

Lattice vibrations: Introduction to phonons

We all know that one can transfer energy to solids on a macroscopic scale and can describe a variety of ways (e.g. heating a cast iron pan, dropping a ball, etc.). Microscopically this energy (heat) is taken up by the lattice in a form of lattice vibrations (and also results in thermal expansion, see L-J potential).

Now, we shall try to connect macroscopically observed picture to the microscopic properties.

Macroscopic parameter of interest in our consideration will be *specific heat* at constant volume which is by definition is a rate of change of the internal energy with the temperature:

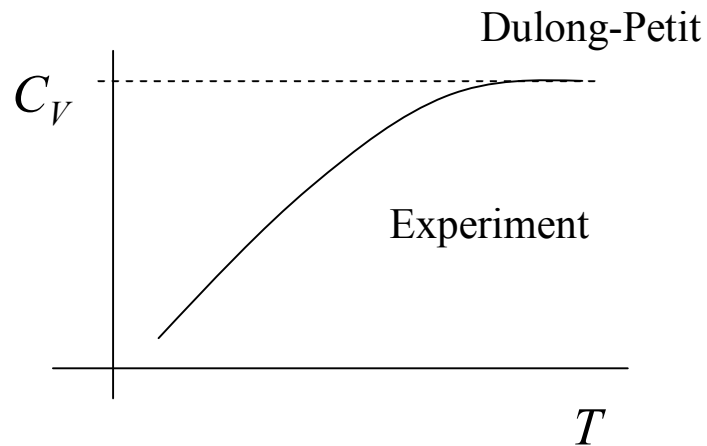
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

First, we shall consider energy per mole within simple classical approach of equipartition of energy where we take kinetic energy per atom to be $\frac{3}{2}k_B T$ (follows from kinetic theory of gasses, see previous lectures). For solids we also must include potential energy which results in total energy per mole = $3k_B T N_A$ (since $KE=PE$ for a system of oscillators, see homework problem from week 5)

This gives for specific heat per mole the Law of Dulong and Petit (early 19th century):

$$C_V = \frac{\partial}{\partial T} (3k_B T N_A) = 3k_B N_A$$

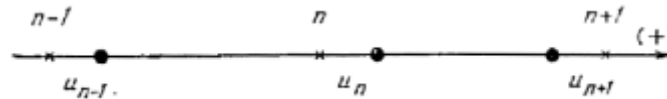
We remember that we like to use graphs together with math and so here is one:



What is wrong with Dulong-Petit? Ans: Assumption of applicability of the *Maxwell-Boltzmann statistics* and of *equipartition of energy* even at low temperatures.

Microscopic picture

Now let's look at the atomic vibrations on microscopic scale. We have already done that before for a single atom vibrating around equilibrium position using *harmonic approximation* (remember parabola in place of LJ potential?). Now let's look into at a more complicated picture: 1D linear chain



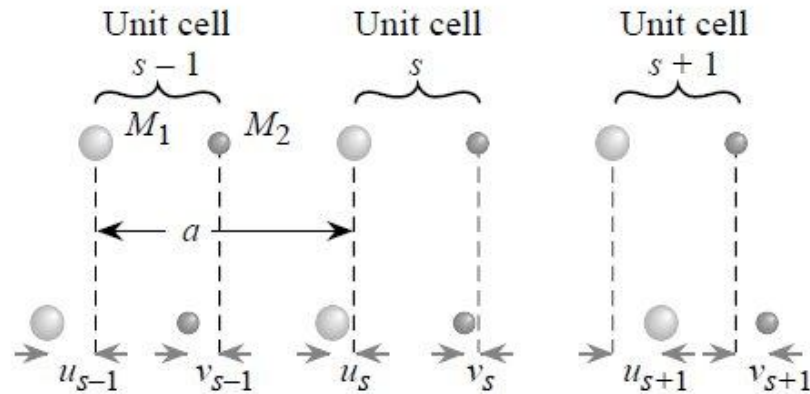
$$m\ddot{u}_n = -C(u_n - u_{n-1}) + C(u_{n+1} - u_n)$$

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

N coupled differential equations in total. What about 2D and 3D? 3D and effectively have N coupled 3D oscillators. We can replace this by a system of equivalent $3N$ one-dimensional oscillators, but they will still be coupled.

Microscopic picture

Now lets throw in the fact that atoms can be different. Then in 1D.



$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s)$$

We can see that picture becomes increasingly complicated.

