Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

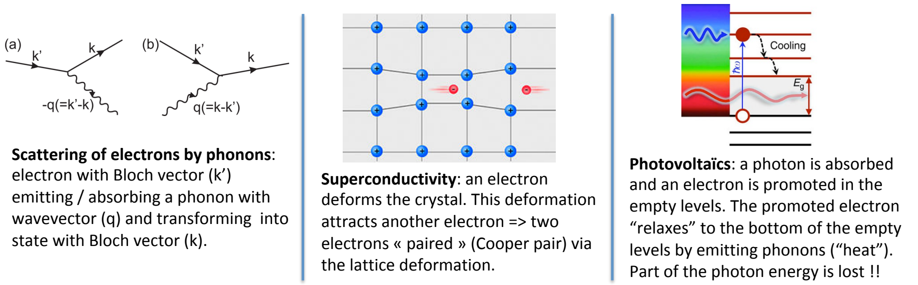
Lecture notes 2020 by Xavier Blase

6 Chapter 6 : Vibrational modes. Phonons.

We assumed so far that the atoms were frozen (rigid positions). However clearly at finite temperature, atoms vibrate around their equilibrium positions with an amplitude proportional to the temperature. This explain for example the thermal dilatation of solids and the melting at high temperature. Atomic vibrations also explain other properties :

- the fact that the mean-free path and electronic conductivity decreases with increasing temperature: electrons do not "bump" on atoms but on atomic vibrations.
- the T^3 dependence of the specific heat in solids at low temperature (electrons contributes to a dependence in T in metals; see Chapter 2)
- the superconductivity (BCS=Bardeen-Cooper-Schrieffer theory, Nobel 1972)
- the limitation of efficiency of photovoltaic cells by transformation of part of photon energy into "vibrational" heat thermoelectricity, etc.

While qualitatively, we picture thermal agitation as some random motion of the atoms, all the above effects can be precisely quantified using quantum mechanics and Bose-Einstein quantum statistical physics, introducing the elementary quanta of vibrations in solids, namely the phonons !!



Scattering of electrons by phonons: electron with Bloch vector (k') emitting / absorbing a phonon with wavevector (q) and transforming into state with Bloch vector (k).

Superconductivity: an electron deforms the crystal. This deformation attracts another electron => two electrons « paired » (Cooper pair) via the lattice deformation.

Photovoltaïcs: a photon is absorbed and an electron is promoted in the empty levels. The promoted electron "relaxes" to the bottom of the empty levels by emitting phonons ("heat"). Part of the photon energy is lost !!

Figure 1: Schematic representation of important physical properties governed by the interaction of electrons with the vibrations of the ions.

6.1 Classical versus quantum mechanics for atoms

6.1.1 Atoms are much heavier than electrons and can often be treated classically

The question of knowing if a particle should be treated classically or quantum mechanically can be addressed (at least qualitatively) by considering the de Broglie wavelength $\lambda = h/p$ associating a wavelength with the momentum p and the Plank constant h. If λ is larger than the typical distance between particles, then quantum interferences will take place and the quantum regime must be used.

In the present case of atoms vibrating at finite temperature, we must use the **thermal de Broglie wavelength** λ_{th} where the impulsion is qualitatively related to the temperature by the equipartition relation (in the classical limit) :

$$\frac{p^2}{2M} = \frac{3}{2}k_BT \implies p = \frac{1}{\sqrt{3Mk_BT}}$$

The de Broglie thermal wavelength is defined as:

$$\lambda_{th} = \frac{h}{\sqrt{2\pi Mk_BT}}$$

(where the 2π factor is somehow arbitrary, I think). Clearly, large masses and large temperatures will reduce λ_{th} and drive the particle to a classical regime. On the contrary, small temperatures or masses will push towards a quantum regime. Putting actual values, one finds that a "thermal neutron" at room temperature possesses a thermal wavelength $\lambda_{th}^{neutron,300K} \simeq 1.8$ Å. Taking now carbon atoms, that are relatively light atoms with a mass number A=12 (namely 6 protons and 6 neutrons), one obtains $\lambda_{th}^{carbon,300K} \simeq 1.8/\sqrt{12} \simeq 0.52$ Å which is smaller than typical interatomic distances in carbon systems. **As such, carbon atoms, and *a fortiori* heavier atoms, can be treated generally classically at room temperature, quantum effects becoming important at low temperatures.**

6.1.2 The quantum oscillator (Reminder)

What we now show is that even in the quantum regime, the classical vibrational frequency is a central quantity. We illustrate this with a brief reminder of the quantum oscillator. Assuming (Figure 2) a spring of constant k with a mass M, its classical vibrational frequency is $\omega_0 = \sqrt{k/M}$. In the quantum approach, the energy of the quantum oscillator is quantized with energy levels given by:

$$E_n = (n + \frac{1}{2})\hbar\omega_0$$

where n is an integer that can be zero.[1]

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[1] The n=0 energy $\hbar\omega_0/2$ is called the zero-point motion : even at rest, a quantum oscillator has an energy. As a matter of fact, uncertainty principle forbids the mass to have both a well defined position and zero velocity !!

