Lattice vibrations and phonons

Additional reading

- Ashcroft, chapters 23 and 24
- Any book on solid state physics
- the field theoretic aspects are well discussed in chapter 1 of Altland

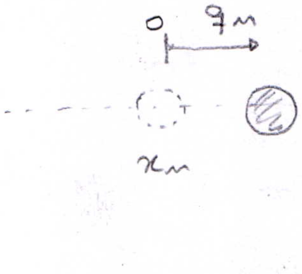
Phonons in one dimension

The atoms in a solid are allowed to vibrate slightly around their equilibrium positions. These are mechanical vibrations, which you hear and feel whenever you kick a material. We will learn that these vibrations are actually quantized. A quanta of lattice vibration is called a phonon.

Phonons are an essential part of condensed matter physics. They contribute to most of the specific heat of a solid and most of the thermal conductivity. Moreover, they interact with the electrons and this is the origin of superconductivity and other interesting effects.

To understand phonons we are going to look at the simplest possible model: a 1D chain of particles connected by springs

Let $x_n = an$ denote the equilibrium position of each atom and let q_n denote the displacement of this atom from equilibrium



$q_n = 0$ if atom n is at x_n

We assume each particle interacts with it's two neighbors by a potential of the form $\frac{g}{2}(q_m - q_{m+1})^2$, where g is the spring constant. This is the harmonic approximation. It will be a good one provided the vibrations are small.

We will study this problem using the classical Lagrangian formulation. The reason I do this is because it well teach us about how to quantize a theory and how to construct a field description of our model.

Thus, we shall take the Lagrangian of our system to be

$$\mathcal{L} = \sum_{m=1}^{N} \frac{m}{2}(\partial_t q_m)^2 - \frac{g}{2}\sum_{m=1}^{N}(q_m - q_{m+1})^2 \tag{1}$$

In this formula I am already assuming periodic boundary conditions, by putting a term $(q_N - q_{N+1})^2$, with the assumption that $q_{N+1} = q_1$.

From (1) we can find the classical equations of motion using the Euler Lagrange equations

$$\frac{\partial\mathcal{L}}{\partial q_m} - \partial_t\left(\frac{\partial\mathcal{L}}{\partial(\partial_t q_m)}\right) = 0 \tag{2}$$

they read (exercise):

$$m\,\partial_t^2 q_m = g\,(q_{m-1} - 2q_m + q_{m+1}) \tag{3}$$

this is a system of N coupled equations for $q_1, \dots, q_N$.

If we want we can quantize our theory at any time using the standard steps of <u>canonical quantization</u>. First we define the momentum associated to q_n as

$$p_n = \frac{\partial \mathcal{L}}{\partial(\partial_t q_n)} \qquad (4)$$

then we construct the Hamiltonian

$$H = \sum_n p_n \dot{q}_n - \mathcal{L}$$

$$= \sum_{n=1}^{N} \frac{p_n^2}{2m} + \frac{g}{2} \sum_{n=1}^{N} (q_n - q_{n+1})^2 \qquad (5)$$

Finally, we promote q_n and p_n to operators satisfying

$$[q_n, p_m] = i\,\delta_{n,m} \qquad (6)$$

we will then have a quantum mechanical Hamiltonian.

However, we don't need to quantize our theory right away. We can first try to simplify the classical Lagrangian (1) and then quantize in the end.

We do that by moving to Fourier space

$$q_n = \frac{1}{\sqrt{N}} \sum_k e^{ikx_n} Q_k \qquad (7)$$

As always, $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ with $\Delta k = \frac{2\pi}{Na}$.

Note: since $q_n^* = q_n$, it follows that $Q_k^* = -Q_k$

we insert this into the Lagrangian (1). The kinetic energy changes as follows:

$$\partial_t q_m = \frac{1}{\sqrt{N}} \sum_k e^{ikx_m} (\partial_t Q_k)$$

so

$$\sum_{m=1}^{N} (\partial_t q_m)^2 = \sum_{k,k'} \underbrace{\frac{1}{N} \sum_m e^{i(k+k')x_m}}_{\delta_{k,-k'}} (\partial_t Q_k)(\partial_t Q_{k'})$$

$$\therefore \quad \sum_{m=1}^{N} \frac{m}{2} (\partial_t q_m)^2 = \sum_k \frac{m}{2} (\partial_t Q_k)(\partial_t Q_{-k}) \qquad (8)$$

As for the potential energy

$$q_m - q_{m+1} = \frac{1}{\sqrt{N}} \sum_k e^{ikx_m} (1 - e^{ika}) Q_k$$

Thus

$$\sum_{m=1}^{N} (q_m - q_{m+1})^2 = \sum_{k,k'} \underbrace{\frac{1}{N} \sum_m e^{i(k+k')x_m}}_{\delta_{k,-k'}} (1 - e^{ika})(1 - e^{ika}) Q_k Q_{k'}$$

$$= \sum_k |1 - e^{ika}|^2 Q_k Q_{-k}$$

we can also write $|1 - e^{ika}|^2 = 2(1 - \cos ka)$

Thus, the Lagrangian in Fourier space becomes

$$\boxed{\mathcal{L} = \frac{m}{2} \sum_{k} \left\{ (\partial_t Q_{-k})(\partial_t Q_k) - \omega_k^2 Q_{-k} Q_k \right\}} \qquad (9)$$

where

$$\boxed{\omega_k^2 = \frac{2g}{m} (1 - \cos ka)} \qquad (10)$$

Eq (9) is traditionally known as the <u>normal mode decomposition</u>. We have sepparated the coupled dynamics of the N oscillators into N uncoupled equations for independent harmonic oscillators, each with frequency ω_k.

To see that more explicitly we can look at the equations of motion. The Euler-Lagrange equations for Q_{-k}, for instance, give

$$\frac{\partial \mathcal{L}}{\partial Q_{-k}} - \partial_t \left(\frac{\partial \mathcal{L}}{\partial (\partial_t Q_{-k})} \right) = m \left\{ - \omega_k^2 Q_k - \partial_t^2 Q_k \right\} = 0$$

Thus we get

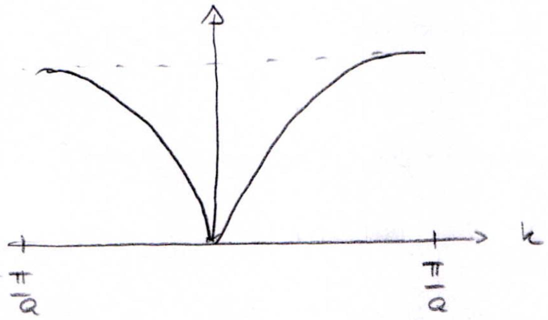
$$\partial_t^2 Q_k = - \omega_k^2 Q_k \qquad (11)$$

this is the equation for a harmonic oscillator of frequency ω_k.

The quantities ω_k therefore represent the dispersion relation for our normal modes:

$$\boxed{\omega_k = \sqrt{\frac{2g}{m}(1-\cos ka)} = 2\sqrt{\frac{g}{m}}\,|\sin(ka/2)|} \qquad (12)$$

It looks like this:



In the long wavelength limit we may expand $\sin(ka/2) \simeq$ $\simeq \frac{ka}{2}$. We then get

$$\boxed{\omega_k \simeq c|k| \qquad c = a\sqrt{\frac{g}{m}}} \qquad (13)$$

This is like the dispersion relation for light. These vibrations represent sound waves and c is the sound velocity in the material. For long wavelengths ($ka \ll 1$) sound waves behave similarly to light. But for ka not small the dispersion relation bends, like in the figure.

So far this is all classical. But now it is straightforward to quantize our theory. We simply follow the usual recipe. Starting with (9) we define the momenta

$$\Pi_k = \frac{\partial \mathcal{L}}{\partial(\partial_t Q_k)} = m\, \partial_t Q_{-k}$$

← careful! $\partial_t Q_k$ appears twice, for $k>0$ and $k<0$.

