CMP PS2

Richard Fern

1 Chemical Bonding

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

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

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

Type	How	Where	What
Ionic	Electrons transfer, ions attract	Electronegative atoms (group 7) steal weakly bound e^- (from group 1,2)	Brittle, hard to melt, insulating and soluble
Covalent	Electrons shared, delocalisation preferred	Atoms with similar electronegativities (groups 3-5)	Brittle, hard to melt, insulating
Metallic	Electrons delocalise, sticking ions together	Metals (see most of periodic table)	Soft, easy to melt, conductive
Van der Waals	Dipoles induce dipoles, dipoles attract	Noble gases and molecules	Soft, easy to melt, insulating
Hydrogen	H slightly positive, attracts to things	Organics and liquids	Soft, easy to melt, insulating

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

An atom or molecule can have a very small fluctuating dipole due to electronic motion about the nucleus of size P_1, which creates small electric fields at a distance r of the form $E_1 \sim \frac{P_1}{r^3}$. This induces a polarisation in atoms or molecules nearby, linear in the field strength (to first order), so $P_2 \sim E_1$. Therefore the energy between the two dipoles is roughly

$$U \sim -E_1 P_2 \sim E_1^2 \sim \frac{P_1^2}{r^6}$$

and so the force falls off as $\frac{1}{r^7}$.

(c) The ionisation energy of a sodium (Na) atom is 5.14eV. The electron affinity of a chlorine (Cl) atom is 3.62eV. The bond length of a sodium-chloride molecule (i.e, one Na atom and one Cl atom) is 0.236nm. Assuming the cohesive energy is purely Coulomb energy, calculate the total energy released when a Na atom and a Cl atom come together to form a NaCl molecule. The actual experimental value is 4.26eV. Qualitatively account for the sign of your error.

Removing the electron from sodium and placing it on chlorine costs us an energy of

$$\Delta E_{\text{Na}} - \Delta E_{\text{Cl}} = 1.52\text{eV}.$$

The subsequent attractive energy however, is

$$\Delta E_{\text{Coulomb}} = -\frac{e^2}{4\pi\epsilon_0 R} = 6.10\text{eV}.$$

Therefore, the energy release is

$$\Delta E_{\text{Bond}} = 4.58\text{eV}.$$

This is slightly more than is actually released because we cannot treat the ions as point particles so we have ignored the repulsion of the electron clouds of the atoms, which will sit quite close to each other at such short separations. However, even without this picture we know some repulsion must exist as the particles do not sit exactly on each another, so this must make the Coulomb energy larger (less negative) at these separations.

2 Covalent Bonding in Detail

(a) **Linear Combination of Atomic Orbitals (LCAO)** In class 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 wavefunction $|n\rangle$ for $n = 1, \ldots, N$. For simplicity, let us assume this basis is orthogonal $\langle n|m\rangle = \delta_{n,m}$.

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). We would like to find the lowest energy wavefunction we can construct of this form, that is 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 Schrödinger equation

$$\mathcal{H}\phi = E\phi \tag{2.1}$$

where ϕ is the vector of N coefficients ϕ_n, and $\mathcal{H}$ is the $N \times N$ 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

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

i) Show that minimising this energy with respect to each ϕ_n gives the same eigenvalue equation, Eq. (2.1) (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 Schrödinger equation will be an approximation to the first excited state.

This technique is known as the molecular orbital approach, or the LCAO (linear combination of atomic orbitals) approach. It is used heavily in numerical simulation of molecules. However, more generally, one cannot assume that the basis set of orbitals is orthonormal (see problem 6.5 from the book for handling the LCAO without this assumption).

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i) Let's write everything out in full,

$$E = \left(\sum_{n,m} \phi_n^* \phi_m \langle n|H|m\rangle \right) \left(\sum_{n',m'} \phi_{n'}^* \phi_{m'} \left\langle n'|m'\right\rangle \right)^{-1}.$$

We are told to assume that the basis is orthonormal, which simplifies the denominator. We are then looking for an equation in terms of ϕ_n so we will differentiate with respect to ϕ_n^*,

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so

$$\frac{\partial E}{\partial \phi_n^*} = 0 = \frac{\partial}{\partial \phi_n^*} \left(\sum_{n',m'} \phi_{n'}^* \phi_{m'} \mathcal{H}_{n',m'} \right) \left(\sum_m \phi_m^* \phi_m \right)^{-1}$$

$$= \left(\sum_{m'} \phi_{m'} \mathcal{H}_{n,m'} \right) \left(\sum_n |\phi_n|^2 \right)^{-1} - \phi_n \left(\sum_{nm} \phi_n^* \phi_m \mathcal{H}_{n,m} \right) \left(\sum_n \phi_n^* \phi_n \right)^{-2}.$$

We then recognise the first term as $\frac{1}{\langle \psi | \psi \rangle} (\mathcal{H}\phi)_n$ and the second term as $\frac{E}{\langle \psi | \psi \rangle} \phi_n$ and so indeed we find

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

(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

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r} - \boldsymbol{R}_1) + V(\boldsymbol{r} - \boldsymbol{R}_2) = K + V_1 + V_2$$

where V is the Coulomb interaction between the electron and the nucleus, $\boldsymbol{R}_1$ is the position of the first nucleus and $\boldsymbol{R}_2$ 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

$$(K + V_1)|1\rangle = \epsilon|1\rangle,$$
$$(K + V_2)|2\rangle = \epsilon|2\rangle.$$