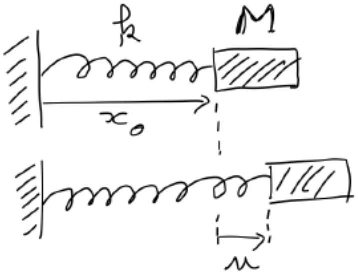


Figure 2: A simple mass M and spring system with a spring constant k. The equilibrium mass position is x_0 and the elongation of the spring with respect to the equilibrium position is labeled "u". The equation of motion is $Md^2u/dt^2 = -ku$ with solution $u(t) = A\cos(\omega_0 t + \phi)$ where $\omega_0 = \sqrt{k/M}$ and where the constants A and ϕ depend on the initial (t=0) position and velocity.

It is a quantum energy (presence of the $\hbar$ and quantization, or discretization, of energy) but it relies on the classical frequency ω_0. In the quantum mechanics treatment, $\hbar\omega_0$ is the vibrational quanta : when interacting with the outside world, the quantum oscillator can only exchange an integer number of $\hbar\omega_0$ energy with the outside world. In the n-th state, the average displacement is given by

$$\langle \Delta X^2 \rangle_n = \langle \phi_n | (\Delta \hat{X})^2 | \phi_n \rangle = (n + \frac{1}{2}) \frac{\hbar}{M\omega_0}$$

where ϕ_n is the quantum wavefunction for the oscillator in the n-th quantum state : in quantum mechanics, one cannot give the elongation u of the spring with the mass in a precise location, but only the probability $|\phi_n(u)|^2$ to have the mass inposition $(x_0 + u)$ where x_0 is the equilibrium position and u the elongation associated with the operator $\Delta\hat{X}$ (see Figure 3). This corresponds to the intuitive picture that when the oscillator energy increases, its displacement increases as well.

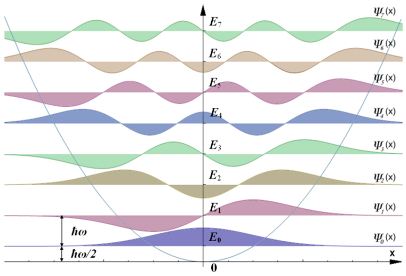


Figure 3: Wavefunction for the first eight bound ϕ_n eigenstates of a 1D quantum harmonic oscillator. The horizontal axis shows the elongation x (noted -u- in the main text) away from x_0 the equilibrium position. When the index n increases, the energy increases and the probability to find the mass far away from x_0 increases as well (from https://en.wikipedia.org/wiki/Quantum_harmonic_oscillator.)

A second important issue is to recover the intuitive idea that when the temperature increases, the vibrational energy increases as well. The relation between temperature and quantum mechanics is the job of quantum statistical physics. For vibrational modes, which are bosons (and not fermions), the **Bose-Einstein distribution theory** tells that the average number of vibrational quanta stored in an harmonic oscillator at temperature T is given by:

$$\langle n \rangle = \frac{\sum_n n e^{-\beta\hbar\omega_0}}{\sum_n e^{-\beta\hbar\omega_0}} = \frac{1}{e^{\beta\hbar\omega_0} - 1}$$

where $\beta = 1/k_B T$. This gives the average energy and average elongation of the quantum spring. We will be using the Bose-Einstein distribution when discussing the specific heat associated with vibrational modes.

One important feature of the quantum treatment is thus that one need to know the classical frequency of the oscillator !! This is what we now discuss for solids, namely we try to find all the vibrational modes associated with the N atoms in a solid.

6.2 Reminder : 2 masses connected by a spring on a line yield 2 vibrational modes

We start with a simple exercise of 2 masses connected by a spring (see Fig. 4). We label u_1 and u_2 the displacement out-of-equilibrium of the mass on the left and on the right. The equation of motion (Newton) are:

$$M\frac{d^2u_1}{dt^2} = k(u_2 - u_1) \quad \text{and} \quad M\frac{d^2u_2}{dt^2} = -k(u_2 - u_1)$$

We note that stretching the spring ($u_2 - u_1 > 0$) pulls the mass 2 towards mass 1 (negative force for mass 2) and mass 1 towards mass 2 (positive force for mass 1). Adding/subtracting the two equations, one finds :

$$\frac{d^2(u_2 + u_1)}{dt^2} = 0 \quad \text{and} \quad \frac{d^2(u_2 - u_1)}{dt^2} = -\frac{2k}{M}(u_2 - u_1)$$

