Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

Lecture notes 2020 by Xavier Blase

6.9 Debye model of phonon specific heat (Exercise 27)

The failure of the Einstein model at low temperature being related to the lack of phonon modes below the ω_E Einstein frequency, Debye proposed a better model by replacing the bands by "linear" bands with the same slope at $q \to 0$ as the true phonon bands (see Fig. 15). As shown in the next paragraph, this slope is the sound velocity v_S in the material, leading to label these bands **acoustic** phonon bands. By linear bands, we mean that the dispersion relation is linear, that is $\omega(\vec{q}) = v_S|\vec{q}|$ in every direction with a maximum Debye frequency ω_D.

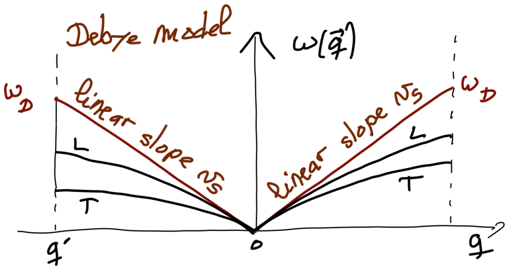


Figure 15: Phonon band structure according to the Debye model. The longitudinal (L) and 2 transverse (T) bands are replaced by a 3-fold degenerate band with linear dispersion $\omega(\vec{q}) = v_S|\vec{q}|$ in every direction with a maximum Debye frequency ω_D.

Calculating the specific heat in the Debye model is more complicated than in the Einstein model, since the phonon energy depends on the wavevector. We start by calculating the phonon density of states $\mathcal{D}(\omega)$, where $\mathcal{D}(\omega)d\omega$ counts the number of phonon modes with an energy within $[\hbar\omega, \hbar(\omega + d\omega)]$. The treatment is very close to the one performed for the density of states associated with the free electrons in a box, but with a linear (not quadratic) dispersion relation between the phonon frequency and the modulus of the wavevector.

6.9.1 Density of phonon states $\mathcal{D}(\omega)$ in the Debye model

We start by counting the number of phonon modes $\mathcal{N}(\omega)$ with an energy lower than $\hbar\omega$. Since the energy grows with the wavector magnitude, $\omega(\vec{q}) = v_S|\vec{q}|$, this is equivalent to counting the number of phonon modes with a wavevector magnitude q lower than ω/v_S. Due to the discretization of the wavevectors in every directions:

$$q_x, q_y, q_z = \text{integer} \times \frac{2\pi}{L} \qquad \text{with L the length of the cristal in each direction}$$

there is only one $\vec{q}$-vector in an elementary volume $(2\pi)^3/V$ in wavevector space, where V is the volume of the crystal. As such the number of wavevectors with magnitude lower than ω/v_S is just :

$$\frac{\frac{4}{3}\pi(\omega/v_S)^3}{(2\pi)^3/V} = \frac{V(\omega/v_S)^3}{6\pi^2} = \frac{V\omega^3}{6\pi^2 v_S^3} \quad \Longrightarrow \quad \mathcal{N}(\omega) = 3 \times \frac{V\omega^3}{6\pi^2 v_S^3} = \frac{V\omega^3}{2\pi^2 v_S^3}$$

where the factor 3 in $\mathcal{N}(\omega)$ accounts for the fact that for any wavevector $\vec{q}$ there are 1 longitudinal and 2 transverse modes. Using the obvious relation $\mathcal{D}(\omega)d\omega = \mathcal{N}(\omega + d\omega) - \mathcal{N}(\omega)$, one obtains:

$$\mathcal{D}(\omega) = \frac{d\mathcal{N}(\omega)}{d\omega} = \frac{3V}{2\pi^2}\frac{\omega^2}{v_s^3} = \frac{3V}{2\pi^2}\frac{(\hbar\omega)^2}{v_s^3\hbar^2}$$

6.9.2 Debye specific heat

We can now calculate the thermal energy stored in the vibrational modes at a given temperature by summing over all phonon modes up to ω_D. Each of the $\mathcal{D}(\omega)d\omega$ phonon modes with an energy within $[\hbar\omega, \hbar(\omega + d\omega)]$ can store a thermal energy given by $(\langle n\rangle_{\omega,T} + 1/2)\hbar\omega$, where $\langle n\rangle_{\omega,T}$ is the average number of $\hbar\omega$ vibrational quanta of energy stored in a vibrational (phonon) mode at a the temperature T as measured by the Bose-Einstein distribution. As a result :

$$U(T) = \int_0^{\omega_D} \mathcal{D}(\omega)\hbar\omega\Big(\langle n\rangle_{\omega,T} + \frac{1}{2}\Big)d\omega = \int_0^{\omega_D} \mathcal{D}(\omega)\hbar\omega\Big(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\Big)d\omega$$