Define also the cross-energy element

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

and the hopping matrix element

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

i) Why can we write V_{cross} and t equivalently using either one of the expressions given on the right hand side?
ii) Show that the eigenvalues of our Schrödinger equation (2.1) are given by

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

iii) Argue (perhaps using Gauss' 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.
iv) This approximation must fail when the atoms get sufficiently close. Why?

i) We can use either of the expressions for t or V_{cross} because of the reflection symmetry in the problem. Sites 1 and 2 are equivalent.
ii) From our effective Schrödinger equation we have

$$\mathcal{H} = \begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix} = \begin{pmatrix} \epsilon + V_{\text{cross}} & -t \\ -t^* & \epsilon + V_{\text{cross}} \end{pmatrix}.$$

Thus, the eigenvalues are indeed

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

iii) Assuming the charge distributions of the electrons about the nuclei are spherical, Gauss'
law tells us that we can treat the charge due to the cloud as a point charge at the position of
the nucleus (when viewed from outside the cloud). Therefore, the charge seen by the other
nucleus outside the cloud is $+Ze$ from the nucleus and $-Ze$ from the electrons, both charges
sitting at the same position and hence cancelling out.

iv) As a first approximation, let's assume that the charge distribution stays spherical. There-
fore, as nucleus 2 begins to penetrate into the charge cloud of atom 1 the effective negative
charge due to the electrons becomes smaller (again, using Gauss' law) and so there is some
overall repulsion (of course, the charge distribution won't stay exactly spherical but this
might even make things worse as it's centre of mass will probably be pushed away from
nucleus' position due to the repulsion from electron cloud 2).

As a model of thermal expansion, we study the distance between two nearest neighbour atoms in an anharmonic potential that looks roughly like this
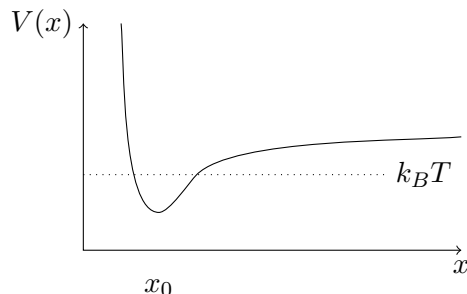
where x is the distance between two neighbouring atoms. This potential can be expanded around its minimum as

$$V(x) = \frac{\kappa}{2}(x - x_0)^2 - \frac{\kappa_3}{3!}(x - x_0)^3 + \dots \tag{3.1}$$

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 we are defining the energy at the bottom of the well to be zero here).
A very accurate approximate form for the inter-atomic potentials (particularly for inert atoms such as helium or argon) is given by the so-called Lennard-Jones potential

$$V(x) = 4\epsilon \left[\left(\frac{\sigma}{x}\right)^{12} - \left(\frac{\sigma}{x}\right)^6 \right] + \epsilon \tag{3.2}$$

where ϵ and σ are constants that depend on the particular atoms we are considering.
i) 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).
ii) By expanding Eq. (3.2) around its minimum, and comparing to Eq. (3.1), 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.

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i) The exponent of 6 is chosen to replicate the long range behaviour of the Van der Waals interaction we discussed in the first question. That the attraction is unlikely to be of this form for small separations is not important because the x^{12} term takes over here.
ii) Firstly we must find the minimum.

$$\frac{dV}{dx} = 4\epsilon \left[-12\sigma^{12}x^{-13} + 6\sigma^6 x^{-7} \right] = 0$$

$$\implies x_0 = 2^{\frac{1}{6}}\sigma.$$

The simplest way to find the next coefficients is then to calculate the higher differentials,

$$V(x_0 + \delta x) = \frac{\delta x^2}{2} \left.\frac{d^2V}{dx^2}\right|_{x_0} + \frac{\delta x^3}{3!} \left.\frac{d^3V}{dx^3}\right|_{x_0} + \dots.$$

So,

$$\left.\frac{\mathrm{d}^2 V}{\mathrm{d}x^2}\right|_{x_0} = \kappa = 4\epsilon \left[156\sigma^{12}x_0^{-14} - 42\sigma^6 x_0^{-8}\right]$$

$$\kappa = 4\epsilon \left[\frac{39}{2^{\frac{1}{3}}\sigma^2} - \frac{21}{2^{\frac{1}{3}}\sigma^2}\right] = \frac{72}{2^{\frac{1}{3}}}\frac{\epsilon}{\sigma^2}.$$

Furthermore,

$$-\left.\frac{\mathrm{d}^3 V}{\mathrm{d}x^3}\right|_{x_0} = \kappa_3 = 4\epsilon \left[2184\sigma^{12}x_0^{-15} - 336\sigma^6 x_0^{-8}\right]$$

$$\kappa_3 = 4\epsilon \left[\frac{546}{\sqrt{2}\,\sigma^3} - \frac{168}{\sqrt{2}\,\sigma^3}\right] = \frac{1512}{\sqrt{2}}\frac{\epsilon}{\sigma^3}.$$

4 Classical Model of Thermal Expansion

In classical statistical mechanics we write the expectation of x as

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

Although one cannot generally do such integrals for arbitrary potential $V(x)$ as in Eq. (3.1), one can expand the exponentials as

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

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

i) Why is the expansion of the exponent and the extension of the limits of integration allowed?

ii) 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

$$\alpha = \frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}T} \simeq \frac{1}{x_0}\frac{\mathrm{d}\langle x \rangle_\beta}{\mathrm{d}T} = \frac{1}{x_0}\frac{k_B\kappa_3}{2\kappa^2}$$

with k_B Boltzmann's constant.

iii) In what temperature range is the above expansion valid?

iv) 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!)

