Condensed Matter Physics : Answers to Examples 1

1 See figures in handout - overhead 5. The fcc structure has atoms in the face centre, giving a nearest neighbour distance of a/√2, and the bcc has one in the centre of the primitive cube, giving a nearest neighbour distance of a√3/2.

2 (a). The reciprocal lattice is an infinite, periodic lattice of points in 'k' (wavevector) space that is associated with a particular crystal lattice structure in real space that gives the wavevectors of the plane wave components needed to make up the Fourier transform of a structure (for example its electron density) that has the periodicity of that particular crystal structure.

Examples of use:
- In setting up a Fourier transform of a periodic structure.
- Each point also represents a set of planes with a particular set of 'Miller' indices – the direction of the reciprocal lattice point is normal to the planes, and its magnitude is $2\pi/d$ where d is the spacing between planes.
- In diffraction the difference between the incoming and outgoing wavevectors of the scattering particle must be a reciprocal lattice vector – and this combined with conservation of energy for elastic scattering gives the 'Ewald Sphere' construction.
- Used to determine the 'back folding' of any quantum state due to the periodicity of the lattice.

(b) 4, $a^3/4$.

(c) Use expression for reciprocal lattice basis vectors (A, B, C) in terms of real lattice basis vectors (a, b, c) as given in the question:
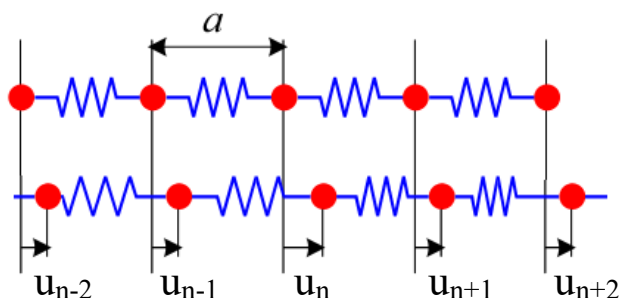
$$A = 2\pi \frac{b \times c}{a \cdot b \times c}$$

Gives:

$$A = \frac{2\pi}{a}\begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix} \quad B = \frac{2\pi}{a}\begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix} \quad C = \frac{2\pi}{a}\begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}$$

These vectors link the corner of a cube, side length $4\pi/a$ to its centre and vice versa – i.e. describe a *bcc* lattice.

(d) fcc: finding the reciprocal lattice vectors of the bcc ones found in (c) will take you back to the starting lattice.

(3) First section: see lecture handout.

$$m\ddot{u}_n = -k_1(2u_n - u_{n-1} - u_{n+1}) - k_2(2u_n - u_{n-2} - u_{n+2})$$

But:

And:
$$u_{n\pm1} = u_n e^{\pm iqa}$$

So:
$$u_{n+2} = u_n e^{\pm i2qa}$$

$$m\ddot{u}_n = -k_1 u_n \left(2 - e^{-iqa} - e^{iqa}\right) - k_2 u_n \left(2 - e^{-2iqa} - e^{2iqa}\right)$$
$$m\ddot{u}_n = -2u_n \left(k_1(1 - cosqa) + k_1(1 - cos2qa)\right)$$

$$m\ddot{u}_n = -4u_n \left(k_1 sin^2(qa/2) + k_2 sin^2(qa)\right)$$

Looking for normal modes means $\ddot{u} = -\omega^2 u$ hence:
$$\omega^2 = -\frac{4}{m}\left(k_1 sin^2(qa/2) + k_2 sin^2(qa)\right)$$

The wavevector q is a way of representing the phase shift between identical positions in a periodic structure – if the spacing between identical positions is a then the phase shift between positions is given by qa. As such it only has a unique meaning over a range corresponding to a range in phase shift of 2π.

Looking for a max in ω^2 is easier than ω, so:
$$\frac{d\omega^2}{dq} = -\frac{4}{m}\left(k_1 a\, sin(qa/2)\, cos(qa/2) + 2k_2 a\, sin(qa)cos(qa)\right)$$
and we are looking for
$$0 = \frac{k_1\, sin(qa)}{2} + 2k_2\, sin(qa)cos(qa)$$
$$0 = sin(qa)\frac{k_1}{2}\left[1 + 4\frac{k_2}{k_1}\, cos(qa)\right]$$
$qa = 0$ is a minimum, and we have a max for
$$0 = 1 + 4\frac{k_2}{k_1}\, cos(0.8\pi)$$
$$0 = 1 - 3.24\frac{k_2}{k_1}$$
and
$$k_2 = \frac{k_1}{3.24}$$
which is much as you would expect – as the effective force constant should be greater for nearest neighbours than for second nearest neighbours.