Then we construct the Hamiltonian

$$H = \sum_k \Pi_k\, \partial_t Q_k - \mathcal{L}$$

which gives

$$\boxed{H = \sum_k \left\{ \frac{\Pi_k \Pi_{-k}}{2m} + \frac{1}{2} m \omega_k^2 Q_k Q_{-k} \right\}} \qquad (14)$$

and finally we promote Q_k, Π_k to operators satisfying

$$[\hat{Q}_k, \hat{\Pi}_{k'}] = i\, \delta_{kk'} \qquad (15)$$

To finish we introduce creation and annihilation operators as

$$a_k = \sqrt{\frac{m\omega_k}{2}} \left[Q_k + \frac{i\, \Pi_{-k}}{m\omega_k} \right]$$
$$a_k^{\dagger} = \sqrt{\frac{m\omega_k}{2}} \left[Q_{-k} - \frac{i\, \Pi_k}{m\omega_k} \right] \qquad (16)$$

[Recall that $Q_k^\dagger = Q_{-k}$. See comment at the end of page 8].

The inverse relations are

$$Q_k = \frac{1}{\sqrt{2m\omega_k}} (a_k + a^\dagger_{-k})$$

$$\Pi_k = i\sqrt{\frac{m\omega_k}{2}} (a^\dagger_k - a_{-k}) \qquad (17)$$

I leave for you to check that Eq (15) implies

$$\boxed{[a_k, a^\dagger_{k'}] = \delta_{kk'}} \qquad (18)$$

Thus, these a_k are exactly <u>Bosonic operators</u>.

The Hamiltonian (14) becomes

$$\boxed{H = \sum_k \omega_k (a_k^\dagger a_k + 1/2)} \qquad (19)$$

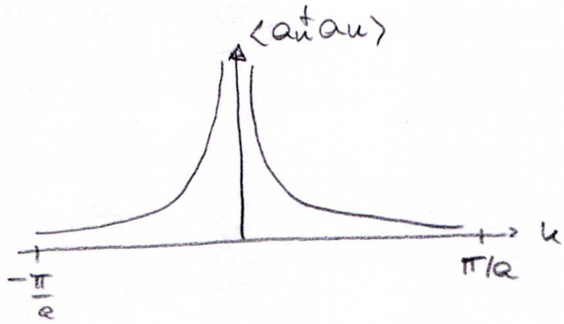
This is now a diagonal Hamiltonian describing independent Bosons with momentum k. These quasi-particles are the <u>phonons</u>.

We therefore emerge from this with the picture that the lattice vibrations, when quantized, are described by quasi-particles that propagate through the material with a dispersion relation ω_k. The solid is nothing but a big city with phonons traveling around. In (19) the phonons do not interact. But is just the first approximation. Anharmonic terms would lead to interactions among phonons.

Now that we have H as a diagonal Hamiltonian, we may use everything we learned about 2^{nd} quantization. In particular, we know that in thermal equilibrium we will have

$$\boxed{\langle a_k^\dagger a_k \rangle = \frac{1}{e^{\beta\omega_k} - 1}} \qquad (20)$$

where, now, there is no chemical potential because the number of phonons in the system is free to fluctuate. This thermal occupation will look like this



It diverges at $k=0$. This actually has a fun physical interpretation: at $k=0$, $\omega_0 = 0$. The $k=0$ mode corresponds to an oscillation where all atoms are displaced by the same amount. Our crystal is not nailed to the table top, so such a displacement will simply translate the crystal somewhere else.

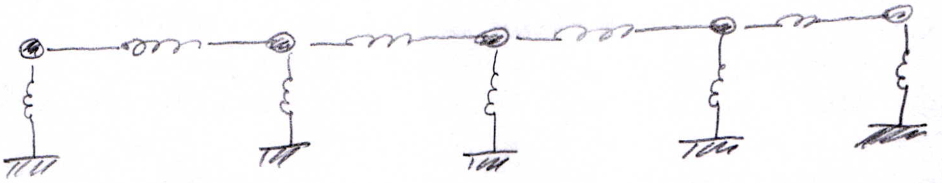
If we now consider our system in the presence of a heat bath, the thermal fluctuations of the bath will cause our system to drift away like a big molecule undergoing Brownian motion in a fluid. That is why $\langle a_0^\dagger a_0 \rangle = \infty$.

Sometimes that is fixed by hand by neglecting the $k=0$ mode in the calculations. Another fun way of fixing this is by adding a pinning term

$$V = \frac{g'}{2}\sum_m q_m^2 \tag{21}$$

This may look a bit like this

(This is not very precise. the drawing is 2D but the effect of (21) is 1D)

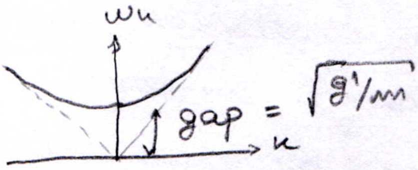


We nail the crystal to a table. I will leave for you to check that the inclusion of the pinning term (21) modifies the dispersion relation to

$$\omega_k = \sqrt{\frac{2g}{m}(1-\cos ka) + \frac{g'}{m}} \tag{22}$$

Thus, now, $\omega_{k=0} \neq 0$ and $\langle a_0^\dagger a_0 \rangle$ will remain finite

In the long wavelength limit, $ka \ll 1$, ω_k may be approximated as



$$\omega_k \simeq \sqrt{c^2k^2 + \frac{g'}{m}} \tag{23}$$

This is a massive relativistic dispersion relation, $E = \sqrt{c^2p^2 + m^2c^4}$. Thus, g'/m actually play the role of a mass term for the phonons. When there is no pinning, phonons are massless particles. But when there is pinning, they became massive and a gap opens: there is a minimum energy $\sqrt{g'/m}$ which we must give in order to create a phonon.

The continuum limit

Consider again the full Lagrangian (1), but including also the pinning term:

$$L = \sum_{n=1}^{N} \frac{m}{2} (\partial_t q_n)^2 - \frac{g}{2} \sum_{n=1}^{N} (q_n - q_{n+1})^2 - \frac{g'}{2} \sum_n q_n^2 \qquad (24)$$

Now we are going to take the continuum limit by assuming that a is very tiny and that q_n is a smooth function of $x_n = an$.

We define

$$\phi(x_n) = \frac{q_n}{\sqrt{a}} \qquad (25)$$

where the factor of $\sqrt{a}$ is placed for convenience. The kinetic energy in (24) then transforms trivially as

$$\sum_{n=1}^{N} \frac{m}{2} (\partial_t q_n)^2 = \frac{1}{2} \sum_{n=1}^{N} m a (\partial_t \phi)^2$$

The pinning term becomes

$$\frac{g'}{2} \sum_n q_n^2 = \frac{g'}{2} \sum_n a \phi^2$$

Finally, the g-term will transform as:

$$\begin{aligned} q_{n+1} - q_n &= \sqrt{a} \left[\phi(x_n + a) - \phi(x_n) \right] \\ &= \sqrt{a}\, a \left[\frac{\phi(x_n + a) - \phi(x_n)}{a} \right] \end{aligned}$$

In the limit $a \to 0$ this becomes a derivative

$$(q_{n+1} - q_n) \simeq \sqrt{a}\, a \;\partial_x \phi$$

Thus

$$\frac{g}{2}\sum_{n=1}^{N} (q_{n+1} - q_n)^2 = \frac{g}{2}\sum_{n} a\, a^2 (\partial_x \phi)^2$$

combining everything we get

$$L = \sum_{n} a \left\{ \frac{m}{2}(\partial_t \phi)^2 - \frac{g a^2}{2}(\partial_x \phi)^2 - \frac{g'}{2}\phi^2 \right\}$$

This now has the form of a Riemann sum, with $\Delta x = a$. Thus we may approximate

$$L = \int dx \left\{ \frac{m}{2}(\partial_t \phi)^2 - \frac{g a^2}{2}(\partial_x \phi)^2 - \frac{g'}{2}\phi^2 \right\}$$

$$= \frac{m}{2}\int dx \left\{ (\partial_t \phi)^2 - \frac{g a^2}{m}(\partial_x \phi)^2 - \frac{g'}{m}\phi^2 \right\}$$

we see here two terms that we have already seen before : $c^2 = \frac{g a^2}{m}$ and the "mass term" $\frac{g'}{m} := \mu^2$

$$\boxed{L = \frac{m}{2}\int dx \left\{ (\partial_t \phi)^2 - c^2 (\partial_x \phi)^2 - \mu^2 \phi^2 \right\}} \qquad (26)$$

We have therefore arrived at a (classical) field theory to describe the lattice vibrations. The field $\phi(x)$ measures the displacement of the lattice at position x. The continuum limit is also called the low energy approximation because at low energies the displacements are smooth enough to allow us to approximate q_n by the continuous function $\phi(x)$.