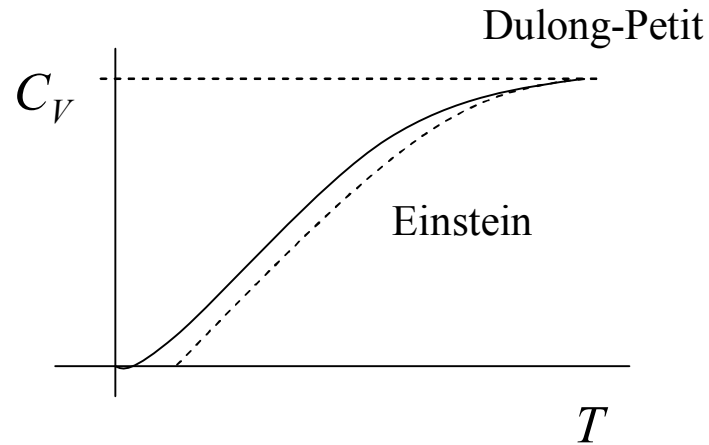
First approach to the problem of the temperature-dependence of specific heat was due to Einstein and came in 1906 as he considered in details microscopic picture of atomic vibrations.

We remember from the lecture on bulk modulus and elastic properties that frequency of atomic vibrations can be linked to interatomic potential. The picture was very simple for pair of atoms in one dimension. However, in a bulk material situation is complicated as we've shown above.

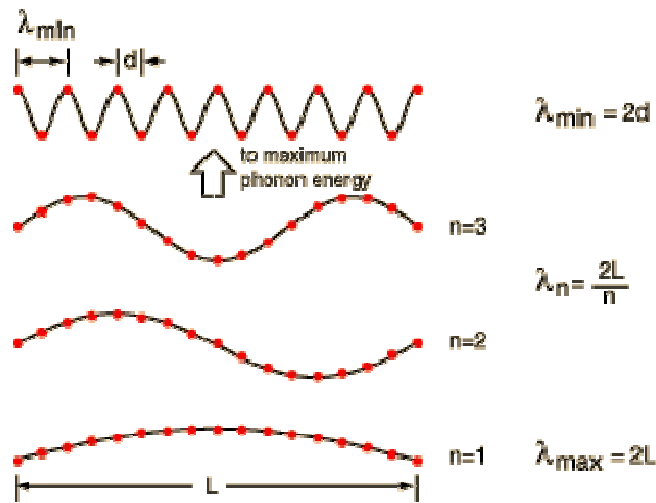
Mathematically that means that we have a system of coupled linear equations.

What we would like to do is to obtain a system of $3N$ independent linear equations which we can solve and find all the frequencies which will characterise the system. In order to do that we have to sacrifice the picture of vibrating atoms and introduce one of collective motion of atoms in a crystal – vibrational modes or sound waves or *phonons*. This latter can be treated in much the same way as photons and have associated wavelength, frequency, velocity and momentum. Moreover, symmetry of a given crystal will affect dependence of frequency on momentum ($\omega(k)$, e. g. optical modes as well as acoustic).

In the Einstein's model all the vibrations are considered to be of the same frequency ω_E . Remarkably (or not), even this model provides significant improvement over Dulong-Petit approach.



Still, there was a room for improvement particularly at very low T and in 1912 Debye came up with another model from an opposite point of view. He treated a solid as continuum and ignored its atomic structure (but not completely). Continuum, would of course possess vibrational modes with frequencies from 0 to infinity.



If, by analogy with photons we assign kinetic energy to these particles (phonons) as:

$$E = h\nu = h \frac{c_s}{\lambda} \approx k_B T, \text{ then at } T = 1\text{K}, \lambda = \frac{hc_s}{k_B T} = \frac{6.6 \cdot 10^{-34} \times 2 \cdot 10^3}{1.4 \cdot 10^{-23} \times 1} \approx 10^{-7} \text{ m} = 0.1 \mu\text{m} = 10^3 \text{ \AA}$$

However, in case of real structure there will be a limit for the highest possible frequency (or shortest possible wavelength) – interatomic distance. Hence there will be a cut-off frequency of (you guessed it!) ν_D ($\nu_D > \nu_E$).

Debye model works very well for metals and is very useful in description of x-ray, neutron diffraction patterns

Note: At low T one has also take into account electronic contribution to the specific heat of a solid.

Summary

- Specific heat of the lattice $C_V = \left(\frac{\partial U}{\partial T} \right)_V$
- Vibrations of monoatomic and diatomic lattices
- Einstein and Debye models of lattice vibrations
- Phonon – a collective lattice excitation