0$ and room temperature of a few percent (and indeed, the measurements could even be done above room temperature!). In the literature X-ray measurements of the lattice constant of alumium give numbers of about .404 nm at room temperature (which would match the stated density much more closely). Thus I suspect the data given above was measured at low temperature, hence the disagreement.

(14.6) More Neutron Scattering

The conventional unit cell dimension for a particular bcc solid is .24nm. Two orders of diffraction are observed. What is the minimum energy of the neutrons? At what temperature would such neutrons be dominant if the distribution is Maxwell–Boltzmann.

For bcc, the lowest two order diffraction peaks are the (110) and the (200). The corresponding plane spacings are

$$d = a/\sqrt{h^2+k^2+l^2}$$

Or $d = a/\sqrt{2}$ and $d = a/2$. Using Bragg's law,

$$d = \lambda/(2\sin\theta)$$

the wavelength must be at least as small as $2d$ in order to see a particular peak. Or in other words $\lambda \leq a = .24\text{nm}$. The corresponding energy of neutrons is

$$E = \frac{\hbar^2 k^2}{2m_n} = \frac{\hbar^2 (2\pi)^2}{2m_n \lambda^2} = 2.28 \times 10^{-21}\text{J}$$

and

$$E/k_B = 165\text{K}$$

(14.7) Lattice and Basis
Prove that the structure factor for any crystal (described with a lattice and a basis) is the product of the structure factor for the lattice times the structure factor for the basis (i.e., prove Eq. 14.14).

We have the definition of the structure factor

$$S_{(hkl)} = \sum_{\text{atoms } j \text{ in (conventional) unit cell}} f_j \; e^{2\pi i(hx_j + ky_j + lz_j)}$$

When we have a lattice and a basis, all of the positons $\mathbf{r_j}$ of atoms j in the unit cell can be written as the sum of a lattice point $\mathbf{R_a}$ and a basis vector $\mathbf{u}_\alpha$. Thus we can write

$$\mathbf{r_j} = \mathbf{R_a} + \mathbf{u}_\alpha$$

and the sum over j becomes a sum over a and α. Thus we have

$$S_{(hkl)} = \sum_{\alpha,a} f_\alpha \; e^{2\pi i(h(R_{x,a}+u_{x,\alpha})+k(R_{y,a}+u_{y,\alpha})+l(R_{z,a}+u_{z,\alpha}))}$$

Note that the atom type depends only on the basis vector not on the lattice point. We split this sum into two

$$S_{(hkl)} = \sum_{\alpha} f_\alpha \; e^{2\pi i(hu_{x,\alpha})+ku_{y,\alpha}+lu_{z,\alpha})} \sum_{a} \; e^{2\pi i(hR_{x,a}+kR_{y,a}+lR_{z,a})}$$

which is simply the product of basis and lattice structure factors

$$S_{(hkl)} = S^{basis}_{(hkl)} S^{lattice}_{(hlk)}$$

(14.8) Cuprous Oxide and Fluorine Beta

(a) The compound Cu_2O has a cubic conventional unit cell with the basis:

$$\begin{array}{ll} \text{O} & [000] \;;\; [\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}] \\ \text{Cu} & [\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}] \;;\; [\tfrac{1}{4},\tfrac{3}{4},\tfrac{3}{4}] \;;\; [\tfrac{3}{4},\tfrac{1}{4},\tfrac{3}{4}] \;;\; [\tfrac{3}{4},\tfrac{3}{4},\tfrac{1}{4}] \end{array}$$

Sketch the conventional unit cell. What is the lattice type? Show that certain diffraction peaks depend only on the Cu form factor f_{Cu} and other reflections depend only on the O form factor f_O.

(b) Consider fluorine beta phase as described in exercise 12.5. Calculate the structure factor for this crystal. What are the selection rules?

(a) the conventional unit cell of Cu_2O is shown in Figure 14.3. The structure factor is

$$\begin{aligned} S_{(hkl)} &= f_O(1+e^{i\pi(h+k+l)}) \\ &\quad + f_{Cu}\left[e^{i\frac{\pi}{2}(h+k+l)} + e^{i\frac{\pi}{2}(h+3k+3l)} + e^{i\frac{\pi}{2}(3h+k+3l)} + e^{i\frac{\pi}{2}(3h+3k+l)}\right] \end{aligned}$$

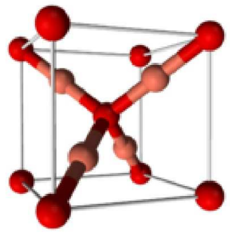


Fig. 14.3 Conventional unit cell of Cu_2O. The darker atoms at the corners and the center are O and the lighter colored atoms are Cu.

Note that sqaure bracketed expression can be simplified to

$$e^{i\frac{\pi}{2}(h+k+l)}\left[1+e^{i\pi(k+l)}+e^{i\pi(h+l)}+e^{i\pi(k+l)}\right]$$

Note that the coefficient of f_0 vanishes unless $h+k+l$ is even. Indeed, this tells us that the oxygens alone form a bcc lattice. The coefficient of the f_{Cu} vanish unless h,k,l are all even or all odd, which tells us that the Cu alone form an fcc lattice (perhaps less obvious!). Thus peaks such as (110) depend only on f_O wheras peaks such as (111) depend only on f_{Cu}.

(b) From 12.5 the basis of Flourine beta is

$$\begin{gathered} [0,0,0],\ [0,1/2,1/4],\ [0,1/2,3/4],\ [1/4,0,1/2], \\ [3/4,0,1/2],\ [1/2,1/4,0],\ [1/2,3/4,0],\ [1/2,1/2,1/2] \end{gathered}$$

The structure factor is then

$$\begin{aligned} &1+e^{i\pi k+i\pi l/2}+e^{i\pi k+i\pi 3l/2}+e^{i\pi l+i\pi h/2}+e^{i\pi l+i\pi 3h/2} \\ &+e^{i\pi h+i\pi k/2}+e^{i\pi h+i\pi 3k/2}+e^{i\pi(h+k+l)} \end{aligned}$$

which can be simplified to

$$1+(-1)^{h+k+l}+(-1)^k[i^l+i^{-l}]+(-1)^l[i^h+i^{-h}]+(-1)^h[i^k+i^{-k}]$$

Note that the first two terms cancel if $h+k+l$ is odd and otherwise give 2. Let us examine the last three terms. Note that

$$i^k+i^{-k}=\begin{cases} 0 & l=\text{odd} \\ 2 & l=0 \mod 4 \\ -2 & l=2 \mod 4 \end{cases}$$

Thus we obtain the following rules for (hkl) where the structure factor does not vanish

one even two odd if the even one is 2 mod 4

one odd two even if the two even indices are not the same mod 4

all even with either one or all three indices being 2 mod 4

(14.9) Form Factors

(a) Assume that the scattering potential can be written as the sum over the contributions of the scattering from each of the atoms in the system. Write the positions of the atoms in terms of a lattice plus a basis so that

$$V(\mathbf{x}) = \sum_{\mathbf{R},\alpha} V_\alpha(\mathbf{x} - \mathbf{R} - \mathbf{y}_\alpha)$$

where $\mathbf{R}$ are lattice points, α indexes the particles in the basis and $\mathbf{y}_\alpha$ is the position of atom α in the basis. Now use the definition of the structure factor Eq. 14.5 and derive an expression of the form of Eq. 14.8 and hence derive expression 14.9 for the form factor. (Hint: Use the fact that an integral over all space can be decomposed into a sum over integrals of individual unit cells.)

(b) Given the equation for the form factor you just derived (Eq. 14.9), assume the scattering potential from an atom is constant inside a radius a and is zero outside that radius. Derive Eq. 14.10.

(c)* Use your knowledge of the wavefunction of an electron in a hydrogen atom to calculate the X-ray form factor of hydrogen.

(a) Start with 14.5

$$S(\mathbf{G}) = \int_{unitcell} \mathbf{dx}\, e^{i\mathbf{G}\cdot\mathbf{x}} V(\mathbf{x}) = \sum_{\mathbf{R},\alpha} \int_{unitcell} \mathbf{dx}\, e^{i\mathbf{G}\cdot\mathbf{x}} V_\alpha(\mathbf{x} - \mathbf{R} - \mathbf{y}_\alpha)$$

we then using $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$ we have

$$S(\mathbf{G}) = \sum_{\mathbf{R},\alpha} \int_{unitcell} \mathbf{dx}\, e^{i\mathbf{G}\cdot(\mathbf{x}-\mathbf{R})} V_\alpha(\mathbf{x} - \mathbf{R} - \mathbf{y}_\alpha)$$

Now we note that the integral $\mathbf{dx}$ over a unit cell summed over all possible unit cells indexed by $\mathbf{R}$ is equivalent to a single integral over all of space, so we have

$$\begin{aligned} S(\mathbf{G}) &= \sum_\alpha \int \mathbf{dx}\, e^{i\mathbf{G}\cdot\mathbf{x}} V_\alpha(\mathbf{x} - \mathbf{y}_\alpha) = \sum_\alpha \int \mathbf{dx}\, e^{i\mathbf{G}\cdot(\mathbf{x}+\mathbf{y}_\alpha)} V_\alpha(\mathbf{x}) \\ &= \sum_\alpha e^{i\mathbf{G}\cdot\mathbf{y}_\alpha} f_\alpha(\mathbf{G}) \end{aligned}$$

with

$$f_\alpha(\mathbf{G}) = \int \mathbf{dx}\, e^{i\mathbf{G}\cdot\mathbf{x}} V_\alpha(\mathbf{x})$$

as required.

(b) Assuming the potential is V_0 inside a radius a and zero outside we have

$$f_\alpha(\mathbf{G}) = V_0 \int_0^{radius=a} \mathbf{dx}\, e^{i\mathbf{G}\cdot\mathbf{x}} = 2\pi V_0 \int_0^a r^2 dr \int \sin\theta d\theta e^{irGcos\theta}$$

where θ is the angle between $\mathbf{x}$ and $\mathbf{G}$. So we have

$$\begin{aligned} f_\alpha(G) &= 2\pi V_0 \int_0^a r^2 dr \int_{-1}^1 dz e^{irGz} = 2\pi V_0 \int_0^a r^2 dr \frac{2\sin(rG)}{rG} \\ &= 4\pi V_0 a^3 \, \frac{\sin(x) - x\cos(x)}{x^3} \end{aligned}$$

where $x = Ga$. Now comparing this to 14.10, it looks identical except for the prefactor. Note however, that the charge of atom is spread out over a volume $4\pi a^3/3$. So setting $V_0 4\pi a^3/3 = Z$ makes the two equations match.

(c) The normalized wavefunction for an electron in the ground state of a hydrogen atom is

$$\psi = \frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

with a_0 the Bohr radius. The scattering potential is proportional to the electron density $|\psi|^2$. Let us call the constant of proportionality K. We then have (using similar calculation as above)

$$f(\mathbf{G}) = K \int \mathbf{dx}\, e^{i\mathbf{G}\cdot\mathbf{x}} |\psi(r)|^2 = K 2\pi \int_0^\infty r^2 dr \frac{2\sin(rG)}{rG} |\psi(r)|^2$$

So we want

$$f(\mathbf{G}) = \frac{2K}{a_0^3} \int_0^\infty r^2 dr \frac{2\sin(rG)}{rG} e^{-2r/a_0}$$

The integration is not too difficult and gives the result

$$f(\mathbf{G}) = \frac{16K}{(a_0^2 G^2 + 4)^2}$$

(14.10) Error Analysis
Imagine you are trying to measure the lattice constant a of some crystal using X-rays. Suppose a diffraction peak is observed at a scattering angle of 2θ. However, suppose that the value of θ is measured only within some uncertainty $\delta\theta$. What is the fractional error $\delta a/a$ in the resulting measurement of the lattice constant? How might this error be reduced? Why could it not be reduced to zero?

See 14.3.e.

(e) From Bragg's law $d \sim 1/\sin\theta$ so

$$\frac{1}{d}\frac{\partial d}{\partial \theta} = \cot\theta$$

So if there is an error in measurement of θ one ends up with a fractional error in d given by

$$\delta \log d = (\cot\theta)(\delta\theta)$$

As a result, error is minimized if one can work as close as possible to scattering angle of 90 degrees. Although at 90 degrees one could have this expression be exactly zero. However, this does not mean the error is actually zero. One has only made the error in measurement zero to lowest order. One also has to worry about higher derivative term

$$\frac{1}{d}\frac{\partial^2 d}{\partial \theta^2} = 1 \neq 0$$

at 90 degrees.

Electrons in a Periodic Potential

15

(15.1) ‡Nearly Free Electron Model

Consider an electron in a weak periodic potential in one dimension $V(x) = V(x+a)$. Write the periodic potential as

$$V(x) = \sum_G e^{iGx} V_G$$

where the sum is over the reciprocal lattice $G = 2\pi n/a$, and $V_G^* = V_{-G}$ assures that the potential $V(x)$ is real.

(a) Explain why for k near to a Brillouin zone boundary (such as k near π/a) the electron wavefunction should be taken to be

$$\psi = Ae^{ikx} + Be^{i(k+G)x} \tag{15.1}$$

where G is a reciprocal lattice vector such that $|k|$ is close to $|k+G|$.

(b) For an electron of mass m with k exactly at a zone boundary, use the above form of the wavefunction to show that the eigenenergies at this wavevector are

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \pm |V_G|$$

where G is chosen so $|k| = |k+G|$.

$\triangleright$ Give a qualitative explanation of why these two states are separated in energy by $2|V_G|$.

$\triangleright$ Give a sketch (don't do a full calculation) of the energy as a function of k in both the extended and the reduced zone schemes.

(c) *Now consider k close to, but not exactly at, the zone boundary. Give an expression for the energy $E(k)$ correct to order $(\delta k)^2$ where δk is the wavevector difference from k to the zone boundary wavevector.

$\triangleright$ Calculate the effective mass of an electron at this wavevector.

(a) A periodic lattice can only scatter a wave by a reciprocal lattice vector (Bragg diffraction). In the nearly free electron picture, the scattering perturbation is weak, so that we can treat the scattered wave in perturbation theory. In this case, there is an energy denominator which suppresses mixing of k-vectors which have greatly different unperturbed energies. Thus, the only mixing that can occur is between two states with similar energies that are separated by a reciprocal lattice vector. Degenerate perturbation theory tells us that we should first diagonalize within the degenerate space spanned by only these two eigenstates.

(b)We have our (variational) trial wavefunction given by

$$|\psi\rangle = A|k\rangle + B|k+G\rangle \tag{15.2}$$

or equivalently

$$\psi = (Ae^{ikx} + Be^{i(k+G)x})/\sqrt{L}$$

To maintain normalization we can insist that $|A|^2 + |B|^2 = 1$. Taking k and $k+G$ both on a Brillouin zone boundary we have $k = n\pi/a$ and $k+$

$G = -n\pi/a$, where here we have chosen the n^{th} zone boundary, and we must have $G = -2n\pi/a$ the reciprocal lattice vector. The Hamiltonian H in question is the usual Kinetic term plus $V(x)$.

Approach 1: Diagonalize H within the 2d degenerate space

$$\begin{aligned}
\langle k|H|k\rangle &= \hbar^2(n\pi/a)^2/(2m) + V_0 \\
\langle k+G|H|k+G\rangle &= \hbar^2(n\pi/a)^2/(2m) + V_0 \\
\langle k|H|k+G\rangle &= V_{2n\pi/a} \\
\langle k+G|H|k\rangle &= V_{-2n\pi/a}
\end{aligned}$$

Diagonalizing this two by two matrix

$$\begin{pmatrix} \hbar^2(\pi/a)^2/(2m) + V_0 & V_{2n\pi/a} \\ V_{-2n\pi/a} & \hbar^2(\pi/a)^2/(2m) + V_0 \end{pmatrix}$$

gives eigenstates

$$E = \frac{\hbar^2(n\pi/a)^2}{2m} + V_0 \pm |V_{2n\pi/a}|$$

where we have used $V_G = V^*_{-G}$. The eigenstates are correspondingly

$$|\psi_\pm\rangle = |k\rangle + |k+G\rangle$$

which are (proportional to) the functions $\sin(2n\pi x/a)$ and $\cos(2n\pi x/a)$.

Interpretation: If we have considered only the $V_{2n\pi/a}$ and $V_{-2n\pi/a}$ Fourier modes of the potential then we have $V = 2V_{2n\pi/a}\cos(2n\pi r/a)$. Assuming $V_{2n\pi/a} > 0$, then the higher energy state is the $\psi = \cos(2n\pi r/a)$ which puts the maximum amplitude of the wavefunction exactly at the maxima of the potential. Similarly, the lower energy wavefunction is the $\sin(2n\pi r/a)$ which has the minimum amplitude of the wavefunction at the maximum of the potential. In the case of $V_{2n\pi/a} < 0$ the sin is the higher energy wavefunction.

Approach 2: Variational.

If we simply calculate the expectation value of H in the trial state given by Eq. 15.2 we obtain

$$\langle\psi|H|\psi\rangle \quad = \quad \hbar^2(n\pi/a)^2/(2m) + V_0 + A^*B\,V^*_{2n\pi/a} + B^*A\,V_{2n\pi/a}$$

Using the variational principle, the eigenstate is the trial wavefunction which minimizes the total energy while preserving the normalization. One way to do this is to write $A = \cos(\theta)$ and $B = e^{i\chi}\sin(\theta)$ which is the most general form we can write while still preserving $|A|^2 + |B|^2 = 1$ (we can arbitrarily choose A to be real, since that only introduces an irrelevant overall phase). In terms of these parameters we have

$$\langle\psi|H|\psi\rangle = \hbar^2(n\pi/a)^2/2m + V_0 + 2\mathrm{Re}[V_{2n\pi/a}e^{i\chi}\sin(\theta)\cos(\theta)]$$

for $V_{2n\pi/a} > 0$ this is minimized for $\chi = \pi$ and $\theta = \pi/4$ (or equivalently $\chi = 0$ and $\theta = 3\pi/4$). It gives minimum energy states for $\psi = \sin(2n\pi r/a)$ as above.

See figure 15.1 for a sketch of the bands in the extended zone scheme.

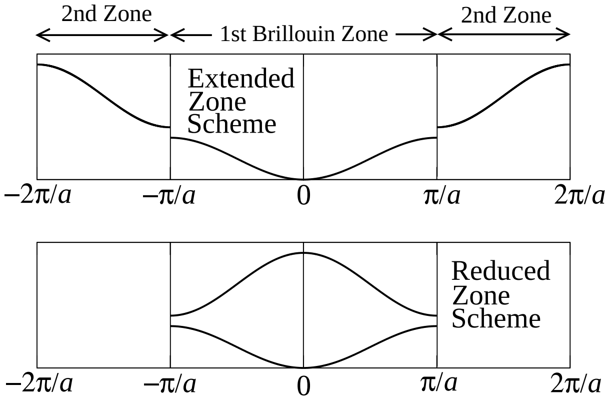


Fig. 15.1 Diagram of the dispersion in a nearly free electron model. Top: extended zone scheme. Bottom: reduced zone scheme. Note that gaps open up at all zone boundaries

(c) This calculation is entirely analogous to that above, only here we need to consider k not on the zone boundary. Letting $k = n\pi/a + \delta k$ and $k + G = -n\pi/a + \delta k$ we have

$$\begin{aligned}\langle k|H|k\rangle &= \hbar^2(\delta k + n\pi/a)^2/(2m) + V_0 \\ \langle k+G|H|k+G\rangle &= \hbar^2(\delta k - n\pi/a)^2/(2m) + V_0 \\ \langle k|H|k+G\rangle &= V_{2n\pi/a} \\ \langle k+G|H|k\rangle &= V_{-2n\pi/a}\end{aligned}$$

which we now need to diagonalize. We obtain

$$E_\pm = \frac{\hbar^2[(\delta k)^2 + (n\pi/a)^2]}{2m} + V_0 \pm \sqrt{\left[\frac{\hbar^2 2(\delta k)n\pi/a}{2m}\right]^2 + |V_{2n\pi/a}|^2}$$

expanding the square-root we obtain

$$E_\pm = \frac{\hbar^2(n\pi/a)^2}{2m} + V_0 \pm |V_{2n\pi/a}| + \frac{\hbar^2(\delta k)^2}{2m}\left(1 \pm \frac{\hbar^2(n\pi/a)^2}{m|V_{2n\pi/a}|}\right)$$

which is a quadratic correction as we move away from the Brillouin zone. Note that for this expansion to remain valid we must have the bracketed term in the square root two equations up small compared to the $|V_{2n\pi/a}|^2$ term.

The effective mass is then obtained by setting

$$\frac{1}{2m^*} = \frac{1}{2m}\left(1 \pm \frac{\hbar^2(n\pi/a)^2}{m|V_{2n\pi/a}|}\right)$$

or equivalently

$$m^* = \left| \frac{m}{1 \pm \frac{\hbar^2 (n\pi/a)^2}{m |V_{2n\pi/a}|}} \right|$$

with the + being for the upper band.

(15.2) Periodic Functions
Consider a lattice of points $\{\mathbf{R}\}$ and a function $\rho(\mathbf{x})$ which has the periodicity of the lattice $\rho(\mathbf{x}) = \rho(\mathbf{x}+\mathbf{R})$. Show that ρ can be written as

$$\rho(\mathbf{x}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}\, e^{i\mathbf{G}\cdot\mathbf{x}}$$

where the sum is over points $\mathbf{G}$ in the reciprocal lattice.

