Lattice vibrations: Introduction to phonons
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The energy transfer to solids on a macroscopic scale and can be described in 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 the macroscopically observed picture to the microscopic properties. The macroscopic parameter of interest in our consideration will be specific heat at a 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 a simple classical approach of equipartition of energy where we take the kinetic energy per atom to be:

\[ \frac{3}{2} k_B T \]

(this follows from the kinetic theory of gasses, see previous lectures). For solids we also must include potential energy which results in the total energy per mole = \(3k_BTN_A\) (since KE=PE for a system of oscillators, see homework problem).

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

\[ C_V = \frac{\partial}{\partial T} \left(3k_BTN_A\right) = 3k_BN_A \]

Which results in a functional dependence of \(C_V(T)\):

What is wrong with Dulong-Petit? Ans: Assumption of applicability of the \textit{equipartition of energy} even at low temperatures.
Atomic Vibrations: microscopic scale
Assumptions:

1. Adiabatic approximation - assume electrons are attached rigidly to the nucleus.
2. Assume the amplitude of the vibrations is small.
3. Harmonic approximations - terms of order higher than $\Delta x^2$ in the interatomic potential are neglected.

1. Harmonic approximation
Now let's look at the atomic vibrations on microscopic scale. The restoring force in case of an atom being displaced from an equilibrium position will be due to interatomic interactions. These in turn can be described by a potential ($V(x)$ in 1D). In earlier lectures we mentioned that it's convenient to introduce what is called a harmonic approximation if atomic displacements from the equilibrium position are small ($\Delta x = x - a_0 \ll a_0$). Mathematically this means that we can expand the potential in Taylor series as:

$$V(x) = V(a_0) + \left[ \frac{dV(x)}{dx} \right]_{a_0} \Delta x + \frac{1}{2} \left[ \frac{d^2V(x)}{dx^2} \right]_{a_0} \Delta x^2 + \frac{1}{3!} \left[ \frac{d^3V(x)}{dx^3} \right]_{a_0} \Delta x^3 + ...$$

$$V(x) \approx V(a_0) + \frac{1}{2} \left[ \frac{d^2V(x)}{dx^2} \right]_{a_0} \Delta x^2$$

Now, introducing the restoring force acting on an atom:

$$F(x) = -\frac{dV(x)}{dx} = -\left[ \frac{d^2V(x)}{dx^2} \right]_{a_0} \Delta x = -k \Delta x$$

Hence we see that the problem of finding the total energy of the lattice is reduced to finding the total energy of harmonic oscillators. Let's find the total energy of a harmonic oscillator.

$F = ma, F = -kx \Rightarrow m \frac{d^2x}{dt^2} + kx = 0$, define $\omega^2 = \frac{k}{m}$ and so we can either be clever and seek solution $x(t) = A\sin(\omega t + \phi)$ where $A$ and $\phi$ will depend on the initial conditions. We then substitute this into equation and check that solution is correct. Or we do it properly by:

$$\frac{d^2x}{dt^2} = \frac{dx}{dt} \frac{dx}{dt} = \frac{d^2x}{dx} \frac{dx}{dt} = \frac{dx}{dx} \frac{dx}{dt} = \frac{dx}{dx} \Rightarrow \frac{dx}{dt} \right\{ x + \omega^2 x = 0 \Rightarrow \frac{dx}{dx} \ast \frac{dx}{dt} + \omega^2 x \frac{dx}{dx} = 0 \text{ and after integrating} \frac{x^2}{x^2} + \omega^2 x^2 = C, \text{ where } C = (A \omega)^2$$
\[ x^2 = A^2 \omega^2 - \omega^2 x^2 \]
\[ \dot{x} = \pm \omega \sqrt{A^2 - x^2} \]
\[ \frac{dx}{\pm \sqrt{A^2 - x^2}} = \omega dt \]
\[ \begin{align*}
\text{arcsin} \frac{x}{A} &= \omega t + \phi \\
\text{arccos} \frac{x}{A} &= \omega t + \phi
\end{align*} \]

With solution \( x(t) = A \sin(\omega t + \phi) \) or \( x(t) = A \cos(\omega t + \phi) \)

kinetic energy \( K = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 = \frac{1}{2} kA^2 \sin^2 (\omega t + \phi) \)

potential energy \( P = -\int F(x)dx = \int kxdx = \frac{1}{2} kx^2 = \frac{1}{2} kA^2 \cos^2 (\omega t + \phi) \)

Total energy \( E = K + P = \frac{1}{2} kA^2 \)

2. More than one atom, linear chain
Let's consider the following simple system:

Under the conditions \( k_2 = k_3 = k_{13} = k \) Newton tells us that:
\[ m\ddot{x}_1 = -2kx_1 + kx_2 \]
\[ m\ddot{x}_2 = kx_1 - 2kx_2 \]

We now have two coupled differential equations to solve in order to find the necessary parameters. The way to solve this is to uncouple the equations. In this case it's relatively easy:
\[ m(\ddot{x}_1 + \ddot{x}_2) = -k(x_1 + x_2) \]
\[ m(\ddot{x}_1 - \ddot{x}_2) = -3k(x_1 - x_2) \]
Similarly to the example for a single oscillator we will get:

\[ x_1 + x_2 = A_1 \cos(\omega t + \varphi_1) \]
\[ x_1 - x_2 = A_2 \cos(\sqrt{3}\omega t + \varphi_2) \]

or

\[ x_1 = \frac{1}{2} \left[ A_1 \cos(\omega t + \varphi_1) + A_2 \cos(\sqrt{3}\omega t + \varphi_2) \right] \]

This shows that \( x_1 \) is a superposition of motions with two different frequencies. We can see that for two coupled oscillators already an expression for \( x(t) \) becomes rather complicated and so an expression for the total energy.

Let's now consider a monoatomic linear chain with \( N \) atoms:

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

What we now have for a system of \( N \) atoms is \( N \) coupled differential equations in total. What about 2D and 3D? We can replace this by a system of equivalent \( 3N \) one-dimensional oscillators, but they will still be coupled.

Now let's throw in the fact that atoms can be different. Then in 1D:

\[ M_1 \frac{d^2u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s) \]
\[ M_2 \frac{d^2v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s) \]

We can see that the picture becomes increasingly complicated.

The first approach to the problem of the temperature-dependence of specific heat was due to \( \text{Einstein} \) and came in 1906 as he considered in details microscopic picture of atomic vibrations. We remember from the lecture on the bulk modulus and elastic properties that the frequency of atomic vibrations can be linked to interatomic potential. The picture was very simple for a 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 $\omega_E$. 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:

$$E = h\nu = h\frac{c}{\lambda} \approx k_BT,$$

then at $T = 1\text{K}$, 

$$\frac{hc_s}{k_BT} = \frac{6.6 \times 10^{-34} \times 2 \times 10^3}{1.4 \times 10^{-23} \times 1} \approx 10^{-7} \text{m} = 0.1\mu\text{m} = 10^3\text{angst}$$

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!) $\nu_D$ (\(\nu_D > \nu_E\)).

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