The equation on the left says that the center of mass as no acceleration. Assuming the center of mass with no velocity at t=0 one finds $u_2 + u_1 = 0$. The second equation means that $u_2 - u_1 = Ae^{i\omega_0 t}$ with $\omega_0^2 = 2k/M$. Adding/subtracting the $(u_2 + u_1)$ and $(u_2 - u_1)$ expressions, we obtain :

$$u_2 = Be^{i\omega_0 t} \quad \text{and} \quad u_1 = -Be^{i\omega_0 t} \quad \text{with } B = A/2 \quad \text{(complex numbers).}$$

If B=0 one has the zero motion solution, or a constant velocity motion of the center of mass assuming that the center of mass has some initial velocity : this is a zero energy mode since the spring is never compressed/stretched (see Fig. 4b). If B is non zero, then it is a mode where the two masses move in phase opposition with maximum stretching/compression of the spring (see Fig. 4b). Assuming that $B = u_0 e^{i\phi}$ (that depends on initial conditions), then for this mode the real-valued displacements (taking the real part of the complex solution) read:

$$u_2 = -u_1 = u_0 \cos(\omega_0 t + \phi) \quad \text{with} \quad \omega_0^2 = 2k/M$$

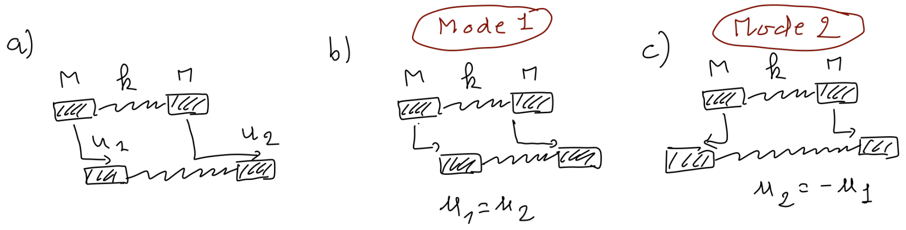


Figure 4: (a) Representation of the 2 masses connected by a spring at equilibrium (top) and with the displacement u_1 and u_2 of the 2 masses (bottom). (b) Zero-energy "in phase" mode: the 2 masses move in parallel and the spring is never compressed. (c) Maximum energy mode : the 2 masses move in phase opposition with frequency $\omega_0 = \sqrt{2k/M}$ and maximum stretching/compression of the spring.

With 2 masses and a spring, we have thus one zero-energy vibrational mode and one high-energy vibrational mode. So now what are the modes for N masses connected by springs, with N$\simeq 10^{23}$? We should find 3N vibrational modes if each mass can move along the (x,y,z) directions, corresponding to the total number of degrees of freedom. But we must first define what is the "spring constant" between neighboring atoms !

6.3 The harmonic crystal : atoms are masses connected by springs

We now consider a crystal with N atoms as in Fig. 5a. The interatomic distance is labeled "d." At equilibrium, that is the zero temperature minimum energy geometry, the distance d is equal to "a" following our notations in previous chapters. At finite temperature, the atoms vibrates around their equilibrium positions, with an amplitude of oscillation that increases with temperature. The **potential of interaction** between two neighboring atoms looks qualitatively like the one represented in Fig. 5b. At moderate temperature, where oscillations are small, the atoms vibrate around the equilibrium bond length and a Taylor expansion of the potential around its minimum value is legitimate :

$$V(d) = V(a) + (d-a)\frac{\partial V}{\partial d}\Big|_a + \frac{1}{2}(d-a)^2\frac{\partial V^2}{\partial^2 d}\Big|_a + \cdots$$

The first order derivative at the minimum (equilibrium) energy is zero by definition so that :

$$V(d) - V(a) \simeq \frac{1}{2}ku^2 \quad \text{with} \quad k = \frac{\partial V^2}{\partial^2 d}\Big|_a \quad \text{and} \quad u = (d-a)$$

This is the potential energy of a spring with spring constant "k" and elongation "u". As such, for small vibrations, that is energies well below the melting temperature, the bonds in solids can be approximated by springs with a constant equal to the curvature at the minimum of the interatomic potential. The approximation that consists in stopping the Taylor expansion of the interatomic potential to the second order is called the **harmonic approximation**. Exploring higher orders means accounting for **anharmonic effects**. Studying the vibrational properties of solids within the harmonic approximation, that is representing the crystal as atomic masses connected by springs, is the central approach to the physics of vibrational modes in solids. We are now facing the problem of finding the vibrational energies and vibrational modes of a collection of N atoms (or masses) connected by springs. We will start again with the model of the 1D chain of atoms.