Generally we can always write $\rho(\mathbf{x})$ in terms of its Fourier transform

$$\rho(\mathbf{x}) = V \int \frac{\mathbf{dk}}{(2\pi)^3} \rho_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}}$$

Now by periodicity we know that $\rho(\mathbf{x}) = \rho(\mathbf{x}+\mathbf{R})$ for any lattice vector $\mathbf{R}$, so let us take a sum over all N lattice vectors in the system

$$\begin{aligned} \rho(\mathbf{x}) &= \frac{1}{N}\sum_{\mathbf{R}} \rho(\mathbf{x}+\mathbf{R}) = \frac{V}{N}\sum_{\mathbf{R}} \int \frac{\mathbf{dk}}{(2\pi)^3} \rho_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{x}+\mathbf{R})} \\ &= \frac{V}{N}\int \frac{\mathbf{dk}}{(2\pi)^3} \rho_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \end{aligned}$$

The sum gives

$$\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} = \frac{(2\pi)^3}{v} \sum_{\mathbf{G}} \delta^3(\mathbf{k}-\mathbf{G})$$

where the sum is over all $\mathbf{G}$ which are reciprocal lattice vectors and v is the volume of the unit cell. Letting the delta function act and cancelling some factors, we then directly obtain

$$\rho(\mathbf{x}) = \sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{x}} \rho_{\mathbf{G}}$$

(15.3) Tight Binding Bloch Wavefunctions
Analogous to the wavefunction introduced in Chapter 11, consider a tight-binding wave ansatz of the form

$$|\psi\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\mathbf{R}\rangle$$

where the sum is over the points $\mathbf{R}$ of a lattice, and $|\mathbf{R}\rangle$ is the ground-state wavefunction of an electron bound to a nucleus on site $\mathbf{R}$. In real space this ansatz can be expressed as

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \varphi(\mathbf{r}-\mathbf{R}).$$

Show that this wavefunction is of the form required by Bloch's theorem (i.e., show it is a modified plane wave).

Start by writing the function φ in its fourier representation

$$\varphi(\mathbf{r}) = V \int \frac{\mathbf{dq}}{(2\pi)^3} e^{i\mathbf{q}\cdot\mathbf{r}} \varphi_{\mathbf{q}}$$

so that

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} V \int \frac{\mathbf{dq}}{(2\pi)^3} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R})} \varphi_{\mathbf{q}}$$

The sum over $\mathbf{R}$ gives

$$\sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{R}} = \frac{(2\pi)^3}{v} \sum_{\mathbf{G}} \delta^3(\mathbf{k}-\mathbf{q}-\mathbf{G})$$

and we allow the delta function to act, giving

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \frac{V}{v} \sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \varphi_{\mathbf{k}-\mathbf{G}}$$

The sum over $\mathbf{G}$ is a function periodic in $\mathbf{r} \to \mathbf{r}+\mathbf{R}$ (since $e^{i\mathbf{G}\cdot\mathbf{R}} = 1$) hence this is in Bloch form.

(15.4) *Nearly Free Electrons in Two Dimensions Consider the nearly free electron model for a square lattice with lattice constant a. Suppose the periodic potential is given by

$$\begin{aligned} V(x,y) &= 2V_{10}[\cos(2\pi x/a) + \cos(2\pi y/a)] \\ &+ 4V_{11}[\cos(2\pi x/a)\cos(2\pi y/a)] \end{aligned}$$

(a) Use the nearly free electron model to find the energies of states at wavevector $\mathbf{G} = (\pi/a, 0)$.

(b) Calculate the energies of the states at wavevector $\mathbf{G} = (\pi/a, \pi/a)$. (Hint: You should write down a 4 by 4 secular determinant, which looks difficult, but actually factors nicely. Make use of adding together rows or columns of the determinant before trying to evaluate it!)

Note, we should not call the points $(\pi/a, 0)$ and $(\pi/a, \pi/a)$ as $\mathbf{G}$ since they are not reciprocal lattice vectors!

(a) The first part of this problem is no different from the one dimensional problem posed in 15.1! The fourier components V_{10} couple $(\pi/a, 0)$ and $(-\pi/a, 0)$. The energies of the states are

$$E = \hbar^2(\pi/a)^2/(2m) \pm |V_{10}|$$

(b) The second part of the problem is more complicated. Here, all four points $(\pm\pi/a, \pm\pi/a)$ all have the same energy and are coupled together by the scattering potential. Therefore we must treat all of these states in degenerate perturbation theory. Let us label the points

$$\begin{aligned} |1\rangle &= (+\pi/a, +\pi/a) \\ |2\rangle &= (+\pi/a, -\pi/a) \\ |3\rangle &= (-\pi/a, -\pi/a) \\ |4\rangle &= (-\pi/a, +\pi/a) \end{aligned}$$

Writing a general wavefunction within this space as $\sum_i \phi_i|i\rangle$ the Hamiltonian matrix within this reduced Hilbert space is

$$\begin{pmatrix} \epsilon & V_{10} & V_{11} & V_{10} \\ V_{10} & \epsilon & V_{10} & V_{11} \\ V_{11} & V_{10} & \epsilon & V_{10} \\ V_{10} & V_{11} & V_{10} & \epsilon \end{pmatrix}$$

where $\epsilon = \hbar^2(\pi/a)^2/m$. To find the eigenenergies we would thus like to solve the determinant equation

$$0 = \begin{vmatrix} \epsilon - E & V_{10} & V_{11} & V_{10} \\ V_{10} & \epsilon - E & V_{10} & V_{11} \\ V_{11} & V_{10} & \epsilon - E & V_{10} \\ V_{10} & V_{11} & V_{10} & \epsilon - E \end{vmatrix}$$

Adding and subtracting rows and columns leaves the determinant unchanged. So we can subtract row 3 from row 1 and subtract row 4 from row 2. Then add column 3 to column 1 and add column 4 to column 2. The result is

$$0 = \begin{vmatrix} 0 & 0 & V_{11} - \epsilon + E & 0 \\ 0 & 0 & 0 & V_{11} - \epsilon + E \\ V_{11} + \epsilon - E & 2V_{10} & \epsilon - E & V_{10} \\ 2V_{10} & V_{11} + \epsilon - E & V_{10} & \epsilon - E \end{vmatrix}$$

Because of all the zeros, method of minors can then evaluate the determinant easily to given

$$0 = (V_{11} - \epsilon + E)^2 \left[(V_{11} + \epsilon - E)^2 - 4V_{10}^2\right]$$

Thus giving solutions

$$\begin{aligned} E &= \epsilon + V_{11} \qquad \text{(two solutions)} \\ E &= \epsilon - V_{11} \pm 2|V_{10}| \end{aligned}$$

(15.5) Decaying Waves

As we saw in this chapter, in one dimension, a periodic potential opens a band gap such that there are no plane-wave eigenstates between energies $\epsilon_0(G/2) - |V_G|$ and $\epsilon_0(G/2) + |V_G|$ with G a reciprocal lattice vector. However, at these forbidden energies, decaying (evanescent) waves still exist. Assume the form

$$\psi(x) = e^{ikx - \kappa x}$$

with $0 < \kappa \ll k$ and κ real. Find κ as a function of energy for $k = G/2$. For what range of V_G and E is your result valid?

Here, we can think of the wavevector k as taking an imaginary part (i.e., absorb κ into k)

$$k = -G/2 + i\kappa$$

so that

$$\begin{aligned}
\epsilon_0(k) &= \tfrac{\hbar^2 k^2}{2m} = \frac{\hbar^2((G/2)^2 - iG\kappa - \kappa^2)}{2m} = \epsilon_R - i\epsilon_I \\
\epsilon_0(k+G) &= \tfrac{\hbar^2 (k+G)^2}{2m} = \frac{\hbar^2((G/2)^2 + iG\kappa - \kappa^2)}{2m} = \epsilon_R - i\epsilon_I
\end{aligned}$$

where we have defined

$$\epsilon_R = \frac{\hbar^2((G/2)^2 - \kappa^2)}{2m}$$

$$\epsilon_I = \frac{\hbar^2(G\kappa)}{2m}$$

As worked out in the text (Eq. 15.8), the characteristic equation is

$$\begin{aligned}
0 &= (\epsilon_0(k) - E)\,(\epsilon_0(k+G) - E) - |V_G|^2 \\
&= (\epsilon_R - i\epsilon_I - E)(\epsilon_R + i\epsilon_I - E) - |V_G|^2 \\
&= (\epsilon_R - E)^2 + \epsilon_I^2 - |V_G|^2 \qquad (15.3)
\end{aligned}$$

Thus, we have

$$E = \epsilon_R \pm \sqrt{|V_G|^2 - \epsilon_I^2}$$

Note here that for $|\epsilon_I| > |V_G|$ the energy becomes imaginary and the solution is not valid. Thus we must have

$$|V_G| \geq |\hbar^2 G\kappa/(2m)|$$

In Eq. 15.3 we have a quadratic equation for κ^2 (there are no lone factors of κ), which can be solved to then give only one (possibly) positive solution

$$\frac{\hbar^2\kappa^2}{2m} = -\frac{\hbar^2(G/2)^2}{2m} - E + \sqrt{4E\frac{\hbar^2(G/2)^2}{2m} + |V_G|^2}$$

In order for this solution to be valid, we must have the right hand side be positive. We can write this condition as

$$\left(\frac{\hbar^2(G/2)^2}{2m} + E\right)^2 \leq 4E\frac{\hbar^2(G/2)^2}{2m} + |V_G|^2$$

Or equivalently

$$\left|\frac{\hbar^2(G/2)^2}{2m} - E\right| \leq |V_G|$$

or in other words, that the energy is inside the gap!

(15.6) Kronig–Penney Model*
Consider electrons of mass m in a so-called "delta-function comb" potential in one dimension

$$V(x) = aU\sum_n \delta(x - na)$$

(a) Argue using the Schroedinger equation that in-between delta functions, an eigenstate of energy E is always of a plane wave form $e^{iq_E x}$ with

$$q_E = \sqrt{2mE}/\hbar.$$

Using Bloch's theorem conclude that we can write an eigenstate with energy E as

$$\psi(x) = e^{ikx} u_E(x)$$

where $u_E(x)$ is a periodic function defined as

$$u_E(x) = A\sin(q_E x) + B\cos(q_E x) \qquad 0 < x < a$$

and $u_E(x) = u_E(x+a)$ defines u outside of this interval.

(b) Using continuity of the wavefunction at $x = 0$ derive

$$B = e^{-ika}[A\sin(q_E a) + B\cos(q_E a)],$$

and using the Schroedinger equation to fix the discontinuity in slope at $x = 0$ derive

$$q_E A - e^{ika} k[A\cos(q_E a) - B\sin(q_E a)] = 2maUB/\hbar^2$$

Solve these two equations to obtain

$$\cos(ka) = \cos(q_E a) + \frac{mUa}{\hbar^2 q_E}\sin(q_E a)$$

The left-hand side of this equation is always between -1 and 1, but the right-hand side is not. Conclude that there must be values of E for which there are no solutions of the Schroedinger equation—hence concluding there are gaps in the spectrum.

(c) For small values of the potential U show that this result agrees with the predictions of the nearly free electron model (i.e., determine the size of the gap at the zone boundary).

Oops another error in this problem. Actually this one is really bad. The first part of the problem should ask you to show that

$$\psi(x+a) = e^{ika}\psi(x)$$

and it should be ψ that has the form $A\sin(qx) + B\cos(qx)$ not u. Then in the second to last equation there is an extra random factor of k in front of the brackets, it should be q_E not k. AND the exponent is e^{-ika}. . Probably too many martinis.

(a) Bloch's theorem tells us

$$\psi(x) = e^{ikx} u(x)$$

with u periodic in the unit cell. This then implies $\psi(x+a) = e^{ika}\psi(x)$ as required.

Between delta functions, there is no potential so the solution must be plane waves $e^{\pm iq_E x}$. Since the Hamiltonian is time reversal invariant we can choose the wavefunction to be real. As a result, we must have ψ of the form $A\sin(q_E x) + B\cos(q_E x)$.

(b) Using $\psi(a^+) = e^{ika}\psi(0) = Be^{ika}$ and $\psi(a^-) = A\sin(q_E a) + B\cos(q_E a)$ gives the required result immediately. The Schroedinger equation evaluated near $x = a$

$$\frac{\hbar^2}{2m}\partial_x^2\psi(x) = aU\delta(x-a)\psi(x)$$

is equivalent to

$$\frac{\hbar^2}{2m}\left[\partial_x\psi(a^+) - \partial_x\psi(a^-)\right] = aU\psi(a)$$

Using

$$\begin{aligned}\psi(a) &= Be^{ika}\\ \partial_x\psi(a^+) &= e^{ika}q_E A\\ \partial_x\psi(a^-) &= q_E[A\cos(q_E a) - B\sin(q_E a)]\end{aligned}$$

gives the desired result which now reads (after removing errors!)

$$A - e^{-ika}[A\cos(q_E a) - B\sin(q_E a)] = 2maUB/(q_E\hbar^2)$$

The two equations (with errors removed) have the required solution.

(c) First we note that for $G = \pi/a$, we have

$$V_G = \frac{1}{L}\int dx V(x)e^{iGx} = \frac{1}{L}\sum_n Ua = U$$

Note this is true also at $V_0 = U$, so we expect an overall energy shift of U (from V_0) and then a gap of magnitude $2|U|$ opening at the zone boundary as well.

Setting $k = \pi/a$ and $q_E = k + \delta$ we have

$$-1 = \cos(\pm\pi + \delta a) + \frac{mUa}{\hbar^2(\pi/a + \delta)}\sin(\pi + \delta)$$

Expanding for small δ and solving to lowest order we get two solutions

$$\delta = 0 \quad or \quad \frac{2mUa}{\hbar^2\pi}$$

Substituting back into $E = \hbar^2(\pi/a + \delta)^2/(2m)$ we obtain

$$E = E_0 \quad or \quad E_0 + 2U$$

giving the gap of $2|U|$ at the zone boundary as expected (and the midpoint of the gap shifted up by U due to V_0 as well).

Insulator, Semiconductor, or Metal

16

(16.1) Metals and Insulators

Explain the following:

(a) sodium, which has two atoms in a bcc (conventional cubic) unit cell, is a metal;

(b) calcium, which has four atoms in a fcc (conventional cubic) unit cell, is a metal;

(c) diamond, which has eight atoms in a fcc (conventional cubic) unit cell with a basis, is an electrical insulator, whereas silicon and germanium, which have similar structures, are semiconductors. (Try to think up several possible reasons!)

▷ Why is diamond transparent?

(a) The conventional bcc unit cell contain 2 atoms, but the primitive unit cell contains only a single atom. Thus sodium, as a monovalent atom, results in a half-filled 1st BZ – and thus gives a metal.

(b) The conventional fcc unit cell contains 4 atoms, but the primitive unit cell contains only one atom. So calcium, which is divalent, could be either a metal or an insulator — depending on the strength of the periodic potential. The fact that it is a metal tells us that the potential is not strong enough to make it an insulator.

(c) C,Si, and Ge are group IV elements and are therefore 4-valent. The fcc unit cell has 4 atoms, but the primitive unit cell has 1 atom, and therefore 4 electrons. This could therefore constitute 2 completely filled bands. In the case of C (diamond) this is indeed an insulator with a large band gap (5.5 eV). For Si and Ge, the band gap is smaller (1.1 eV and .67 eV respectively), hence they are semiconductors.

There are various explanations for this effect. One argument is that for carbon, the periodic potential is extremely strong (no inner shell electrons to screen it, and atoms much closer together) therefore it is an insulator with a large band gap. For Si and Ge, the potential is less strong, so the gap is smaller. Hence they are semiconductors.

Another argument is given by thinking in the tight binding picture. Before you bring the atoms together to make a solid, one needs to consider single-electron orbitals. The higher orbitals in an atom are typically closer together in energy (as they are for hydrogen). For C the valence electrons are in the 2p shell whereas for Si and Ge, the valence electrons are 3p and 4p respectively. Hence we expect smaller gaps for Si and Ge.

In a more chemical language, 4 electrons per atom can therefore form 4 covalent bonds with each of the 4 neighbors in the diamond lattice structure. The electrons are all therefore tied up in covalent bonds, making the material an insulator.

Diamond is transparent because it is an insulator with band gap that is larger than any visible light frequency. Thus light cannot be absorbed (or reflected) by any electronic transition.

(16.2) Fermi Surface Shapes

(a) Consider a tight binding model of atoms on a (two-dimensional) square lattice where each atom has a single atomic orbital. If these atoms are monovalent, describe the shape of the Fermi surface.

(b) Now suppose the lattice is not square, but is rectangular instead with primitive lattice vectors of length a_x and a_y in the x and y directions respectively, where $a_x > a_y$. In this case, imagine that the hoppings have a value $-t_x$ in the x-direction and a value $-t_y$ in the y-direction, with $t_y > t_x$. (Why does this inequality match $a_x > a_y$?)

▷ Write an expression for the dispersion of the electronic states $\epsilon(\mathbf{k})$.

▷ Suppose again that the atoms are monovalent, what is the shape of the Fermi surface now?

(a) The dispersion of the tight binding model is given by

$$\epsilon(k_x, k_y) = -2t\left(\cos(k_x a) + \cos(k_y a)\right)$$

A contour plot of this energy is given in the left of Fig. 16.1. If we are considering a monovalent unit cell, then the Brillouin zone is half filled. This then gives a Fermi surface in the shape of a diamond, as shown in the right of Fig. 16.1.

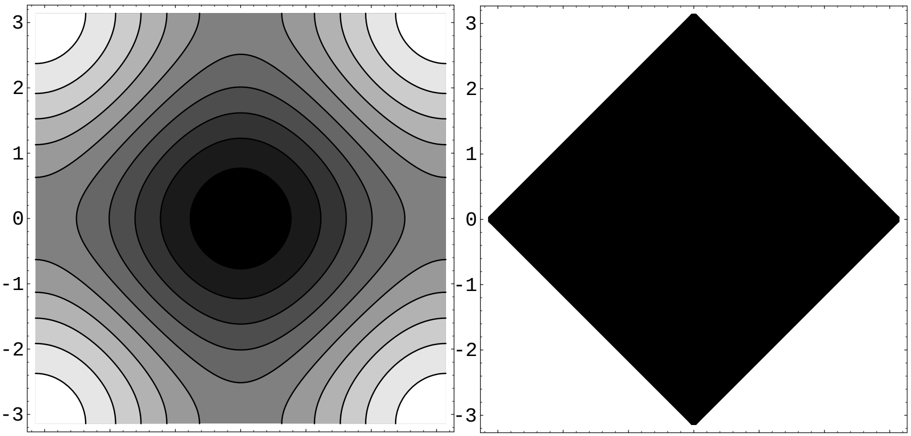


Fig. 16.1 Left: Dispersion of a 2D tight binding model on a square lattice. Right: the Fermi surface for one electron per unit cell.

(b) If $a_x > a_y$ one expects the hopping magnitude to be smaller in the x direction since the atoms are further apart (although this is not holy, as the orbitals, such as p_x orbitals, may not be isotropic). We then expect a dispersion of the form

$$\epsilon(k_x, k_y) = -2t_x \cos(k_x a_x) - 2t_y \cos(k_y a_y)$$

As an example, let us choose $t_y = 2t_x$ but $a_x = a_y = a$ for simplicity. A contour plot of the energy is given in the left of Fig. 16.2. If we are considering a monovalent unit cell, then the Brillouin zone is half filled. This then gives a Fermi surface in the shape of ... well, i'm not sure what to call it. But it is shown in the right of Fig. 16.2.

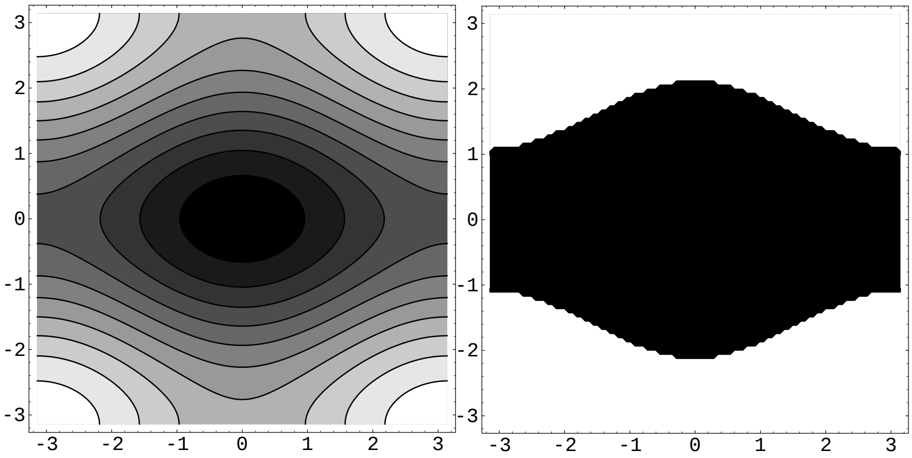


Fig. 16.2 Left: Dispersion of a 2D tight binding model on a square lattice with anisotropic hoppings. Right: the corresponding Fermi surface for one electron per unit cell.

(16.3) More Fermi Surface Shapes*
Consider a divalent atom, such as Ca or Sr, that forms an fcc lattice (with a single atom basis). In the absence of a periodic potential, would the Fermi surface touch the Brillouin zone boundary? What fraction of the states in the first Brillouin zone remain empty?

This is some nasty geometry. First, recall that the reciprocal lattice of an FCC lattice with lattice constant a is a BCC lattice with lattice constant $4\pi/a$ (See excercise 13.1). The BCC lattice has two lattice points per conventional unit cell, so the primitive unit cell (or the Brillouin zone in this case) has volume $\frac{1}{2}(4\pi/a)^3$ in k-space. Now since we have a divalent unit cell in real space, we should have enough electrons to fill exactly the volume of the Brillouin zone. Thus for electrons in the absence of a periodic potential we have

$$\frac{4\pi k_F^3}{3} = \frac{1}{2}\left(\frac{4\pi}{a}\right)^3 \approx 992/a^3$$

or

$$k_F = (24\pi^2)^{1/3}/a \approx 6.187/a$$

We would like to know if this hits the Brillouin zone boundary or not. For a BCC lattice, the nearest neighbor of the point [0,0,0] is the point

[1/2,1/2,1/2] in units of the lattice constant. The perpendicular bisector to this point is thus a distance $\sqrt{3}/4$. For our reciprocal lattice with lattice constant $4\pi/a$, the distance to this perpendicular bisector (i.e., to the Brillouin zone boundary) is then

$$dk = \pi\sqrt{3}/a \approx 5.441/a$$

which is less than the Fermi wavevector, thus telling us that the Fermi surface hits the Brillouin zone boundary (it is obvious that it must hit the Brillouin zone boundary since the volume of the fermi surface must equal the volume of the Brillouin zone and they are not the same shape!).

