

## I. PHONONS

We want to make our way towards considering electrons in solids, and therefore electrons in lattices. As a warm up, but also for their own sake, let's talk first about phonons.

Phonons are the sound waves propagating in a solid. They are mechanical motion of the lattice atoms. Unlike sound waves in gas, solids could support transverse waves as well as longitudinal. Also, their velocity is not independent of their frequency. Let's derive the equations of motion for these objects.

### A. Acoustic phonons dispersion

Solids can be terribly complicated. Let's consider phonons in a simple model for a solid. We'll consider a simple solid. Square lattice in 3d, with an isotropic mass and also isotropic spring constant. Denote by  $\vec{r}_{\vec{n}}$ ,  $\vec{p}_{\vec{n}}$  the locations and momenta of the ions in a 3d cubic lattice, with  $\vec{n}$  the indices of the atoms. The kinetic energy is then:

$$H_k = \sum_{\vec{n}} \frac{p_{\vec{n}}^2}{2m} \quad (1)$$

and for the elastic energy of the system we assume that two atoms feel a restoring force proportional to the difference of their displacements. So the kinetic energy of a bond between two atoms - one at  $\vec{n}$  and one at  $\vec{n} + \hat{\alpha}$  (with  $\alpha = x, y, z$ ) is:

$$E_{pot} = \sum_{\alpha=x,y,z} \frac{1}{2} k (\vec{r}_{\vec{n}+\hat{\alpha}} - \vec{r}_{\vec{n}})^2 \quad (2)$$

The total hamiltonian is then:

$$H = \sum_{\vec{n}} \frac{p_{\vec{n}}^2}{2m} + \sum_{\vec{n}, \alpha=x,y,z} \frac{1}{2} k (\vec{r}_{\vec{n}+\hat{\alpha}} - \vec{r}_{\vec{n}})^2 \quad (3)$$

What should we do with this? Well, Fourier transform!

Let us rewrite this hamiltonian using a discrete Fourier transform. This is very common in solids, so it is a good opportunity to get some practice. Again we assume a cube of sizes  $L_\alpha$  with periodic boundary conditions. If we are looking at the discrete set of  $L/a$  atoms in each direction, then we need to sum over momenta  $-\frac{\pi}{a} < q < \frac{\pi}{a}$ . How do we see this? We need to preserve the number of degrees of freedom. We recall that

$$dq = \frac{2\pi}{L} \quad (4)$$

Therefore we see that the number of Fourier components for a 3d sample is:

$$N = \left( \frac{2\pi}{a} / dq \right)^3 = \left( \frac{L}{a} \right)^3 \quad (5)$$

which is indeed the number of particles we need to account for. So then we can write:

$$\vec{r}_{\vec{n}} = a^3 \int_{q_{x,y,z}=-\pi/a}^{\pi/a} \frac{d^3 q}{(2\pi)^3} e^{i\vec{q} \cdot \vec{n} a} \vec{r}_{\vec{q}} \quad (6)$$

with  $\vec{n}a$  is the location of the atoms in real space. and this comes along with the definition of  $\vec{r}_{\vec{q}}$ :

$$\vec{r}_{\vec{q}} = \sum_{\vec{n}} e^{-i\vec{q} \cdot \vec{n} a} \vec{r}_{\vec{n}} \quad (7)$$

With the same equations applying to the momentum as well.

And we can easily confirm using the methods above that

$$\int_{q_{x,y,z}=-\pi/a}^{\pi/a} \frac{d^3 q}{(2\pi)^3} e^{i\vec{q} \cdot \vec{n} a} = \frac{1}{a^3} \delta_{\vec{n},0} \quad (8)$$

and

$$\sum_{\vec{n}} e^{-i\vec{q}\cdot\vec{n}a} = \left(\frac{2\pi}{a}\right)^3 \delta_{(\vec{q})}^{(3)} \quad (9)$$

The next thing is the commutation relation. Moving from the real space and the location of individual atoms, to momentum space:

$$[p_{\alpha,\vec{q}}, r_{\beta,\vec{q}}^*] = -i\hbar \left(\frac{2\pi}{a}\right)^3 \delta_{(\vec{q}-\vec{q}')} \delta_{\alpha,\beta} \quad (10)$$

Now let's express the energies in terms of the Fourier components. First, the kinetic energy:

$$H_{kin} = \sum_{\vec{n}} \frac{p_{\vec{n}}^2}{2m} = \int_{q_{x,y,z}=-\pi/a}^{\pi/a} \frac{d^3q}{(2\pi)^3} \frac{1}{2m} \vec{p}_{\vec{q}} \vec{p}_{\vec{q}}^* \quad (11)$$

