Lecture 09

Tuesday, February 02, 2010

What we did: Einstein phonons and Debye phonons
What we will cover here: Debye phonons, Anharmonic effects, Phonon transport

Qualitative understanding of the Debye T^3 law

What is the essential reason for this amazing law? The following table summarizes the qualitative physics at low T *and* at high T. The key idea here? Qualitatively speaking, phonons with $\hbar\omega < k_B T$ are excited, and have the typical energy $k_B T$ while phonons with $\hbar\omega > k_B T$ are not excited. In the following table, N_m is the total number of normal modes, i.e. the number of atoms times the spatial dimension.

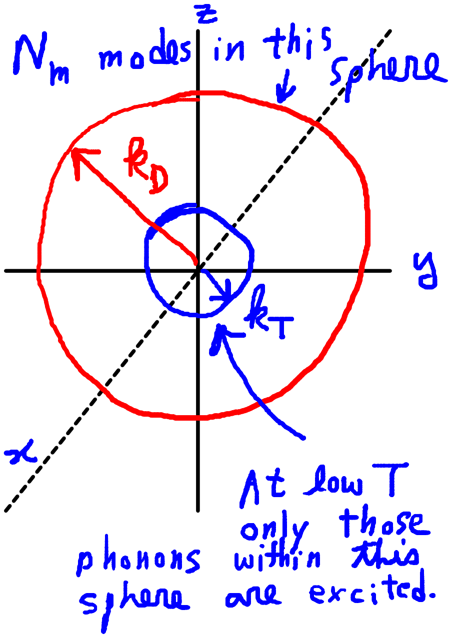
↱ ☆☆ IMPORTANT! ☆☆

Qualitative table (up to a numerical factor)

	$T \ll \theta_D$	$T \gg \theta_D$
(1) Typical phonon mode energy	$k_B T$	$k_B \theta_D$
(2) Number of phonon modes excited	$N_m \left(\frac{T}{\theta_D}\right)^3$	N_m
(3) Typical energy per phonon mode	$k_B T$	$k_B T$
Total Energy E = (2) x (3)	$N_m \left(\frac{T}{\theta_D}\right)^3 k_B T$	$N_m k_B T$
Heat Capacity $C_V = \partial E / \partial T$	$N_m \left(\frac{T}{\theta_D}\right)^3 k_B$	$N_m k_B$
The total number of phonons excited = $E/(1)$	$N_m \left(\frac{T}{\theta_D}\right)^3$	$N_m \left(\frac{T}{\theta_D}\right)$

The key observation is that at high temperature all phonon modes become excited, while at low temperature the number of phonons modes excited becomes $N_m \left(\frac{k_T}{k_D}\right)^3 \sim N_m \left(\frac{T}{\theta_D}\right)^3$ since $vk_D = k_B\theta_D$ and vk_T is defined as $k_B T$ (k_T is the "thermal" wave length). At low T, only those phonon modes with wave vector up to $\sim k_T$ are excited.

Qualitatively Speaking



N_m modes in this sphere

At low T only those phonons within this sphere are excited.

Anharmonic effects

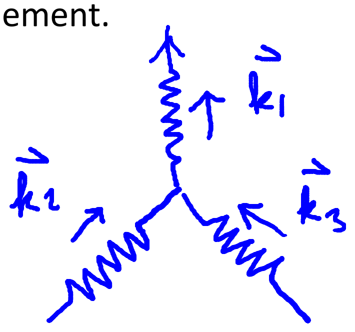
Normal modes, each of which is a simple harmonic oscillator, oscillating as an independent mode is quite nice. Only if that was true... Common sense tells us that the inter-atomic/inter-ionic potential energy does not end at the quadratic term, but will have a cubic term and a quartic term, etc. These terms become increasingly important as temperature goes up. Effects coming from these additional terms are called **anharmonic effects**, as the potential energy is now no longer reducible to a simple harmonic potential.

The following list enumerates some phenomena due to the anharmonicity.

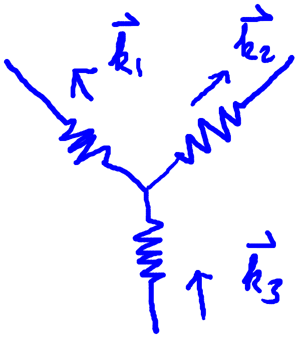
- **Thermal expansion** of materials arise due to the anharmonicity. If the harmonic potential applicable at T=0 were valid at all temperatures, then there would be no thermal expansion!
- **Finite thermal conductivity** arises due to the anharmonicity, among other things (defects, impurities, size effect). This is related to the next item.
- **Phonons** as we defined in previous lectures are not eigenstates any more. Instead, they **acquire a finite lifetime**, whose inverse is proportional to the width of phonon absorption peak or emission peak in inelastic neutron/X-ray/electron spectroscopy.
- The high T limit of heat capacity never quite shows the Du Long Petit law. Instead of approaching a constant, the heat capacity tends to have a finite slope, albeit a small slope. See the figure in the last lecture (fit to the Debye model).
- $\kappa_T \neq \kappa_S$ (iso-thermal compressibility and adiabatic compressibility) and

$C_P \neq C_V$ (constant pressure heat capacity and constant volume heat capacity). This fact is related to thermal expansion (see Appendix A).