We performed a very similar calculation to this one in the first class. The methods used there are easy to apply to this question, using some generating function and differentiating to pull down factors of x. However, let's do it in the spirit intended instead.

i) The expansion is allowed because the series is convergent. To see this we note that Gaussian integrals over $x^{3n}e^{-x^2}$ are finite and the tails, which we might not expect to be part of the true system, give only a small correction to this. Therefore, the parts that we are ignoring (by only expanding) and the parts we are introducing (by assuming we can take the limits to ∞) are both negligible (but only if something is small, see the later part).

ii) For this calculation we need to find the expectation value. Consider the form of the numerator in $\langle x \rangle_\beta$,

$$\int \mathrm{d}x\, x e^{-\beta V(x)} = \int_{-\infty}^{\infty}\mathrm{d}x\, x\left[1 + \frac{\beta\kappa_3}{6}(x-x_0)^3\right]e^{-\frac{\beta\kappa}{2}(x-x_0)^2}$$

$$= \sqrt{\frac{2}{\beta\kappa}}\int_{-\infty}^{\infty}\mathrm{d}y\left(\sqrt{\frac{2}{\beta\kappa}}y + x_0\right)\left[1 + \frac{\kappa_3}{3\kappa}\sqrt{\frac{2}{\beta\kappa}}y^3\right]e^{-y^2}.$$

Now we can ignore all the integrals here which are odd in y, leaving only two contributions,

$$\int \mathrm{d}x\, x e^{-\beta V(x)} = \sqrt{\frac{2}{\beta\kappa}}\int_{-\infty}^{\infty}\mathrm{d}y\left(x_0 + \frac{2\kappa_3}{3\beta\kappa^2}y^4\right)e^{-y^2}$$

$$= \sqrt{\frac{2\pi}{\beta\kappa}}\left(x_0 + \frac{\kappa_3}{2\beta\kappa^2}\right)$$

(where we integrated by parts twice for the second integral to find $\int y^4 e^{-y^2} = \frac{3}{2}\times\frac{1}{2}\times\sqrt{\pi}$).

We then need to find the denominator, which is simple from our previous expression, getting rid of x

$$\int \mathrm{d}x e^{-\beta V(x)} = \sqrt{\frac{2}{\beta\kappa}} \int_{-\infty}^{\infty} \mathrm{d}y \left[1 + \frac{\kappa_3}{3\kappa}\sqrt{\frac{2}{\beta\kappa}}y^3\right] e^{-y^2}$$

$$= \sqrt{\frac{2\pi}{\beta\kappa}}$$

as, once again, odd terms vanish.

Thus,

$$\langle x \rangle_\beta = x_0 + \frac{\kappa_3}{2\beta\kappa^2}$$

$$\alpha \simeq \frac{1}{x_0}\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\kappa_3 k_B T}{2\kappa^2}\right) = \frac{k_B \kappa_3}{2\kappa^2 x_0}.$$

iii) When we made this expansion we claimed that the extra terms were small. Therefore, to find the range in which this is valid we must check that the sub-leading terms are much smaller, so require

$$\kappa(x - x_0)^2 \gg \kappa_3 (x - x_0)^3.$$

We estimate the size of $(x - x_0)$ by assuming that the quadratic term is indeed dominant, suggesting $\kappa(x - x_0)^2 \sim k_B T$ and so we need

$$k_B T \gg \frac{\kappa_3}{\kappa^{\frac{3}{2}}}(k_B T)^{\frac{3}{2}} \qquad \Longrightarrow \qquad k_B T \ll \frac{\kappa^3}{\kappa_3^2}.$$

iv) For the many-atom chain we find many normal modes, which we call phonons, which determine the expansion of the lattice. We must therefore solve for these in that case and consider the finite temperature occupation of these modes to calculate the nonlinear effects.
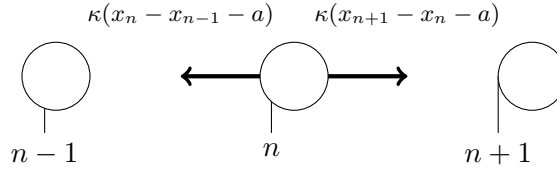
5 Modes of a 1D Monatomic Chain

(a) Explain what is meant by a "normal mode" and by "phonon".
Explain briefly why phonons obey Bose statistics.

> A normal mode is a collective oscillation of a system at a given frequency. It is generally characterised by some dispersion relation $\omega(\boldsymbol{k})$ where $\boldsymbol{k}$ is the wavevector. A phonon is a quantum of this vibration, carrying both the energy and momentum of an oscillation.
> The mode of vibration can be excited multiple times, allowing one mode to be occupied by multiple phonons, which simply corresponds to a larger amplitude of vibration. Therefore, as there is no exclusion, the phonons must be bosonic.

(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).