We can observe that when T=0 (that is $\beta = +\infty$):

$$U(T = 0) = \int_0^{\omega_D} \mathcal{D}(\omega)\hbar\omega\Big(0 + \frac{1}{2}\Big)d\omega$$

the zero-temperature vibrational energy associated with the "zero-point motion" : even at zero temperature, due to quantum uncertainty, a mass cannot have both a fixed position and a zero-velocity, which means that atoms cannot be completely at rest ! We can thus write :

$$U(T) - U(T = 0) = \frac{3V}{2\pi^2}\frac{1}{v_s^3\hbar^3}\int_0^{\omega_D} \frac{(\hbar\omega)^3 d(\hbar\omega)}{e^{\beta\hbar\omega} - 1}$$

The mathematical trick is to put all the integral temperature dependance in the upper limit of the integral by making a change of variable with $X = \beta\hbar\omega$. The energy difference becomes then:

$$U(T) - U(T = 0) = \frac{3V}{2\pi^2}\frac{1}{v_s^3\hbar^3}\frac{1}{\beta^4}\int_0^{\beta\hbar\omega_D} \frac{X^3 dX}{e^X - 1}$$

The Debye specific heat is the temperature derivative of this expression. It is represented in the Figure where the Einstein specific heat was represented, showing better agreement with experiment, in particular at low temperature.

Low temperature Debye model. In the low temperature limit, $\beta\hbar\omega_D$ goes to infinity and:

$$U(T) - U(T=0) \Longrightarrow \frac{3V}{2\pi^2}\frac{1}{v_s^3\hbar^3}\frac{1}{\beta^4}\int_0^{+\infty}\frac{X^3dX}{e^X-1}$$

The integral is now just a constant and U(T) depends on $(1/\beta)^4$ that is on T^4. By derivation, one correctly recovers the T^3 dependence at low temperature of the phonon-related contribution to the specific heat.

High temperature Debye model. In the classical limit, the integral upper limit $\beta\hbar\omega_D$ goes to zero and the X variable inside the integral takes vanishingly small values, allowing to do a Taylor expansion of the integrand :

$$\frac{X^3}{e^X-1} \Longrightarrow \frac{X^3}{(1+X+\cdots)-1} = X^2$$

leading to the high-T limit:

$$\int_0^{\beta\hbar\omega_D}\frac{X^3dX}{e^X-1} \Longrightarrow \frac{(\beta\hbar\omega_D)^3}{3}$$

so that

$$U(T) - U(T=0) \Longrightarrow \frac{3V}{2\pi^2}\frac{1}{v_s^3\hbar^3}\frac{1}{\beta^4}\frac{(\beta\hbar\omega_D)^3}{3} = \frac{V}{2\pi^2\hbar^3}\frac{(\hbar\omega_D)^3}{v_s^3}k_BT$$

We can see that U(T) is linear in T at high-temperature. As such, the specific heat, the derivative of U(T), is independent of T in the classical high-temperature limit. We recover the Dulong-Petit law. To see if we have the correct $3Nk_B$ limit for the specific heat at high-temperature, we must know the Debye frequency. This can be obtained by saying that one should have exactly 3N vibrational modes, so that:

$$3N = \int_0^{\omega_D}\mathcal{D}(\omega)d\omega = \frac{3V}{2\pi^2}\frac{1}{v_s^3}\int_0^{\omega_D}\omega^2d\omega = \frac{V}{2\pi^2}\frac{\omega_D^3}{v_s^3}$$

We have thus

$$\frac{(\hbar\omega_D)^3}{v_s^3} = \frac{6N\pi^2\hbar^3}{V} \qquad \text{and} \qquad U(T) - U(T=0) \Longrightarrow 3Nk_BT$$

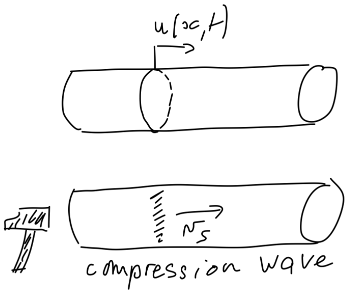
which by derivation provides the correct Dulong-Petit high-temperature limit for the specific heat.