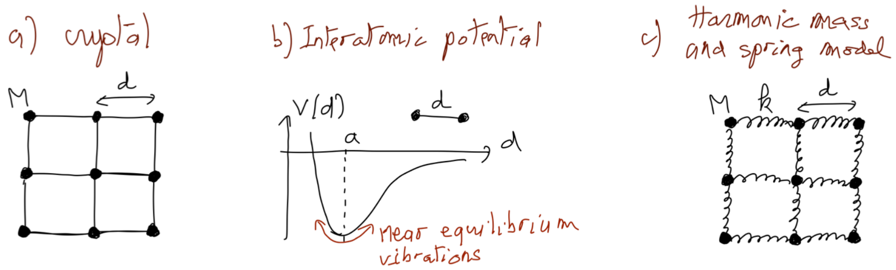


Figure 5: (a) A crystal with atoms connected by bonds. The interatomic distance is ”d” with an equilibrium (minimum energy) distance d=a. At finite temperature, atoms vibrate around their equilibrium position and the bond length d oscillates around the equilibrium d=a value. (b) Interatomic potential V(d), that is the interaction potential between two atoms (accounting for ionic and electronic interactions). The potentiel is repulsive (positive) at short distance and attractive around the equilibrium bond length, that is the minimum energy. (c) For small vibrations around the equilibrium position (well below the melting temperature), the potentiel V(d) is harmonic and the bond can be assimilated to a spring with a spring constant $k = (\partial^2 V/\partial d^2)|_a$.

6.4 Vibrational modes of the 1D chain of atoms: phonons

We start again with the 1D chain of atoms described now as classical masses M (the atomic mass) connecting by springs (see Fig. 6). To avoid making a confusion between wavevectors k and the spring constant, we now use the letter ”C” to quantify the spring constant. We study **longitudinal** displacements of atoms, that is along the chain direction, not perpendicularly to the chain direction. The amplitude of the displacement out-of-equilibrium of atom ”n” is noted u_n. As such, the elongation of the spring connecting the (n-1)-th atom to the n-th atom is $(u_n - u_{n-1})$. In the classical limit, the equation of motion (Newton equation) for atom ”n” is just

$$M\frac{d^2u_n}{dt^2} = C(u_{n+1} - u_n) - C(u_n - u_{n-1}) = C(u_{n+1} + u_{n-1} - 2u_n)$$

Inspired by the Bloch theorem for electrons, accounting for the translation

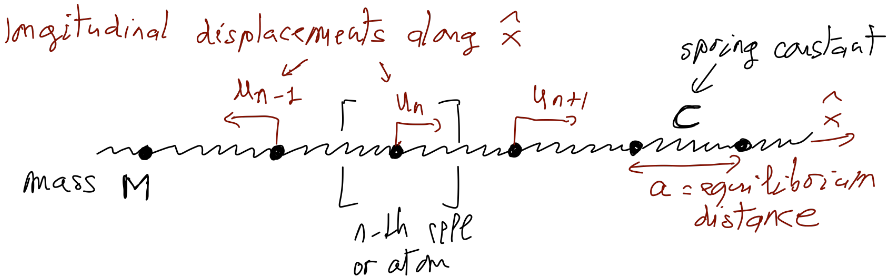


Figure 6: Masses M connected by springs with spring constant C. The equilibrium distance is "a". The longitudinal displacement of atom n is labeled u_n.

properties of the chain, we try out solutions of the form:

$$\boxed{u_n = u_0 e^{iqna} e^{-i\omega t}}$$

with **q the vibrational mode wavevector and ω the vibrational frequency**. The e^{iqna} phase factor for the n-th atom in position (na) is indeed reminiscent of the Bloch theorem. Plugging this solution into the equation of motion, one obtains:

$$-M\omega^2 u_0 e^{iqna} e^{-i\omega t} = C\Big(u_0 e^{iq(n+1)a} e^{-i\omega t} + u_0 e^{iq(n-1)a} e^{-i\omega t} - 2u_0 e^{iq(n+1)a} e^{-i\omega t}\Big)$$

Simplifying by $u_n = u_0 e^{iqna} e^{-i\omega t}$ one obtains:

$$-M\omega^2 = C\Big(e^{iqa} + e^{-iqa} - 2\Big) = 2C\Big(\cos(qa) - 1\Big)$$

so that:

$$\omega^2 = \frac{2C}{M}\Big(1 - \cos(qa)\Big)$$

with $\Big(1 - \cos(qa)\Big)$ always positive or zero. Using the identity $\cos(qa) = 1 - 2\sin^2(qa/2)$ one obtains:

$$\boxed{\omega(q) = \sqrt{\frac{4C}{M}}|\sin(qa/2)|}$$

This is the **dispersion relation**, that is the relation between the frequency ω and the wavevector q, for the 1D harmonic chain with 1-atom/cell. The dispersion relation is represented in Fig. 7. We have verified that $u_n = u_0 e^{iqna} e^{-i\omega t}$ is a solution of the equation of motion. In practice, for real-valued displacements, it is necessary to take the real value of u_n. **These vibrational solutions for the crystal are called the "phonon modes"** and the dispersion relation is also called the **"phonon band-structure" relating phonon frequency ω with the phonon momentum q.** As for the simple one-mass and spring