> We construct the problem using Newtonian mechanics. The force F_n on atom n is a restoring force from the atoms at $n-1$ and $n+1$,
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> Thus,
> $$F_n = m\frac{\mathrm{d}^2 x_n}{\mathrm{d}t^2} = \kappa(x_{n+1} + x_{n-1} - 2x_n).$$
> This looks remarkably like a wave equation and so we make that ansatz,
> $$x_n = Ae^{i(\omega t - kna)}$$
> which results in
> $$-m\omega^2 = \kappa\left(e^{-ika} + e^{ika} - 2\right)$$
> $$\implies \omega = \sqrt{-\frac{\kappa}{m}\left(e^{\frac{ika}{2}} - e^{-\frac{ika}{2}}\right)^2} = 2\sqrt{\frac{\kappa}{m}}\left|\sin\frac{ka}{2}\right|$$

(c) Show that the mode with wavevector k has the same pattern of mass displacements as the mode with wavevector $k + \frac{2\pi}{a}$. Hence show that the dispersion relation is periodic in reciprocal space (k-space).
How many different normal modes are there?

> Recall our ansatz was of the form
> $$x_n = \left(Ae^{i\omega t}\right)e^{-ikna}.$$

Thus, considering this shifted momentum we notice that

$$x_n = \left(A e^{i(\omega t - kna)} \right) e^{-2\pi i n} = A e^{i(\omega t - kna)}.$$

Therefore, the dispersion is indeed periodic (and the extra periods are redundant because our calculation only makes sense at the atomic positions).

As for the number of modes, we assume periodic boundary conditions, which demands that

$$x_n = x_{n+L} \qquad \Longrightarrow \qquad e^{-ikL} = 1.$$

Therefore, k is quantised to be

$$k = \frac{2\pi}{L} n$$

which means that there must be

$$N = \frac{L}{a}$$

distinct modes (which constitutes one full period of our dispersion relation).

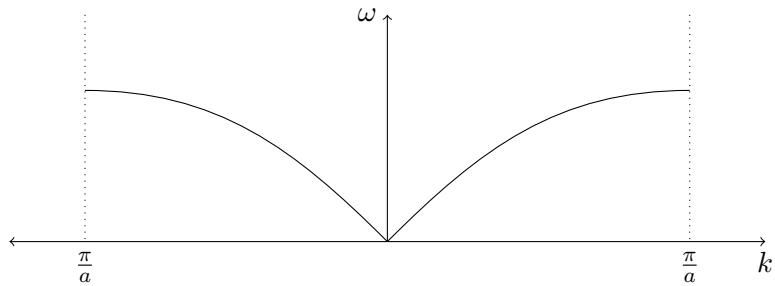(d) Derive the phase and group velocities and sketch them as a function of k.

What is the sound velocity?

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

Recall that

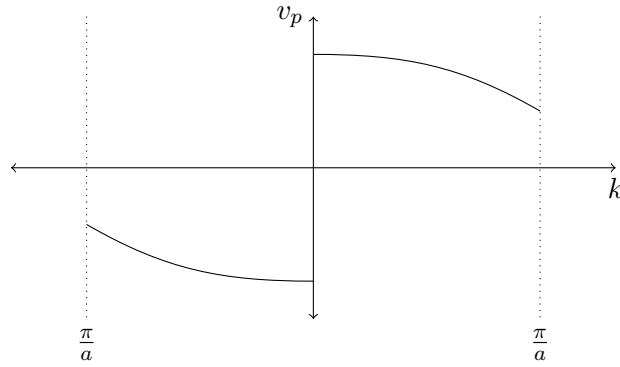$$\omega = 2 \sqrt{\frac{\kappa}{m}} \left| \sin \frac{ka}{2} \right|.$$

Let's sketch this first,

The phase velocity is then

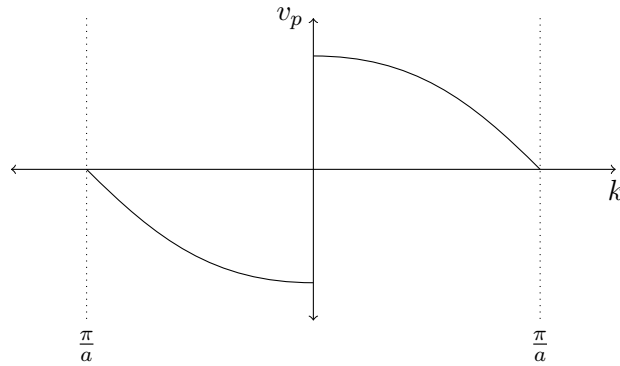$$v_p = \frac{\omega}{k} = 2 \sqrt{\frac{\kappa}{m}} \frac{1}{k} \left| \sin \frac{ka}{2} \right|$$

and this looks like

The group velocity is the gradient

$$v_g = \frac{\mathrm{d}\omega}{\mathrm{d}k} = a\sqrt{\frac{\kappa}{m}}\,\left|\cos\frac{ka}{2}\right|\,\frac{k}{|k|}$$

and this looks like this,

The sound velocity is then the speed as small-k, namely

$$v_s = a\sqrt{\frac{\kappa}{m}}.$$

Finally we consider that the density of the chain is clearly $\rho = \frac{m}{a}$. The compressibility is a little trickier,

$$\beta = -\frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}F}$$

where this F is the force to compress the chain. We can think about this for just one of the links (the chain is translationally invariant and this is an intensive quantity) and hence

$$\beta = \frac{1}{a}\left(\frac{\mathrm{d}(\kappa a)}{\mathrm{d}a}\right)^{-1} = \frac{1}{\kappa a}.$$