When we have a field theory, instead of working with the total Lagrangian L, we may work with a Lagrangian density

this is how masses appear in QFT ↙

$$\boxed{\mathcal{L} = \frac{1}{2}\left[(\partial_t \phi)^2 - c^2 (\partial_x \phi)^2\right] - \frac{\mu^2}{2}\phi^2} \qquad (27)$$

where I got rid of the m in (26) since it simply rescales the units of L.

In quantum field theory Eq (27) is called the scalar field. It is the first field theory you find in any QFT book.

The Euler Lagrange equations now involve a derivative with respect to t and one with respect to x:

$$\frac{\partial \mathcal{L}}{\partial \phi} - \partial_t\left(\frac{\partial \mathcal{L}}{\partial(\partial_t \phi)}\right) - \partial_x\left(\frac{\partial \mathcal{L}}{\partial(\partial_x \phi)}\right) = 0 \qquad (28)$$

using (27) then gives

$$-\mu^2\phi - \partial_t^2\phi + c^2\partial_x^2\phi = 0$$

or

$$\boxed{\partial_t^2\phi - c^2\partial_x^2\phi + \mu^2\phi = 0} \qquad (29)$$

This is called the Klein-Gordon equation. If the pinning is zero, $\mu = 0$, we get the wave equation

$$\partial_t^2\phi - c^2\partial_x^2\phi = 0 \qquad (30)$$

This is another way of thinking about the lattice vibrations: they are just waves propagating through the material with speed of sound c.

We can also set $c = 1$. This simply rescales the units of position or time. We are then left with

$$(\partial_t\phi)^2 - (\partial_x\phi)^2 = (\partial_\mu\phi)(\partial^\mu\phi)$$

which is a manifestly Lorentz invariant quantity. I will not use this anymore because I don't know how familiar you are with relativity.

Quantum field theory

The Lagrangian density (27) describes a classical field theory. We may now quantize it using the usual recipe. First we define the momentum $\Pi(x)$ associated to the field $\phi(x)$, as

$$\Pi(x) = \frac{\partial \mathcal{L}}{\partial(\partial_t \phi)} = \partial_t \phi \qquad (31)$$

Then we construct the Hamiltonian density

$$\mathcal{H} = \Pi(x)\,(\partial_t \phi) - \mathcal{L}$$

which gives

$$\mathcal{H} = \frac{1}{2}\left\{ \Pi^2 + c^2 (\partial_x \phi)^2 + \nu^2 \phi^2 \right\} \qquad (32)$$

Finally, we promote ϕ and Π to operators satisfying

$$[\phi(x), \Pi(y)] = i\delta(x-y) \qquad (33)$$

We then got ourselves a quantum field theory. the total Hamiltonian is simply

$$\boxed{H = \int dx\, \mathcal{H} = \int dx\, \frac{1}{2}\left\{ \Pi(x)^2 + c^2(\partial_x \phi)^2 + \nu^2 \phi^2 \right\}} \qquad (32')$$

We can also diagonalize our Hamiltonian by moving to Fourier space. We define

$$\phi(x) = \frac{1}{\sqrt{L}} \sum_k e^{ikx} \phi_k$$

$$\Pi(x) = \frac{1}{\sqrt{L}} \sum_k e^{ikx} \Pi_k \qquad (34)$$

As usual, $k = \frac{2\pi l}{L}$. But now k is no longer restricted to the first BZ since x may vary continuously.

I will leave for you as an exercise to check that, introducing (34) in (32) leads to

$$\boxed{H = \sum_k \frac{1}{2} \left\{ \Pi_k \Pi_{-k} + \omega_k^2 \phi_k \phi_{-k} \right\}} \qquad (35)$$

where, now,

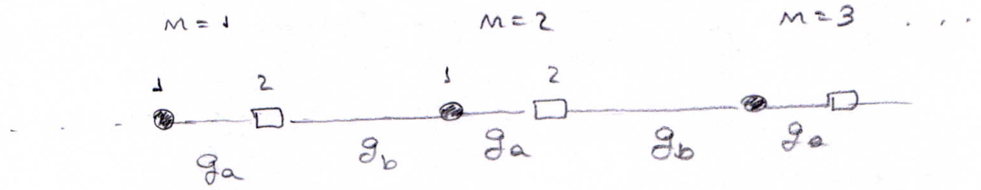
$$\boxed{\omega_k^2 = c^2 k^2 + \mu^2} \qquad (36)$$

Thus, in the continuum limit we obtain the long wavelength dispersion relation. In this sense, when we start with a dispersion relation like (22) and expand to get (23), we are implicitly taking the continuum limit.

The last step is to introduce creation and annihilation operators, exactly like in (17). One will then obtain the phonon Hamiltonian (19)

1D crystal with 2 atoms in the basis

We now consider a different model. We take a 1D crystal but assume there are two different atoms in the basis



For simplicity we assume the two atoms have the same mass, but the spring constants are different. We label the atoms as $q_{n,1}$ and $q_{n,2}$, where n is the Bravais lattice site.

The Lagrangian now reads

$$\boxed{\mathcal{L} = \sum_{n=1}^{N} \frac{m}{2}\left[(\partial_t q_{n,1})^2 + (\partial_t q_{n,2})^2\right] - \frac{g_a}{2}\sum_{n=1}^{N}(q_{n,1}-q_{n,2})^2 + - \frac{g_b}{2}\sum_{n=1}^{N}(q_{n,2}-q_{n+1,1})^2} \qquad (37)$$

We proceed as before, by moving to Fourier space according to

$$q_{n,i} = \frac{1}{\sqrt{N}}\sum_k e^{ikx_n} Q_{k,i} \qquad i = 1,2 \qquad (38)$$

The kinetic energy is modified exactly as before [Eq (9)]

$$\sum_{m=1}^{N} \frac{m}{2}\left[(\partial_t q_{m,1})^2 + (\partial_t q_{m,2})^2\right] = \sum_k \frac{m}{2}\Big[(\partial_t Q_{k,1})(\partial_t Q_{-k,1}) +$$

$$+ (\partial_t Q_{k,2})(\partial_t Q_{-k,2})\Big] \qquad (39)$$

As for the potential energy,

$$(q_{m,1} - q_{m,2}) = \frac{1}{\sqrt{N}} \sum_k e^{ikx_m} (Q_{k,1} - Q_{k,2})$$

so

$$\frac{g_a}{2} \sum_m (q_{m,1} - q_{m,2})^2 = \frac{g_a}{2} \sum_{kk'} \underbrace{\frac{1}{N} \sum_m e^{i(k+k')x_m}}_{\delta_{k,-k'}} (Q_{k,1} - Q_{k,2}) \times$$

$$\times (Q_{k',1} - Q_{k',2})$$

$$= \frac{g_a}{2} \sum_k (Q_{k,1} - Q_{k,2})(Q_{-k,1} - Q_{-k,2})$$

and

$$(q_{m,2} - q_{m+1,1}) = \frac{1}{\sqrt{N}} \sum_k e^{ikx_m} (Q_{k,2} - e^{ika} Q_{k,1})$$

so

$$\frac{g_b}{2} \sum_m (q_{m,2} - q_{m+1,1})^2 = \sum_{k,k'} \frac{1}{N} \sum_m e^{i(k+k')x_m} (Q_{k,2} - e^{ika} Q_{k,1}) \times$$

$$\times (Q_{k',2} - e^{ik'a} Q_{k',1})$$

$$= \frac{g_b}{2} \sum_k (Q_{k,2} - e^{ika} Q_{k,1})(Q_{-k,2} - e^{-ika} Q_{-k,1})$$