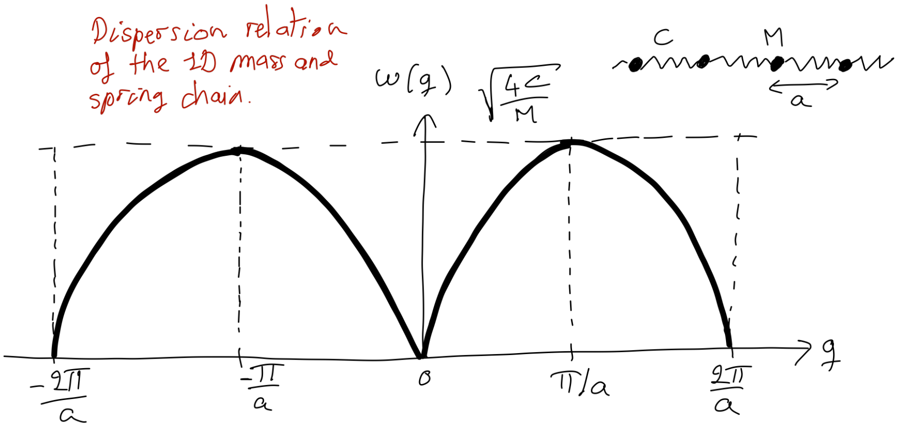


Figure 7: Dispersion $\omega(q)$ or "phonon band structure" for the 1D chain with 1-atom/cell.

model with eigenfrequency $\omega_0 = \sqrt{k/M}$, a crystal excited in a phonon (or vibrational) mode will keep oscillating with the same frequency and the same displacements provided that there is no dissipation of energy. Phonons are the stationary collective vibrational modes of the crystal.

We can further plot (Figure 8) the atomic displacements associated with the phonon mode $\omega(q)$ with its oscillatory behaviour in space along the chain and in time. It is like a discretized vibrating string with wavelength $\lambda = 2\pi/q$. We note that the ratio of the displacement of atom (n+1) by that of atom (n) is :

$$\frac{u_{n+1}}{u_n} = e^{iqa}$$

For zero phonon wavevector (q=0), this ratio is equal to one and all atoms have the same displacement : springs are not compressed/elongated and it is a zero energy mode. At maximum vibrational energy, $q = \pi/a$ and the ratio $u_{n+1}/u_n = -1$. Neighbouring atoms move in phase opposition with a maximum compression/elongation of the springs, namely indeed a maximum energy. These two modes are reminiscent of the 2-masses/1-spring vibrational modes.

We however need to answer a question similar to the one we asked for electrons with the LCAO method : with N atoms vibrating along a 1D chain (longitudinal displacements), that is N degrees of freedom, one should find N vibrational modes (phonons) and related energies and momentum. The dispersion relation $\omega(q)$ is continuous so we have an infinite number of possible frequencies and modes. Again, **we need to discretize the phonon momentum q**.

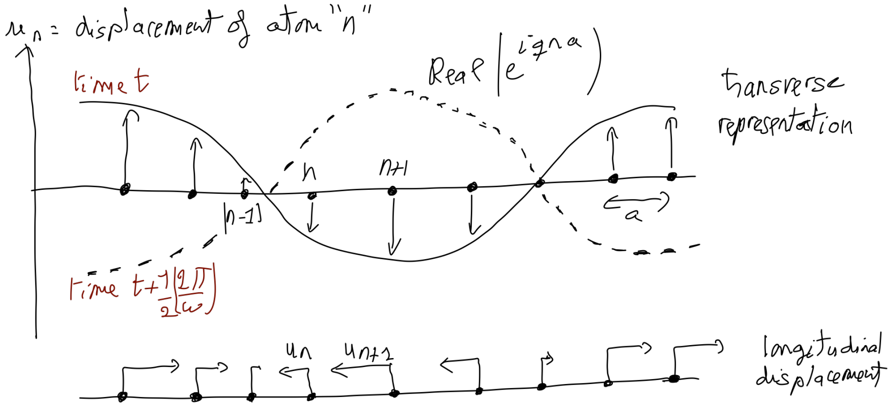


Figure 8: Representation of the phonon modes $u_n = u_0 e^{iqna} e^{-i\omega t}$. The displacements associated with the full/dashed lines correspond to times (t) and (t+T/2) where $T = 2\pi/\omega$ the period of oscillation. WARNING: in the upper part of the figure, we plot the displacements perpendicularly to the chain for better visibility, but really we have been studying longitudinal (along the chain) displacements as in the lower figure.

6.5 Phonon wavevector Brillouin zone

The reasoning is the same as we did for the momentum of electrons. The crucial observation is that defining $b = 2\pi/a$ one observes that:

$$\omega(q+b) = \sqrt{\frac{4C}{M}} |\sin(qa/2 + \pi)| = \sqrt{\frac{4C}{M}} |-\sin(qa/2)| = \omega(q)$$

and further

$$u_n(q+b) = u_0 e^{i(q+b)na} e^{-i\omega t} = u_0 e^{iqna} e^{in2\pi} e^{-i\omega t} = u_n(q)$$

As such, the phonons with wavevectors (q) and (q+b) are exactly the same. This leads to define a phonon wavevector Brillouin zone (BZ), i.e. $q \in [-b/2, b/2[$, exactly as we did for electrons. In the present case of a 1D system with a unit-cell of length a, we restrict $q \in [-\pi/a, \pi/a[$.