The Fermi surface thus goes into the 2nd Brillouin zone as a spherical cap of radius $6.187/a$ where the Brillouin zone boundary is of radius $5.441/a$. Note that the center of this spherical cap is in the L direction (in the language of Brillouin zones, see fig 13.6 of the book). We should check that the spherical cap remains on the L-face. We can check this by noting that the angle subtended by this spherical cap is only $\theta = \cos^{-1}(5.441/6.187) \approx 28.425$ degrees, which is much smaller than the angle to say the K point.

The height of the spherical cap is $h = 6.187/a - 5.441/a = 0.745/a$. A well known geometric formula gives us that the volume of a cap is

$$V = \frac{\pi h^2}{3}(3r - h) = 10.4/a^3$$

However, note that we have 8 such spherical caps in all of the 8 equivalent L directions, thus giving a total volume of

$$V = 83/a^3$$

in the 2nd Brillouin zone, compared to the total volume of the fermi surface which is $992/a^3$. Thus the caps in the second Brillouin zone account for roughly 8% of the filled states.

Semiconductor Physics

17

(17.1) Holes

(a) In semiconductor physics, what is meant by a hole and why is it useful?

(b) An electron near the top of the valence band in a semiconductor has energy

$$E = -10^{-37}|\mathbf{k}|^2$$

where E is in Joules and k is in m^{-1}. An electron is removed from a state $\mathbf{k} = 2 \times 10^8 \text{m}^{-1}\hat{x}$, where $\hat{x}$ is the unit vector in the x-direction. For a hole, calculate (and give the sign of!)

(i) the effective mass
(ii) the energy
(iii) the momentum
(iv) the velocity.

▷ If there is a density $p = 10^5 \text{m}^{-3}$ of such holes all having almost exactly this same momentum, calculate the current density and its sign.

(a) A hole is the absence of an electron in an otherwise filled valence band. This is useful since instead of describing the dynamics of all the (many) electrons in the band, it is equivalent to describe the dynamics of just the (few) holes.

(b) Effective mass $\hbar^2 k^2/(2m*) = (10^{-37}\text{Joule} \cdot \text{meter}^2)k^2$. So $m^* = 5 \times 10^{-32}$ kg or .05 the mass of the electron. This mass is *positive* in the usual convention. The energy is $E = (10^{-37}\text{Joule}\cdot\text{meter}^2))k^2 = 4\times10^{-21}$ J, or about 0.025 eV. This energy is positive (it takes energy to ”push” the hole down into the fermi sea, like pushing a balloon under water).

Getting the momentum and velocity right are tricky. First, note that the velocity of an eigenstate is the same whether or not the state is filled with an electron. It is always true that the velocity of an electron in a state is $\nabla_k E_k/\hbar$ where E_k is the electron energy. Thus the hole velocity here is negative $v = -\hbar k/m^* = -3.8 \times 10^5$ m/s (i.e the velocity is in the negative $\hat{x}$) direction.

For momentum, since a filled band carries no (crystal) momentum, and for electrons crystal momentum is always $\hbar k$, the removal of an electron leaves the band with net momentum $-\hbar k$ which we assign as the momentum of the hole. Thus we obtain hole momentum $-\hbar k = -2.1 \times 10^{-26}$ kg-m/s which is also in the negative $\hat{x}$ direction. (this matches well to the intuition that $p = mv$ with a positive effective mass for holes). With p the density of such holes, the total current density is $pev = -6 \times 10^{-9}$ Amp/m^2 also in the negative $\hat{x}$ direction (noting that the charge of the hole is positive).

Note that it is typical to define the wavevector of a hole to be negative of the wavevector of the missing electron.

(17.2) Law of Mass Action and Doping of Semiconductors

(a) Assume that the band-gap energy E_g is much greater than the temperature $k_B T$. Show that in a pure semiconductor at a fixed T, the product of the number of electrons (n) and the number of holes (p) depends only on the density of states in the conduction band and the density of states in the valence band (through their effective masses), and on the band-gap energy.

▷ Derive expressions for n for p and for the product np. You may need to use the integral $\int_0^\infty dx\, x^{1/2} e^{-x} = \sqrt{\pi}/2$.

(b) The band gaps of silicon and germanium are 1.1 eV and 0.75 eV respectively. You may assume the effective masses for silicon and germanium are isotropic, roughly the same, and are roughly .5 of the bare electron mass for both electrons and holes. (Actually the effective masses are not quite the same, and furthermore the effective masses are both rather anisotropic, but we are just making a rough estimates here.)

▷ Estimate the conduction electron concentration for intrinsic (undoped) silicon at room temperature.

▷ Make a rough estimate of the maximum concentration of ionized impurities that will still allow for this "intrinsic" behavior.

▷ Estimate the conduction electron concentration for germanium at room temperature.

(c) The graph in Fig. 17.1 shows the relationship between charge-carrier concentration for a certain n-doped semiconductor.

▷ Estimate the band gap for the semiconductor and the concentration of donor ions.

▷ Describe in detail an experimental method by which these data could have been measured, and suggest possible sources of experimental error.

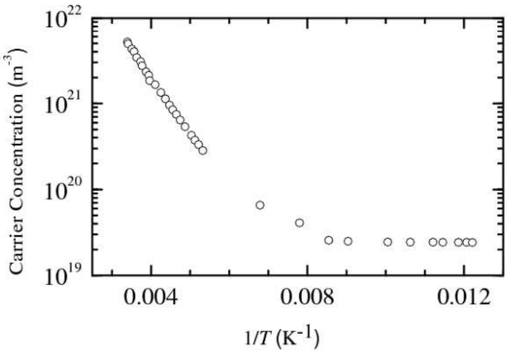


Fig. 17.1 Figure for Exercise 17.

(a) The density of states per unit volume of free electron with dispersion $E = \hbar^2 k^2/(2m)$ is given by (including spin)

$$g(E) = \sqrt{2E}\,\frac{m^{3/2}}{\hbar^3 \pi^2}$$

So if the dispersion near the valence band edge and conduction band edges are

$$\begin{aligned} E_e(k) &= E_c + \hbar^2 k^2/(2m_e) \\ E_h &= E_v - \hbar^2 k^2/(2m_h) \end{aligned}$$

we obtain density of states for conduction electrons and valence holes given by

$$\begin{aligned} g_e(E > E_c) &= \sqrt{2(E - E_c)}\,\frac{m_e^{3/2}}{\hbar^3 \pi^2} \\ g_h(E < E_v) &= \sqrt{2(E_v - E)}\,\frac{m_h^{3/2}}{\hbar^3 \pi^2} \end{aligned}$$

At fixed chemical potential μ and temperature β the number density of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} g_e(E) n_F(\beta(E-\mu)) dE$$

where $n_F(x) = 1/(e^x + 1)$ is the Fermi occupation factor. Assuming that μ is well below the conduction band (by at least energy $k_b T$), then $x = \beta(E - \mu)$ is very positive and it is acceptable to replace $n_F(x)$ by the Boltzmann factor e^{-x}, thus we obtain.

$$n = \int_{E_c}^{\infty} g_e(E) e^{-\beta(E-\mu)} dE$$

Similarly, the number of holes in valence band is given by

$$p = \int_{-\infty}^{E_v} g_h(E)(1 - n_F(\beta(E-\mu)) dE$$

Assuming that μ is well above the valence band (by at least energy $k_b T$) then $x = \beta(E - \mu)$ is very negative and we can replace the fermi factor $1 - n_F(x)$ by e^x resulting in

$$p = \int_{-\infty}^{E_v} g_h(E) e^{\beta(E-\mu)} dE$$

It is then clear immediately, that when we multiply np the variable μ completely vanishes.

A bit more manipulation obtains

$$n = \frac{e^{\beta\mu}\sqrt{2} m_e^{3/2}}{\hbar^3 \pi^2} \int_{E_c}^{\infty} \sqrt{(E - E_c)}\, e^{-\beta E} dE$$

redefining variables $y = E - E_c$ and performing the integral, one obtains

$$n = \frac{1}{4}\left(\frac{2 m_e k_b T}{\pi \hbar^2}\right)^{3/2} e^{-\beta(E_c - \mu)} \tag{17.1}$$

and similarly

$$p = \frac{1}{4}\left(\frac{2 m_h k_b T}{\pi \hbar^2}\right)^{3/2} e^{-\beta(\mu - E_v)} \tag{17.2}$$

Obtaining

$$np = \frac{1}{16}\left(\frac{2\sqrt{m_h m_e} k_b T}{\pi \hbar^2}\right)^{3} e^{-\beta(E_c - E_v)}$$

which depends only on the band gap, T and the effective masses.

(b) In the undoped case $n = p$, and we are assuming $m_h = m_e = m/2$ as well so we have

$$n = \frac{1}{4}\left(\frac{2(m/2) k_b T}{\pi \hbar^2}\right)^{3/2} e^{-\beta(E_g/2)}$$

with E_g the gap value. Plugging in numbers gives

$$n = 5.26 \times 10^{15} \mathrm{m}^{-3}$$

for Silicon and

$$n = 4.54 \times 10^{18} \mathrm{m}^{-3}$$

for Germanium. When the doping level gets to on the order of the expected intrinsic level, then you no longer have intrinsic behavior.

(c) The concentration of donor atoms is simply the saturation concentration at low T (which I estimate from the figure to be about 2×10^{19} m^{-3}). Note that at very low temperature one could get carrier freeze-out where the density drops again.

To estimate the gap, we need to measure the slope of the curve at high temperature.

Extracting a slope

$$\log n/(m^3) = -1500K/T + Constant.$$

Or equivalently

$$n \sim e^{-1500K/T}$$

We then set $1500K = E_g/(2k_b)$ and obtain a band gap of about .26 eV.

It might be useful to also mention to the students that Si and Ge both have valley degeneracies (i.e, multiple equi-energy minima in the conduction band). These may add an additional factor to the law of mass action.

The concentration is most likely measured by a Hall effect measurement. Several possible sources of error can occur here. First, when there are both electrons and holes present, then you measure some (nontrivial) combination of the Hall resistivities weighted by their concentrations and by their mobilities (in a very nontrivial way).

$$R_H = \frac{R_e \rho_e^2 + R_h \rho_h^2}{(\rho_e + \rho_h)^2}$$

(See exercise 17.9). One only gets an accurate absolute measurement of the electron concentration to the extent that the electron resistivity is much lower than the hole resistivity.

There are other more obvious sources of experimental error such as heating when one runs current through a sample to measure it – thus it requires measuring small voltages accurately. To measure hall resistivity, without mixing in longitudinal resisitivity, one needs to align contacts exactly parallel to each other in a hall bar. One has to also make sure that the voltages being measured are due to the sample and not the contacts/wires/amplifiers etc.

(17.3) Chemical Potential

(a) Show that the chemical potential in an intrinsic semiconductor lies in the middle of the gap at low temperature.

(b) Explain how the chemical potential varies with temperature if the semiconductor is doped with (i) donors (ii) acceptors.

(c) A direct-gap semiconductor is doped to produce a density of 10^{23} electrons/m^3. Calculate the hole density at room temperature given that the gap is 1.0 eV, and the effective mass of carriers in the conduction and valence band are 0.25 and 0.4 electron masses respectively. Hint: use the result of Exercise 17.2.a.

(a) In an intrinsic semiconductor $n = p$ so we can set

$$\frac{n}{p} = 1$$

Referrring back to the previous problem we can insert the expressions Eq. 17.1 and Eq. 17.2 for n and p respectively. Almost all of the nasty prefactors cancel and we obtains

$$\frac{m_e^{3/2} e^{-\beta(E_c-\mu)}}{m_h^{3/2} e^{-\beta(\mu-E_v)}} = 1$$

We can solve this trivially to obtain

$$\mu = \frac{E_c + E_v}{2} + \frac{3}{4}(k_B T)\log(m_h/m_e)$$

So at low temperature the chemical potential lies mid-gap. (Incidentally, this is why it is never a good idea to say that the fermi energy is the energy of the highest filled state. There may be a very large difference between the highest filled state and the chemical potential!).

(b) Let us assume for a moment we are well above the freezeout temperature, so the doping can be thought of as going directly into the conduction band. For simplicity let us assume $m_e = m_h$, so the intrinsic behavior is then simply that the chemical potential is fixed as a function of temperature. If the doner density is much higher than n_{int} then $n \approx n_{dopant}$ (i.e., the thermally excited electrons are irrelevant compared to those that are there from doping). Then looking at Eq. 17.1 fixing n to be n_{dopant} and solving for μ we have

$$\mu \approx E_c - k_B T \log\left[\frac{n_{dopant}}{\frac{1}{4}\left(\frac{2m_e k_b T}{\pi\hbar^2}\right)^{3/2}}\right]$$

Similarly for acceptor impurities

$$\mu \approx E_v + k_B T \log\left[\frac{p_{acceptor}}{\frac{1}{4}\left(\frac{2m_h k_b T}{\pi\hbar^2}\right)^{3/2}}\right]$$

So at low tempearture, the chemical potential is essentially right at the conduction (donor) or valence (acceptor) band and moves towards mid-gap as the temperature is increased. When the intrinsic density exceeds the dopant density, then one expects to have μ given by the intrinsic expression from part a, which is roughly to have the chemical potential mid-gap with a small slope dependent on the ratio of masses.

Now the story is a bit more complicated if one wants to think about the very low temperature regime where there is carrier freezeout. At zero temperature all of the electrons are bound to their dopant nuclei and one can think of this as being a filled "impurity band" playing the role of a filled valence band, and the nearby conduction band is empty. As is usually the case, at zero temperature the chemical potential is midway between the top of the impurity band and the bottom of the conduction band. As the temperature is increased, since the real valence band is very far away compared to the temperature so we can ignore it. It is then only a matter of figuring out how the chemical potential moves between the filled impurity band and the empty conduction band. Since the density of states in the conduction band is larger than the those in the sparse impurity band, as the temperature is raised, the chemical potential moves up towards the conduction band.

(c) We first calculate the undoped intrinsic carrier concentration using the law of mass action with $n = p = n_{intrinsic}$. At T =293 Kelvin, I obtained

$$n_{intrinsic} = 10^{16} m^{-3}$$

Then since $n_{dopant} \gg n_{intrinsic}$ we can set $p = n^2_{intrinsic}/n$ (from the law of mass action) to obtain

$$p = 10^9 m^{-3}$$

(17.4) Energy Density
Show that the energy density of electrons in the valence band of a semiconductor is

$$(\epsilon_c + \frac{3}{2} k_B T)\, n$$

where n is the density of these electrons and ϵ_c is the energy of the bottom of the conduction band.

In short this is just a matter of realizing that the electrons in the conduction band are essentially classical (are activated with Boltzmann factors not fermi factors), so classical stat mech applies and one can apply the equipartition theorem. One obtains ϵ_c for each particle excited, then an extra $\frac{3}{2} k_B T$ for the translational degrees of freedom as usual in equipartition theorem.

One can, of course, do the calculation more rigorously writing the total energy density as (compare problem 17.2)

$$E/V = \int_{E_c}^{\infty} E g_e(E) n_F(\beta(E - \mu)) dE$$

where $n_F(x) = 1/(e^x + 1)$ is the Fermi occupation factor. As in 17.2 it is acceptable to replace $n_F(x)$ by the Boltzmann factor to get

$$E/V = \int_{E_c}^{\infty} E g_e(E) e^{-\beta(E-\mu)} dE$$

The same manipulation obtains

$$E/V = \frac{e^{\beta(\mu-E_c)}\sqrt{2} m_e^{3/2}}{\hbar^3 \pi^2} \int_{E_c}^{\infty} [(E-E_c)+E_c]\sqrt{(E-E_c)}\, e^{-\beta(E-E_c)} dE$$

Note the second term in brackets, the E_c term (compare 17.2) gives the same integral as the above calcualtion of n in 17.2 so we obtain nE_c. To evaluate the remaining term we redefine variables $y = E - E_c$ and performing the integral, whixh we recognize as being precisely $\partial/\partial\beta$ of the prior integral from 17.2. Since the prior integral was proportional to $T^(3/2)$ we obtain $(3/2)(k_B T)$ times the prior integral and thus a total of $(3/2)(k_B T)n$ proving the result.

(17.5) Semiconductors
Describe experiments to determine the following properties of a semiconductor sample: (i) sign of the majority carrier (ii) carrier concentration (assume that one carrier type is dominant) (iii) band gap (iv) effective mass (v) mobility of the majority carrier.

(i,ii) Sign of majority carrier and carrier concentration (assuming there is only one type of carrier) are both easily measured with Hall effect. (iii) band gap may be measured optically. Or by carrier concentration (essentially conductance) as a function of temperature. (iv) Effective mass is measured with cyclotron resonance (v) mobility is easily measured via resistivity once concentration of carriers is known.

(17.6) More Semiconductors
Outline the absorption properties of a semiconductor and how these are related to the band gap. Explain the significance of the distinction between a direct and an indirect semiconductor. What region of the optical spectrum would be interesting to study for a typical semiconducting crystal?

Optical absorbtion can occur when a photon is absorbed while exciting an electron out of the valence band into the conduction band. This requires a minimum of the gap energy (Small amounts of absorbtion can occur below the gap for impure semiconductors if there are impurity or defect states within the gap – also very weak nonlinear processes can allow multiple photons to be absorbed while exciting a single electron).

In the absorbtion process energy and momentum must both be conserved. Since photons carry very little momentum given a certain energy (being that c is very large) one should think of this absorbtion as not tranferring any momentum to the system. This means that direct gap absorbtion (where the momentum of the electron does not change) is highly favored over indirect gap absorbtion. Indirect gap absorbtion can occur, but it must be assisted by a phonon or some other process that can account for the necessary momentum.

Semiconductor gaps tend to be in the optical, or infra-red range (somewhere from 400 nm to 3 micron, or roughly 3 eV to .5 eV). Only a very few wide gap semiconductors reach the optical blue range and UV.

(17.7) Yet More Semiconductors

Outline a model with which you could estimate the energy of electron states introduced by donor atoms into an n-type semiconductor. Write down an expression for this energy, explaining why the energy levels are very close to the conduction band edge.

One can consider a simple hydrogenic schroedinger equation with an attractive proton being the ionized donor and the single electron. The main differences are that the mass of the electron is replaced by the band electron mass, and ϵ_0 is multiplied by the dielectric constant ϵ_r of the semiconductor. As a result, the Rydberg becomes replaced by an effective Rydberg

$$R^* = R_0(m^*/m)(1/\epsilon_r^2)$$

This gives us a hydrogenic binding energy that can be extremely small for typical semiconductors, hence the bound states remain very close the conduction band edge.

(17.8) Maximum Conductivity*

Suppose holes in a particular semiconductor have mobility μ_h and electrons in this semiconductor have mobility μ_e. The total conductivity of the semiconductor will be

$$\sigma = e\,(n\,\mu_e + p\,\mu_h)$$

with n and p the densities of electrons in the conduction band and holes in the valence band. Show that, independent of doping, the maximum conductivity that can be achieved is

$$\sigma = 2e\,n_{intrinic}\sqrt{\mu_e\mu_h}$$

with $n_{intrinsic}$ the intrinsic carrier density. For what value of $n - p$ is this conductivity achieved?

Actually this is easy. Using law of mass action $np = n_{intrinsic}^2$. Thus we write

$$\sigma = e\left(n\,\mu_e + \frac{n_{intrinsic}}{n}\,\mu_h\right)$$

Now set $d\sigma/dn = 0$ to maximize and solve to obtain

$$n = n_{intrinsic}\sqrt{\mu h/\mu_e}$$

Which correspondingly results in

$$p = n_{intrinsic}\sqrt{\mu e/\mu_h}$$

plugging into the original expression for σ with a tiny bit of algebra we obtain

$$\sigma = 2e\, n_{intrinic} \sqrt{\mu_e \mu_h}$$

as required, and we also obtain

$$n - p = n_{intrinsic} \left(\sqrt{\mu h/\mu_e} - \sqrt{\mu e/\mu_h} \right)$$

(17.9) Hall Effect with Both n- and p-Dopants* Suppose a semiconductor has a density p of holes in the valence band with mobility μ_h and a density n of electrons in the conduction band with mobility μ_n. Use Drude theory to calculate the Hall resistivity of this sample.

See also exercise 3.3c. For a single species, we have (See exercise 3.1)

$$\rho = \begin{pmatrix} r & BR \\ -BR & r \end{pmatrix}$$

where $r = n\mu$ and $R = q/n$ with q the charge on the charge carrier and n the carrier density. We define tensors ρ_e and ρ_h for the two species with $r_e = n\mu_n$ and $r_h = p\mu_h$ and $R_e = e/n$ and $R_h = -e/p$. The conductivity tensors are $\sigma_j = \rho_j^{-1}$ and then the total conductivity tensor is $\sigma = \sigma_e + \sigma_i$. Finally this is inverted to give the tensor $\rho_{total} = \sigma^{-1}$. There is a lot of algebra involved in this. I obtained

$$\begin{aligned} \rho_{xx} &= \frac{B^2(r_e R_h^2 + r_h R_e^2) + r_h r_e (r_e + r_h)}{B^2(R_e + R_h)^2 + (r_e + r_h)^2} \\ \rho_{xy} &= \frac{B\left(B^2 R_e R_h (R_e + R_h) + R_h r_e^2 + R_e r_h^2\right)}{B^2(R_e + R_h)^2 + (r_e + r_h)^2} \end{aligned}$$

Semiconductor Devices

18

(18.1) Semiconductor Quantum Well

(a) A quantum well is formed from a layer of GaAs of thickness L nm, surrounded by layers of $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ (see Fig. 18.2). You may assume that the band gap of the $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ is substantially larger than that of GaAs. The electron effective mass in GaAs is 0.068 m_e whereas the hole effective mass is 0.45 m_e with m_e the mass of the electron.