6.10 Acoustic modes and sound velocity

Exercise 25 allows to better understand the origin of the wording "acoustic modes" by demonstrating that the slope of the acoustic band for ($q \to 0$) is the velocity of sound in the material. The propagation of sound in a continuous medium is governed by the equation:

$$\frac{1}{v_s^2}\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2}$$

where v_s is the sound velocity and $u(x;t)$ is the instantaneous displacement of a piece a matter at position x when the material is perturbed by a sound compression wave (see e.g. Feynman in www.feynmanlectures.caltech.edu/I_47.html).



To make the link between our 1D chain of atoms and the continuous limit, we just assume that the atomic position is a continuous variable, namely:

$$u_n = u(x) \quad \text{with} \quad x = na \qquad \Longrightarrow \quad u_{n+1} = u(x+a) \quad \text{and} \quad u_{n-1} = u(x-a)$$

taking the simplest chain with identical atoms of mass M. The equation of motion :

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

can be rewritten as:

$$M\frac{d^2 u(x)}{dt^2} = C\Big(u(x+a) + u(x-a) - 2u(x)\Big)$$

In the continuous limit with $a \to 0$, we make a Taylor expansion:

$$u(x \pm a) = u(x) \pm a\frac{\partial u}{\partial x} + \frac{a^2}{2}\frac{\partial^2 u}{\partial x^2} + \cdots$$

The equation of motion becomes

$$M\frac{d^2 u(x)}{dt^2} = Ca^2\frac{\partial^2 u}{\partial x^2}. \qquad \Longrightarrow \quad \Big(\frac{1}{Ca^2/M}\Big)\frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2}$$

This is precisely the continuous sound wave equation given above with $v_s = \sqrt{Ca^2/M}$. Let's consider now the phonon band structure for the simple 1D chain:

$$\omega(q) = \sqrt{\frac{4C}{M}}|\sin(qa/2)| \simeq \sqrt{\frac{4C}{M}}|qa/2| = \sqrt{\frac{Ca^2}{M}}|q| \quad \text{when } \ q \to 0.$$

We see that the slope of the acoustic band at low momentum is precisely the velocity of sound. This is why it is called the acoustic phonon branch.

6.11 Optical modes

We now address the case of **acoustic** modes, starting by considering the phonon band structure of Silicon, an FCC (face-centered cubic) crystal with 2-atoms per cell. We represent in Fig. 16(Left) the corresponding Brillouin zone (with the traditional name of high-symmetry **q**-vectors) and in Fig. 16(Right) the phonon band-structure, or dispersion relation $\omega(\mathbf{q})$, along specific directions in the Brillouin zone. An important feature is that, contrary to our previous examples, there are high-energy **q**=0 modes in addition to the phonon bands starting at zero energy in **q**=0. Such high-energy modes at small **q**-vectors are called **optical phonon modes**, while phonon modes with vanishing energy at small wavevector are the acoustic modes, which are the modes we studied in the previous paragraphs. The name ”optical” is explained in Exercise 28 where it is shown that these modes can couple strongly with electromagnetic waves. As discussed previously, acoustic and optical modes can be longitudinal or transverse.

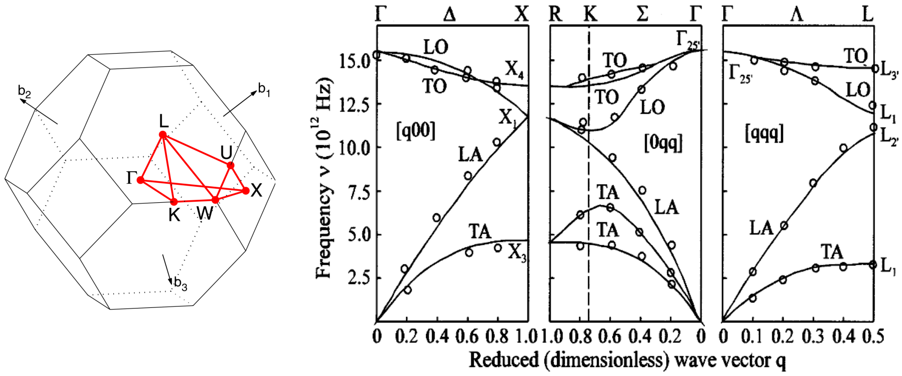


Figure 16: (Left) Silicon Brillouin zone. (Right) Silicon phonon band-structure. The LA, TA and LO, TO letters mean respectively : Longitudinal Acoustic, Transverse Acoustic, Longitudinal Optic, Transverse Optic. The acoustic phonon modes go to zero energy at small wavevector, the optical phonon modes have non-zero energy at small wavevector (from: R Tubino, L Piseri, G Zerbi; J. Chem. Phys. 56 (1972) 1022.)