Thus,

$$v_s = \sqrt{\kappa a\frac{a}{m}} = \sqrt{\frac{1}{\beta\rho}}.$$

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

The modes have a constant density in the k direction,

$$\mathrm{d}N = 2\frac{L}{2\pi}\mathrm{d}k$$

where we need this factor of 2 because we are restricting to k positive (and we have $k \leftrightarrow -k$ symmetry). Therefore,

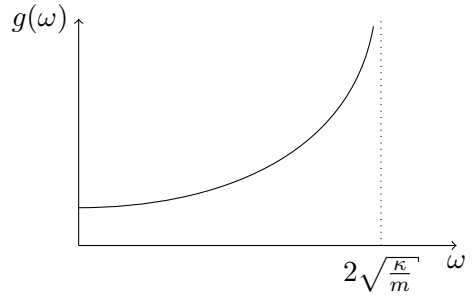$$g(\omega) = \frac{L}{\pi}\left(\frac{\mathrm{d}\omega}{\mathrm{d}k}\right)^{-1} = \frac{L}{\pi v_g}.$$

Now we notice that

$$\left(\frac{v_g}{a}\right)^2 + \left(\frac{\omega}{2}\right)^2 = \frac{\kappa}{m}$$

(this is just getting rid of the cos and sin) so

$$g(\omega) = \frac{L}{\pi a}\left(\frac{\kappa}{m} - \left(\frac{\omega}{2}\right)^2\right)^{-\frac{1}{2}}.$$

Therefore, the density of states will diverge at $k = \frac{\pi}{a}$ at $\frac{\omega}{2} = \sqrt{\frac{\kappa}{m}}$ here. This is what we expect as the dispersion relation is flat here. Sketching this we find

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

Recall that the stored energy is

$$U = \int \mathrm{d}\omega g(\omega)\hbar\omega\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$$

which we must differentiate with respect to T to find the heat capacity. We then make this a differentiation with respect to β and find

$$C = -\frac{\beta}{T}\int \mathrm{d}\omega g(\omega)\hbar\omega\frac{-\hbar\omega e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

$$= k_B \int \mathrm{d}\omega g(\omega)(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}.$$

(g) Show that at high temperature the law of Dulong-Petit (for one dimension) is recovered.

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Large T means small β so we expand,

$$C \simeq k_B \int \mathrm{d}\omega g(\omega).$$

Therefore, we are integrating the density of states over all states and just receive N. Therefore,

$$C = N k_B.$$

(This is why Debye's model worked. The low-temperature regieme only required him to get that the dispersion was linear and didn't care about high temperatures. The high-temperature regieme on the other hand only needs to know that the total number of states is N, and doesn't care so much how you formulate it, whether with a proper density of states as we do here or with some constant approximation cut off at the right point.)

6 Modes of a 1D Diatomic Chain

(a) What is the difference between an acoustic and an optical mode?
Describe how particles move in each case.

An acoustic mode is one for which atoms move slowly and in phase with little spatial modulation. $\omega \sim k$ for small k. For example

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An acoustic mode is one for which the motion of atoms is out of phase, which looks like fast spatial modulation but is slow when looking at every other atom. $\omega \sim \text{const}$ for small k. This looks like this

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(b) Derive the dispersion relation for the longitudinal oscillations of a one-dimension 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 (all springs are the same, and motion of particles is in one dimension only).

Once again, we must write down the equations of motion, denoting m_1 particles as x and m_2 particles as y. So

$$m_1 \ddot{x}_n = \kappa \left(y_n + y_{n-1} - 2x_n \right)$$

$$m_2 \ddot{y}_n = \kappa \left(x_{n+1} + x_n - 2y_n \right)$$

where we have assumed that the unit cell is an m_1 followed by an m_2 and n refers to which unit cell we are in. We now make a wave ansatz,

$$x_n = A_x e^{i(\omega t - kan)}$$

$$y_n = A_y e^{i(\omega t - kan)}$$

and substitute this in to find

$$-m_1 \omega^2 A_x = \kappa \left(A_y + A_y e^{-ika} - 2A_x \right)$$

$$-m_2 \omega^2 A_y = \kappa \left(A_x e^{ika} + A_x - 2A_y \right)$$

which we formulate as the matrix equation

$$\begin{pmatrix} 2\frac{\kappa}{m_1} & -\frac{\kappa}{m_1}(1 + e^{-ika}) \\ -\frac{\kappa}{m_2}(1 + e^{ika}) & 2\frac{\kappa}{m_2} \end{pmatrix} \boldsymbol{A} = \omega^2 \boldsymbol{A}.$$

We then solve,

$$\left(\frac{2\kappa}{m_1} - \omega^2 \right) \left(\frac{2\kappa}{m_2} - \omega^2 \right) - \frac{\kappa^2}{m_1 m_2} \left(2 \cos \frac{ka}{2} \right)^2 = 0$$

$$\omega^4 - 2 \left(\frac{\kappa}{m_1} + \frac{\kappa}{m_2} \right) \omega^2 + \frac{4\kappa^2}{m_1 m_2} \sin^2 \frac{ka}{2} = 0.$$

We then solve using the quadratic formula to find

$$\omega^2 = \frac{\kappa}{\mu}\left[1 \pm \sqrt{1 - \frac{4\mu}{M}\sin^2\frac{ka}{2}}\right]$$

where $\mu = \left(m_1^{-1} + m_2^{-1}\right)^{-1}$ is the reduced mass and $M = m_1 + m_2$ the total mass of the unit cell.