▷ Sketch the shape of the potential for the electrons and holes.

▷ What approximate value of L is required if the band gap of the quantum well is to be 0.1 eV larger than that of GaAs bulk material?

(b) *What might this structure be useful for?

(a) This is a particle in a box problem. Both electron and holes are particles in a box of length L. Thus the lowest lying electron in the well is

$$E_e = E_c + \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m_e^*}$$

with E_c the bulk conduction band minimum. Similarly the highest lying hole state in the well is

$$E_h = E_v - \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m_h^*}$$

Thus the difference in energy is

$$E_e - E_h = E_{bulkgap} + \frac{\hbar^2}{2}\left(\frac{\pi}{L}\right)^2 \left(\frac{1}{m_e^*} - \frac{1}{m_h^*}\right)$$

Setting $E_e - E_h - E_{bulkgap}$ to 1eV and solving for L gives 8 nm.

(b) This type of quantum well device is useful to precisely design a band gap for example for a laser where one wants to fix the emission wavelength. If one puts donor impurities outside of the well (on both sides, say) the donated electrons can reduce their energies by falling into the well, but the ionized dopants remain behind. This is known as modulation doping. It is useful because one can obtain extremely high mobility electrons within the quantum well since there are no ionized dopants in the well to scatter off of. One uses these structures heavily for fundamental physics studies of clean (unperturbed) electrons.

(18.2) Density of States for Quantum Wells
(a) Consider a quantum well as described in the previous exercise. Calculate the density of states for electrons and holes in the quantum well. Hint: It is a 2D electron gas, but don't forget that there are several particle-in-a-box states.

(b) Consider a so-called "quantum wire" which is a one-dimensional wire of GaAs embedded in surrounding AlGaAs. (You can consider the wire cross-section to be a square with side 30nm.) Describe the density of states for electrons or holes within the quantum wire. Why might this quantum wire make a very good laser?

(a) For a 2D electron gas for electrons with mass m, we quickly calcualte the density of states.

$$N = 2A \int_0^{k_F} \frac{\mathbf{dk}}{(2\pi)^2}$$

with A the area and the factor of 2 out front for spin and $\mathbf{k}$ a two dimensional vector. This can be converted to

$$n = N/A = \frac{k_F^2}{2\pi}$$

When the energy of an electron is given by

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m}$$

we have $k^2 = 2mE/\hbar^2$ and we then have a density of states per unit volume of

$$g = \frac{dn}{dE} = \frac{m}{\pi\hbar^2}$$

This is the correct answer for any $E \geq 0$ and the density of states is zero for any $E < 0$. We then write more precisely that

$$g(E) = \frac{m}{\pi\hbar^2}\Theta(E)$$

where Θ is the step function which has value 1 for nonnegative argument and value 0 for negative argument.

In our quantum well we must make a few minor changes. First of all, we should use the effective mass rather than the actual mass of the electron. Secondly the energy of the particle in the quantum well also includes its particle-in-a-box energy for its motion transverse to the 2D quantum well. Thus for an electron in the conduction band of the quantum well we have

$$E = E_c + \frac{\hbar^2\pi^2}{2m_e^*}\frac{a^2}{L^2} + \frac{\hbar^2\mathbf{k}^2}{2m_e^*}$$

where E_c is the bulk conduction band bottom, and $a = 1, 2, 3, \ldots$ is the transverse quantum number of the particle in the well. Fixing the transverse quantum number a, the density of states would be

$$g(E) = \frac{m_e^*}{\pi\hbar^2}\Theta\left(E - E_c - \frac{\hbar^2\pi^2}{2m_e^*}\frac{a^2}{L^2}\right)$$

Now accounting for the fact that there may be many transverse modes we have

$$g(E) = \frac{m_e^*}{\pi\hbar^2}\sum_{a>0}\Theta\left(E - E_c - \frac{\hbar^2\pi^2}{2m_e^*}\frac{a^2}{L^2}\right)$$

and this expression remains true up to an energy where the transverse modes spill out of the box.

Analogously the density of holes in the valuence band in the quantum well is

$$g(E) = \frac{m_h^*}{\pi\hbar^2}\sum_{a>0}\Theta\left(E_v - \frac{\hbar^2\pi^2}{2m_h^*}\frac{a^2}{L^2} - E\right)$$

(b) First we determine the density of states for a one dimensional electron gas.

$$N = 2L\int_{-k_F}^{k_F}\frac{dk}{2\pi}$$

with L the Length of the system and the factor of 2 out front for spin. This can be converted to

$$n = N/L = \frac{2k_F}{\pi}$$

using $k = \sqrt{2mE}/\hbar$ we then obtain a density of states

$$g(E) = \frac{dn}{dE} = \frac{\sqrt{2m}}{\pi\hbar}E^{-1/2}\,\Theta(E)$$

Now in the seminconductor quantum wire we must consider the transverse modes. In general the energy of an electron in the wire is then given by

$$E = E_c + \frac{\hbar^2\pi^2}{2m_e^*}\frac{a_1^2 + a_2^2}{L^2} + \frac{\hbar^2k^2}{2m_e^*}$$

where a_1 and a_2 are the mode indices (integers greater than zero) in the two transverse directions. Adding the density of states associated with all of these modes we obtain

$$g(E) = \frac{\sqrt{2m_e^*}}{\pi\hbar}\sum_{a_1,a_2>0}\left(E - E_c - \frac{\hbar^2\pi^2}{2m_e^*}\frac{a_1^2 + a_2^2}{L^2}\right)^{-1/2}\Theta\left(E - E_c - \frac{\hbar^2\pi^2}{2m_e^*}\frac{a_1^2 + a_2^2}{L^2}\right)$$

and similarly in the valence band

$$g(E) = \frac{\sqrt{2m_h^*}}{\pi\hbar}\sum_{a_1,a_2>0}\left(E_v - \frac{\hbar^2\pi^2}{2m_h^*}\frac{a_1^2 + a_2^2}{L^2} - E\right)^{-1/2}\Theta\left(E_v - \frac{\hbar^2\pi^2}{2m_h^*}\frac{a_1^2 + a_2^2}{L^2} - E\right)$$

(18.3) ***p*-*n* Junction***

Explain the origin of the depletion layer in an abrupt *p*-*n* junction and discuss how the junction causes rectifcation to occur. Stating your assumptions, show that the total width w of the depletion layer of a *p*-*n* junction is:

$$w = w_n + w_p$$

where

$$w_n = \left(\frac{2\epsilon_r\epsilon_0 N_A\phi_0}{eN_D(N_A+N_D)}\right)^{1/2}$$

and a similar expression for w_p Here ϵ_r is the relative permittivity and N_A and N_D are the acceptor and donor densities per unit volume, while ϕ_0 is the difference in potential across the *p*-*n* junction with no applied voltage. You will have to use Poisson's equation to calculate the form of ϕ given the presence of the ion charges in the depletion region.

▷ Calculate the total depletion charge and infer how this changes when an additional voltage V is applied.

▷ What is the differential capacitance of the diode and why might it be useful to use a diode as a capacitor in an electronic circuit?

Let us set the position x to be zero, where we have an n doped region to the left (negative x) and a p doped region to the right (positive x). Let the depletion widths be w_n and w_p respectively, and the doping densitities be N_D and N_A respectively. Within the depletion widths there is a net charge built up (see Fig 18.4 of the book for example). We must solve the Poisson equation $\partial_x^2\phi = \rho/(\epsilon_0\epsilon_r)$ where ρ is the local charge density (which is constant in each region). Setting $\phi(x=0)=0$ for simplicity, we immediately obtain

$$\begin{aligned}\phi(x) &= \frac{-eN_D}{2\epsilon_0\epsilon_r}x^2 + C_D x \qquad && x<0\\ \phi(x) &= \frac{eN_A}{2\epsilon_0\epsilon_r}x^2 + C_A x && x>0\end{aligned}$$

where C_D and C_D are constants to be fixed here. We have additional boundary conditions that the electric field must go to zero at the edge of the depletion region, so we have $\partial_x\phi(x=-w_n) = \partial_x(x=w_a) = 0$. This fixes the constants so that we now have

$$\begin{aligned}\phi(x) &= \frac{-eN_D}{2\epsilon_0\epsilon_r}\left(x^2+2w_n x\right) \qquad && x<0\\ \phi(x) &= \frac{eN_A}{2\epsilon_0\epsilon_r}\left(x^2-2w_a x\right) && x>0\end{aligned}$$

The total potential drop across both regions is then

$$\phi_0 = \phi(-w_n) - \phi(w_a) = \frac{e}{2\epsilon_0\epsilon_r}\left(N_D w_n^2 + N_A w_a^2\ \right) \tag{18.1}$$

We also note that the total charge in the two depletion regions must sum to zero (since the depletion occurs by annihilation of opposite charges) so we have

$$w_a N_A = w_n N_D \tag{18.2}$$

Plugging Eq. 18.2 into Eq. 18.1 and solving for w_n yields the desired expression.

$$w_n = \left(\frac{2\epsilon_r\epsilon_0 N_A\phi_0}{eN_D(N_A+N_D)}\right)^{1/2}$$

and similarly

$$w_a = \left(\frac{2\epsilon_r\epsilon_0 N_D\phi_0}{eN_A(N_A+N_D)}\right)^{1/2}$$

When an additional voltage is added, it simply shifts ϕ_0 to $\phi_0 + eV$.

The total depletion charge per unit cross sectional area is then

$$q = w_n N_D = w_a N_A = \left(\frac{2\epsilon_r \epsilon_0 N_D N_A (\phi_0 + eV)}{e(N_A + N_D)} \right)^{1/2}$$

The differential capacitance per unit cross sectional area is

$$C = \frac{\partial q}{\partial V} = \left(\frac{\epsilon_r \epsilon_0 N_D N_A}{2e(N_A + N_D)} \right)^{1/2} (\phi_0 + eV)^{-1/2}$$

This provides a useful circuit element as it allows one to control a capacitance by applying a DC voltage.

(18.4) Single Heterojunction*

Consider an abrupt junction between an n-doped semiconductor with minimum conduction band energy ϵ_{c1} and an undoped semiconductor with minimum conduction band energy ϵ_{c2} where $\epsilon_{c1} < \epsilon_{c2}$. Describe qualitatively how this structure might result in a two-dimensional electron gas at the interface between the two semiconductors. Sketch the electrostatic potential as a function of position.

It should say, $\epsilon_{c1} > \epsilon_{c2}$.

In this problem, nothing interesting happens in the valence band — so we only draw the conduction band. The situation is quite similar to the p-n junction. Before the two semiconductors are brought together, there are electrons in the conduction band on the left (or in dopant orbitals slightly below the conduction band as shown in the figure), but empty states on the right at lower energy because the conduction band energy

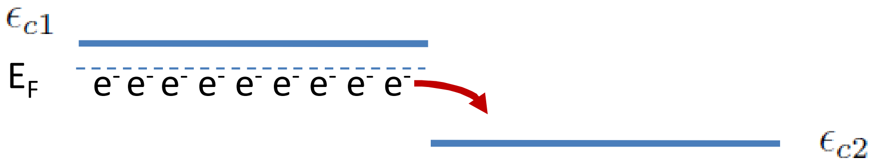


Fig. 18.1 Before electrons are allowed to flow between the two seminconductors, there are electrons on the left at higher energy than empty states on the right. The blue lines indicate the conduction band minima. The dotted line is the fermi energy (slighly below the conduction band assuming that electrons are bound to dopants).

As in the p-n junction, electrons want to flow between the two semiconductors in order to lower their energies, but in so doing charge builds up (a postive charge is left on the left and negative charged electrons accumulate on the right. When equilibrium is established the electrochemical potential is as shown in figure 18.2. The electrons are back attracted to the positive charges they left behind, thus accumulating in a roughly triangular well that forms near the interface. If the confinement is sufficiently strong, this becomes a particle in a box problem and the electrons in the well may become restricted to a single transverse wavefunction — thus becoming a strictly two dimensional electron gas.

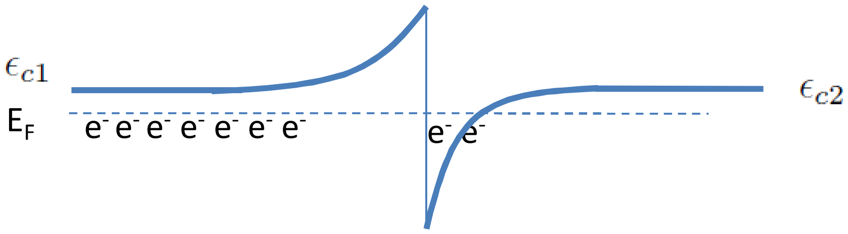


Fig. 18.2 Electrochemical potential of a semiconductor heterostructure. There is net postive charge on the left where electrons have left their donor atoms behind and net negative charge on the right where electrons have accumulated without positively charged nuclei.

(18.5) Diode Circuit
Design a circuit using diodes (and any other simple circuit elements you need) to convert an AC (alternating current) signal into a DC (direct current) signal.

▷ *Can you use this device to design a radio reciever?

For the purpose of this problem we will make the crude assumption that a diode (arrow in a circuit diagram) is an ideal circuit element that allows current flow one way but no current flow the other way.

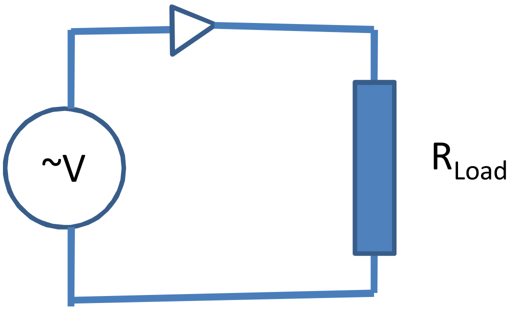
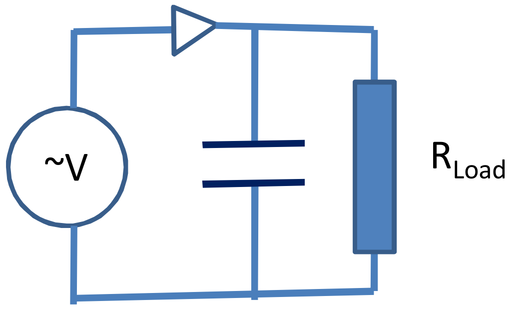


Fig. 18.3 A half-wave rectifier.

The circuit shown in Fig. 18.3 is known as “half-wave rectifier”. If the source voltage is sinusoidal, $V = V_0 sin(\omega t)$, the voltage across the load



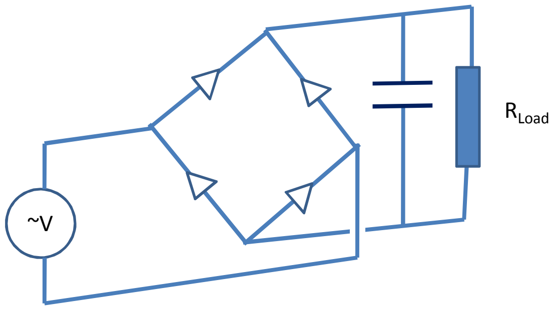


Fig. 18.5 A full-wave rectifier.

In this case, in the absence of the smoothing capacitor, the voltage across the load is given by

$$V = |V_0 \sin(\omega t)|$$

a smoothing capacitor can be used as above. This scheme has the advantage that the resulting DC voltage ends up being of higher magnitude than that of the half-wave, and the fluctuating DC component ends up being smaller.

▷ In order to design a radio, we must first think about how radios encode information. The simplest encoding system is AM or amplitude modulation. In this case a signal $A(t)$ (for simplicity let us assume the signal is everywhere positive) is multiplied by a high frequency carrier wave $\sin(\omega t)$ and the product $A(t)\sin(\omega t)$ is transmitted and then received by an antenna. To convert the received signal back into $A(t)$ one simply puts it through a rectifier. If one wants to do a slightly better job, one wants to recieve only signals where the carrier frequency is very close to some given frequency ω_0. To do this, one needs to build a resonant (LC) circuit which will respond only to frequencies near its resonance. A sample 1-diode radio circuit (often known as a "crystal" radio after the fact that the diode was often made of a small crystal) is shown in Fig. 18.6. In this figure the right hand side (D1,C3,E1) is just a half-wave rectifier as discussed above. Here E1 is the "earphone" or output load of the circuit. The middle of the circuit L2,C2 is the resonant LC circuit, which is inductively coupled to the incoming signal from the antenna. Note that the capacitors are made tunable here so that the resonance frequencies can be modified. Many other designs are possible as well.

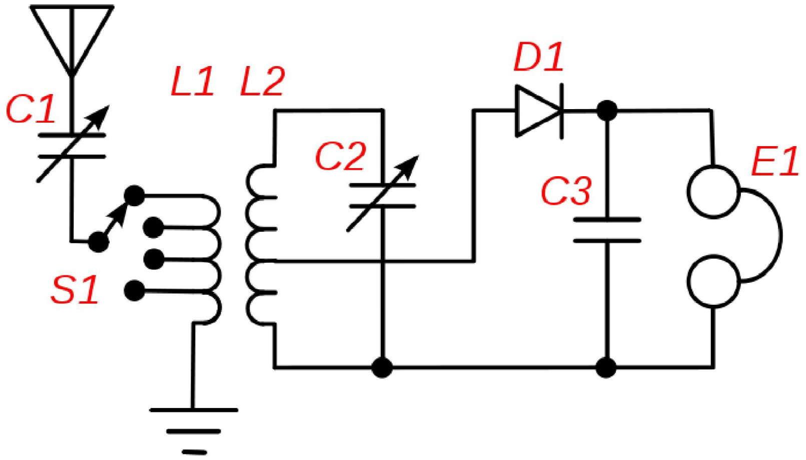


Fig. 18.6 A radio circuit. Here E1 is the "earphone" or output load of the circuit. The incoming antenna is on the far left. A very crude radio could be made by with only the rectifier (D1,C3) attached directly to an incoming antenna and an outgoing earphone E1.

(18.6) CMOS Circuit*

Design a circuit made of one n-MOSFET and one p-MOSFET (and some voltage sources etc.) which can act as a latch—meaning that it is stable in two possible states and can act a single bit memory (i.e., when it is turned on it stays on by itself, and when it is turned off it stays off by itself).

A simple (and very rough) CMOS latch circuit (also known as an SCR or silicon-controlled rectified) is shown in Fig. 18.7. When the switch (S1) is closed no current flows. The reason for this is that there is no voltage on either of the two gates, so both transistors are "off" meaning they prevent current flow (and therefore prevent voltage from being transmitted). However, when a voltage is momentarily applied to the ON input, then this activates the P-MOSFET, allowing current to flow to the gate of the N-MOSFET, which then activates it, allowing current to flow to the gate of the P-MOSFET even when the ON voltage is removed. Thus the circuit is latched in the "On" state. To put the circuit back in the "Off" state, one must disconnect the switch S1 momentarily.

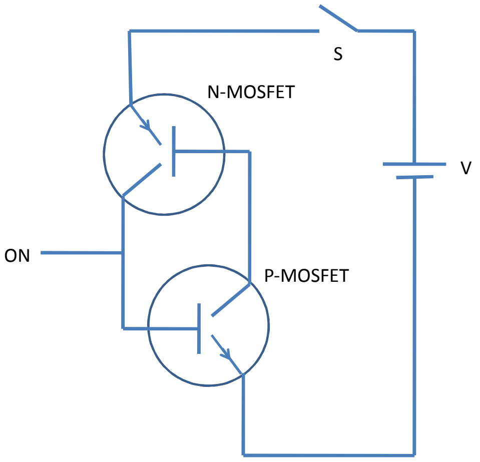


Fig. 18.7 A CMOS latch circuit.

Magnetic Properties of Atoms: Para- and Dia-Magnetism

19

(19.1) ‡ **Atomic Physics and Magnetism**

(a) Explain qualitatively why some atoms are paramagnetic and others are diamagnetic with reference to the electronic structure of these materials.

(b) Use Hund's rules and the Aufbau principle to determine L, S, and J for the following isolated atoms:

(i) Sulfur (S) atomic number = 16
(ii) Vanadium (V), atomic number = 23
(iii) Zirconium (Zr), atomic number = 40
(iv) Dysprosium (Dy), atomic number = 66

(a) To a first approximation, paramagnetic atoms have net moment $J \neq 0$ which can be re-aligned, whereas the typical diamagnetic atoms have no moment.

If an atom has completely filled shells (say, the noble gases), then $J = L = S = 0$, and the atom is diamagnetic due to Larmor Diamagnetism.

If an atom has a net moment $J \neq 0$, from unfilled shells, then it is paramagnetic. This is almost all other atoms.

However (more advanced answer): it is also possible to have $J = 0$ while having L and S nonzero. In this case, the atom can either be paramagnetic or diamagnetic. Both para and dia terms are weak and either one can win in this case. This can occur for atoms that are one electron short of half-filled shells. (Known as Van Vleck Paramagnetism).

In metals one can have Pauli paramagnetism associated with re-orientation of the spins of the conduction electron. One can also have Landau diamagnetism (beyond the scope of the course) which is the diamagnetic response of the orbital motion of the conduction electrons. Pauli paramagnetism in a metal is much weaker than Curie paramagnetism and can be roughly the same size as diamagnetic effects.