Recall that $Q_{-k,i} = Q^*_{k,i}$. So we may write things in a slightly more pleasant way as

$$\mathcal{L} = \sum_k \Big\{ \frac{m}{2}\Big[(\partial_t Q_{k,1})(\partial_t Q^*_{k,1}) + (\partial_t Q_{k,2})(\partial_t Q^*_{k,2})\Big] - \frac{g_a}{2}\left(Q^*_{k,1} - Q^*_{k,2}\right)\left(Q_{k,1} - Q_{k,2}\right) - \frac{g_b}{2}\left(Q^*_{k,2} - e^{-ika} Q^*_{k,1}\right)\left(Q_{k,2} - e^{ika} Q_{k,1}\right)\Big\} \tag{40}$$

we can also write this as

$$\mathcal{L} = \sum_k \Big\{ \frac{m}{2}\Big[(\partial_t Q^*_{k,1})(\partial_t Q_{k,1}) + (\partial_t Q^*_{k,2})(\partial_t Q_{k,2})\Big] - V_k \Big\} \tag{41}$$

where the potential V_k is written as a quadratic form

$$V_k = \frac{1}{2}\begin{pmatrix} Q^*_{k,1} & Q^*_{k,2} \end{pmatrix} W(k) \begin{pmatrix} Q_{k,1} \\ Q_{k,2} \end{pmatrix} \tag{42}$$

the matrix $W(k)$ can be read off directly from (40). It reads

$$W(k) = \begin{bmatrix} g_a + g_b & -(g_a + g_b e^{ika}) \\ -(g_a + g_b e^{-ika}) & g_a + g_b \end{bmatrix} \tag{43}$$

This situation is entirely analogous to the tight-binding model. Now that we have more than one internal degree of freedom, going to Fourier space is not enough to give us a "diagonal" Lagrangian. Instead, this was just the first step. Now we need to diagonalize the matrix $w(k)$.

I will call the 2 eigenvalues of $W(k)$ as $m\omega_{k+}^2$ and $m\omega_{k,-}^2$. They read

$$\boxed{m\omega_{k\pm}^2 = g_a + g_b \pm \sqrt{g_a^2 + g_b^2 + 2 g_a g_b \cos ka}} \tag{44}$$

The matrix W can be diagonalized by a unitary transformation of the form

$$S = \frac{1}{\sqrt{2}} \begin{bmatrix} e^{-i\phi/2} & -e^{-i\phi/2} \\ e^{i\phi/2} & e^{i\phi/2} \end{bmatrix} \tag{45}$$

where

$$\tan\phi = \frac{-g_b \sin ka}{g_a + g_b \cos ka} \tag{46}$$

It is possible to derive all these results using the Pauli matrices trick that I discuss in Sec 1.3 of my PDF notes on quantum mechanics.

We now define a new set of variables $Q_{k,\pm}$ according to

$$\begin{pmatrix} Q_{k,1} \\ Q_{k,2} \end{pmatrix} = S^{\dagger} \begin{pmatrix} Q_{k,+} \\ Q_{k,-} \end{pmatrix} \qquad (47)$$

We then get

$$V_k = \frac{1}{2} \begin{pmatrix} Q^*_{k,+} & Q^*_{k,-} \end{pmatrix} S\, W(k)\, S^{\dagger} \begin{pmatrix} Q_{k,+} \\ Q_{k-} \end{pmatrix}$$

But

$$S W(k) S^{\dagger} = \begin{pmatrix} m\omega_{k+}^2 & 0 \\ 0 & m\omega_{k-}^2 \end{pmatrix} \qquad (48)$$

Thus the potential energy becomes

$$V_k = \frac{1}{2} m\omega_{k+}^2 Q^*_{k+} Q_{k+} + \frac{1}{2} m\omega_{k-}^2 Q^*_{k-} Q_{k-} \qquad (49)$$

The kinetic energy in (40) transforms trivially under (47), so we finally get

$$\boxed{\begin{aligned} \mathcal{L} = \sum_k \Big\{ & \frac{m}{2} (\partial_t Q^*_{k+})(\partial_t Q_{k+}) - \frac{1}{2} m\omega_{k+}^2 Q^*_{k+} Q_{k+} \\ & + \frac{m}{2} (\partial_t Q^*_{k-})(\partial_t Q_{k-}) - \frac{1}{2} m\omega_{k-}^2 Q^*_{k-} Q_{k-} \Big\} \end{aligned}} \qquad (50)$$

We have therefore decomposed our interacting system into 2N non-interacting harmonic oscillators. The steps to write a quantum theory are now exactly as before. We define creation and annihilation operators a_{k+} and a_{k-} for each mode, which then gives us a diagonal Hamiltonian

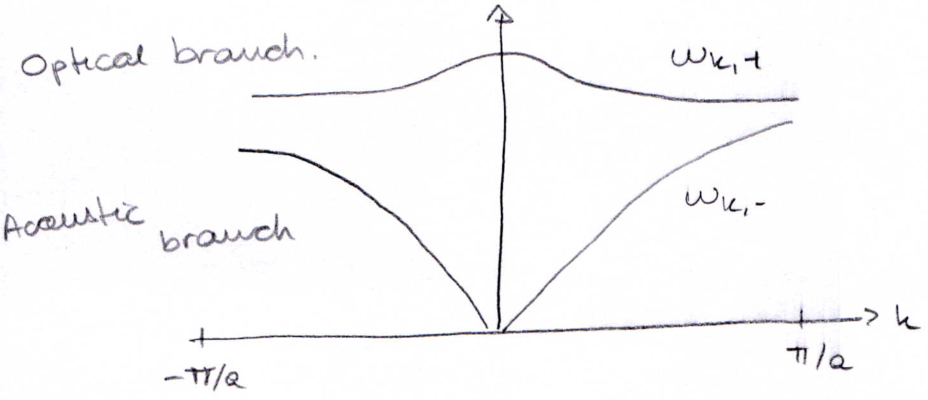
$$\boxed{\mathcal{H} = \sum_{k,\lambda} \omega_{k,\lambda} \left(a^{\dagger}_{k\lambda} a_{k\lambda} + 1/2 \right)} \qquad (51)$$

where $\lambda = +, -$ describes the two bands.

The dispersion relations for the two bands are given by Eq (44)

$$\boxed{\omega_{k\pm} = \frac{1}{\sqrt{m}} \left[g_a + g_b \pm \left(g_a^2 + g_b^2 + 2 g_a g_b \cos ka \right)^{1/2} \right]^{1/2}} \qquad (52)$$

It looks something like this



The lower band $\omega_{k,-}$ is somewhat similar to what we had before. At low k it behaves like

$$\omega_{k,-} \simeq c\,|k| \tag{53}$$

Hence it describes the propagation of <u>sound waves</u> in the material. For this reason it is called the <u>acoustic branch</u>.

The upper band, on the other hand, tends to a constant when $k \to 0$:

$$\omega_{k,+} \to \omega_0 \quad \text{when } k \to 0 \tag{54}$$

This therefore represents a high-frequency oscillation with zero momentum. It is the "internal" oscillation of the two atoms in the unit cell

Each basis pair oscillates like an independent molecule. This type of oscillation couples well with electromagnetic radiation. For this reason ω_{k+} is known as the <u>optical branch</u>.

Phonons in more general situations

It is possible to compute the phonon spectra of any crystal system you want. However, the calculations become quite cumbersome. There are no conceptual difficulties, just big ugly formulas that you need to manipulate. Nowadays we never do this by hand anymore. We simply plug the crystal in a computer and let it do the job. For this reason, all you need to know is the general idea.