(c) Determine the frequencies of the acoustic and optical modes at $k = 0$ as well as at the Brillouin zone boundary.
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 $v_s = \sqrt{\frac{1}{\beta\rho}}$ where ρ is the chain density and β is the compressibility.

At $k = 0$

$$\omega_{\text{optical}} = \sqrt{2\frac{\kappa}{\mu}} \qquad\qquad \omega_{\text{accoustic}} = 0$$

whereas at $k = \frac{\pi}{a}$ we have that

$$\omega^2 = \frac{\kappa}{\mu}\left[1 \pm \sqrt{1 - \frac{4\mu}{M}}\right].$$

This can be simplified by using the fact that

$$1 - \frac{4\mu}{M} = \frac{(m_1 - m_2)^2}{(m_1 + m_2)^2}$$

so

$$\omega^2 = \frac{\kappa}{\mu M}\left(m_1 + m_2 \pm |m_1 - m_2|\right)$$

and therefore

$$\omega_{\text{optical}} = \sqrt{\frac{2\kappa m_1}{m_1 m_2}} \qquad\qquad \omega_{\text{accoustic}} = \sqrt{\frac{2\kappa m_2}{m_1 m_2}}$$

assuming $m_1 > m_2$.
For the sound velocity we take the small-k expansion of the accoustic mode,

$$\omega^2 = \frac{\kappa}{\mu}\left(1 - \sqrt{1 - \frac{\mu(ka)^2}{M}}\right) = \frac{\kappa(ka)^2}{2M}$$

and so

$$v_s = a\sqrt{\frac{\kappa}{2M}}.$$

For the group velocity we differentiate ω^2 and find

$$v_g = -\frac{\kappa a}{M\omega}\left(1 - \frac{4\mu}{M}\sin^2\frac{ka}{2}\right)^{-\frac{1}{2}}\sin\frac{ka}{2}\cos\frac{ka}{2}.$$

Therefore, given that $\cos\frac{ka}{2} = 0$ at the zone boundary whilst all the other quantities in the expression are finite, $v_g = 0$.

Once again we can consider the density as $\rho = \frac{M}{a}$ but the compressibility is trickier. We need to recall that two springs in series have $\kappa_{\text{eff}} = \frac{\kappa}{2}$ (or we could make the dodgy assumption that each spring occupies a region of $\frac{a}{2}$ if we don't remember this). Therefore, $\beta = \frac{2}{\kappa a}$ here and so indeed
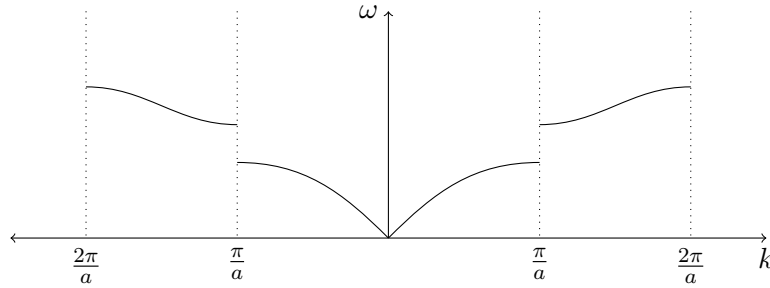
$$v_s = \sqrt{\frac{1}{\rho\beta}}\,.$$

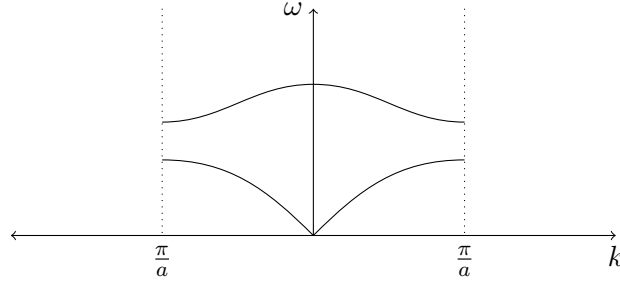(d) Sketch the dispersion in both reduced and extended zone scheme.
If there are N unit cells, how many different normal modes are there?
How many branches of excitations are there? (i.e, in reduced zone scheme, how many modes are there at each k).

The extended zone scheme picture looks like this

and the reduced zone scheme looks like this

Given N unit cells there are $2N$ modes (one per degree of freedom, N cells, 2 degrees of freedom per site).
There are two branches of excitation (2 modes per k for 2 degrees of freedom per unit cell).

(e) What happens when $m_1 = m_2$?

When $m_1 = m_2$ the gap between the modes closes. The extended zone scheme is then the natural one to consider because the unit cell is now $\frac{a}{2}$. As the gap closes then the dispersion returns to the single sinusoid we have already seen. To see this notice that

$$\frac{\mu}{M} = \frac{1}{4}$$

when $m_1 = m_2$ and so

$$\omega_- = 2\sqrt{\frac{\kappa}{m}}\,\sin\frac{ka}{4}$$

$$\omega_+ = 2\sqrt{\frac{\kappa}{\mu}}\cos\frac{ka}{4}.$$

So we see that $a \to \frac{a}{2}$ from the old accoustic mode and we can see that the old optical mode is simply a sin but shifted to conform to the reduced zone scheme (which no longer really applies).