(b) Shells are filled in the order

$$1\mathrm{s}, 2\mathrm{s}, 2\mathrm{p}, 3\mathrm{s}, 3\mathrm{p}, 4\mathrm{s}, 3\mathrm{d}, 4\mathrm{p}, 5\mathrm{s}, 4\mathrm{d}\ldots$$

with s,p,d shells containing 2,6,10 electrons respectively.

(i) ${}_{16}$S: [Ne]$3s^2 3p^4$
(ii) ${}_{23}$V: [Ar]$4s^2 3d^3$
(iii) ${}_{40}$Zr: [Kr]$5s^2 4d^2$

(iv) $_{54}$Xe: [Xe] (All filled shells)
(v) $_{66}$Dy: [Xe]6s^{2}4f^{10}

Where filled shell configurations [Ne] contains 10 electrons, [Ar] contains 18, [Kr] contains 36 and [Xe] contains 54.

Thus

(i) Sulfer has 4 electrons in a p-shell, these fill $l_z = -1, 0, 1$ with spin up and $l_z = 1$ with spin down. Thus $L = 1$ and $S = 1$, and since the shell is more than half full $J = L + S = 2$.

(ii) Vanadium has 3 electrons in a d-shell, these fill $l_z = 2, 1, 0$ with spin up giving $L = 3$ and $S = 3/2$. Since the shell is less than half filled $J = L - S = 3/2$.

(iii) Zirconium has 2 electrons in a d-shell, these fill $l_z = 2, 1$ with spin up giving $L = 3$ and $S = 1$. Since the shell is less than half filled $J = L - S = 2$.

(iv) Xenon is a noble gas, meaning all shells are filled, so $J = L = S = 0$.

(v) Dysprosium has 10 electrons in an f-shell, these fill all the spin up state (7 of them) and $l_z = 3, 2, 1$ for spin down giving $L = 6$ and $S = 2$. Since the shell is more than half filled $J = L + S = 8$.

Note that none of these atoms violate the Madelung rule which dictates the filling order or violates Hund's rules when the atoms are isolated. (Violations do sometimes occur but these atoms work as they are supposed to).

(19.2) More Atomic Physics
(a) In solid erbium (atomic number=68), one electron from each atom forms a delocalized band so each Er atom has eleven f electrons on it. Calculate the Landé g-factor for the eleven electrons (the localized moment) on the Er atom.

(b) In solid europium (atomic number =63), one electron from each atom forms a delocalized band so each Eu atom has seven f electrons. Calculate the Landé g-factor for the seven electrons (the localized moment) on the Eu atom.

Er typically is in a +3 state. 2 of those are from the core s-orbitals. 1 is from the f orbital.

(a) For 11 electrons in an f-shell, using Hund's first rule we obtain $S = 3/2$ and Hund's second rule we have $L = 6$. Since the shell is more than half filled, J is given by the sum $J = 6 + 3/2 = 15/2$. Using the formula for the Lande g factor (with $g = 2$) we have

$$\tilde{g} = \frac{1}{2}(g+1) + \frac{1}{2}(g-1)\left[\frac{S(S+1) - L(L+1)}{J(J+1)}\right] = 6/5$$

This is almost exactly right.

(b) The counting here is messed up. There are 7 electrons before losing one. For 7 electrons in an f-shell, $L = 0$ and $S = 7/2$ and $J = S$. is purely spin, so $\tilde{g} = g = 2$ (it also comes out of the above formula as well). In fact, we should have 6 electrons when one is lost, and we get $L = 3 = S$ and $J = 0$. However, This is a van-vleck ion, so in fact the result is not what is predicted here.

(19.3) Hund's Rules*

Suppose an atomic shell of an atom has angular momentum l ($l = 0$ means an s-shell, $l = 1$ means a p-shell etc, with an l shell having $2l + 1$ orbital states and two spin states per orbital.). Suppose this shell is filled with n electrons. Derive a general formula for S, L, and J as a function of l and n based on Hund's rules.

The shell has $2l+1$ orbital states and 2 spin states per orbital. Hund's first rule tells us that

$$S(n,l) = \begin{cases} \frac{n}{2} & 0 \leq n \leq 2l+1 \\ \\ \frac{4l+2-n}{2} & 2l+1 \leq n \leq 4l+2 \end{cases}$$

The second rule tells us that for $n \leq 2l + 1$ we have

$$L(n,l) = \sum_{x=l-n+1}^{x=l} x$$

We can do this sum to obtain

$$L(n,l) = \frac{1}{2} n(2l+1-n)$$

For $2l + 1 \leq n \leq 4l + 2$ we can consider only the electrons in addition to the $L = 0$ half-filled shell, so $L(n,l) = L(n - (2l+1), l)$ So we have in all,

$$L(n,l) = \begin{cases} \frac{1}{2} n(2l+1-n) & 0 \leq n \leq 2l+1 \\ \\ \frac{1}{2}(n-2l-1)(4l+2-n) & 2l+1 \leq n \leq 4l+2 \end{cases}$$

And thus we have (using Hund's third rule) $J = L - S$ for less than half filled and $J = L + S$ for more than half filled so

$$J(n,l) = \begin{cases} \frac{1}{2} n(2l-n) & 0 \leq n < 2l+1 \\ \\ \frac{1}{2}(n-2l)(4l+2-n) & 2l+1 \leq n \leq 4l+2 \end{cases}$$

‡ (19.4) Para and Diamagnetism

Manganese (Mn, atomic number=25) forms an atomic vapor at 2000K with vapor pressure 10^5 Pa. You can consider this vapor to be an ideal gas.

(a) Determine L, S, and J for an isolated manganese atom. Determine the paramagnetic contribution to the (Curie) susceptibility of this gas at 2000K.

(b) In addition to the Curie susceptibility, the manganese atom will also have some diamagnetic susceptibility due to its filled core orbitals. Determine the Larmor diamagnetism of the gas at 2000K. You may assume the atomic radius of an Mn atom is one Ångstrom.

Make sure you know the derivations of all the formulas you use!

Using the ideal gas law, the density of Mn atoms is $n = P/(k_B T)$. We will use this below.

(a) Atomic Mn has orbital configuration ${}_{25}$Mn: [Ar]4s^{2}3d^5, meaning a half filled d-shell. This then has $L = 0$ and $S = 5/2$. Since this is purely spin moment the g-factor is 2.

Now we need to determine the paramagnetic susceptibility of a spin $S = 5/2$. Let us write the partition function

$$Z = \sum_{m=-5/2}^{5/2} e^{-\beta g \mu_B B m}$$

Since we will be concerned with small B, it is probably simplest to expand the partition function directly

$$\begin{aligned} Z &\approx \sum_{m=-5/2}^{5/2} \left[1 - (\beta g \mu_B B m) + \frac{1}{2}(\beta g \mu_B B m)^2 + \ldots \right] \\ &= 6 + \frac{35}{4}(\beta g \mu_B B)^2 \end{aligned}$$

Calculating the moment

$$\text{moment} = -\partial(k_B T \log Z)/\partial B = \frac{35}{12}\beta (g\mu_B)^2 B$$

Yielding a susceptibility of the gas

$$\chi = \partial M/\partial H = n\mu_0 \frac{35}{12}\beta(g\mu_B)^2 = [P/(k_B T)^2]\frac{35}{3}\mu_0 \mu_B^2 = 1.6 \times 10^{-7}$$

(b) Diamagnetism is understood from the schroedinger equation and expanding for small magnetic field

$$H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} = \frac{\mathbf{p}^2}{2m} + \frac{1}{2m}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\mathbf{p}) + \frac{e^2 \mathbf{A}^2}{2m}$$

The middle term is a $\mathbf{L}\cdot\mathbf{B}$, and has zero expectation if there is a filled shell such that $\langle \mathbf{L} \rangle = 0$. The final term is the source of diamagnetism. One can write in circular gauge

$$\mathbf{A} = \frac{1}{2}\mathbf{r} \times \mathbf{B}$$

and the final term ends up being

$$\frac{e^2}{8m}|B|^2 (r_\perp)^2 = \frac{e^2}{6m}|B|^2 r^2$$

where we have used the spherical symmetry of the atom so that $x^2+y^2 = (2/3)r^2$. We thus have the susceptibility

$$\chi = -\mu_0 dE^2/dB^2 = -\mu_0 \frac{\rho e^2}{6m}\langle r^2\rangle$$

where here ρ is the density of *electrons*. Since there are 20 core electrons per atom, we have $\rho = 20n$ with n the gas density (using 25 here would also be sensible). Using 1 angstrom for r we thus obtain

$$\chi = -4.3 \times 10^{-9}$$

which is much much smaller than the paramagnetic contribution, even at 2000K!

‡(19.5) Diamagnetism

(a) Argon is a noble gas with atomic number 18 and atomic radius of about .188 nm. At low temperature it forms an fcc crystal. Estimate the magnetic susceptibility of solid argon.

(b) The wavefunction of an electron bound to an impurity in n-type silicon is hydrogenic in form. Estimate the impurity contribution to the diamagnetic susceptibility of a Si crystal containing 10^{20} m^{-3} donors given that the electron effective mass $m^* = 0.4m_e$ and the relative permittivity is $\epsilon_r = 12$. How does this value compare to the diamagnetism of the underlying silicon atoms? Si has atomic number 14, atomic weight 28.09, and density 2.33 g/cm^3.

(a) First we establish the density of Argon. The radius of the avrgon atom is $r = .188$ nm. For an fcc crystal, the nearest neighbor distance is $r = a/(2\sqrt{2})$ We then have four atoms per conventional unit cell for an overall atomic density of $4/a^3 = 1/(4\sqrt{2}r^3)$. The number of electrons is 18 times the number of atoms, so we have (see 19.4 for derivation)

$$\chi = -\mu_0 \frac{\rho e^2}{6m}\langle r^2\rangle = -\mu_0 18\frac{e^2}{(4\sqrt{2}r^3)6m}\langle r^2\rangle = -\mu_0\frac{3}{4\sqrt{2}}\frac{e^2}{mr} = -1\times 10^{-4}$$

This number is actually a bit too big because the average $\langle r^2\rangle$ is smaller than this number since most of the electrons are further inside the atom than the full atomic radius. Measurement gives us a suscpetability about 10^{-5}, which would correspond to $\sqrt{\langle r^2\rangle} \approx r/3$.

(b) For a hydrogenic orbital (recall $\psi \sim e^{-r/a_0}$) it is easy to calcualte that $\langle r^2\rangle = 3a_0^2$. We need only calculate the Bohr radius of an impurity in a silicon atom. Recalling that the expression for the Bohr radius is

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

we see that the Bohr radius in silicon should be rescaled by

$$a_0^{Si} = a_0\epsilon_r m/m^* = a_0 * 12/.4 = 1.6\text{nm}.$$

Again using the result of the prior problem (and using m^* rather than m)

$$\chi = -\mu_0\frac{\rho e^2}{6m^*}\langle r^2\rangle \approx -10^{-11}$$

Finally we would like to compare this to the diamagnetism of the pure silicon. First let us calculate the density of atoms in the system

$$n = \frac{2.33\text{g}}{\text{cm}^3}\frac{\text{mol}}{28.09\text{g}}\frac{6.02\times10^{23}\text{atoms}}{\text{mol}}\frac{(100\text{cm})^3}{\text{m}^3} = 5\times10^{28}\frac{\text{atoms}}{\text{m}^3}$$

Now we need to determine the atomic radius of silicon from the data given. If we didn't know the crystal structure, we might guess roughly that

$$r = \frac{1}{2}n^{-1/3}$$

which would be exact for a simple cubic lattice. However, we know that Si is diamond structure with 8 atoms per conventional unit cell, so the density is $n = 8/a^3$ with a the lattice constant so $a = 2n^{-1/3}$. The nearest neighbor distance is from $[0,0,0]$ to $[a/4, a/4, a/4]$ or a distance of $a\sqrt{3}/4$, so the atomic radius is $a\sqrt{3}/8 = \frac{1}{4}n^{-1/3} = 1.17$ Angstrom. We then have

$$\chi = -\mu_0\frac{\rho e^2}{6m}\langle r^2\rangle \approx -4\times10^{-6}$$

This is much much greater than the diamagnetism of the few impurities. (Note: I think the table value is almost exactly this, however, this is fortuitous as the table value is usually given in cgs which differs from the SI version by a factor of 4 pi. Again the error is in the estimate of r^2.)

‡(19.6) Paramagnetism
Consider a gas of monatomic atoms with spin $S = 1/2$ (and $L = 0$) in a magnetic field B. The gas has density n.

(a) Calculate the magnetization as a function of B and T. Determine the susceptibility.

(b) Calculate the contribution to the specific heat of this gas due to the spins. Sketch this contribution as a function of $\mu_B B/k_B T$.

"Monatomic atoms" ? What was I smoking when I wrote this? It should say monovalent. Doh! I should have also specified the g-factor (as usual we can take it to be 2).

(a) Same calculation as we have done a million times.

$$\begin{aligned} Z &= e^{+\beta g\mu_B\frac{1}{2}B} + e{-}\beta g\mu_B\frac{1}{2}B \\ F &= -k_B T\log Z \\ m &= -\partial F/\partial B = g\mu_B\frac{1}{2}\tanh(\beta g\mu_B\frac{1}{2}B) \\ M &= mn \\ \chi &= \lim_{B\to0}\mu_0\partial M/\partial B = \mu_0 n(\frac{1}{2}g\mu_B)^2\beta \end{aligned}$$

(b) Similarly, we have

$$\begin{aligned} U &= \partial\log Z/\partial\beta = g\mu_B\frac{1}{2}B\tanh(\beta g\mu_B\frac{1}{2}B) \\ C &= \partial U/\partial T = \frac{1}{k_B T^2}(g\mu_B\frac{1}{2}B)^2\text{sech}^2(\beta g\mu_B\frac{1}{2}B) \end{aligned}$$

(19.7) Spin J Paramagnet*

Given the Hamiltonian for a system of non-interacting spin-J atoms

$$\mathcal{H} = \tilde{g}\mu_B \mathbf{B}\cdot\mathbf{J}$$

(a)* Determine the magnetization as a function of B and T.

(b) Show that the susceptibility is given by

$$\chi = \frac{n\mu_0(\tilde{g}\mu_B)^2}{3}\frac{J(J+1)}{k_B T}$$

where n is the density of spins. (You can do this part of the exercise without having a complete closed-form expression for part a!)

(a) The eigenenergies of a single spin are

$$E_m = \tilde{g}\mu_B B m \qquad m = -J, -J+1\,, -J+2\,, \ldots J-1\,, J$$

So the canonical partition function of the single spin is

$$\begin{aligned} Z &= \sum_{m=-J}^{J} e^{-\beta g \mu_B B m} = e^{\beta\tilde{g}\mu_b B J}\sum_{p=0}^{2J} e^{-\beta\tilde{g}\mu_B p} \\ &= e^{\beta\tilde{g}\mu_b B J}\,\frac{1-e^{-\beta\tilde{g}\mu_B B(2J+1)}}{1-e^{-\beta\tilde{g}\mu_B B}} = \frac{e^{\beta\tilde{g}\mu_B B(2J+1)/2}-e^{-\beta\tilde{g}\mu_B B(2J+1)/2}}{e^{\beta\tilde{g}\mu_B B/2}-e^{-\beta\tilde{g}\mu_B B/2}} \\ &= \frac{\sinh(\beta\tilde{g}\mu_B B(2J+1)/2)}{\sinh(\beta\tilde{g}\mu_B B/2)} \end{aligned}$$

we construct the free energy per spin $F/N = -k_B T \log Z$ and then get the magnetic moment per spin

$$\mathbf{m} = -\frac{\partial(F/N)}{\partial B} = (\tilde{g}\mu_B/2)\left[(2J+1)\coth(\beta\tilde{g}\mu_B B(2J+1)/2) - \coth(\beta\tilde{g}\mu_B B/2)\right]$$

and the total magnetizaton is then the moment per spin times the density of spins n, so

$$M = n(\tilde{g}\mu_B/2)\left[(2J+1)\coth(\beta\tilde{g}\mu_B B(2J+1)/2) - \coth(\beta\tilde{g}\mu_B B/2)\right]$$

(b) To obtain the susceptibility, we want

$$\chi = \lim_{B\to 0}\mu_0\frac{\partial M}{\partial B}$$

To take this limit we take the argument of the coth to be small and we use the expansion

$$\lim_{x\to 0}\coth x = \frac{1}{x} + \frac{x}{3}$$

Note that the two $1/x$ terms cancel when subtracted leaving

$$M \sim n(\tilde{g}\mu_B/2)\left[(2J+1)^2\beta\tilde{g}\mu_B B/6 - \beta\tilde{g}\mu_B B/6\right]$$

So we have

$$\chi = \frac{n\mu_0(\tilde{g}\mu_B)^2}{3}\frac{J(J+1)}{k_B T}$$

as required.

Note, the question claims that part (b) may be achieved without completing part (a). To do this, note that we only concerned with small B so we can expand the partition function directly for small B.

$$Z = \sum_{m=-J}^{J} e^{-\beta\tilde{g}\mu_B Bm} = \sum_{m=-J}^{J} 1 - \beta\tilde{g}\mu_B Bm + \frac{1}{2}(\beta\tilde{g}\mu_B B)^2 m^2 + \ldots$$

The first term in the sum gives $(2J+1)$ and the second term gives 0 by symmetry. The third term is the only hard one. I claim that

$$G[J] = \sum_{m=-J}^{J} = \frac{1}{3}(2J+1)(J+1)J \qquad (19.1)$$

I will derive this below, but for now let us assume it is correct. So we have

$$Z = (2J+1)[1 + \frac{1}{6}(\beta\tilde{g}\mu_B B)^2 J(J+1) + \ldots]$$

Using the free energy per spin is $F/N = -k_B T \log Z$, since B is small we have

$$F/N = -k_B T \log(2J+1) - \frac{1}{6k_B T}(\tilde{g}\mu_B B)^2 J(J+1)$$

And the magnetic moment per site is

$$m = -\frac{\partial(F/N)}{\partial B} = \frac{(\tilde{g}\mu_B)^2 BJ(J+1)}{3k_B T}$$

which multiplying by the density of spins n to give the magnetization, gives the same result as above.

Finally we turn to derive Eqn. 19.1. The result of this sum must be some polynomial in J. Further, approximating it as an integral, it must have a maximum power of J^3, and the coefficient of the J^0 term must be zero since $G[0] = 0$. Thus we propose

$$G[J] = aJ^3 + bJ^2 + cJ$$

Then we can also write the difference of two successive sums as just the new ad

$$G[J+1] - G[J] = 2(J+1)^2$$

which we multiply out to give

$$a(3J^2 + 3J + 1) + b(2J+1) + c = 2(J+1)^2$$

matching coefficients then gives the values of a, b, c which proves Eq. 19.1.

Spontaneous Magnetic Order: Ferro-, Antiferro-, and Ferri-Magnetism

20

(20.1) **Ferromagnetic vs Antiferromagnetic States**

Consider the Heisenberg Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\sum_{\langle i,j \rangle} J\,\mathbf{S}_i \cdot \mathbf{S}_j + \sum_i g\mu_B \mathbf{B}\cdot\mathbf{S}_i \qquad (20.1)$$

and for this exercise set $\mathbf{B} = 0$.

(a) For $J > 0$, i.e., for the case of a ferromagnet, intuition tells us that the ground state of this Hamiltonian should simply have all spins aligned. Consider such a state. Show that this is an eigenstate of the Hamiltonian Eq. 20.1 and find its energy.

(b) For $J < 0$, the case of an antiferromagnet on a cubic lattice, one might expect that (at least for $\mathbf{B} = 0$) the state where spins on alternating sites point in opposite directions might be an eigenstate. Unfortunately, this is not precisely true. Consider such a state of the system. Show that the state in question is not an eigenstate of the Hamiltonian.

Although the intuition of alternating spins on alternating sites is not perfect, it becomes reasonable for systems with large spins S. For smaller spins (like spin 1/2) one needs to consider so-called "quantum fluctuations" (which is much more advanced, so we will not do that here).

It is useful here to recall that

$$\mathbf{S_i}\cdot\mathbf{S_j} = \frac{1}{2}(S_i^+ S_j^- + S_i^- S_j^+) + S_i^z S_j^z$$

(Indeed, students often need to be reminded of this! Maybe it is worth giving this as a hint!)

(a) If each spin is aligned in the $\hat{z}$ direction (it has $S_z = 1$), then the energy is $-g\mu_b B$ per spin and for each bond we have energy $-J\mathbf{S}_i\cdot\mathbf{S}_j = -JS_i^z S_j^z = -JS^2$ since S^+ on the spins all give zero. The system is in an energy eigenstate with energy

$$E = -Ng\mu_B|B| - NzJS^2/2$$

with z the number of neighbors of each site (=6 for a cubic lattice).

(b) Assuming an antiferromagnetic configuration, the key here is to note that there are terms $S_i^+ S_j^-$ which do not vanish (where S^+ is applied to a down spin, and S^- is applied to an up spin). This means that when the hamiltonian is applied to the proposed antiferromagnetic ground states, it generates other spin configurations. Hence this is not an eigenstate.

(20.2) **Frustration**
Consider the Heisenberg Hamiltonian as in Exercise 20 with $J < 0$, and treat the spins as classical vectors.

(a) If the system consists of only three spins arranged in a triangle (as in Fig. 20.2), show that the ground state has each spin oriented 120° from its neighbor.

(b) For an infinite triangular lattice, what does the ground state look like?

Probably here I should have stated explicitly that all three spins have the same $|\mathbf{S}|$ (might be interesting to consider a case where they don't all have the same spin!).