We consider a crystal with B atoms in the basis. Each Bravais site will therefore have 3B "internal degrees of freedom" since each atom may vibrate in the x, y and z directions. We can label these coordinates as $q_{n,\alpha}$ where n is the position $\mathbf{R}_n$ of the Bravais lattice site and $\alpha = 1, \dots, 3B$.

The potential energy may now be written as

$$\boxed{V = \frac{1}{2} \sum_{\substack{n,m \\ \alpha,\beta}} \Phi_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m)(q_{n\alpha} - q_{m\alpha})(q_{n\beta} - q_{m\beta})} \qquad (55)$$

where, due to translation invariance, Φ can only depend on $\mathbf{R}_n - \mathbf{R}_m$. Figuring out the Φ's is actually the hardest part. We will come back to this in a second. For simplicity I will assume all atoms have the same mass. I hate masses. They make everything look ugly.

We now move to Fourier space by defining

$$q_{m,\alpha} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_m} Q_{\mathbf{k},\alpha} \qquad (56)$$

then

$$q_{n,\alpha} - q_{m,\alpha} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \left(e^{i\mathbf{k}\cdot\mathbf{R}_n} - e^{i\mathbf{k}\cdot\mathbf{R}_m}\right) Q_{\mathbf{k},\alpha}$$

Hence

$$V = \frac{1}{2} \sum_{\substack{n,m \\ \alpha,\beta}} \sum_{\mathbf{k},\mathbf{k}'} \frac{1}{N} \Phi_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m)\left(e^{i\mathbf{k}\cdot\mathbf{R}_n} - e^{i\mathbf{k}\cdot\mathbf{R}_m}\right) \times$$
$$\left(e^{i\mathbf{k}'\cdot\mathbf{R}_n} - e^{i\mathbf{k}'\cdot\mathbf{R}_m}\right) Q_{\mathbf{k},\alpha} Q_{\mathbf{k}',\beta}$$

Now change variables to $\mathbf{R}_l = \mathbf{R}_n - \mathbf{R}_m$. We then get

$$V = \frac{1}{2} \sum_{\substack{\mathbf{k},\mathbf{k}' \\ \alpha,\beta}} Q_{\mathbf{k}\alpha} Q_{\mathbf{k}'\beta} \Bigg[\frac{1}{N} \sum_{l,m} \Phi_{\alpha\beta}(\mathbf{R}_l)\left(e^{i\mathbf{k}\cdot(\mathbf{R}_l + \mathbf{R}_m)} - e^{i\mathbf{k}\cdot\mathbf{R}_m}\right)$$
$$\left(e^{i\mathbf{k}'\cdot(\mathbf{R}_l + \mathbf{R}_m)} - e^{i\mathbf{k}'\cdot\mathbf{R}_m}\right)$$

$$= \frac{1}{2} \sum_{\substack{\mathbf{k},\mathbf{k}' \\ \alpha,\beta}} Q_{\mathbf{k}\alpha} Q_{\mathbf{k}'\beta} \underbrace{\left[\frac{1}{N} \sum_{m} e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}_m} \right]}_{\delta_{\mathbf{k},-\mathbf{k}'}} \Bigg[\sum_{l} \Phi_{\alpha\beta}(\mathbf{R}_l) \times$$
$$\times \left(e^{i\mathbf{k}\cdot\mathbf{R}_l} - 1\right)\left(e^{i\mathbf{k}'\cdot\mathbf{R}_l} - 1\right) \Bigg]$$

Define

$$\boxed{\omega_{\alpha\beta}(\mathbf{k}) = 2\sum_{l} \Phi_{\alpha\beta}(\mathbf{R}_l)\left[1 - \cos(\mathbf{k}\cdot\mathbf{R}_l)\right]} \qquad (57)$$

Then we get, recalling also that $Q_{-\mathbf{k},\beta} = Q^*_{\mathbf{k}\beta}$

$$\boxed{V = \frac{1}{2}\sum_{\mathbf{k}}\sum_{\alpha,\beta} W_{\alpha\beta}(\mathbf{k})\, Q_{\mathbf{k}\alpha}\, Q^*_{\mathbf{k}\beta}} \qquad (59)$$

Again, note the similarity with the tight-binding model. To finish the job we must now diagonalize the matrix $W(\mathbf{k})$, which has dimension 3B. This will then give us 3B phonon bands.

Let $\omega_\lambda(\mathbf{k})^2$ denote the eigenvalues of $W(\mathbf{k})$, where λ is the eigenvalue index, with $\lambda = 1, \ldots, 3B$. Also, let $\vec{e}_\lambda(\mathbf{k})$ denote the eigenvectors, Then

$$W(\mathbf{k})\, \vec{e}_\lambda(\mathbf{k}) = \omega_\lambda(\mathbf{k})^2\, \vec{e}_\lambda(\mathbf{k}) \qquad (59)$$

Let us first assume that our crystal only has one atom per unit cell. then the "internal degrees" α are the cartesian positions x, y, z of each atom. that is, $q_{m,1} = q_{m,x}$ and so on. the eigenvector $\vec{e}_\lambda(\mathbf{k})$ will play the role of a polarization vector.

when $ka \ll 1$ we may approximate (57) by

$$\begin{aligned} W_{\alpha\beta}(\mathbf{k}) &\simeq \sum_l \Phi_{\alpha\beta}(\mathbf{R}_l)\,(\mathbf{k}\cdot\mathbf{R}_l)^2 \\ &= |\mathbf{k}|^2 \sum_l \Phi_{\alpha\beta}(\mathbf{R}_l)\,(\hat{\mathbf{k}}\cdot\mathbf{R}_l)^2 \end{aligned} \qquad (60)$$

where $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$.

We therefore see that $\omega_\lambda(\mathbf{k})^2$ will be proportional to $\mathbf{k}^2$. Thus $\omega_\lambda(\mathbf{k}) \propto |\mathbf{k}|$. the 3 modes will therefore be acoustic modes. Each mode will have a sound velocity $c_\lambda(\hat{\mathbf{k}})$ which will, in general, depend on the direction of propagation $\hat{\mathbf{k}}$.

When the crystal has a sufficiently high symmetry, we can in general choose the eigenvectors in such a way that

$$\vec{e}_1(\mathbb{k}) = \text{const} \times \hat{\mathbb{k}} \qquad \vec{e}_2(\mathbb{k}) \perp \vec{e}_3(\mathbb{k}) \perp \vec{e}_1(\mathbb{k}) \tag{61}$$

then we speak of $\vec{e}_1$ as the longitudinal acoustic mode (LA) and $\vec{e}_2, \vec{e}_3$ as the transverse acoustic modes (TA).

If our material has $\mathcal{B}$ atoms in the basis, then the matrix $\mathbb{W}$ will have dimension $3\mathcal{B}$. It can be shown that 3 eigenvalues will continue to be of the acoustic type, and the remaining $3\mathcal{B}-3$ will be optical modes.

How to construct $\Phi_{\alpha\beta}(\mathbf{R}_n - \mathbf{R}_m)$

Let me discuss now how to build the connection matrix appearing in (55). I will consider only the case of one atom per unit cell.

Let $\mathbf{R}_n$ be the equilibrium position of each atom and $\mathbf{r}_n$ the instantaneous position. Then we write

$$\mathbf{r}_n = R_n + q_n \qquad (62)$$

The 3 components of q_n are $q_{n,x}$, $q_{n,y}$, q_{nz}. They are the $q_{n\alpha}$ in Eq (55).