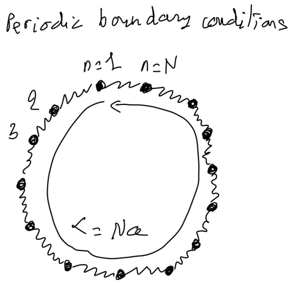
6.6 Boundary conditions

Even though limited to the Brillouin zone, we still have a continuum, i.e. an infinite number of possible q-vectors, that is of phonon modes. Again, we must apply boundary conditions. Boundary conditions for phonons can be very diverse depending on the situations : atoms at the surface are free to move (free boundary conditions) or the atoms at the surface are attached to something (imagine the final spring attached to a "wall'), in which case we have so-called "clamped boundary conditions". As a matter of fact, it does not really matter : there are so many atoms that what happens at the surface should not change much the physics. As for electrons, solid-state-physicists prefer to use the Born-von Karman (BvK) or periodic boundary conditions where the last atom is connected to the first one (see Figure). In such a situation, the first atom is also the (N+1) atom and we should make the displacement of these 2 atoms identical, that is:

$$e^{iqa} = e^{iq(N+1)a}$$

$$\Longrightarrow \quad qNa = \text{integer} \times 2\pi$$

$$\Longrightarrow \quad q = \text{integer} \times \frac{2\pi}{Na}$$



As such there are

$$\frac{2\pi/a}{2\pi/Na} = N$$

possible q-vectors in the Brillouin zone.

We thus confirm that N masses connected by springs with 1D motion (that is N degrees of freedom) yield N phonon modes as expected.

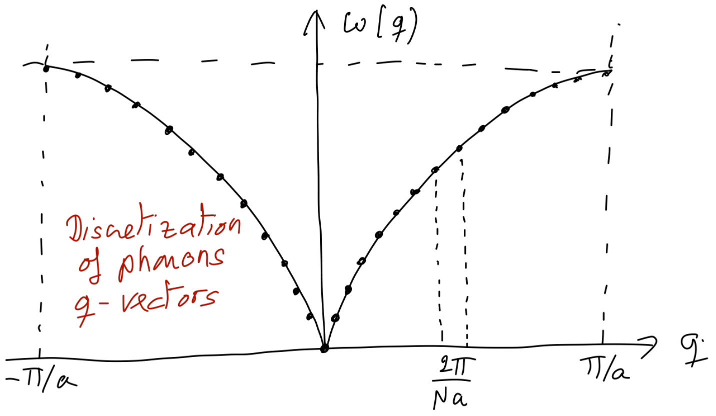


Figure 9: 1D atomic chain phonon band structure restricted to the BZ with discretized phonon q-momentum yielding N phonon modes.

6.7 Phonons in 3D, longitudinal and transverse modes

We explored here above a simple 1D chain of atoms with longitudinal displacements, that is displacements in the direction of the chain. In practice, even for 1D chains, displacements of atoms can be transverse to the chain direction. Assuming that the chain is oriented along the x-direction, we have studied above longitudinal modes with displacements along the $\hat{x}$-direction, but atoms can be displaced along the $\hat{y}$- and $\hat{z}$-directions, generating 2 "transverse" modes. This is a bit analogous to the polarization of light in electromagnetism. In a general 3D solid, phonon modes are of the form:

$$\vec{u}_n = \vec{u}_0 e^{i\vec{q}\cdot\vec{r}} e^{-i\omega t}$$

where we now have vector displacements and vector momentum $\vec{q}$. Considering now 3D crystals with 1 atom/cell, there are thus 3 phonon modes for a given phonon $\vec{q}$-vector in the 3D Brillouin zone : one longitudinal mode such that $\vec{q}$ and $\vec{u}_0$ are parallel, and two transverse modes such that $\vec{q}$ and $\vec{u}_0$ are perpendicular. For N atoms, there are therefore in 3N phonon modes in 3D corresponding to the 3N (x,y,z) degrees of freedom for each atom. Qualitatively, in most situations, transverse modes compress/extend springs less than longitudinal modes, and the energy of the 2 transverse modes is usually smaller than that of the longitudinal mode.