(a) The Hamiltonian is

$$\mathcal{H} = J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_3)$$

Since $\mathbf{S_i} \cdot \mathbf{S_i} = S^2$ is a constant we can write

$$\mathcal{H} = (J/2)(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3)^2 + \text{constant}$$

To minimize the energy, we must have

$$\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 = 0$$

which implies that the spins are at 120 degree angles from each other – but can lie in any plane.

(b) For a triangular lattice, each triangle must have three spins each at 120 degree angles from its neighbors. So choose three directions all at 120 degree angles from each other in any given plane. Call these three directions A, B, C. Now we must assign each site on the triangular lattice one of the three values A, B, or C in such a way that all triangles contain one site of type A, one of type B, and one of type C. One can think of this as being now a crystal whose unit cell has three times the area of the original unit cell, and now contains one spin of each type A, B, C.

(20.3) **Spin Waves***
For the spin-S ferromagnet particularly for large S, our "classical" intuition is fairly good and we can use simple approximations to examine the excitation spectrum above the ground state.

First recall the Heisenberg equations of motion for any operator

$$i\hbar \frac{d\hat{O}}{dt} = [\hat{O}, \mathcal{H}]$$

with $\mathcal{H}$ the Hamiltonian (Eq. 20.1 with $\mathbf{S_i}$ being a spin S operator).

(a) Derive equations of motion for the spins in the Hamiltonian Eq. 20.1. Show that one obtains

$$\hbar \frac{d\mathbf{S_i}}{dt} = \mathbf{S_i} \times \left(J \sum_j \mathbf{S_j} - g\mu_b \mathbf{B} \right) \qquad (20.2)$$

where the sum is over sites j that neighbor i.

In the ferromagnetic case, particularly if S is large, we can treat the spins as not being operators, but rather as being classical variables. In the ground state, we can set all $\mathbf{S_i} = \hat{z}S$ (Assuming $\mathbf{B}$ is in the $-\hat{z}$ direction so the ground state has spins aligned in the $\hat{z}$ direction). Then to consider excited states, we can perturb around this solution by writing

$$\begin{aligned} S_i^z &= S - \mathcal{O}((\delta S)^2/S) \\ S_i^x &= \delta S_i^x \\ S_i^y &= \delta S_i^y \end{aligned}$$

where we can assume δS^x and δS^y are small compared to S. Expand the equations of motion (Eq. 20.2) for small perturbation to obtain equations of motion that are linear in δS_x and δS_y

(b) Further assume wavelike solutions

$$\begin{aligned} \delta S_i^x &= A_x e^{i\omega t - i\mathbf{k}\cdot\mathbf{r}} \\ \delta S_i^y &= A_y e^{i\omega t - i\mathbf{k}\cdot\mathbf{r}} \end{aligned}$$

This ansatz should look very familiar from our prior consideration of phonons.

Plug this form into your derived equations of motion.

▷ Show that S_i^x and S_i^y are out of phase by $\pi/2$. What does this mean?

▷ Show that the dispersion curve for "spin-waves" of a ferromagnet is given by $\hbar\omega = |F(\mathbf{k})|$ where

$$\begin{aligned} &F(\mathbf{k}) = g\mu_b|B| \\ &\quad + JS(6 - 2[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]) \end{aligned}$$

where we assume a cubic lattice.

▷ How might these spin waves be detected in an experiment?

(c) Assume the external magnetic field is zero. Given the spectrum you just derived, show that the specific heat due to spin wave excitations is proportional to $T^{3/2}$.

(a) We need the angular momentum algebra

$$[S^x, S^y] = iS^z$$

and cyclic permutations of this. We then have the Heisenberg equations

$$i\hbar \frac{dS_i^x}{dt} = [S_i^x, \mathcal{H}]$$

The only terms that this does not commute with are those containing S_i^y and S_i^z. Thus we have

$$i\hbar \frac{dS_i^x}{dt} = [S_i^x, g\mu_b(B_y S_i^y + B_z S_i^z) - J\sum_j (S_j^y S_i^y + S_j^z S_i^z)]$$

with the sum over j being over neighbors of i. Thus we obtain

$$i\hbar \frac{dS_i^x}{dt} = i\left[(g\mu_b)(B_y S_i^z - B_z S_i^y) - J\sum_j (S_j^y S_i^z - S_j^z S_i^y)\right]$$

and similar for the other two components of the spin. Thus we conclude

$$\hbar \frac{d\mathbf{S_i}}{dt} = \mathbf{S_i} \times \left(J\sum_j \mathbf{S_j} - g\mu_b \mathbf{B}\right)$$

Writing

$$\mathbf{S_i} = \hat{z}S + \boldsymbol{\delta S_i}$$

we obtain

$$\hbar \frac{d\boldsymbol{\delta S_i}}{dt} = JS\hat{z} \times \sum_j \boldsymbol{\delta S_j} + \boldsymbol{\delta S_i} \times (JZS\hat{z} + g\mu_b|B|)$$

where Z is the number of neighbors of a site.

(b) Plugging in the wave ansatz (for a cubic lattice) we obtain

$$\begin{aligned} i\hbar\omega A_x &= F(\mathbf{k})A_y \\ i\hbar\omega A_y &= -F(\mathbf{k})A_x \end{aligned}$$

where

$$F(\mathbf{k}) = JS(6 - 2[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]) + g\mu_b|B|$$

This system of equations can be solved immediately to give dispersion $\hbar\omega = |F(\mathbf{k})|$

Spin waves are typically detected by inelastic neutron scattering. This is like scattering from phonons except that one uses (spin-polarized) neutrons in order to couple to the spin.

(c) For small $k = |\mathbf{k}|$, and hence small energy, the energy spectrum is quadratic

$$E = JSa^2k^2$$

We will also need

$$k = (E/JSa^2)^{1/2}$$

and

$$dk = dE/(2(EJSa^2)^{1/2})$$

Calculating the total energy stored in spin waves, we have

$$U = V\int_{BZ} \frac{\mathbf{dk}}{(2\pi)^3} E(\mathbf{k}) n_B(E(\mathbf{k})) \approx \frac{V}{2\pi^2}\int_0^\infty dk k^2 E(k) n_B(E(k))$$

with n_B the usual Bose factor and the approximation accurate for low temperatures. We rewrite this as

$$\begin{aligned} U &= \frac{V}{4\pi^2(JSa^2)^{3/2}}\int_0^\infty dE E^{3/2} n_B(E) \\ &= \frac{V(k_bT)^{5/2}}{4\pi^2(JSa^2)^{3/2}}\int_0^\infty dx \frac{x^{5/2}}{e^x - 1} \end{aligned}$$

which we differentiate to get the heat capacity

$$C = dU/dT = k_b \frac{5}{2}\frac{V(k_bT)^{3/2}}{4\pi^2(JSa^2)^{3/2}}\int_0^\infty dx \frac{x^{5/2}}{e^x - 1}$$

(one does not really need to carry all of the constants to see how it scales!). For those who are interested though, the integral can be evaluated in the usual way

$$\int_0^\infty dx \frac{x^{5/2}}{e^x - 1} = \sum_{n=1}^\infty \int_0^\infty dx x^{5/2} e^{-nx} = \sum_{n=1}^\infty \frac{1}{n^{7/2}}\int_0^\infty dy y^{5/2} e^{-y} = \Gamma(7/2)\zeta(7/2)$$

where $\Gamma(7/2) = 15\sqrt{\pi}/8$ and $\zeta(7/2) \approx 1.1267\ldots$.

(20.4) **Small Heisenberg Models**

(a) Consider a Heisenberg model containing a chain of only two spins, so that

$$\mathcal{H} = -J\mathbf{S_1}\cdot\mathbf{S_2} \quad .$$

Supposing these spins have $S = 1/2$, calculate the energy spectrum of this system. Hint: Write $2\mathbf{S_1}\cdot\mathbf{S_2} = (\mathbf{S_1}+\mathbf{S_2})^2 - \mathbf{S_1}^2 - \mathbf{S_1}^2$.

(b) Now consider three spins forming a triangle (as shown in Fig. 20.2). Again assuming these spins are $S = 1/2$, calculate the spectrum of the system. Hint: Use the same trick as in part (a)!

(c) Now consider four spins forming a tetrahedron. Again assuming these spins are $S = 1/2$, calculate the spectrum of the system.

Note the obvious typo, it should read $2\mathbf{S_1}\cdot\mathbf{S_2} = (\mathbf{S_1}+\mathbf{S_2})^2 - \mathbf{S_1}^2 - \mathbf{S_2}^2$.

(a)

$$\mathcal{H} = -(J/2)[(\mathbf{S}_1+\mathbf{S}_2)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2]$$

Since $(\mathbf{S})^2 = S(S+1)$ for spin-1/2 we have $(\mathbf{S})^2 = 3/4$. Further, when two spin 1/2's are added they can form either a spin-0 singlet or a spin-1 triplet (three S_z states). So $(\mathbf{S}_1+\mathbf{S}_2)^2$ takes the values 0 for the singlet or $S(S+1) = 2$ for the $S = 1$ triplet. Thus the Hamiltonian has eigenstates $3J/4$ for the singlet (one eigensate) and $-J/4$ for the triplet (three eigenstates).

(b) Similarly

$$\mathcal{H} = -(J/2)[(\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2 - \mathbf{S}_3^2]$$

Here, again for spin 1/2 we have $(\mathbf{S})^2 = 3/4$. When adding three spin-1/2s, we can obtain spin-1/2 in two ways and spin-3/2 in one way. (To see this, think about adding the first two spin-1/2 to get spin-0 or spin-1. Now adding a spin-1/2 the spin-0 gives spin-1/2 and adding spin-1/2 to the spin-1 gives either spin-1/2 or spin-3/2. Note that counting the total nbumber of eigenstates we should get 8 since each spin-1/2 has two possible S_z states. Each of the two possible spin-1/2's can take two possible S_z states and the spin-3/2 can take 4 possible S_z states, which gives a total of 8 possible S_z states.

In the case that the three spins add to spin-1/2, we obtain energy $3J/4$ (four eigenstates) whereas if the three spins add to spin-3/2, $\mathbf{S}^2 = S(S+1) = 15/4$, so the energy is $-3J/4$ (four eigenstates).

(c) Same story

$$\mathcal{H} = -(J/2)[(\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3+\mathbf{S}_4)^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2 - \mathbf{S}_3^2 - \mathbf{S}_4^2]$$

The sum of the four spins can give spin 0 in two ways, spin 1 in 3 ways, and spin 2 in one way. Again we should add up the total number of eigenstates to check that it is $2^4 = 16$. We have 2 spin 0's + 3 states for spin 1 in 3 ways + 5 states in spin 2. So we have $2+9+5 = 16$. The spin-0 singlets (two eigenstates) have energy $(-J/2)[0-4(3/4)] = 3J/2$. The three spin-1 triplets (9 eigenstates) have energy $(-J/2)[2-4(3/4)] = J/2$ and the spin-2 fiveplets (5 eigenstates) have energy $(-J/2)[2\times 3 - 4(3/4)] = -3J/2$

(20.5) **One-Dimensional Ising Model with $B = 0$**

(a) Consider the one-dimensional Ising model with spin $S = 1$. We write the Hamiltonian for a chain of N spins in zero magnetic field as

$$\mathcal{H} = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}$$

where each σ_i takes the value ±1. The partition function can be written as

$$Z = \sum_{\sigma_1, \sigma_2, \ldots \sigma_N} e^{-\beta H} \quad .$$

Using the transformation $R_i = \sigma_i \sigma_{i+1}$ rewrite the partition function as a sum over the R variables, and hence evaluate the partition function.

▷ Show that the free energy has no cusp or discontinuity at any temperature, and hence conclude that there is no phase transition in the one-dimensional Ising model.

(b) *At a given temperature T, calculate an expression for the probability that M consecutive spins will be pointing in the same direction. How does this probability decay with M for large M? What happens as T becomes small? You may assume $N \gg M$.

(a) The first spin can be either in the spin-up or spin down state, so we leave σ_1 as a variable to be summed over. The remaining spins are defined by R_i for $i = 1, \ldots N-1$ where each R can take the values ±1. The Hamitonian in terms of the R variables is

$$\mathcal{H} = -J \sum_{i=1}^{N-1} R_i$$

So the partition function is

$$Z = 2(e^{-\beta J} + e^{\beta J})^{N-1} = 2(2\cosh(\beta J))^{N-1}$$

with the factor of 2 out front being the sum over the first spin. The free energy is thus

$$F = -k_B T \log Z = -k_B T N \log 2 - k_b T N \log \cosh(\beta J)$$

which is a completely continuous function with no cusps or discontinuities at finite β.

(b) The probability that a given R is in the +1 state is

$$P(R = +1) = \frac{e^{\beta J}}{e^{\beta J} + e^{-\beta J}} = \frac{1}{e^{-2\beta J} + 1}$$

Having R in the +1 state tells us that two consecutive spins are pointing in the same direction. Looking at $M-1$ consecutive values of R, the probability that all of these are +1 is then

$$P(M) = \left(\frac{1}{e^{-2\beta J} + 1} \right)^{M-1}$$

which would put M consecutive spins in the same direction. This probability decays exponentially with M. To see this, rewrite

$$P(M) = \exp[-(M-1)\log(e^{-2\beta J} + 1)]$$

so the decay length is $1/\log(e^{-2\beta J}+1)$. In the low tempearture limit $P(R+1)$ becomes close to unity, and the decay length becomes long. Actually, we can see that for very large β we have $\log(e^{-2\beta J}+1) \approx e^{-2\beta J}$, so the decay length is $e^{2\beta J}$ lattice sites and is exponentially long.

(20.6) **One-Dimensional Ising Model with $B \neq 0$***

Consider the one-dimensional Ising model with spin $S=1$. We write the Hamiltonian (Eq. **??**) for a chain of N spins in magnetic field B as

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i \tag{20.3}$$

where

$$\begin{aligned} \mathcal{H}_1 &= h\sigma_1 \\ \mathcal{H}_i &= -J\sigma_i\sigma_{i-1} + h\sigma_i \qquad \text{for } i > 1 \end{aligned}$$

where each σ_i takes the value ± 1 and we have defined $h = g\mu_B B$ for simplicity of notation.

Let us define a partial partition function for the first M spins (the first M terms in the Hamiltonian sum Eq. 20.3) *given that* the M^{th} spin is in a particular state. I.e.,

$$Z(M,\sigma_M) = \sum_{\sigma_1,\ldots,\sigma_{M-1}} e^{-\beta\sum_{i=1}^{M}\mathcal{H}_i}$$

so that the full partition function is $Z = Z(N,+1) + Z(N,-1)$.

(a) Show that these partial partition functions satisfy a recursion relation

$$Z(M,\sigma_M) = \sum_{\sigma_{M-1}} T_{\sigma_M,\sigma_{M-1}} Z(M-1,\sigma_{M-1})$$

where T is a 2 by 2 matrix, and find the matrix T. (T is known as a "transfer matrix").

(b) Write the full partition function in terms of the matrix T raised to the $(N-1)^{th}$ power.

(c) Show that the free energy per spin, in the large N limit, can be written as

$$F/N \approx -k_B T \log \lambda_+$$

where λ_+ is the larger of the two eigenvalues of the matrix T.

(d) From this free energy, derive the magnetization, and show that the susceptibility per spin is given by

$$\chi \propto \beta e^{2\beta J}$$

which matches the Curie form at high T.

(a) The transfer matrix takes the form

$$T = \begin{pmatrix} e^{-\beta\mathcal{H}(+,+)} & e^{-\beta\mathcal{H}(+,-)} \\ e^{-\beta\mathcal{H}(-,+)} & e^{-\beta\mathcal{H}(-,-)} \end{pmatrix} = \begin{pmatrix} e^{-\beta(-J+h)} & e^{-\beta(J-h)} \\ e^{-\beta(J+h)} & e^{-\beta(-J-h)} \end{pmatrix}$$

(b) The full partition function is then

$$Z = vT^{N-1}v^T$$

where $v = (1,1)$. Although T is not hermitian, it can still be brought to diagonal form via a Jordon decomposition

$$T = J\Lambda J^{-1}$$

where Λ is a diagonal matrix of the eigenvalues of T and J is a matrix made of the eigenvectors of T (these are no longer orthonormal!). (c) Assuming these two eigenvalues are not degenerate, we then have for large N that

$$Z \sim \lambda_+^{N-1}$$

where λ_+ is the larger of the two eigenvalues. Thus the free energy per site is

$$F/N \sim -k_B T \log \lambda_+$$

For the record, the value of the larger eigenvalue is

$$\lambda_+ = \frac{e^{-\beta(h+J)}}{2}\left(1 + e^{2\beta h} + \sqrt{1 - 2e^{2\beta h} + e^{4\beta h} + 4e^{4\beta(h+J)}}\right)$$

Just to check that this agrees with the previous problem, note that setting $h = 0$ we correctly obtain

$$\lambda_+ = e^{-\beta J} + e^{\beta J}$$

(d) Probably we want to derive the magnetic moment per spin which is

$$m = -\frac{\partial(F/N)}{\partial B} = g\mu_B k_b T \frac{\partial \log \lambda_+}{\partial h}$$

The result is a bit of a mess. Then once we have this, we want the susceptibility per spin

$$\chi = \mu_0 \partial m / \partial B$$

which one evaluates at $B = 0$. It is much easier to make expansions for small h since this is all we will need. In the end we will obtain

$$\chi = g^2 \mu_B^2 \mu_0 k_b T \frac{\partial^2 \log \lambda_+}{\partial h^2} = g^2 \mu_B^2 \mu_0 \beta e^{-2\beta J}$$

as claimed.

Domains and Hysteresis

21

(21.1) **Domain Walls and Geometry**

Suppose a ferromagnet is made up of a density ρ of spins each with moment μ_B.

(a) Suppose a piece of this material forms a long circular rod of radius r and length $L \gg r$. In zero external magnetic field, if all of the moments are aligned along the L-direction of the rod, calculate the magnetic energy of this ferromagnet. (Hint: a volume of aligned magnetic dipoles is equivalent to a density of magnetic monopoles on its surface.)

(b) Suppose now the material is shaped such that $r \gg L$. What is the magnetic energy now?

(c) If a domain wall is introduced into the material, where might it go to minimize the magnetic energy in the two different geometries. Estimate how much magnetic energy is saved by the introduction of the domain wall.

(d) Suppose the spins in this material are arranged in a cubic lattice, and the exchange energy between nearest neighbors is denoted J and the anisotropy energy is very large. How much energy does the domain wall cost? Comparing this energy to the magnetic energy, what should we conclude about which samples should have domain walls?

(e) Note that factors of the lattice constant a are often introduced in quoting exchange and anisotropy energies to make them into energies per unit length or unit volume. For magnetite, a common magnetic material, the exchange energy is $JS^2/a = 1.33 \times 10^{-11}$ J/m and the anisotropy energy is $\kappa S^2/a^3 = 1.35 \times 10^4$ J/m^3. Estimate the width of the domain wall and its energy per unit area. *Make sure you know the derivation of any formulas you use!*

(a) Following the hint, the magnetic energy between two monopoles of charge q_m and q'_m separated by distance r is given by

$$E = \frac{\mu_0}{4\pi} \frac{q_m q'_m}{r}$$

Here we have charge of magnitude $q_m = \mu_B A \rho$ where $A = \pi r^2$ is the area of the end. Check that this has the right dimensions, recall that a dipole is a charge times a length, so q_m correctly has dimension of a charge.

Thus the energy is

$$\frac{\mu_0}{4\pi} \frac{(\mu_B \rho(\pi r^2))^2}{L}$$

(b) This problem, on the other hand is analogous to the energy of a capacitor. The energy stored in a capacitor is $q^2/(2C)$ where electrically the capacitance is $\epsilon_0 A/d$ with A the area and d the spacing. The analogy here is thus $A/(d\mu_0)$. Thus the total energy stored is

$$E = q_m^2 \mu_0 d/(2A) = \frac{\mu_0 (\mu_B \rho)^2 (\pi r^2) L}{2}$$

(c) First, let us consider a domain wall that cuts L in half (i.e., a plane parallel to the A surface). This puts two magnetic charges of the same sign right next to each other and is therefore energetically unfavorable. Now consider a domain wall perpendicular to this plane — i.e., that runs along the L axis. In the (a) case we can view this as, instead of having a single charge at each end of the rod, now we have two opposite charges along each end of the rod (each with charge $\pm q_m/2$). This completely kills the leading energy cost and now we have instead some sort of dipolar interaction between the two ends — with energy typically on the much smaller order

$$E = \frac{\mu_0}{4\pi}\frac{(\mu_B \rho(\pi r^2/2))^2 r^2}{L^3}$$

Similarly with the capacitor configuration of part (b), we can convert "charge" energy to "dipole" energy by placing a domain wall in the diraction along the axis (in the direction of L). However, here we will not be able to consider the system "dipolar" until the size of the domains d is smaller than L. Once we do this, the energy will again drop as in the (a) case proportional to d^6/L^3

(d) Since the lattice spacing will be $a = \rho^{-1/3}$, the energy of introducing a domain wall of area $\mathcal{A}$ is $\mathcal{A}J\rho^{2/3} = 2LrJ\rho^{2/3}$. In the (a) case, for large enough L, the magnetic energy is not very large to begin with, so introducing an energy cost proportional to L is not a very good idea. Now let us consider the (b) case. Let us consider introducing a domain wall network spaced by d. The number of domains is $\pi r^2/d^2$ and the total aread of the walls will be $\pi r^2 L/d$ and their total domain wall energy will be $\pi r^2 LJ\rho^{2/3}/d$. As a function of d, as discussed in part (c) then magnetic energy drops strongly when $d < L$. Thus, there will be some happy medium which optimizes the total energy.

(e) As mentioned in the text, the width of a domain wall should be $\sqrt{J/\kappa}$ which here is 3100 lattice spacings. The energy per unit area is then $\sqrt{J\kappa} = 4 \times 10^7$ Joules per a^2 area.