6.11.1 The 1D chain model with 2-atoms per cell

To understand the presence of these low-momentum high-energy optical modes, we now consider a 1D system with 2 atoms per unit cell, with mass M_1 and M_2, connected by a spring of strength C. The length of the unit-cell is now 2a, with -a- the equilibrium bond length, and the Brillouin zone is $q \in [-\pi/2a, \pi/2a[$. We label u_n and v_n the longitudinal displacement of the atoms with mass M_1 and M_2, respectively, in the n-th unit-cell (see Figure 17). We can now use the

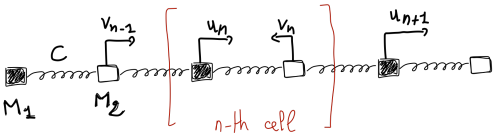


Figure 17: Representation of a chain with two atoms per cell with mass M_1 and M_2. We label u_n and v_n the longitudinal displacement of the atoms with mass M_1 and M_2 in the n-th unit-cell.

Newton classical equation-of-motion for the 2 atoms in the n-th cell:

$$M_1 \frac{d^2 u_n}{dt^2} = C(v_n - u_n) - C(u_n - v_{n-1}) = C(v_n + v_{n-1} - 2u_n)$$
$$M_2 \frac{d^2 v_n}{dt^2} = C(u_{n+1} - v_n) - C(v_n - u_n) = C(u_{n+1} + u_n - 2v_n)$$

where in the right-hand-side we always see the displacement of the two neighboring atoms minus twice the displacement of the atom of interest. Following what we did in the previous paragraphs, we postulate[1] the form of the vibrational modes for atoms with mass M_1 and atoms with mass M_2.

$$u_n = Ae^{iq2na}e^{-i\omega t} \qquad v_n = Be^{iq(2n+1)a}e^{-i\omega t}$$

We again see in the phase factor e^{iq2na} and $e^{iq(2n+1)a}$ the position at equilibrium of the 2 atoms in the n-th cell. Plugging these expressions in the 2 equation of motion, we find :

$$-\omega^2 M_1 Ae^{iq2na} = C(Be^{iq(2n+1)a} + Be^{iq(2n-1)a} - 2Ae^{iq2na})$$
$$-\omega^2 M_2 Be^{iq(2n+1)a} = C(Ae^{iq2(n+1)a} + Ae^{iq2na} - 2Be^{iq(2n+1)a})$$

where we have removed the common $e^{-i\omega t}$. Simplifying now by e^{iq2na} the first line and by $e^{iq(2n+1)a}$ the second line, one obtains:

$$-\omega^2 M_1 A = C(Be^{iqa} + Be^{-iqa} - 2A)$$
$$-\omega^2 M_2 B = C(Ae^{iqa} + Ae^{-iqa} - 2B)$$

that is, defining $K_1 = C/M_1$ and $K_2 = C/M_2$:

$$-\omega^2 A = K_1(2B\cos(qa) - 2A)$$
$$-\omega^2 B = K_2(2A\cos(qa) - 2B)$$

This leads to the system:

$$(\omega^2 - 2K_1)A + 2K_1\cos(qa)B = 0$$
$$2K_2\cos(qa)A + (\omega^2 - 2K_2)B = 0$$

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[1] This is not really postulating since it can be demonstrated using again the translation invariance. Similarly to what we said for electrons with several atomic orbitals per cell, the u_n displacements and v_n displacements are not connected by translation properties and appear as independent variables that are however inter-dependent in the 2 equations of motion.

that has non-zero (A,B) solutions provided that:

$$(\omega^2 - 2K_1)(\omega^2 - 2K_2) - 4K_1K_2\cos^2(qa) = 0$$

leading to:

$$\omega^4 - 2(K_1+K_2)\omega^2 + 4K_1K_2\Big(1-\cos^2(qa)\Big) = 0$$

Using: $\omega^4 - 2(K_1+K_2)\omega^2 = \Big(\omega^2 - (K_1+K_2)\Big)^2 - (K_1+K_2)^2$, and further $1-\cos^2(qa) = \sin^2(qa)$, we obtain:

$$\Big(\omega^2 - (K_1+K_2)\Big)^2 = (K_1+K_2)^2 - 4K_1K_2\sin^2(qa)$$

with the right-hand-side always positive since:

$$(K_1-K_2)^2 \leq (K_1+K_2)^2 - 4K_1K_2\sin^2(qa)$$

As a result:

$$\boxed{\omega^2 = (K_1+K_2) \pm \sqrt{(K_1+K_2)^2 - 4K_1K_2\sin^2(qa)}}$$

which is represented in Fig. 18 in the case $M_1 < M_2$.