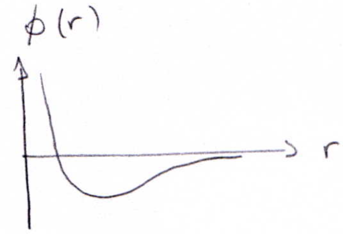
We now assume the atoms in the crystal interact by means of a pairwise interaction $\phi(\mathbf{r}_n - \mathbf{r}_m)$. The total interaction then has the form

$$V = \sum_{n \neq m} \phi(\mathbf{r}_n - \mathbf{r}_m) \qquad (63)$$

We know V has a minimum when $\mathbf{r}_n = \mathbf{R}_n$, since this is the equilibrium configuration. We therefore expand V assuming the q_n are small. To do that we use the formula

$$\phi(\mathbf{R} + q) \simeq \phi(\mathbf{R}) + \sum_i \frac{\partial \phi}{\partial R_i} q_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 \phi}{\partial R_i \partial R_j} q_i q_j + \cdots \qquad (64)$$

We do this with $\mathbf{R} = \mathbf{R}_n - \mathbf{R}_m$ and $q = q_n - q_m$.



we then get

$$\mathcal{V} \simeq \sum_{n,m} \phi(\mathbb{R}_n - \mathbb{R}_m) + \sum_{n,m} \sum_{i} \partial_i \phi(\mathbb{R}_n - \mathbb{R}_m) \quad (q_{n,i} - q_{m,i})$$

$$+ \frac{1}{2} \sum_{n,m} \sum_{ij} \partial_{ij} \phi(\mathbb{R}_n - \mathbb{R}_m) \quad (q_{n,i} - q_{m,i})(q_{n,j} - q_{m,j})$$

(65)

The first term is just a constant and may be neglected. The 2^{nd} term is zero because it represents the total force acting on the system. But since we expanded around the minimum of $\mathcal{V}$, the force must be zero.

Thus we get

$$\mathcal{V} \simeq \frac{1}{2} \sum_{n,m} \sum_{i,j} \partial_{ij} \phi(\mathbb{R}_n - \mathbb{R}_m) \quad (q_{n,i} - q_{m,i})(q_{n,j} - q_{m,j}) \quad (66)$$

Comparing with (55) we therefore conclude that

$$\boxed{\Phi_{ij}(\mathbb{R}_n - \mathbb{R}_m) = \partial_{ij} \phi(\mathbb{R}_n - \mathbb{R}_m)} \quad (67)$$

It is the second derivative of the potential evaluated at $\mathbb{R}_n - \mathbb{R}_m$.

The interatomic potential $\phi(r)$ depends only on the magnitude of the distance $r = \sqrt{x_1^2 + x_2^2 + x_3^2}$. Thus

$$\partial_i \phi = \frac{\partial \phi}{\partial x_i} = \frac{\partial r}{\partial x_i} \frac{\partial \phi}{\partial r}$$

Hence

$$\partial_i \phi = \frac{x_i}{r} \phi'(r)$$

Similarly

$$\partial_{ij} \phi = \partial_j (\partial_i \phi) = \frac{\partial}{\partial x_j} \left(\frac{x_i}{r} \phi'(r) \right)$$

$$= \delta_{ij} \frac{\phi'(r)}{r} + x_i \left(\frac{\partial}{\partial x_j} \frac{1}{r} \right) \phi' + \frac{x_i}{r} \frac{\partial}{\partial x_j} (\phi')$$

$$= \delta_{ij} \frac{\phi'}{r} - \frac{x_i x_j}{r^3} \phi' + \frac{x_i}{r} \frac{x_j}{r} \phi''$$

Thus

$$\boxed{\partial_{ij} \phi = \frac{x_i x_j}{r^2} \phi''(r) + \frac{\phi'}{r} \left(\delta_{ij} - \frac{x_i x_j}{r^2} \right)} \qquad (68)$$

This formula is useful when figuring out the Φ_{ij}

In summary, the recipe to construct the phonon spectra is

1) For each connection between sites n, m, construct

$$\Phi_{ij}(\mathbb{R}_n - \mathbb{R}_m) = \partial_{ij}\phi(\mathbb{R}_n - \mathbb{R}_m)$$

where

$$\partial_{ij}\phi(r) = \frac{x_i x_j}{r}\phi''(r) + \frac{\phi'(r)}{r}\left(\delta_{ij} - \frac{x_i x_j}{r}\right)$$

2) construct the matrix (69)

$$W_{ij}(\mathbb{k}) = 2\sum_m{}' \Phi_{ij}(\mathbb{R}_n)\left[1 - \cos \mathbb{k}\cdot\mathbb{R}_n\right]$$

3) the phonon bands will be the eigenvalues of W_{ij}

In step (1) you must choose if you keep nearest neighbors, next-nearest neighbors and so on.

Example : cubic lattice

Consider a cubic lattice and assume only nearest-neighbor interactions.

Let us look at the interaction of atom $\mathbb{R}_n$ with $\mathbb{R}_n + \mathbb{Q}_1$. We thus need to compute $\Phi_{ij}(\mathbb{Q}_1)$. We use (67) and (68). But must evaluate our function at $\mathbb{r} = \mathbb{Q}_1 = a(1,0,0)$. Thus, for instance

$$\Phi_{11}(\mathbb{Q}_1) = \phi''(a) + \frac{\phi'(a)}{a}\left(1 - \frac{a^2}{a^2}\right) = \phi''(a)$$

$$\Phi_{12}(\mathbb{Q}_1) = \Phi_{13}(\mathbb{Q}_1) = \Phi_{23}(\mathbb{Q}_1) = 0$$

$$\Phi_{22}(\mathbb{Q}_1) = \frac{\phi'(a)}{a} = \Phi_{33}(\mathbb{Q}_1)$$

Note how the connection of $\mathbb{R}_n$ with the guy on $\mathbb{R}_n + \mathbb{Q}_1$ will produce oscillations for the y and z directions as well. The potential (66) will look like

$$V = \frac{1}{2}\phi''(a)\left[q_x(\mathbb{R}_n) - q_x(\mathbb{R}_n + \mathbb{Q}_1)\right]^2 +$$
$$+ \frac{1}{2}\frac{\phi'(a)}{a}\left[q_y(\mathbb{R}_n) - q_y(\mathbb{R}_n + \mathbb{Q}_1)\right]^2$$
$$+ \frac{1}{2}\frac{\phi'(a)}{a}\left[q_z(\mathbb{R}_n) - q_z(\mathbb{R}_n + \mathbb{Q}_2)\right]^2 + \dots$$

this is only the interaction with one neighbor what we need is to construct the matrix $W_{\alpha\beta}$ in Eq (57).

So we need the interaction with all neighbors:

$$W_{\alpha\beta}(\mathbf{k}) = 2\,\Phi_{\alpha\beta}(Q_1)\left[1-\cos k_x a\right] + 2\Phi_{\alpha\beta}(-Q_1)\left[1-\cos k_x a\right]$$

$$+\,2\,\Phi_{\alpha\beta}(Q_2)\left[1-\cos k_y a\right] + \cdots$$

there will be 6 terms, one for each nearest neighbor. Based on the symmetry of the lattice we can already guess that

$$W_{11}(\mathbf{k}) = 4\,\Phi_{11}(Q_1)\left[1-\cos k_x a\right] + 4\,\Phi_{11}(Q_2)\left[1-\cos k_y a\right]$$

$$+\,4\,\Phi_{11}(Q_3)\left[1-\cos k_z a\right]$$

$$= 4\,\phi''(a)\,(1-\cos k_x a) + \frac{4\phi'}{a}\,(2-\cos k_y a-\cos k_z a)$$

The other digonal terms will be symmetrical and the off-digonals will be zero. Thus we get 3 acoustic branches.

$$\omega_1(k) = \sqrt{4\,\phi''(a)\,(1-\cos k_x a) + \frac{4\phi'}{a}\,(2-\cos k_y a-\cos k_z a)}$$

$$\omega_2(k) = \sqrt{4\,\phi''(a)\,(1-\cos k_y a) + \frac{4\phi'}{a}\,(2-\cos k_x a-\cos k_z a)}$$

$$\omega_3(k) = \sqrt{4\,\phi''(a)\,(1-\cos k_z a) + \frac{4\phi'}{a}\,(2-\cos k_x a-\cos k_y a)}$$

It is possible that $\phi'(a)$ may be almost zero (it will be identically zero if only n.n. interactions are present, but will deviate from zero if 2^{n} n.n. is taken into account, since then $|\mathbf{R}_m-\mathbf{R}_n| = a$ will only be the local minimum of V, which is not necessarily the local minimum of ϕ.