(21.2) **Critical Field for Crystallite**

(a) Given that the energy of a crystallite in a magnetic field is given by

$$E/V = E_0 - |M||B|\cos\theta - \kappa'|M|^2(\cos\theta)^2$$

show that for $|B| < B_{crit}$ there is a local energy minimum where the magnetization points opposite the applied field, and find B_{crit}.

(b)* In part (a) we have assumed **B** is aligned with the anisotropy direction of the magnetization. Describe what can occur if these directions are not aligned.

(c) For small B, roughly how large (in energy per unit volume) is the activation barrier for the system to get from the local minimum to the global minimum.

(d) Can you make an estimate (in terms of actual numbers) of how big this activation barrier would be for a ferromagnetic crystal of magnetite that is a sphere of radius 1 nm ? You may use the parameters given in Exercise 31.1.e (you may need to estimate some other parameters as well).

(a) Let $\cos\theta = z$. The function $E(z)$ is an upside-down parabola with maxium at $z = -B/(2\kappa'|M|) < 0$. If this parameter is $z > -1$ then there are two minima, one at $\theta = 0$ and the other at $\theta = \pi$. The absolute minium is always at $\theta = 0$.

(b) Let us consider B again pointing in the $\hat{z}$ direction and the anisotropy direction oriented at an angle ϕ from $\hat{z}$. In this case we have an energy functional

$$E/V = E_0 - |M||B|\cos\theta - \kappa'|M|^2[\cos(\theta-\phi)]^2$$

If $y = \kappa|M|/(2B)$ is small, then the minimum will always be close to 0. If this parameter is greater than 1/2, then there may be a metastable minimum as well, although for y close to 1/2 then there is only a metastable minimum if ϕ is close to zero. If y is large, then the metastable minima always exist near to ϕ and $\phi + \pi$.

(c) Consider small B, so z is close to zero. In this case, $E_{min} = E_0 - \kappa|M|^2$ and $E_{max} = E_0$. So the activation barrier is $\kappa|M|^2$.

(d) The activation barrier is just the total anisotropy energy. This is $1.35 \times 10^4 \mathrm{J/m}^3$ and the size is $(4/3)\pi \times 1nm^3 \approx 10^{-26}m^3$, so we have a total energy of about $10^{-22}J \approx 10$Kelvin activation energy.

(21.3) **Exact Domain Wall Solution***

The approximation used in Section 21.1.1 of the energy of the anisotropy (κ) term is annoyingly crude. To be more precise, we should instead write $\kappa S^2(\cos\theta_i)^2$ and then sum over all spins i. Although this makes things more complicated, it is still possible to solve the problem so long as the spin twists slowly so that we can replace the finite difference $\delta\theta$ with a derivative, and replace the sum over sites with an integral. In this case, we can write the energy of the domain wall as

$$E = \int \frac{dx}{a}\left\{\frac{JS^2a^2}{2}\left(\frac{d\theta(x)}{dx}\right)^2 - \kappa S^2[\cos\theta(x)]^2\right\}$$

with a the lattice constant.

(a) Using calculus of variations show that this energy is minimized when

$$(Ja^2/\kappa)d^2\theta/dx^2 - \sin(2\theta) = 0$$

(b) Verify that this differential equation has the solution

$$\theta(x) = 2\tan^{-1}\left(\exp\left[\sqrt{2}(x/a)\sqrt{\frac{\kappa}{J}}\right]\right)$$

thus demonstrating the same $L \sim \sqrt{J/\kappa}$ scaling.

(c) Show that the total energy of the domain wall becomes $E_{tot}/(A/a^2) = 2\sqrt{2}S^2\sqrt{J\kappa}$.

It is better to write the first equation as $+\sin^2$ instead of $-\cos^2$. These differ only by a constant, but in the former case, the background energy is zero whereas as written the background energy is finite.

(a) This is a trivial exercise in calculus of variations. To clarify it, write $\theta = \theta_0 + \delta\theta$ and expand to linear order in $\delta\theta$. Isolating the terms inside the integral linear in $\delta\theta$, and then integrating by parts to remove the derivatives gives

$$\left\{-JS^2a^2\left(\frac{d^2\theta(x)}{dx^2}\right) + 2\kappa S^2\cos\theta(x)\sin\theta(x)\right\}\delta\theta(x)$$

Setting this variation to zero immediately gives the desired result.

(b) This is an exercise in nasty algebra. First write $b = \sqrt{2}(1/a)\sqrt{\frac{\kappa}{J}}$ so that we have

$$\theta(x) = 2\tan^{-1}(e^{bx})$$

From this we obtain on the left of the equation

$$d\theta/dx = 2b\frac{e^{bx}}{1+e^{2bx}} = \frac{b}{\cosh(bx)} \tag{21.1}$$

$$d^2\theta/dx^2 = -\frac{b^2\sinh(bx)}{\cosh^2(bx)} \tag{21.2}$$

On the right of the equation we need to evaluate

$$\sin 2\theta = 2\sin\theta\cos\theta = 4\sin\frac{\theta}{2}\cos\frac{\theta}{2}(\cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2}) \tag{21.3}$$

We have $\theta/2 = \tan^{-1}(e^{bx})$ so $e^{bx} = \tan\frac{\theta}{2}$ so we have $1 + e^{2bx} = \sec^2\frac{\theta}{2}$ so

$$\begin{aligned}\cos\frac{\theta}{2} &= \frac{1}{\sqrt{1+e^{2bx}}}\\ \sin\frac{\theta}{2} &= \frac{e^b x}{\sqrt{1+e^{2bx}}}\end{aligned}$$

Plugging these results into the prior expression for $\sin 2\theta$ the gives

$$\sin 2\theta = 4\frac{e^{bx}}{1+e^{2bx}}\frac{1-e^{2bx}}{1+e^{2bx}} = \frac{-2\sinh(bx)}{\cosh^2(bx)}$$

Comparing this result to Eq. 21.2 along with the expression for b immediately confirms the desired solution.

(c) Starting with

$$E = \int \frac{dx}{a}\left\{\frac{JS^2a^2}{2}\left(\frac{d\theta(x)}{dx}\right)^2 + \kappa S^2[\sin\theta(x)]^2\right\}$$

we have $d\theta/dx = \frac{b}{\cosh(bx)}$ and

$$\sin\theta = 2\cos\theta/2\sin\theta/2 = \frac{2e^{bx}}{1+e^{2bx}} = 1/\cosh(bx)$$

This then naturally gives

$$E = \int \frac{dx}{a}\left\{\frac{JS^2a^2}{2}\left(\frac{b}{\cosh(bx)}\right)^2 + \kappa S^2\frac{1}{\cosh^2(bx)}\right\}$$

Plugging in the value of b this simplifies to

$$E = 2\kappa S^2\int\frac{dx}{a}\frac{1}{\cosh^2 bx} = \frac{2\kappa S^2}{ab}\int dx\frac{1}{\cosh x}$$

plug in the value of b to get a prefactor of $S^2\sqrt{2\kappa J}$ and the integral of sech^2 is tanh thus giving a factor of 2, yielding the desired result.

Mean Field Theory

22

(22.1) ‡ **Weiss Mean Field Theory of a Ferromagnet**

Consider the spin-1/2 ferromagnetic Heisenberg Hamiltonian on the cubic lattice:

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j \rangle} \mathbf{S_i}\cdot\mathbf{S_j} + g\mu_B \mathbf{B}\sum_i \mathbf{S_i} \qquad (22.1)$$

Here, $J > 0$, with the sum indicated with $\langle i,j\rangle$ means summing over i and j being neighboring sites of the cubic lattice, and $\mathbf{B}$ is the externally applied magnetic field, which we will assume is in the $\hat{z}$ direction for simplicity. The factor of 1/2 out front is included so that each pair of spins is counted only once. Each site i is assumed to have a spin $\mathbf{S_i}$ of spin $S = 1/2$. Here μ_B is the conventional Bohr magneton defined to be positive. The fact that the final term has a + sign out front is from the fact that the electron charge is negative, therefore the magnetic moment opposes the spin direction. If one were to assume that these were nuclear spins the sign would be reversed (and the magnitude would be much smaller due to the larger nuclear mass).

(a) Focus your attention on one particular spin $\mathbf{S_i}$, and write down an effective Hamiltonian for this spin, treating all other variables $\mathbf{S_j}$ with $j \neq i$ as expectations $\langle \mathbf{S_j}\rangle$ rather than operators.

(b) Calculate $\langle \mathbf{S_i}\rangle$ in terms of the temperature and the fixed variables $\langle \mathbf{S_j}\rangle$ to obtain a mean-field self-consistency equation. Write the magnetization $M = |\mathbf{M}|$ in terms of $\langle \mathbf{S}\rangle$ and the density of spins.

(c) At high temperature, find the susceptibility $\chi = dM/dH = \mu_0 dM/dB$ in this approximation.

(d) Find the critical temperature in this approximation.

▷ Write the susceptibility in terms of this critical temperature.

(e) Show graphically that in zero external field ($\mathbf{B} = 0$), below the critical temperature, there are solutions of the self-consistency equation with $M \neq 0$.

(f) Repeat parts (a)–(d) but now assuming there is an $S = 1$ spin on each site (meaning that S_z takes the values $-1, 0, +1$).

(a) The effective Hamiltonian for one spin-1/2 is

$$\mathcal{H}_i = \mathbf{S_i}\cdot\left[-J\sum_j \langle \mathbf{S_j}\rangle + g\mu_b\mathbf{B}\right] = +\mathbf{S_i}\cdot g\mu_b\mathbf{B}_{i,eff}$$

where

$$g\mu_b\mathbf{B}_{i,eff} = g\mu_b\mathbf{B} - J\sum_j \langle \mathbf{S_j}\rangle$$

with the sums being over sites j neighboring site i. (Note the factor of 1/2 out front is now missing).

(b)Assuming $\mathbf{B}$ aligned with $\hat{z}$ tells us that $\langle \mathbf{S_k}\rangle$ should be aligned with $-\hat{z}$ if nonzero. Thus we can treat these quantities as scalars rather than vectors. We then have the usual calculation

$$\begin{aligned} Z_i &= \exp(\beta g\mu_b B_{i,eff}(1/2)) + \exp(-\beta g\mu_b B_{i,eff}(1/2)) \qquad (22.2) \\ \langle S_i^z\rangle &= -\frac{1}{2}\tanh[\beta g\tilde{\mu}_b B_{eff}(1/2)] \end{aligned}$$

which gives us the self consistency equation

$$\langle S_z \rangle = -\frac{1}{2} \tanh[\beta(g\mu_b B - Jz\langle S_z \rangle)(1/2)] \tag{22.3}$$

where z is the number of neighboring spins for each site (which is $z = 6$ for a cubic lattice).

(c) At high T the magnetization is zero in the absence of a field. Thus for small field we can expand the tanh for small argument to obtain.

$$\langle S_z \rangle = -\frac{1}{2}[\beta(g\mu_b B - Jz\langle S_z \rangle)(1/2)]$$

or

$$\langle S_z \rangle = \frac{(-1/4)\beta(g\mu_b B)}{1 - \beta Jz/4}$$

The moment per site is thus

$$m = -g\mu_b \langle S_z \rangle = \frac{(1/4)(g\mu_b)^2 B}{k_b T - Jz/4}$$

giving the susceptibility

$$\chi = \frac{(\mu_0/4)(g\mu_b)^2 N}{k_b T - Jz/4} = \frac{(1/4)(g\mu_b)^2 N}{k_b(T - T_c)} \tag{22.4}$$

refWeissMeanFerro where N is the density of spins.

(d) the critical temperature is the point where the susceptibility diverges, or $k_b T_c = Jz/4$.

(e) Graphically we plot the right and left sides of Eq. 22.3 as shown roughly in Fig. 22.1. The horizontal axis is $-\langle S \rangle$. The left side of the equation is a straight line, the right side is a tanh. At high enough T, these intersect only at $\langle S \rangle = 0$, however at $T < T_c$ they intersect as well at a finite value of $\langle S \rangle$. Note that the point at which the curves are tangent is the critical temperature. We will show in the next problem that below T_c the solution with $\langle S \rangle = 0$ is unstable.

(f) The procedure is the same for $S = 1$. In this case, the partition function Eq. 22.2 is replaced by

$$Z_i = \exp(\beta g\mu_b B_{i,eff}) + 1 + \exp(-\beta g\mu_b B_{i,eff}) \tag{22.5}$$

leading to

$$\langle S_i^z \rangle = \frac{-2\sinh(x)}{2\cosh(x) + 1}$$

with $x = \beta g\mu_b B_{eff} = \beta(g\mu_b B - Jz\langle S_i^z \rangle)$. At high T we expand for small x we obtain the equation

$$\langle S^z \rangle = \frac{-2x}{3} = \frac{-2}{3}\beta(g\mu_b B - Jz\langle S^z \rangle)$$

which then gives us

$$\langle S^z \rangle = \frac{(-2/3)\beta g\mu_b B}{1 - \frac{2}{3}\beta Jz}$$

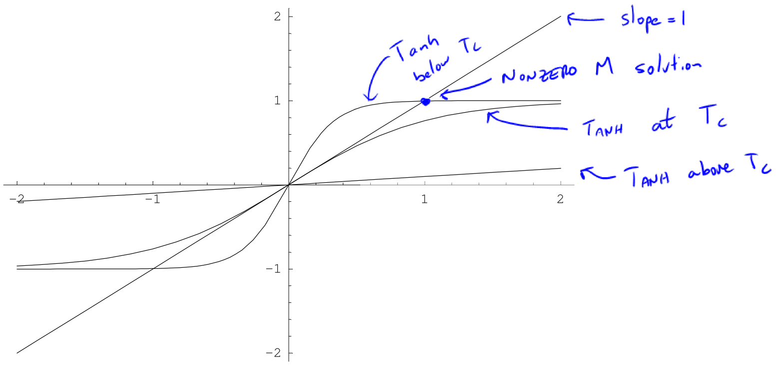


Fig. 22.1 graphical solution of Eq. 22.3

or a susceptibility of

$$\chi = \frac{(2/3)\mu_0(g\mu_b)^2 N}{k_b T - \frac{2}{3}Jz}$$

and a critical temperature of $k_b T_c = (2/3)Jz$ (where N is the density of spins).

(22.2) **Bragg-Williams Approximation**

This exercise provides a different approach to obtaining the Weiss mean-field equations. For simplicity we will again assume spin 1/2 variables on each site.

Assume there are N lattice sites in the system. Let the average spin value be $\langle S_i^z \rangle = s$. Thus the probability of a spin being an up spin is $P_\uparrow = 1/2 + s$ whereas the probability of a spin being a down spin is $P_\downarrow = 1/2 - s$. The total number of up spins or down spins is then $NP_\uparrow$ and $NP_\downarrow$ respectively where there are N total lattice sites in the system.

(a) Consider first a case where sites do not interact with each other. In the micro-canonical ensemble, we can count the number of configurations (microstates) which have the given number of spin-ups and spin-downs (determined by s). Using $S = k_B \ln \Omega$, calculate the entropy of the system in the large N limit.

(b) Assuming all sites have independent probabilities $P_\uparrow$ and $P_\downarrow$ of pointing up and down respectively, calculate the probability that two neighboring sites will point in the same direction and the probability that two neighboring sites will point in opposite directions.

▷ Use this result to calculate an approximation to the expectation of the Hamiltonian. Note: This is not an exact result, as in reality, sites that are next to each other will have a tendency to have the same spin because that will lower their energies, but we have ignored this effect here.

(c) Putting together the results of (a) and (b) above, derive the approximation to the free energy

$$\begin{aligned} F &= E - TS \\ &= Nk_BT\left[(\frac{1}{2}+s)\log(\frac{1}{2}+s)\right. \\ &\quad \left. + (\frac{1}{2}-s)\log(\frac{1}{2}-s)\right] \\ &\quad + g\mu_B B_z N s - JNzs^2/2 \end{aligned}$$

where z is the number of neighbors each spin has, and we have assumed the external field $\mathbf{B}$ to be in the $\hat{z}$ direction. (Again we assume the spin is electron spin so that the energy of a spin interacting with the external field is $+g\mu_b\mathbf{B}\cdot\mathbf{S}$.)

(d) Extremize this expression with respect to the variable s to obtain the Weiss mean field equations.

▷ Below the critical temperature note that there are three solutions of the mean field equations.

▷ By examining the second derivative of F with respect to s, show that the $s = 0$ solution is actually a maximum of the free energy rather than a minimum.

▷ Sketch $F(s)$ both above and below the critical temperature for $B = 0$. At non-zero B?

(a) The number of configurations is

$$\Omega = \begin{pmatrix} N \\ N_\uparrow \end{pmatrix} = \frac{N!}{(N(1/2+s))!(N(1/2-s))!}$$

giving the entropy (using Stirling's approximation)

$$S = k_b \ln\Omega = -k_b N\left[(\frac{1}{2}+s)\log(\frac{1}{2}+s) + (\frac{1}{2}-s)\log(\frac{1}{2}-s)\right]$$

(b) The expected energy per bond is $-J(1/2)^2$ times the probability of having like spins on neighboring sites plus $J(1/2)^2$ times the probability of having unlike spins. We thus have

$$E/bond = -(J/4)[P_\uparrow P_\uparrow + P_\downarrow P_\downarrow] + 2(J/4)P_\uparrow P_\downarrow = -(J/4)(P_\uparrow - P_\downarrow)^2 = -Js^2$$

If there are $Nz/2$ bonds in the whole system (with z being the number of neighbors of each site) we thus obtain a total energy

$$E = -JNzs^2/2$$

We must add to this the coupling to the external field which is simply $Ng\mu_B s$. Adding these terms together $F = E - TS$ gives us the desired result.

(c)

$$\frac{1}{N}\frac{dF}{ds} = g\mu_b B - sJz + k_b T\left[\log(\frac{1}{2}+s) - \log(\frac{1}{2}-s)\right]$$

Setting this to zero we obtain

$$\beta(-g\mu_b B + sJz) = \left[\log(\frac{1}{2}+s) - \log(\frac{1}{2}-s)\right]$$

defining the left to be x, we exponentiate both sides to get

$$e^x = \frac{1/2+s}{1/2-s}$$

which we rearrange to

$$s = \frac{1}{2}\frac{e^x-1}{e^x+1} = \frac{1}{2}\tanh(x/2) = \frac{1}{2}\tanh(\beta(-g\mu_b B + sJz)/2)$$

which is the same self-consistency condition.

(d) Look at the second derivative

$$\frac{1}{N}\frac{d^2F}{ds^2} = -Jz + k_bT\left[\frac{1}{1/2+s} + \frac{1}{1/2-s}\right]$$

Now examine this at $s = 0$, we obtain

$$\left.\frac{1}{N}\frac{d^2F}{ds^2}\right|_{m=0} = -Jz + 4k_bT$$

Note that this changes sign exactly at the critical temperature! Thus below T_c the $s = 0$ solution becomes a maximum of the free energy rather than a minimum as it is as above T_c. The free energy as a function of s is plotted in Fig. 22.2.

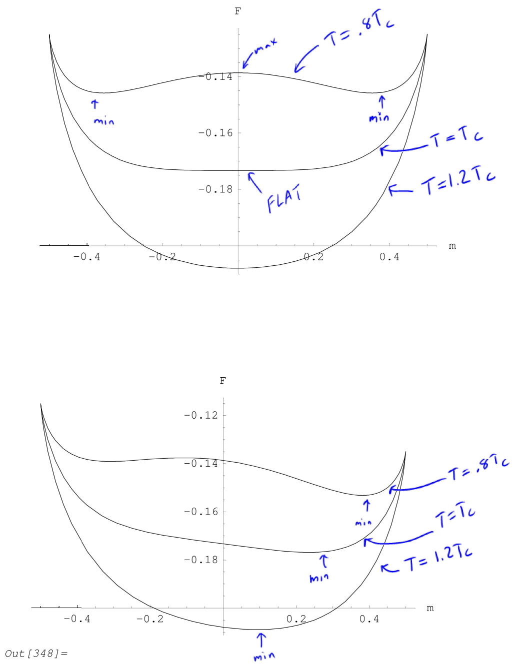


Fig. 22.2 Free energy (vertical axis) as a function of s (horizontal axis), at, and below T_c. Left: in zero applied B. Right: In $g\mu_b B = 0.02T_c$

(22.3) **Spin S Mean Field Theory**
Using the result of Exercise 19.7 use mean field theory to calculate the critical temperature for a spin S ferromagnet with a given g-factor g, having coordination number z and nearest-neighbor exchange coupling J_{ex}. (It may be useful to re-solve Exercise 19.7 if you don't remember how this is done.)

From Exercise 19.7, in a field B the resulting $\langle S \rangle$ per site (for small perturbation B) is given by

$$\langle S \rangle = \frac{S(S+1)}{3} \beta g \mu_B B$$

And in mean field theory, the effective field seen from neighboring spins is

$$g\mu_B B_{eff} = J_{ex} z \langle S \rangle$$

Thus we have at the crtical point

$$\langle S \rangle = \frac{S(S+1)}{3} \beta J_{ex} z \langle S \rangle$$

which has the solution for the critical temperature

$$k_b T_c = \frac{S(S+1)}{3} J_{ex} z$$

(22.4) **Low-Temperature Mean Field Theory**
Consider the $S = 1/2$ ferromagnet mean field calculation from Exercise 22.1. At zero temperature, the magnet is fully polarized.

(a) Calculate the magnetization in the very low temperature limit. Show that the deviation from fully polarized becomes exponentially small as T goes to zero.

(b)* Now consider a spin S ferromagnet. Determine the magnetization in the low T limit. You can express your result conveniently in terms of the result of Exercise 22.3.

(c)* In fact this exponential behavior is not observed experimentally! The reason for this has to do with spin-waves, which are explored in Exercise 20.3, but are not included in mean field theory. Using some results from that exercise, determine (roughly) the low-temperature behavior of the magnetization of a ferromagnet.