4 For first part see notes

A is the speed of sound for both transverse waves in the <111> directions, measureable by, for example, exciting transverse standing waves on a NaCl crystal. (Note – this figure is somewhat schematic – the gradient of the LA and TA modes is actually different as they approach $q =0$ – see overhead 46 in the handout for a more accurate plot.)

B relates to the difference in mass between the Na and Cl ions – the [111] direction is perpendicular to planes containing either just Na or just Cl ions – so it looks very much like

the 1D diatomic chain. The upper mode at 'B' corresponds to the lighter atoms (Na) moving and the heavier ones (Cl) stationary – and the lower mode vice-verse.

C relates to the difference between the force constants for shearing a Na (111) plane with respect to its Cl plane neighbours and that for compressing the planes together.

D relates to the reduced mass of the Na/Cl system as it contains Na planes moving against Cl planes.

E is the Brillouin zone boundary in the [111] direction – given by π/d_{111} where d_{111} is the separation of successive Na (111) planes. This plane spacing can be worked out either from the lattice parameter as derived from x-ray scattering, or given one knows the Avogadro number and formula weight for NaCl, the lattice parameter can be derived from the density of NaCl.

Parameters D, B and C can only be determined from the actual phonon dispersion curves as measured by neutron scattering.

At high temperatures (i.e. above the Debye temperature for NaCl, which is, for the record, 321K) the heat capacity is $3k_B$ per atom – i.e. 6R per mole of NaCl. At lower temperatures the speeds of sound (for transverse and longitudinal waves), as estimated from the gradients fo the TA and LA modes as q tends to zero, can be used in the Debye model. These speed are however only estimates of the average transverse and longitudinal sound velocities as these will depend (in general, and indeed for cubic crystals) on the direction of propagation – crystals are not isotropic media.

To determine the thermal conductivity one needs a value for the mean free path. At high temperatures this is determined by phonon-phonon scattering – and there is no information on this in the measured phonon dispersion curves as this arises from the anharmonicity of the ion-ion interactions. At low temperatures, and for low defect crystals, the mean free path is simply the physical dimensions of the crystal.

Firstly, at the zone centre and at the zone boundary the ratio between transverse and longitudinal mode frequencies should always be the same as in each case the same single transverse or longitudinal nearest neighbour force constant should be used.

The actual ratios are:

Zone centre LO/TO= 7.93/5.17=1.54
Zone edge LO/TO=6.99/4.27=1.64
Zone edge LA/TA=5.35/3.61=1.48

Whilst these are clearly not the same they are reasonably close (ranging +/- 5% from the mean)

At the zone centre the frequencies go as one over the square root of the reduced mass – which for NaCl is 23*35.5/(23+35.5)=13.95, at the zone centre the higher mode is the one with Na moving, so its frequency goes as one over the square root of the Na mass and the lower frequency mode goes as one over the square root of the chlorine mass. i.e. the ratio of frequencies is:

1D model value for Zone centre : optical at zone edge: acoustic at zone edge
= 1/√13.95:1/√23:1/√35.5
= 1: 0.78: 0.63
= 1.60: 1.28: 1

Experimental longitudinal phonon frequency ratios
= 7.93:6.99:5.35
= 1 :0.88: 0.67
= 1.48: 1.31: 1

Experimental transvers phonon frequency ratios
= 5.17: 4.27: 3.61
= 1: 0.83: 0.70
= 1.43: 1.16: 1

The longitudinal frequency ratio of the LO and LA modes at the zone edge is very close to the simple model one, but otherwise there are fractional discrepancies of the order of 10%. The ion-ion force is an inverse square one, which has, as force fields go, a long range – so it would not be surprising if the effective spring constant between next nearest neighbours was significant.

The long range forces between ions are coulomb ones – so are indeed pairwise forces – but there are other forces, however, particularly the short range ones, which are really many body forces and the basic premise of these calculations (pairwise forces) is not strictly true. As two ions approach each other, the electrons between them will re-arrange themselves, and how they do this will depend on where other neighbouring ions are.

5. The periodicity of the superlattice is 4 times that of a lattice in which each layer of atoms is identical –and so the Brillouin zone is 4 times smaller.