Summary of phonon formulas

As you have probably seen, computing realistic phonon curves is quite cumbersome. Lucky for us, this is something we seldom need in practice.

All we need to remember is this: if there are B atoms per unit cell, then there will be 3B phonon modes. 3 will be acoustic, with

$$\omega_\lambda(\mathbb{k}) \simeq c_\lambda(\hat{\mathbb{k}})\,|\mathbb{k}|$$

where the speed of sound may in general depend on $\hat{\mathbb{k}}$. The remaining 3B - 3 will be optical, with

$$\omega_\lambda(0) = \text{const.}$$

The Hamiltonian may be written as

$$\boxed{H = \sum_{\mathbb{k},\lambda} \omega_\lambda(\mathbb{k})\, a^\dagger_{\mathbb{k}\lambda} a_{\mathbb{k}\lambda}} \qquad (70)$$

where $\lambda = 1, \dots, 3B$ and I neglected the ½ term since it is just a constant.

Another property we might need in the future is the relation between q_M and the a operators. It may be written in a more organized way as

$$\boxed{q_M = \frac{1}{\sqrt{vol}} \sum_{k,\lambda} \frac{\vec{e}_\lambda(k)}{\sqrt{2\omega_\lambda(k)}} \left[a_{k\lambda} e^{ik\cdot r} + a^{+}_{k\lambda} e^{-ik\cdot r} \right]} \qquad (71)$$

where $e_\lambda(k)$ is the polarization vector.

The specific heat of phonons

Consider a single bosonic mode with $H = \omega a^\dagger a$. We have seen that

$$\langle a^\dagger a \rangle = \bar{n} = \frac{1}{e^{\beta\omega}-1} \tag{72}$$

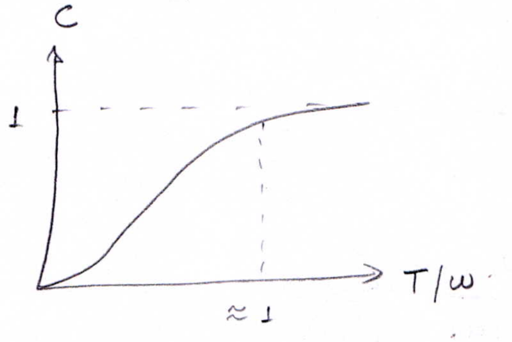
Hence, the average energy will be

$$U = \omega \bar{n} = \frac{\omega}{e^{\beta\omega}-1} \tag{73}$$

The heat capacity is then found from

$$C = \frac{\partial U}{\partial T} = \left(\frac{\omega}{T}\right)^2 \frac{e^{\beta\omega}}{(e^{\beta\omega}-1)^2} \tag{74}$$

This looks like this:



At high temperatures we recover the value $C \simeq 1$ (or $C \simeq k_B$), which is the classical result.

the Dulong and Petit law for solids gives $c = 3Nk_B$. this led Einstein to propose that the solid could be interpreted as a collection of 3N oscillators. At high temperatures we get $c = 3Nk_B$ and at low temperatures the specific heat falls down, like in the figure.

this is the Einstein model for the specific heat of solids.

the curve I drew in the previous page indeed looks like an experimental curve. But they have one fundamental difference: Eq (74) predicts that c will fall down exponentially with T, whereas experiments predict that at low T we should have $c \sim T^3$.

The idea of treating a solid like 3N oscillators is not a bad one. Indeed, we just saw that this is exactly what the phonon picture gives us. the problem of the Einstein model is that it assumes all modes have the same frequency, and that, we know is not true.

the correct formula for the energy is therefore

$$U = \sum_{k,\lambda} \frac{\omega_\lambda(k)}{e^{\beta\omega_\lambda(k)} - 1} \tag{75}$$

If we look at the figure in page 37 we note that c is only significant when $\frac{T}{\omega} \gtrsim 1$. This means that at low T the significant contributions will come from terms with small ω. Consequently, the optical modes will have only a minor contribution. This means we only need to consider $\lambda = 1, 2, 3$. Moreover, even for the acoustic modes, the main contribution will come from the tiniest of ω's, which are those close to $k = 0$. Thus we may approximate $\omega_k \simeq c\,|k|$ (I also assume for simplicity that all c are equal).

If we do all this and also convert the sum to an integral, we get

$$U = \frac{V}{(2\pi)^3} \underset{\lambda=1,2,3}{\underset{\uparrow}{3}} \int d^3k \, \frac{c\,k}{e^{\beta c k}-1}$$

$$= \frac{V}{(2\pi)^3}\, 3\,(4\pi)\, c \int dk \, \frac{k^3}{e^{\beta c k}-1}$$

Now change variables to $x = \beta c k$. We get

$$U = \frac{3V}{2\pi^2} \frac{T^4}{c^3} \int_0^\infty dx \, \frac{x^3}{e^x - 1}$$

Thus we see that, apart from a bunch of constants,

$U \propto T^4$

Consequently

$$C = \frac{\partial U}{\partial T} \propto T^3$$

Hence, assuming a dispersion relation $\omega_k = c|k|$ reproduces the T^3 behavior found experimentally result, we are left with

$$U = \frac{V}{(2\pi)^3} 4\pi \sum_{\lambda=1,2,3} \int_0^\infty \frac{\hbar c_\lambda k}{e^{\hbar c_\lambda k/t} - 1} k^2 \, \mathrm{d}k$$

Now change variables in each integral to $x = \hbar c_\lambda k / T$. This removes the temperature dependence from the integral completely

$$U \frac{V}{2\pi^2} \sum_{\lambda=1,2,3} \frac{T^4}{(\hbar c_\lambda)^3} \int_0^\infty \frac{x^3}{e^x - 1} \mathrm{d}x$$

Forget the pre-factors for now. All that matters is that $U \propto T^4$. Consequently,

$$c \propto T^3 \tag{5.109}$$

which is indeed what is observed experimentally. We therefore conclude that the quantum description of the lattice vibrations yields the correct specific heat of a solid, both at high *and* low temperatures.

The Debye model

Without knowing anything about the dispersion characteristics, we have shown that the phonon descriptions adequately describes both low and high temperatures. If you do know the entire phonon spectra of all branches, then you can use Eq. (5.105) to compute the exact specific heat over all temperature ranges. People rarely do this however. Crystal defects, impurities and other complications, make such an application restricted only to very well prepared samples. Instead, it would be nice to have an approximate formula to describe the specific heat over the entire temperature range, but which does not require a deep knowledge of the phonon branches.

This formula was proposed by Peter Debye in 1912.[5] Debye's result is an **interpolation** formula. That is, a formula which gives the correct result at both low and high temperatures and which fills the space in between with a smooth good looking function. His idea is as follows. The approximation that we just did to assume that $c_\lambda(\hat{\boldsymbol{k}})$ is roughly independent of $\hat{\boldsymbol{k}}$ is not bad, even at higher temperatures. It is also not bad to assume that all c_λ are equal to a single velocity c, since this roughly corresponds to assuming that c is an average of the c_λ. Finally, distorting the first BZ to make it look like a sphere is again not all bad. After all, every object can be approximate as a sphere!

The really important aspect of the approximation we just did was that extended the limit of the k-integration to $+\infty$. Debye's idea was to restrict this upper limit to a finite value k_D called the Debye wavelength (very creative name). And the value of k_D is determined by noting that the first BZ has exactly N (not N_{at}) phonon modes. Thus, the volume of the first BZ must be

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[5] P. Debye, *Annalen der Physik* (1912) **39** 789. This paper is in German. Your years of listening to Rammstein will finally pay off!