(a) In absence of external field, using the results of 22.1, the self consistency equation is

$$S_z = \frac{1}{2} \tanh(\beta J z S_z / 2)$$

For large argument x we have

$$\tanh x = \frac{1 - e^{-2x}}{1 + e^{-2x}} \approx 1 - 2e^{-2x}$$

So at low temperature we have

$$S_z \approx \frac{1}{2} - e^{-\beta J z S_z}$$

Since at low temperature, S_z is very close to $1/2$, this becomes

$$S_z \approx \frac{1}{2} - e^{-\beta J z / 2}$$

Another way to see this is to note that, if all the neighbors are aligned, then $g\mu B_{eff} = Jz\frac{1}{2}$. Thus the energy for flipping a given spin in this effective field is $Jz/2$. So the activated deviation from fully aligned is $e^{-\beta Jz/2}$.

(b) Probably the easiest way to do this one is to use the final comment of part (a). If all the spins are aligned to extremize S_z, the effective field is $g\mu B_{eff} = JzS$. The low energy excitations excite S_z by a single step at activation energy JzS, thus we obtain

$$S_z = S - e^{-\beta JzS}$$

I have no idea what the comment about expressing the answer in terms of 22.3!

(c) As noted in problem 20.3 the low energy spectrum of spin waves (in absence of external field) is given by

$$\hbar\omega = JSa^2|\mathbf{k}|^2$$

Each excitation reduces the magnetization by one step. The total number of spins is $V/(a^3)$ and the number of excitations (the number of lost steps) at finite T is

$$V\int \frac{\mathbf{dk}}{(2\pi)^3} n_B(\hbar\omega_k)$$

with n_B the bose factor. Thus, for each spin the reduction in magnetization is

$$a^3\frac{4\pi}{(2\pi)^3}\int_0^\infty dk k^2 \frac{1}{e^{\beta JS^2a^2k^2}-1} = \frac{1}{2\pi^2}\left(\frac{k_bT}{JS^2}\right)^{3/2}\int_0^\infty dx \frac{x^2}{e^x-1}$$

and the final integral gives $2\zeta(3) \approx 2.4$.

(22.5) **Mean Field Theory for the Antiferromagnet**

For this Exercise we use the molecular field (Weiss mean field) approximation for the spin-1/2 *antiferromagnetic* model on a three-dimensional cubic lattice. The full Hamiltonian is exactly that of Eq. 22.1, except that now we have $J < 0$, so neighboring spins want to point in opposite directions (compared to a ferromagnet where $J > 0$ and neighboring spins want to point in the same direction). For simplicity let us assume that the external field points in the $\hat{z}$ direction.

At mean field level, the ordered ground state of this Hamiltonian will have alternating spins pointing up and down respectively. Let us call the sublattices of alternating sites, sublattice A and sublattice B respectively (i.e, A sites have lattice coordinates (i, j, k) with $i+j+k$ odd whereas B sites have lattice coordinates with $i+j+k$ even).

In mean field theory the interaction between neighboring spins is replaced by an interaction with an average spin. Let $s_A = \langle S^z\rangle_A$ be the average value of the spins on sublattice A, and $s_B = \langle S^z\rangle_B$ be the average value of the spins on sublattice B (we assume that these are also oriented in the $\pm\hat{z}$ direction).

(a) Write the mean field Hamiltonian for a single site on sublattice A and the mean field Hamiltonian for a single site on sublattice B.

(b) Derive the mean-field self-consistency equations

$$\begin{aligned} s_A &= \frac{1}{2}\tanh(\beta[JZs_B - g\mu_B B]/2) \\ s_B &= \frac{1}{2}\tanh(\beta[JZs_A - g\mu_B B]/2) \end{aligned}$$

with $\beta = 1/(k_BT)$. Recall that $J < 0$.

(c) Let $B = 0$. Reduce the two self-consistency equations to a single self-consistency equation. (Hint: Use symmetry to simplify! Try plotting s_A versus s_B.)

(d) Assume $s_{A,B}$ are small near the critical point and expand the self-consistency equations. Derive the critical temperature T_c below which the system is antiferromagnetic (i.e., $s_{A,B}$ become non-zero).

(e) How does one detect antiferromagnetism experimentally?

(f) In this mean-field approximation, the magnetic susceptibility can be written as

$$\chi = -(N/2) g \mu_0 \mu_B \lim_{B \to 0} \frac{\partial (s_A + s_B)}{\partial B}$$

(why the factor of 1/2 out front?).

▷ Derive this susceptibility for $T > T_c$ and write it in terms of T_c.

▷ Compare your result with the analogous result for a ferromagnet (Exercise 22). In fact, it was this type of measurement that first suggested the existence of antiferromagnets!

(g)* For $T < T_c$ show that

$$\chi = \frac{(N/4)\mu_0 (g\mu_b)^2 (1 - (2s)^2)}{k_B T + k_B T_c (1 - (2s)^2)}$$

with s the staggered moment (ie, $s(T) = |s_A(T)| = |s_B(T)|$).

▷ Compare this low T result with that of part f.

▷ Give a sketch of the susceptibility at all T.

This follows very much problem 22 (a)

$$\begin{aligned} \mathcal{H}_{i,A} &= \mathbf{S_i} \cdot \left[-J \sum_j \langle \mathbf{S_j}_B \rangle + g\mu_b \mathbf{B} \right] \\ \mathcal{H}_{i,B} &= \mathbf{S_i} \cdot \left[-J \sum_j \langle \mathbf{S_j}_A \rangle + g\mu_b \mathbf{B} \right] \end{aligned}$$

(b) solving as above gives the desired self-consistency equations.

(c) For $B = 0$ we have

$$\begin{aligned} s_A &= \frac{1}{2} \tanh(\beta J Z s_B / 2) \\ s_B &= \frac{1}{2} \tanh(\beta J Z s_A / 2) \end{aligned}$$

These are solved by

$$s_A = -s_B = \frac{1}{2} \tanh(\beta J Z s_B / 2) = -\frac{1}{2} \tanh(\beta J Z s_A / 2)$$

Recall that $J < 0$. (Since tanh is an odd function these are the only possible solutions for $J < 0$, which one can check graphically by plotting s_A versus s_B).

Thus the problem is reduced to

$$s_A = -\frac{1}{2} \tanh(\beta J Z s_A / 2) = \frac{1}{2} \tanh(\beta |J| Z s_A / 2)$$

which is identical to the relation we obtained in the ferromagnetic case.

(d) As in the ferromagnet $k_b T_c = z|J|/4$.

(e) This staggered moment is most easily observed with neutron scattering where the scattering will be spin-dependent. Going into the antiferromagnetic phase there is a new unit cell of lattice constant $2a$, thus one sees new diffraction peaks at $k = n2\pi/(2a)$ (with n odd) which are not present above T_c.

(f)The factor of 1/2 is because we have only $N/2$ A sites or B sites. Expanding the self consistency equations for high T we obtain

$$\begin{aligned} s_A &= \beta[JZs_B - g\mu_b B]/4) \\ s_B &= \beta[JZs_A - g\mu_b B]/4) \end{aligned}$$

One can solve this system of two equations in two unknowns to obtain

$$s_A = s_B = \frac{-\beta g\mu_b B}{4 - \beta Jz}$$

Thus giving

$$\chi = \frac{(1/4)\mu_0 (g\mu_b)^2 N}{k_b(T + T_c)}$$

compare to the $T - T_c$ factor in Eq. 22.4.

(g) This required implicit differentiation. Differentiating our two self-consistency equations gives

$$\begin{aligned} \left.\frac{\partial s_A}{\partial B}\right|_{B=0} &= \left(\frac{\beta JZ}{4} \left.\frac{\partial s_B}{\partial B}\right|_{B=0} - \frac{\beta g\mu_b}{4}\right) \operatorname{sech}^2(\beta JZ s_B/4) \\ \left.\frac{\partial s_B}{\partial B}\right|_{B=0} &= \left(\frac{\beta JZ}{4} \left.\frac{\partial s_A}{\partial B}\right|_{B=0} - \frac{\beta g\mu_b}{4}\right) \operatorname{sech}^2(\beta JZ s_A/4) \end{aligned}$$

Noting that $s_A = -s_B = s$ so both sech terms are the same, we add both equations together to get

$$\left.\frac{\partial(s_A + s_B)}{\partial B}\right|_{h=0} = \left(\frac{\beta JZ}{4} \left.\frac{\partial(s_A + s_B)}{\partial B}\right|_{B=0} - \frac{\beta g\mu_b}{2}\right) \operatorname{sech}^2(\beta JZ s/4)$$

Making note that $\operatorname{sech}^2 + \tanh^2 = 1$, we then have

$$\operatorname{sech}^2(\beta JZ s/4) = 1 - \tanh^2(\beta JZ m/4) = 1 - (2s)^2$$

where we have used the self-consistency equation to replace the tanh by s. We thus have

$$\left.\frac{\partial(s_A + s_B)}{\partial B}\right|_{B=0} = \left(\frac{\beta JZ}{4} \left.\frac{\partial(s_A + s_B)}{\partial B}\right|_{B=0} - \frac{\beta g\mu_b}{2}\right) (1 - (2s)^2)$$

This then can be rearranged into

$$\left(\left.\frac{\partial(s_A + s_B)}{\partial B}\right|_{B=0}\right) \left(1 - \beta JZ(1 - (2s)^2)/4\right) = -(\beta g\mu_b/2)(1 - (2s)^2)$$

or

$$\chi = \frac{(N/4)\mu_0 (g\mu_b)^2 (1 - (2s)^2)}{k_b T + k_b T_c(1 - (2s)^2)}$$

with s the staggered moment (with N the density of spins). Above T_c, we have $s = 0$ and we have the same behavior as part f above. Below T_c, the factor $1 - (2s)^2$ goes quickly down to zero, and the susceptibility drops rapidly. At T_c there is a cusp. This behavior is illustrated in the figure 22.3

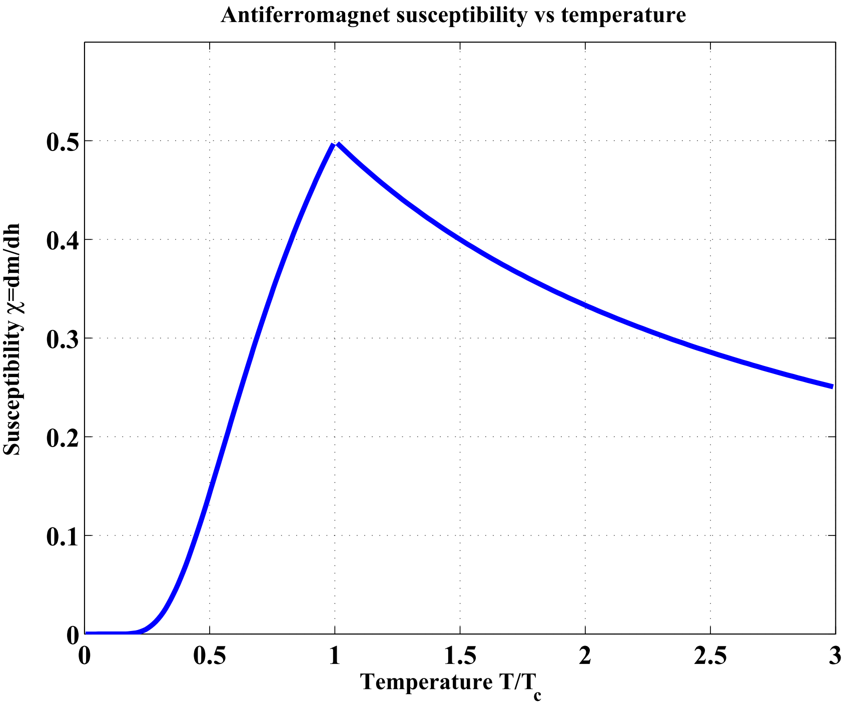


Fig. 22.3 Susceptibility of an Antiferromagnet.

(22.6) **Correction to Mean Field***
Consider the spin-1/2 Ising ferromagnet on a cubic lattice in d dimensions. When we consider mean field theory, we treat exactly a single spin σ_i and the $z = 2d$ neighbors on each side will be considered to have an average spin $\langle\sigma\rangle$. The critical temperature you calculate should be $k_B T_c = Jz/4$.

To improve on mean field theory, we can instead treat a block of two connected spins σ_i and $\sigma_{i'}$ where the neighbors outside of this block are assumed to have the average spin $\langle\sigma\rangle$. Each of the spins in the block has $2d - 1$ such averaged neighbors. Use this improved mean field theory to write a new equation for the critical temperature (it will be a transcendental equation). Is this improved estimate of the critical temperature higher or lower than that calculated in the more simple mean-field model?

We have to consider four configurations in our partition function:

$$(\uparrow,\uparrow),(\uparrow,\downarrow),(\downarrow,\uparrow),(\downarrow,\downarrow)$$

Correspondingly, the partition function is

$$Z = e^{-\beta(J\langle\sigma\rangle(z-1)+g\mu_B B)-\beta J/4} + 2e^{\beta J/4} + e^{\beta(J\langle\sigma\rangle(z-1)+g\mu_B B)-\beta J/4}$$

From this we calculate the magnetization per site (note that this partition function represents two sites), and then setting B to zero we obtain

$$m = \langle\sigma\rangle = \frac{e^{-\beta J/4}\sinh(\beta(J\langle\sigma\rangle(z-1))}{2e^{-\beta J/4}\cosh(\beta(J\langle\sigma\rangle(z-1)) + 2e^{\beta J/4}}$$

Expanding for small $\langle\sigma\rangle$ we find equality (which finds T_c) when

$$k_B T = \frac{J(z-1)}{4}\left[\frac{e^{-\beta J/4}}{\cosh(\beta J/4)}\right]$$

The final factor in brackets is always less than unity, so this expression always gives a lower prediction for T_c than our prior mean field theory.

Magnetism from Interactions: The Hubbard Model

23

(23.1) **Itinerant Ferromagnetism**

(a.i) Review 1: For a three-dimensional tight binding model on a cubic lattice, calculate the effective mass in terms of the hopping matrix element t between nearest neighbors and the lattice constant a.

(a.ii) Review 2: Assuming the density n of electrons in this tight binding band is very low, one can view the electrons as being free electrons with this effective mass m^*. For a system of spinless electrons show that the total energy per unit volume (at zero temperature) is given by

$$E/V = nE_{min} + Cn^{5/3}$$

where E_{min} is the energy of the bottom of the band.

$\triangleright$ Calculate the constant C.

(b) Let the density of spin-up electrons be $n_\uparrow$ and the density of spin-down electrons be $n_\downarrow$. We can write these as

$$\begin{aligned} n_\uparrow &= (n/2)(1+\alpha) \qquad (23.1)\\ n_\downarrow &= (n/2)(1-\alpha) \qquad (23.2)\end{aligned}$$

where the total net magnetization of the system is given by

$$M = -\mu_b n\alpha B.$$

Using the result of part (a), fixing the total density of electrons in the system n,

$\triangleright$ calculate the total energy of the system per unit volume as a function of α.

$\triangleright$ Expand your result to fourth order in α.

$\triangleright$ Show that $\alpha = 0$ gives the lowest possible energy.

$\triangleright$ Argue that this remains true to all orders in α

(c) Now consider adding a Hubbard interaction term

$$H_{Hubbard} = U \sum_i N_\uparrow^i N_\downarrow^i$$

with $U \geq 0$ where N_σ^i is the number of electrons of spin σ on site i.

Calculate the expectation value of this interaction term given that the up and down electrons form Fermi seas with densities $n_\uparrow$ and $n_\downarrow$ as given by Eqns. 23.1 and 23.2.

$\triangleright$ Write this energy in terms of α.

(d) Adding together the kinetic energy calculated in part b with the interaction energy calculated in part c, determine the value of U for which it is favorable for α to become non-zero.

$\triangleright$ For values of U not too much bigger than this value, calculate the magnetization as a function of U.

$\triangleright$ Explain why this calculation is only an approximation.

(e) Consider now a two-dimensional tight binding model on a square lattice with a Hubbard interaction. How does this alter the result of part (d)?

(a.i) The tight binding spectrum is

$$E = E_0 - 2t\left[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right]$$

which we expand to get

$$E = E_{min} + ta^2|\mathbf{k}|^2$$

where $E_{min} = E_0 - 6t$ is the bottom of the band. We thus have

$$ta^2|\mathbf{k}|^2 = \hbar^2|\mathbf{k}|^2/(2m^*)$$

or

$$m^* = \frac{\hbar^2}{2ta^2}$$

(a.ii) As we have calculated many times (note we are considering spin polarized electrons here, so there is no factor of 2 out front)

$$N = \frac{V}{(2\pi)^3}\int_0^{kf} \mathbf{dk} = \frac{V}{(2\pi)^3}\int_0^{kf} 4\pi k^2 dk = \frac{V}{(2\pi)^3}\frac{4\pi k_f^3}{3}$$

or

$$k_f = (6\pi^2 n)^{1/3}$$

The total energy is given by

$$\begin{aligned} E - E_{min}N &= \frac{V}{(2\pi)^3}\int_0^{kf} \frac{\hbar^2 k^2}{2m^*}\mathbf{dk} = \frac{V}{(2\pi)^3}\int_0^{kf} \frac{\hbar^2 k^2}{2m^*}4\pi k^2 dk \\ &= \frac{V}{(2\pi)^3}\frac{\hbar^2}{2m^*}\frac{4\pi k_f^5}{5} = \frac{V}{20\pi^2}\frac{\hbar^2}{m^*}k_f^5 \end{aligned}$$

Thus we have

$$E/V = E_{min}n + Cn^{5/3}$$

with

$$C = \frac{1}{20\pi^2}\frac{\hbar^2}{m^*}(6\pi^2)^{5/3} = \frac{ta^2}{10\pi^2}(6\pi^2)^{5/3}$$

(b) Note that n remains fixed. So we have

$$\begin{aligned} E/V - E_{min}n &= +C\left[n_\uparrow^{5/3} + n_\downarrow^{5/3}\right] \\ &= C(n/2)^{5/3}\left[(1+\alpha)^{5/3} + (1-\alpha)^{5/3}\right] \end{aligned}$$

Taylor expanding here, note that the odd terms of the expansion cancel leaving only even terms

$$\begin{aligned} E/V - E_{min}n &= 2C(n/2)^{5/3}\left[1 + (1/2!)(5/3)(2/3)\alpha^2 + \right. \\ &\quad \left.(1/4!)(5/3)(2/3)(-1/3)(-4/3)\alpha^4 + \ldots\right] \\ &= 2C(n/2)^{5/3}\left[1 + (5/9)\alpha^2 + (5/243)\alpha^4 + \ldots\right] \end{aligned}$$

Note that successive terms of the expansion always have positive coefficient.

(c) The expected number of electrons per unit site is na^3 and similarly $n_\uparrow a^3$ and $n_\downarrow a^3$ are the expected number of spin up and spin down electrons per site. Thus, the expectation of the hubbard interaction per unit volume is

$$\begin{aligned} E_{hubbard}/V &= (U/a^3)(n_\uparrow a^3)(n_\downarrow a^3) = Ua^3 n_\uparrow n_\downarrow \\ &= Ua^3(n/2)^2(1+\alpha)(1-\alpha) = Ua^3(n/2)^2(1-\alpha^2) \end{aligned}$$

(d) We thus obtain a total energy given by

$$E_{total}/V = \text{constant} + \alpha^2 \left[2C(5/9)(n/2)^{5/3} - Ua^3(n/2)^2\right] + \alpha^4 \left[2C(n/2)^{5/3}(5/243)\right] + \ldots \quad (23.3)$$

And taking the limit of small α we see that $\alpha = 0$ is the solution only for

$$U \leq 2C(5/9)(n/2)^{-1/3}$$

For U not too much bigger than this, we can use the quartic form of the energy given in Eq. 23.3. Minimizing with respect to α gives

$$\alpha = \sqrt{\frac{-2C(5/9)(n/2)^{5/3} + Ua^3(n/2)^2}{4C(n/2)^{5/3}(5/243)}}$$

and $M = -\mu_b n\alpha$.

(e) In the 2d case, the key here is that $N \sim k_f^2$ and $\epsilon \sim E_F^2$, so $E/V \sim n^2$. As a result, we have the kinetic term given by

$$E = \tilde{C}[(1+\alpha)^2 + (1-\alpha^2)] = 2\tilde{C}[1+\alpha^2]$$

and there is no quartic term. Thus, we have a total energy of the form

$$E_{total} = \text{const} + \alpha^2(\tilde{C} - \tilde{K}U)$$

Once U becomes large enough that $\alpha = 0$ is not the lowest energy solution, then α immediately goes to its maximum possible value 1. Thus, the transition is discontinuous going suddenly from unpolarized spins to fully polarized spins.

(23.2) **Antiferromagnetism in the Hubbard Model**

Consider a tight binding model with hopping t and a strong Hubbard interaction

$$H_{Hubbard} = U \sum_i N_\uparrow^i N_\downarrow^i \quad .$$

(a) If there is one electron per site, if the interaction term U is very strong, explain qualitatively why the system must be an insulator.

(b) On a square lattice, with one electron per site, and large U, use second-order perturbation theory to determine the energy difference between the ferromagnetic state and the antiferromagnetic state. Which one is lower energy?

(a) If U is strong enough, there must always be one electron per site. This makes a traffic jam of electrons where no one can move (so long as there is no doping).

(b) For the antiferromagnet, each spin can make a virtual excursion to each of the neighboring sites, at an energy cost of U. If the hopping is t at 2nd order in perturbation theory, this gives a reduction in the ground state energy, per site, of

$$-2zt^2/U$$

where z is the number of neighbors. For a ferromagnet, no excursion is allowed by the Pauli principle, so it is higher energy.