+- π/a   Brillouin zone boundary for monoatomic chain
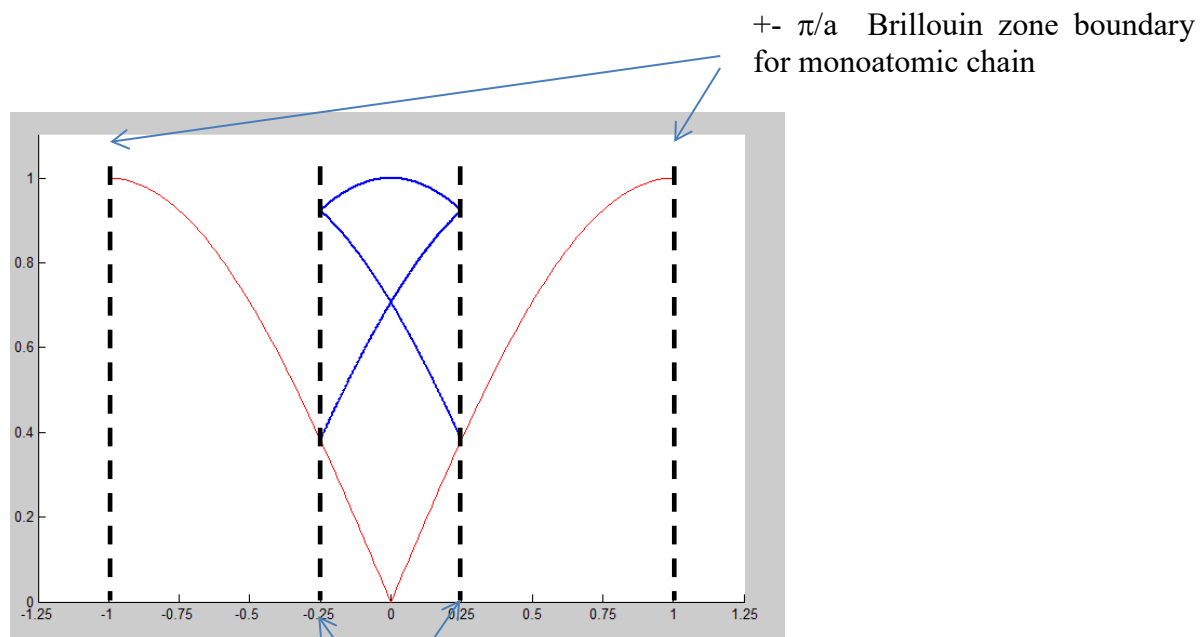
If the superlattice was composed of atoms of equal mass – then all that would happen is that the modes that were   +- π/4a Brillouin zone boundary   π/a would now have to be plotted
for 4 layer superlattice chain

between - $\pi/4a$ and $\pi/4a$ – i.e. sections of the dispersion curve outside the new superlattice Brillouin zone would need to be brought into the superlattice Brillouin zone by moving them by a G vector of the new lattice –i.e. by a multiple of $2\pi/4a$. The fact that the masses of all the layers are not equal means that a gap will open up at the boundary of the new zone – i.e. the degeneracy of the modes at this point is lifted. (a is the spacing between layers of the lattice –i.e. the superlattice has a periodicity of $4a$)

Look at the displacement patterns of I, II, and III you see that in I the direction of motion alternates between atoms – i.e. it is a mode derived from a mode on a monoatomic lattice with wavelength $2a$. Modes II and III are derived form a mode of the monoatomic lattice with wavelength $4a$ – so I is clearly the highest energy mode and therefore must be R.

Which of II and III is of lower energy takes a little thought. One could propose a spring constant k and calculate the frequencies – mode II is has the frequency of a Si-Ge diatomic molecule as the neighbouring Si atoms move together so there is no force between them and the same for the Ge atoms – so the frequency of this mode will by sqrt(k/μ) where μ is the reduced mass $\mu=m_{Si}m_{Ge}/(m_{Si}+m_{Ge})$. For mode III one can place a solid wall between Si atoms and another between Ge atoms as the centre of these springs do not move – and have the Si/Ge atoms attached to the wall with springs of spring constant $2k$, and then solve the dynamical matrix that results – the upper mode that this gives is in fact mode I:

x_{Si} x_{Ge}
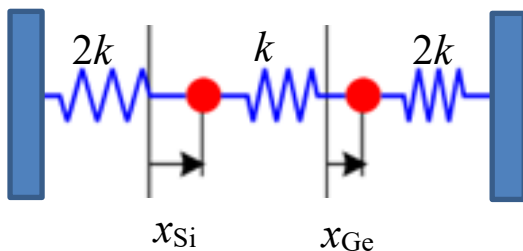
A useful way of thinking about modes II and III is to note that the mass of Ge (72.6 amu) is much larger than that of Si (28.1 amu) and to consider what would happen to the frequencies of these modes if one increased the mass of the Ge. For mode II, as the mass of the heavier Ge atom increases, its frequency tends to sqrt(k/m_{Si}) as we have a mode of a light atom moving with large amplitude attached to a heavy atom that is barely moving. For mode III – and referring to the figure of two masses between two walls above – as the mass of the Ge increases, in the limit the mass of the Si can be ignored for the low frequency mode – giving one very high frequency mode (R) in which the heavy Ge is all but stationary and the light Si moves plus the mode of a Ge atom attached on one side to a wall with a spring of constant $2k$ and on the other to a wall by a spring of constant k attached to a spring of constant $2k$ – of effective spring constant $k*(1/(1/1+1/2))= 2/3k$. The Ge therefore has a total restoring spring constant of $8/3k$ and the frequency of the low frequency mode therefore tends to sqrt($8/3k/m_{Ge}$) which is clearly lower than sqrt(k/m_{Si}) as the mass of Ge increases. If the masses of the Ge and Si were equal modes II and III would have equal frequency – clearly they will not have equal frequency for any other mass ratio – so if for very large mass of Ge III is lower in frequency than II, then for all mass ratios III will be lower in energy than II - so mode II is Q and III is P.

6. Key elements of Debye theory – see handout.

The energy per state is given by the Planck formula: $\dfrac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}$ which in the high temperature limit tends to $k_B T$ (show how-see lecture handout).

At low temperature only the low k modes are excited – suppose the modes are thermally excited out to a particular k –say k_1. The number of modes excited will therefore go as the volume of the sphere in k space of radius k_1. – *i.e.* proportional to k_1^3, and the average energy of these modes will be proportional to k_1 giving overall a thermal energy stored proportional to k_1^4. Now the concept of whether a mode is excited or not is not so easy to define – but whatever it is, since the energy of the mode is proportional to the wave vector then k_1 is proportional to the temperature, giving a thermal energy proportional to T^4 and a heat capacity proportional to T^3.

7 The expression for the coefficient of thermal conductivity is : $\kappa = \dfrac{1}{3} C \langle c \rangle l$ where C is the heat capacity per unit volume <c> is the mean speed of sound and l is the mean free path. At low temperature the scattering of phonons is dominated by geometrical effects – defects in the crystal or in a low defect density crystal, scattering from the edges of the crystal –both of which are temperature independent. The temperature variation of the thermal conductivity is therefore determined by the variation of the heat capacity – and for an insulating crystal the heat is stored in the phonons and at low temperature the heat capacity varies as T^3. At high temperatures the heat capacity tends to a constant value of $3k_B$ per atom in the solid – so the temperature dependence of the thermal conductivity is dominated by the temperature dependence of the phonon mean free path. As the temperature increases the number of phonons in the crystal increases – linearly above the Debye temperature as in this temperature regime the heat capacity is constant - and phonon-phonon interactions dominate the mean free path of the phonons. There mean free path therefore decreases as 1/T, as therefore does the thermal conductivity.

At 1000K the thermal conductivity of germanium is about 0.2W/cmK (reading from the graph). From the density and the relative atomic weight we can calculate the number of germanium atoms per unit volume (n=5300/0.0726*6.022e23=4.40e28/m^3) and hence the heat capacity per unit volume C=n. $3k_B$ = 4.40e28*1.38e-23*3=1.82e6 J/m3/K hence the mean free path l=3*κ/C/<c>=3*200/1.82e6/5400=60nm.

For phonon scattering to be effective large q phonons are needed so that 'unklapp' process can occur which are effective at changing the direction of heat flow. As the temperature drops below the Debye temperature (374K for Ge) the high energy modes start to be excited less and less – so from this point there is an ever increasing lack of phonons with large enough q for the effective umklapp processes to take place and the thermal conductivity rises. Without this effect the actual thermal conductivity would lie under the two asymptotes shown in the figure.