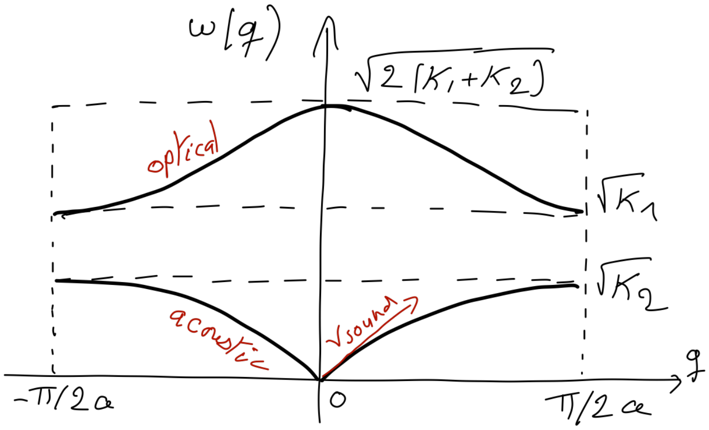

Figure 18: Phonon band structure for the 2-atoms/cell 1D chain with masses M_1 and M_2 and spring constant C, defining $K_1 = C/M_1$ and $K_2 = C/M_2$. We assume here that $K_1 > K_2$. The slope of the acoustic band at small q is the sound velocity v^{sound} as demonstrated previously.

Analysis of specific phonon modes. For (q=0) the two solutions are: $\omega^{ac} = 0$ or $\omega^{opt} = \sqrt{2(K_1+K_2)}$ where ac=acoustic and opt=optical. We verify thus the presence of a low-momentum high-energy mode. Further, with a Brillouin zone $q \in [-\pi/2a, \pi/2a[$, the zone-boundary modes, in e.g. $q = \pi/2a$ where $\sin(qa) = 1$, verify:

$$\omega^2(q = \pi/2a) = (K_1 + K_2) \pm \sqrt{(K_1 - K_2)^2} = (K_1 + K_2) \pm (K_1 - K_2)$$

assuming that $M_1 < M_2$ so that $K_1 > K_2$. For $q = \pi/2a$, the 2 phonon frequencies are consequently $\sqrt{K_1}$ or $\sqrt{K_2}$.

It is interesting to look at the atomic displacements for the phonon modes. Using e.g. the first equation of the system above for the amplitudes A and B :

$$(\omega^2 - 2K_1)A + 2K_1\cos(qa)B = 0 \quad \Longrightarrow \quad \frac{A}{B} = \frac{2K_1\cos(qa)}{2K_1 - \omega^2}$$

and the expression for u_n and v_n, one obtains :

$$\frac{u_n}{v_n} = \frac{A}{B}e^{iqa} = \frac{2K_1\cos(qa)}{2K_1 - \omega^2}e^{iqa}$$

the ratio of the displacements of atoms of mass M_1 and M_2 in a given unit-cell.

Zone-center (q=0) modes.

In that case $\cos(qa) = 1$ and $\omega^{ac} = 0$ or $\omega^{opt} = \sqrt{2(K_1 + K_2)}$, leading to:

$$\left(\frac{u_n}{v_n}\right)^{ac} = \frac{2K_1}{2K_1} = 1 \qquad \text{and} \qquad \left(\frac{u_n}{v_n}\right)^{opt} = \frac{2K_1}{2K_1 - 2(K_1 + K_2)} = -\frac{K_1}{K_2} = -\frac{M_2}{M_1}$$

The zone-center zero-energy optical mode corresponds to a phonon where all atoms move in phase : springs are not compressed nor elongated. This is what we have seen in the previous paragraphs. The zone-center optical mode corresponds to atoms moving in phase opposition, compressing/stretching the springs. This is a high-energy mode reminiscent of the zone-boundary $q = \pi/a$ mode for the simple chain with 1-atom/cell.

Note on band folding. In the case where $M_1 = M_2$, the optical mode for (q=0) in the 2-atoms/cell system, and the zone-boundary (q=π/a) mode for the 1-atom/cell system treated at the beginning, are exactly the same modes with same $\sqrt{4C/M}$ energy and same anti-phase motion of neighbors. Following what we discussed for the band structure of electrons, the phonon band structure in the small $q \in [-\pi/2a, \pi/2a|$ Brillouin zone is just the folding of the band structure in the large $[-\pi/2a, \pi/2a|$ Brillouin-zone.

END OF THE SSP LECTURE FOR THIS YEAR !