Likewise, we can substitute in the potential energy, but notice that the differences give another factor of  $|(e^{i\vec{q}\cdot\hat{\alpha}a} - 1)|^2 = 4 \sin^2\left(\frac{\vec{q}\cdot\hat{\alpha}a}{2}\right)$ . We finally obtain:

$$E_{pot} = \sum_{\alpha=x,y,z} \frac{1}{2} k (\vec{r}_{\vec{n}+\hat{\alpha}} - \vec{r}_{\vec{n}})^2 = \sum_{\alpha=x,y,z} \int_{q_{x,y,z}=-\pi/a}^{\pi/a} \frac{d^3q}{(2\pi)^3} \frac{k}{2} \vec{r}_{\vec{q}} \vec{r}_{\vec{q}}^* 4 \sin^2\left(\frac{\vec{q}\cdot\hat{\alpha}a}{2}\right) \quad (12)$$

And combining the two, we get a decent looking hamiltonian:

$$H = \int_{q_{x,y,z}=-\pi/a}^{\pi/a} \frac{d^3q}{(2\pi)^3} \left[ \frac{1}{2m} \vec{p}_{\vec{q}} \vec{p}_{\vec{q}}^* + \frac{k}{2} \vec{r}_{\vec{q}} \vec{r}_{\vec{q}}^* \left( \sum_{\alpha=x,y,z} 4 \sin^2\left(\frac{\vec{q}\cdot\hat{\alpha}a}{2}\right) \right) \right] \quad (13)$$

So the Fourier transform was effective in breaking the problem down to separate hamiltonians for each Furier component.

Next, we need to define the equations of motion of the momentum and location. To do that, we can use the Heisenberg equations of motion:

$$\frac{d\vec{p}_{\vec{q}}}{dt} = -\frac{i}{\hbar} [\vec{p}_{\vec{q}}, H] = k\vec{r}_{\vec{q}} \left( \sum_{\alpha=x,y,z} 4 \sin^2\left(\frac{\vec{q}\cdot\hat{\alpha}a}{2}\right) \right) \quad (14)$$

[CHECK  $a^3$  everywhere] And similarly:

$$\frac{d\vec{r}_{\vec{q}}}{dt} = -\frac{i}{\hbar} [\vec{r}_{\vec{q}}, H] = \frac{1}{m} \vec{p}_{\vec{q}} \quad (15)$$

Nothing more than the equation of motion for three hammonic oscillators - one for each dimension - with frquency:

$$\omega_{\vec{q}}^2 = \frac{k}{m} \left( \sum_{\alpha=x,y,z} 4 \sin^2\left(\frac{\vec{q}\cdot\hat{\alpha}a}{2}\right) \right) \quad (16)$$

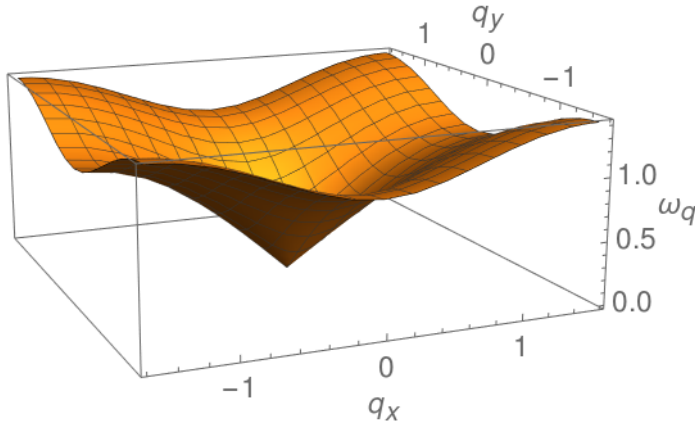
At small momenta we get:

$$\omega_{\vec{q}}^2 = \frac{k}{m} \vec{q}^2 a^2 \quad (17)$$

and a speed of sound:

$$c = \frac{k}{m} a \quad (18)$$

resonant frequency in each lattice site.



The 2d phonon dispersion

### B. Debye frequency

Usually what follows is a calculation of the phonon heat capacity in the Debye approximation. Debye assumed that phonons roughly obey Eq. (17), and that instead of the momenta all set in the range  $-\pi/a < q_{x,y,z} < \pi/a$ , the phonon momenta will be  $|\vec{q}| < q_D$  with the proper volume in momentum space to take into account all degrees of freedom:

$$\frac{1}{(2\pi)^3} \frac{4}{3} \pi q_D^3 = \frac{1}{a^3} \rightarrow q_D = \left(\frac{3}{4\pi}\right)^{1/3} \frac{2\pi}{a} \quad (19)$$