7 One Dimensional Tight Binding Model

(a) **Monatomic Solid:** Consider a one-dimesnional 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 $n = 1, \ldots, N$ (and you may assume periodic boundary conditions, and that $\langle n|m \rangle = \delta_{nm}$). 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 $n = m \pm 1$.

i) Derive and sketch the dispersion curve for electrons (Hint: Use the effective Schrödinger equations of problem 2.2.a. The resulting equation should look very similar to that of problem 2.5 above).

ii) How many different eigenstates are there in this system?

iii) What is the effective mass of the electron near the hottom of this band?

iv) What is the density of states?

v) If each atom is monovalent (it donates a single electron) what is the density of states at the Fermi surface?

vi) Estimate the heat capacity of the system at low temperature.

vii) What is the heat capacity if each atom is divalent? What about the spin susceptibility?

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i) We can do better than the hint. Consider the effect of the Hamiltonian. It takes each site and applies an energy cost to occupying that site. It also hops a spin from site n to $n \pm 1$ with amplitude $-t$. Thus,

$$H = \sum_n \left[\epsilon |n\rangle\langle n| - t|n-1\rangle\langle n| - t|n+1\rangle\langle n| \right].$$

Therefore, given some general state

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

we find

$$H|\psi\rangle = \sum_n \phi_n \left[\epsilon|n\rangle - t|n-1\rangle - t|n+1\rangle \right].$$

Playing around with the sum then we find

$$E\sum_n \phi_n|n\rangle = \sum_n \left[\epsilon\phi_n - t\phi_{n+1} - t\phi_{n-1} \right]|n\rangle.$$
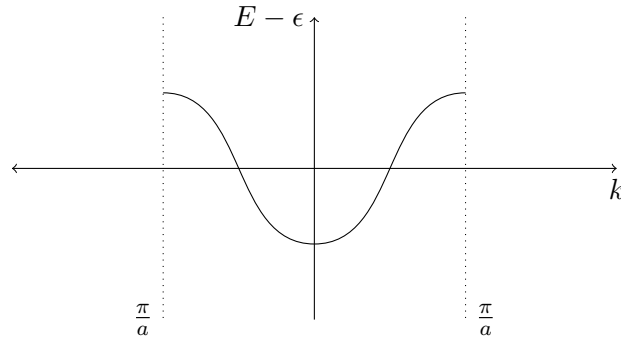
Therefore, given that our states are linearly independent, we find that we must satisfy

$$E\phi_n = \epsilon\phi_n - t\phi_{n+1} - t\phi_{n-1} = 0.$$

We can then make a wave ansatz as per usual, $\phi_n = Ae^{ikna}$ and so

$$E = \epsilon - te^{ika} - te^{-ika} = \epsilon - 2t\cos(ka).$$

This looks like this

.

ii) There are $2N$ eigenstates of this system. We just diagonalised an $N \times N$ matrix (giving N states) but we ignored spins (which gives a degeneracy of 2 per eigenstate).

iii) To find the effective mass we expand,

$$E = \epsilon - 2t \left(1 - \frac{(ka)^2}{2} \right) = \text{const} + ta^2k^2.$$

Therefore, by comparisin with $\frac{\hbar^2 k^2}{2m}$ we find

$$\frac{\hbar^2}{2m^*} = ta^2 \qquad \Longrightarrow \qquad m^* = \frac{\hbar^2}{2ta^2}.$$

iv) We proceed as usual, (remembering the factor of 2 for $k \leftrightarrow -k$ symmetry and 2 for spins)

$$dN = 2 \times 2 \frac{L}{2\pi} dk = \frac{2L}{\pi} dE \left(\frac{dE}{dk} \right)^{-1} = \frac{L}{\pi t a \sin(ka)} dE.$$

So this is our density of states. We then use that

$$\sin(ka) = \sqrt{1 - \left(\frac{E - \epsilon}{2t} \right)^2}$$

to put density of states in terms of E.

v) If each atom is monovalent there are N electrons filling $2N$ states. Therefore we fill halfway to $E = \epsilon$ and so $\sin(ka) = 1$ and

$$g(E_F) = \frac{L}{\pi t a}.$$

vi) This is a formula worth remembering:

$$C_e = \frac{\pi^2}{6} k_B^2 g(E_F) T.$$

We can motivate it all very simply but remember this $\frac{\pi^2}{6}$ prefactor! Therefore,

$$C_e = \frac{\pi k_B^2 L}{6ta} T.$$

vii) If there are two electrons per unit cell we are in the regieme where we've filled the whole band up. Therefore, the density of states at the Fermi surface, $g(E_F)$, is zero. As such the heat capacity and spin susceptibility must be zero as there are no states nearby for electrons to move into to either accept heat or induce a magnetisation.

(b) **Diatomic Solid:** Now consider a model of a diatomic solid as such

$$-A - B - A - B - A - B - .$$

Suppose that the on-site energy of type A is different from the on-site energy of type B, i.e, $\langle n|H|n\rangle = \epsilon_A$ 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).
i) Calculate the new dispersion relation.
ii) Sketch this dispersion relation in both the reduced and extended zone schemes.
iii) What happens in the "atomic" limit when t becomes very small?
iv) What is the effective mass of an electron near the bottom of the lower band?
v) If each atom (of either type) is monovalent, is the system a metal or an insulator?
vi) What happens if $\epsilon_A = \epsilon_B$?