$N(2\pi)^3/V$ and, as Debye argued, this must also be the number of modes in a sphere of radius k_D. With this argument we fix k_D as:

$$\frac{4\pi}{3}k_D^3 = \frac{N}{V}(2\pi)^3 \longrightarrow \frac{N}{V} = \frac{k_D^3}{6\pi^2} \tag{5.110}$$

The Debye wavelength define the entire Debye family: you have the Debye wavelength

$$\omega_D = ck_D \tag{5.111}$$

and the Debye temperature

$$\boxed{\Theta_D = \hbar\omega_D = \hbar ck_D} \tag{5.112}$$

With this approximation, instead of Eq. (5.113), we write

$$U = 3\frac{V}{(2\pi)^3}(4\pi)\int\limits_0^{k_D} \frac{\hbar ck}{e^{\hbar ck/t}-1}k^2\,\mathrm{d}k \tag{5.113}$$

where the factor of 3 is because we have 3 acoustic branches. The heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{3V}{2\pi^2}\int\limits_0^{k_D}\left(\frac{\hbar ck}{T}\right)^2 \frac{e^{\hbar ck/T}}{(e^{\hbar ck/T}-1)^2}k^2\,\mathrm{d}k \tag{5.114}$$

We now change variables to $x = \hbar ck/T$. The upper limit of integration changes from k_D to $\hbar ck_D/T = \Theta_D/T$. Thus we get

$$C = \frac{3V}{2\pi^2}\left(\frac{T}{\hbar c}\right)^2\int\limits_0^{\Theta_D/T}\frac{x^4e^x}{(e^x-1)^2}\,\mathrm{d}x$$

To finish the problem with style we use Eq. (5.110) to write V in terms of k_D:

$$\frac{3V}{2\pi^2} = \frac{3}{2\pi^2}\frac{6\pi^2N}{k_D} = \frac{9N}{k_D^3}$$

But k_D^3, together with $(\hbar c)^3$ will give Θ_D^3. Thus we finally obtain

$$\boxed{c = \frac{C}{N} = 9\left(\frac{T}{\Theta_D}\right)^3\int\limits_0^{\Theta_D/T}\frac{x^4e^x}{(e^x-1)^2}\,\mathrm{d}x} \tag{5.115}$$

This is Debye's famous formula. It expresses the specific heat per particle as begin a function *only* of the ratio T/Θ_D. This formula is shown in Fig. 5.8(a) as a function of T/Θ_D (the integral must be computed numerically). Remember that to convert from our c in dimensionless units, to experimental values in J/mol K, you simply need to multiply by the gas constants [see Sec. ??]. The Debye temperature Θ_D is interpreted as a parameter which changes from one material to another. Thus, we may use Eq. (5.115) to fit Θ_D to experiment. There are different strategies to estimate Θ_D for different materials since the specific heat may also contain other contributions, which must be subtracted (more about this in a second). Typical values are shown in Table 5.1. From Fig. 5.8 we see that when $T \sim \Theta_D$ the specific heat is almost at the Dulong and Petit value. Thus, the Debye temperature may be interpreted as the temperature below which quantum effects become important.

Table 5.1: Debye temperature for selected elements. Stolen from Ashcroft and Mermin.

Element	Θ_D (K)
Li	400
Na	150
K	100
Be	1000
Mg	318
Ca	230
Al	394
Ga	240
C (diamond)	1860
Si	625
Ge	360
Cu	315
Ag	215
Au	170
Cr	460
Fe	420
Co	385
Ni	375

When $T \ll \theta_D$ we may extend the upper limit of integration in Eq. (5.115) to $+\infty$. The remaining integral is tabled and has the funny value

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2}\,\mathrm{d}x = \frac{4\pi^4}{15} \tag{5.116}$$

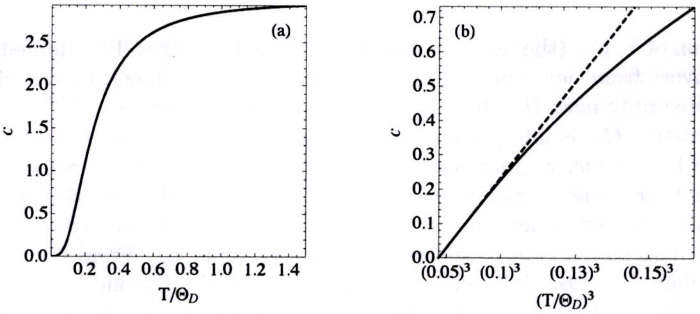

Figure 5.8: (a) The specific heat of the Debye model, Eq. (5.115). (b) Low temperature behavior plotted as a function of $(T/\Theta_D)^3$. The dashed curve is simply a straight line for comparison.

Thus, at low temperatures we obtain

$$\boxed{c \simeq \frac{12\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3} \tag{5.117}$$

This, in an insulating crystal, at low temperatures a plot of c vs. T^3 should yield a straight line with coefficient

$$A = \frac{12\pi^4}{5}\frac{1}{\Theta_D^3}$$

whose fit yields the Debye temperature. This behavior is illustrated in Fig. 5.8(b), which shows that this approximation is reasonable for $T/\Theta_D \sim 0.1$. In metals, on the other hand, there is usually a contribution to the specific heat due to the conduction electrons which has the form $c \sim \gamma T$. Thus, for metals at low temperatures,

$$c = \gamma T + AT^3 \tag{5.118}$$

Thus, for metals one usually plots c/T vs. T^2, which should be a straight line.

The Debye formula is just a rough approximation. It should *not* be taken as an absolute truth of what is happening in a crystal. The absolute truth is (i) the full phonon spectra and (ii) possible anharmonic contributions. An example is shown in Fig. 5.9 for the case of Diamond, which has an unusually high Debye temperature of $\Theta_D = 1860$ K. But this value is only a rough estimate. In fact, in diamond it is *impossible* to find a single value of Θ_D which fits the entire curve. Instead, what some people do is assume that Θ_D itself depends on the temperature. I personally think that is nonsense. If the model is no longer valid, don't force it. Forcing it makes it sound like the model is the whole truth. It is not; it is just a (*very*) rough approximation to reality.

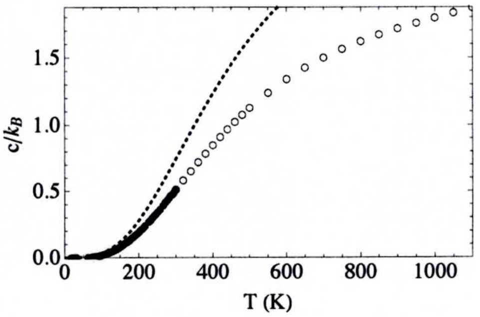

Figure 5.9: The specific heat of diamond. Solid circles were taken from W. DeSorbo, *J. Chem. Phys.* **21** (1953) 876 and open circles were taken from A. C. Victor, *J. Chem. Phys.* **36** (1962) 1903. The dotted curve is the Debye function (5.115) for $\Theta_D = 1860$ K.

5.4 Polarons

I want to discuss with you now a lovely application of the phonon theory: the propagation of electrons in ionic crystals. Ionic crystals, like NaCl, have strong localized polarizations since the Na and the Cl are oppositely charged. If you place an electron inside an ionic crystal it will therefore polarize the region around it. And if this electron moves, it will carry this polarization distortion with it. In ionic crystals there is, therefore a strong coupling between an electron and the optical phonons. The electron, plus its accompanying polarization distortion is called a **polaron**. In this section we will establish a Hamiltonian for the electron-phonon interaction and show that the phonon moves with a mass that is higher than that of the electron, due to the polarization that it has to carry in its back.

This problem was discussed by many people, but the formulation we will study here is due to Herbert Frölich. He has a paper whose name is absolutely beautiful: "*Electrons in lattice fields*".[6] I think that this name captures very well some of the ideas discussed in this chapter.

The first step is to derive the Frölich Hamiltonian. I will give here just a "sketch" of the derivation. A more rigorous calculation requires too many technical details and is filled with a bunch of annoying constants. I refer the reader to Frölich's paper for more details. If you place an electron inside a ionic crystal, the local charge density $\rho(\boldsymbol{r})$ will fluctuate substantially in the atomic level. Let $V(\boldsymbol{r})$ denote the electrostatic felt by the electron. It obeys Poisson's equation

$$\nabla^2 V = -e\rho(\boldsymbol{r}) \tag{5.119}$$

The charge density may also be written in terms of the polarization vector in

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[6] H. Frölich, *Advances in physics.* **3** (1954) 325.