The the energy stored in the phonons is:

$$U \approx 3V \int_0^{q_D} \frac{4\pi q^2 dq}{(2\pi)^3} \frac{\hbar c q}{e^{\hbar c q \beta} - 1} \quad (20)$$

The first thing to do is to look at the classical limit. This gives the Dulong-Petit law. Do you remember it? At high temperature we have equipartition, so each degree of freedom gets the energy  $k_B T$  (half kinetic and half potential), and then the total energy becomes:

$$U \approx 3 \int_0^{q_D} \frac{4\pi q^2 dq}{(2\pi)^3} \frac{\hbar c q}{e^{\hbar c q \beta} - 1} \approx 3V \int \frac{4\pi q^2 dq}{(2\pi)^3} k_B T = 3k_B \frac{V}{a^3} T \quad (21)$$

and

$$C_{D-P} = 3k_B N \quad (22)$$

For this we used  $k_B T \gg \hbar \omega_q$ .

What happens in the opposite limit? Let's change variables to extract the temperature dependence in Eq. (20). Set  $x = \hbar c q \beta$ . Then we have:

$$U \approx 3V \frac{T^3}{\hbar c} \int_0^{x_D} \frac{4\pi x^2 dx}{(2\pi)^3} \frac{T x}{e^x - 1} = 3V \frac{T^4}{2\pi^2 \hbar^3 c^3} \int_0^{\text{inf}} x^3 dx \frac{1}{e^x - 1} = V \frac{\pi^2}{10 \hbar^3 c^3} T^4 \quad (23)$$

And from this we get the heat capacity:

$$C_{\text{phonons}} = N \frac{12\pi^4}{5} \left(\frac{T}{T_D}\right)^3 \quad (24)$$

With  $k_B T_D = \hbar c q_D$ . The Debye temperature sets the scale for crossover between the Debye law and

According to our derivation, the acoustic phonon branch saturates at a maximum frequency of  $\omega_{max} = \sqrt{\frac{3k}{m}}$ . A bit higher than the Debye wave number, which is roughly  $q_D \approx \sqrt{\frac{k}{4^{2/3}m}}$ .

What is this Debye energy scale though? We can estimate it. For the mass, let's take the mass of a decent metal with, say, 30 nucleons. At  $1.6 \cdot 10^{-27} kg$  this gets us to  $5 \cdot 10^{-26} kg$ . The spring constant is a bit trickier to estimate. Given atomic scales, however, we can get a good idea. It should be somewhere between  $1eV$  and  $10eV$  of energy for displacing by  $1\text{\AA}$ . Let's go with  $1eV$  since  $10eV$  just sounds preposterous. Then:

$$k \sim 10^{-19} J/10^{-20} m^2 = 10 N/m \quad (25)$$

Putting this together:

$$\omega_D \sim \sqrt{\frac{10 N/m}{5 \cdot 10^{-26} kg}} \approx 1.4 \cdot 10^{13} Hz \quad (26)$$

and translated to energy and temperature:

$$\hbar\omega_D = 1.4 \cdot 10^{-21} J = k_B 100 K \quad (27)$$

And the  $5eV$  energy scale would have given us  $\sim 200 K$ , which is a bit of a better ball park.

BTW - let's not forget the speed:

$$c = a\sqrt{k/m} \sim 10^3 m/s \quad (28)$$

which is what we would expect.

### C. Optical phonons

Materials are much more complex than a single atomic cubic lattice. What if the unit cell has a structure? What if there are two atoms per unit cell? Then we get an additional branch of phonons to describe the second atom species - we have more degrees of freedom after all. But now, we also need to take into account vibrations within the unit cell.

Again, oversimplifying, but without losing sight of the physics, Let's assume that there are two atoms close together near each lattice site. Also, let's assume that the elastic energy from before describes well the average motion of the two atoms. On top of that, we need to describe the energy in the relative coordinate,  $\vec{\delta}_{\vec{n}}$ . A crude but effective model is simply:

$$E_{rel} = \frac{1}{4} m \dot{\vec{\delta}}_{\vec{n}}^2, E_{pot} = \frac{1}{2} k_{rel} \vec{\delta}_{\vec{n}}^2 \quad (29)$$

per unit cell.

This is all contained within each unit cell! No need to even Fourier transform. These energies just describe  $3N$  oscillators with frequency:

$$\omega_{opt} = \sqrt{k_{rel}/2m} \quad (30)$$

In momentum space this would describe a non-dispersing mode at  $\omega_{opt}$ . For complex materials we can have several bands of optical phonons ranging from  $50meV$  to  $1eV$  even. They are very effective scatterers for electrons at high energy, since they don't conserve momentum. They can just take energy and scatter the electrons without phase space constraints. Also, they appear in spatial absorption lines in the material, and hence the name.