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i) We now need to worry about the different sites A and B in each unit cell. We take our unit cell to be $-A - B-$ and so we formulate our Hamiltonian as such,

$$H = \sum_n \left[\epsilon_A |A_n\rangle\langle A_n| + \epsilon_B |B_n\rangle\langle B_n| - t|A_n\rangle\langle B_{n-1}| - t|A_n\rangle\langle B_n| - t|B_n\rangle\langle A_n| - t|B_n\rangle\langle A_{n+1}| \right].$$

A generic state is then of the form

$$|\psi\rangle = \sum_n \left(\phi_n |A_n\rangle + \psi_n |B_n\rangle \right).$$

Let's put this in and see what we find,

$$H|\psi\rangle = \sum_n \left(\epsilon_A \phi_n |A_n\rangle - t\phi_n |B_n\rangle - t\phi_{n+1}|B_n\rangle + \epsilon_B \psi_n |B_n\rangle - t\psi_{n-1}|A_n\rangle - t\psi_n |A_n\rangle \right).$$

Once again, every state is assumed to be linearly independent and so

$$E\phi_n = \epsilon_A \phi_n - t\psi_{n-1} - t\psi_n,$$

$$E\psi_n = \epsilon_B \psi_n - t\phi_n - t\phi_{n+1}.$$

Into this we insert our wave ansatz and so

$$E \begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} \epsilon_A & -t(1 + e^{-ika}) \\ -t(1 + e^{ika}) & \epsilon_B \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}.$$
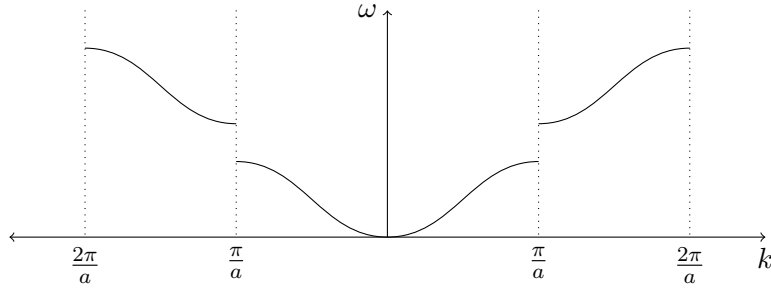
We diagonalise this matrix to find

$$E^2 - (\epsilon_A + \epsilon_B)E + \epsilon_A \epsilon_B - 4t^2 \cos^2 \frac{ka}{2} = 0.$$
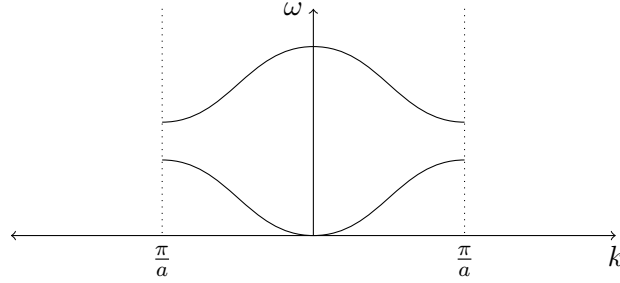
So using the quadratic formula, and defining $\bar{\epsilon} = \frac{\epsilon_A + \epsilon_B}{2}$ and $\Delta\epsilon = \frac{|\epsilon_A - \epsilon_B|}{2}$,

$$E = \bar{\epsilon} \pm \sqrt{\Delta\epsilon^2 + \left(2t \cos \frac{ka}{2} \right)^2}.$$

ii) The extended zone scheme picture looks like this

---

and the reduced zone scheme looks like this

iii) When the hopping becomes very small the electrons reside almost entirely on one atom or the other. We can see this by setting $t = 0$ and we find

$$E = \epsilon_A \text{ or } \epsilon_B.$$

iv) The lower band is the $-$ solution. It is actually slightly easier to expand, though even that will prove horrible. Let's get through this,

$$E = \ldots - \left(\Delta\epsilon^2 + 4t^2 \left(1 - \frac{(ka)^2}{8} \right)^2 \right)^{\frac{1}{2}}$$

$$= \ldots - \left(\Delta\epsilon^2 + 4t^2 - (tka)^2 \right)^{\frac{1}{2}}$$

$$= \ldots - \left(\Delta\epsilon^2 + 4t^2 \right)^{\frac{1}{2}} \left(1 - \frac{1}{2} \frac{(tka)^2}{\Delta\epsilon^2 + 4t^2} \right)$$

$$= \ldots + \frac{(ta)^2}{2\sqrt{\Delta\epsilon^2 + 4t^2}} k^2.$$

Thus,

$$m^* = \frac{\hbar^2}{(ta)^2} \sqrt{\Delta\epsilon^2 + 4t^2}.$$

v) If both atoms are monovalent then we fill up the lower band completely. There is then a gap to the next band and so the system is an insulator.

vi) If $\epsilon_A = \epsilon_B$ then $\Delta\epsilon = 0$ and so

$$E = \epsilon \pm \left| 2t \cos\frac{ka}{2} \right|.$$

Therefore, as expected and as in the phonon question, this is exactly the monatomic case but with a reduced unit cell, $a \to \frac{a}{2}$.