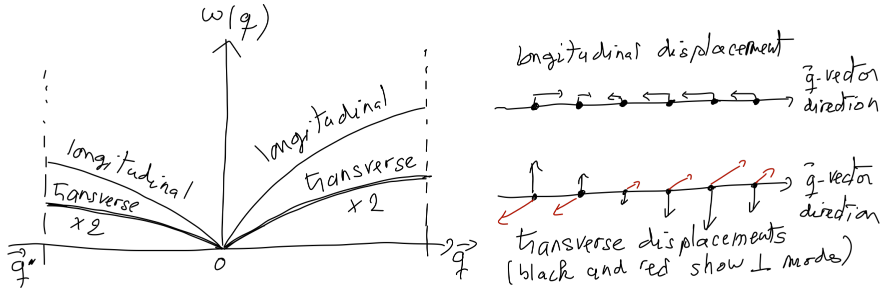


Figure 10: Typical 3D phonon band structure for systems with 1-atom/cell along two different $\vec{q}$-directions in the 3D Brillouin zone. Longitudinal and transverse phonon bands and displacements are shown qualitatively.

We finally plot in Figure 11 the phonon band structure of a real system, Calcium, a typical FCC (cubic face-centered) lattice with 1-atom/cell. The corresponding Brillouin zone is in the Left of the figure and the phonon band structure $\omega(\mathbf{q})$ is plotted for $\mathbf{q}$-vector momentum that varies along high-symmetry directions of the Brillouin zone, e.g. the $\mathbf{\Gamma X}$ or $\mathbf{\Gamma L}$ segments. The symbols T and L indicate Transverse and Longitudinal modes. The 2 transverse modes are degenerate along the $\mathbf{\Gamma X}$ or $\mathbf{\Gamma L}$ $\mathbf{q}$-vector direction, but show different energies along the $\mathbf{XK}$ $\mathbf{q}$-vector direction. The longitudinal mode becomes more energetic than the 2 transverse T_1 and T_2 modes along $\mathbf{K\Gamma}$. The red diamonds are the experimental data obtained typically by neutron diffraction.[2]

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[2] As discussed above, thermal neutrons have the same de Broglie wavelength than typical interatomic spacing so that quantum interference effects can take place in the diffraction spectrum of neutron by crystals. In Grenoble neutron diffraction can be performed at the Institut Laue-Langevin (ILL).

We note finally that the typical energy of phonons is of the order of a few dozens of meVs with the conversion 5 THz = 20.7 meV (experimentalists often give the phonon frequency $\nu = 1/T = \omega/2\pi$ rather than its energy $\hbar\omega$). This is in the infrared that goes from 430 THz to 300 GHz, or in energy from 1.7 eV to 1.24 meV. The Figure is adapted from ”Lattice dynamics of fcc Ca”, C. Stassis, J. Zaretsky, D. K. Misemer, H. L. Skriver, B. N. Harmon, and R. M. Nicklow, Phys. Rev. B 27, 3303.

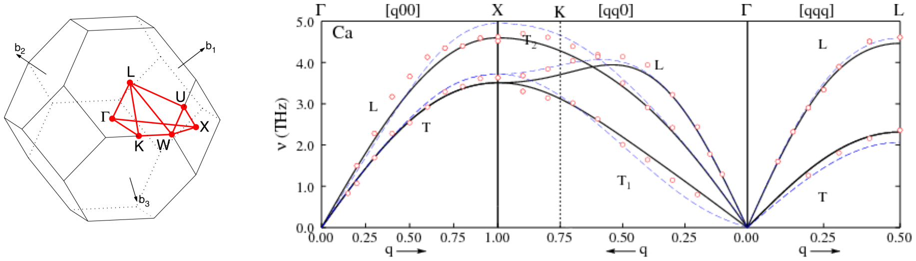

Figure 11: Experimental (red diamonds) and various theoretical (black and dashed blue lines) phonon band structure for Calcium along high-symmetry directions for **q**-vectors in the FCC Brillouin zone (left). Phonon energies are given in THz.

6.8 The Einstein model and specific heat

We now discuss the specific heat C_V associated with the vibrations of atoms in a crystal, a central subject to discuss e.g. heat transport in solids. We already discussed the specific heat in our previous Chapters dealing with electrons, with an electronic contribution to C_V linear in temperature T in metals, leaving a T^3 contribution that we said to be associated to the vibrations of ions.

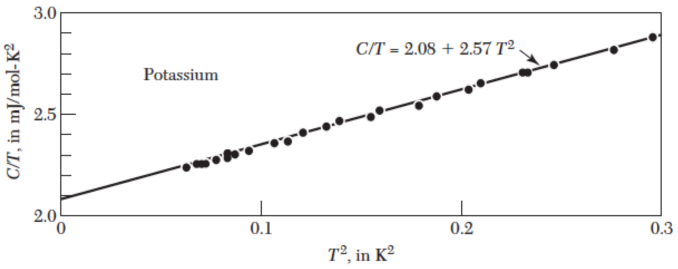

Figure 12: Experimental specific heat for potassium with an electronic T and vibrational T^3 contribution (from Kittel, Chapter 6).

This is what we discuss now using a simple approach, the Einstein model. In this model, we replace the 3N phonon modes (1 longitudinal and 2 transverse per **q**-vector in the BZ) by 3N modes with the same "average" frequency ω_E, the Einstein frequency (see Figure 13).

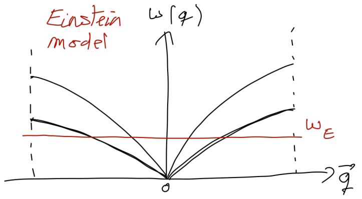

Figure 13: Einstein model for the phonon vibrational modes. This model has been proposed in the early 19-th century (Albert Einstein, Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme , Annalen der Physik, vol. 22, 1907, p. 180).

Using now the Bose-Einstein distribution that tells us how many $\langle n\rangle$ vibrational quanta of energy are stored per vibrational mode at a given temperature T, the total vibrational energy stored in the system is :

$$U(T) = 3N\Big(\langle n\rangle + \frac{1}{2}\Big)\hbar\omega_E = 3N\Big(\frac{1}{e^{\beta\hbar\omega_E}-1} + \frac{1}{2}\Big)\hbar\omega_E$$

By taking the derivative with respect to temperature, the specific heat reads :

$$C_V = \frac{\partial U}{\partial T} = \Big(\frac{\partial U}{\partial e^{\beta\hbar\omega_E}}\Big)\Big(\frac{\partial e^{\beta\hbar\omega_E}}{\partial\beta}\Big)\Big(\frac{\partial\beta}{\partial T}\Big)$$

where we have used the "chain rule" to simplify the calculation, leading to :

$$C_V = 3N\hbar\omega_E\Big(\frac{-1}{(e^{\beta\hbar\omega_E}-1)^2}\Big)\Big(\hbar\omega_E e^{\beta\hbar\omega_E}\Big)\Big(\frac{-1}{k_B T^2}\Big)$$

resulting in :

$$C_V = 3Nk_B\Big(\frac{\hbar\omega_E}{k_B T}\Big)^2\frac{e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E}-1)^2}$$

The Einstein model specific heat is represented in Fig. 14 where it is compared to a typical experiment, showing a very reasonable agreement despite the simplicity of the model. As expected, the specific heat converges to zero at low temperature : at zero temperature, there is no thermal energy to be stored. Another important feature is that at high energy, the specific heat becomes independent of the temperature and saturates at what is called the Dulong-Petit classical value. This is what we now explore using the low and high temperature limits of the Einstein specific heat.

6.8.1 High temperature classical limit

As discussed in the Introduction with the de Broglie wavelength, the high-temperature limit is the classical limit. In this limit:

$$T \Longrightarrow +\infty \qquad \beta \Longrightarrow 0 \qquad e^{\beta\hbar\omega_E} \Longrightarrow 1 + \beta\hbar\omega_E$$

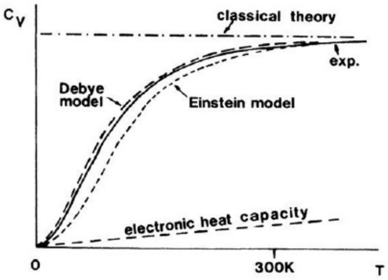

Figure 14: Specific heat of a solid comparing the experimental data to the Einstein and Debye models. The high-temperature classical limit is called the Dulong and Petit law where the specific heat is a constant equal to $3Nk_B$ with N the number of atoms. The two models differ at low temperature (see text and Exercise 27).

As a result:

$$C_V \Longrightarrow 3Nk_B\Big(\frac{\hbar\omega_E}{k_BT}\Big)^2\frac{1}{(\beta\hbar\omega_E)^2} = 3Nk_B$$

which is independent of the temperature. This is what is observed experimentally. We recover the equipartition theorem with 6 degrees of liberty per atom (3 for the kinetic energy and 3 for the potential energy in 3D) yielding an energy, thanks to the classical equipartition theorem, equal to:

$$U^{classic}(T) \simeq 6N \times \frac{k_BT}{2} \Longrightarrow C_V^{classic} = 3Nk_B \quad \text{(classical Dulong-Petit law)}$$

6.8.2 Low temperature quantum limit

In the low temperature limit, that is the quantum limit, one obtains :

$$T \Longrightarrow 0 \qquad \beta \Longrightarrow +\infty \qquad e^{\beta\hbar\omega_E} \Longrightarrow +\infty$$

As a result:

$$C_V \Longrightarrow 3Nk_B\Big(\frac{\hbar\omega_E}{k_BT}\Big)^2 e^{-\beta\hbar\omega_E}$$

We observe that the Einstein specific heat decreases exponentially with temperature, and not as a T^3 power law. The Einstein model is thus qualitatively wrong at low temperature. The explanation is that the Einstein model has no phonons with an energy smaller than the Einstein frequency ω_E. As a result, as soon as the temperature becomes smaller than ω_E, there are no phonon modes that can store thermal energy and the specific heat decays exponentially fast. A better model in this limit is the Debye model that will be studied as an exercise (Exercise 27).