It is important to be able to visualize the anharmonic interactions in a diagrammatic way. Consider a cubic term like x^3. Recall that x is a sum of terms of the form $Aa_k^\dagger + Ba_k$. So, a cubic term will involve terms like $a_{k_1}^\dagger a_{k_2} a_{k_3}$, $a_{k_1}^\dagger a_{k_2}^\dagger a_{k_3}$. In the first order, only these terms have any non-zero matrix element.



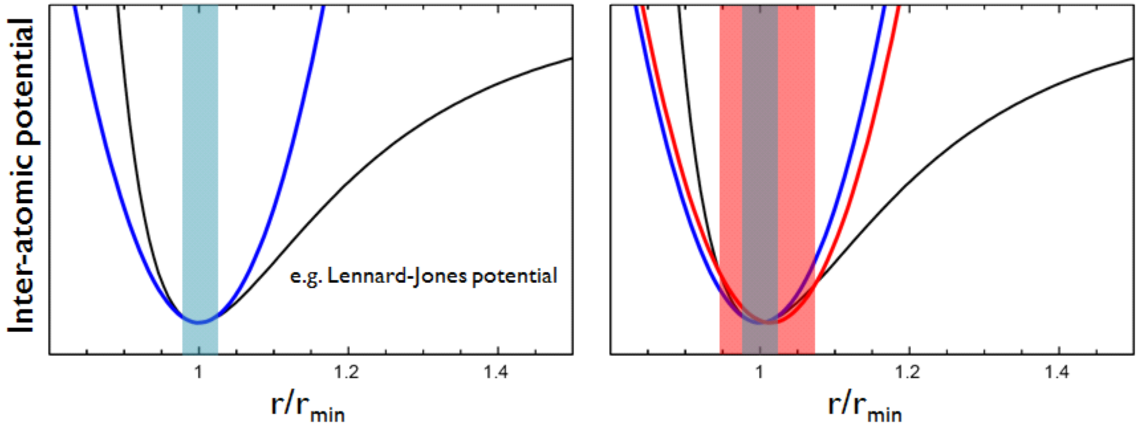
$a^\dagger_{k_1} a_{k_2} a_{k_3}$



$a^\dagger_{k_1} a^\dagger_{k_2} a_{k_3}$

In these scattering processes, **the crystal momentum conservation** and **the energy conservation** hold as for any scattering process in a crystal. These and other higher order scattering processes will impart a finite lifetime to phonon states.

Thermal expansion



The above figure shows the Lennard-Jones potential, $U(r) \propto \left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^{6}$ where σ is the bond length scale. Such a potential is an excellent model for the interaction between two atoms in a molecular crystal. At low temperature, bond length fluctuations are small (blue shade). At high temperature, bond length fluctuations are large (red shade). Given the range of atomic displacements, one can set up an approximate simple harmonic potential as the first approximation.

This **harmonic approximation** will result in a slightly different location of the potential well minimum! This is the source of the thermal expansion. Note also that as the bond length fluctuation becomes greater the harmonic approximation becomes poorer and poorer, which is one reason why phonons will become more and more short-lived at high temperatures.

Grüneisen constant

Often, the dispersion relation has a certain volume dependence, which makes discussion of thermodynamic quantities simple.

Grüneisen ansatz: $\boxed{\omega_k \propto V^{-\gamma}}$ where γ is the Grüneisen constant.

The volume dependence of ω_k comes from $\sqrt{C}$ where C is the spring constant (k is volume dependent also, but it is cancelled by the volume dependence of lattice constant a; i.e. ka is dimensionless and does not depend on volume).

Let us consider the interatomic potential $U(r) = U(a) + \frac{U''(a)}{2}(r-a)^2 + \frac{U'''(a)}{6}(r-a)^3 + \cdots$ where a is the r value corresponding to the minimum of $U(r)$. At a finite temperature, the mean bond length $= a'$, which would be similar to a but not quite the same. The spring constant $C = U''(a') = U''(a) + U'''(a)(a'-a) + \cdots$. We assume that the system volume $V \propto a'^3$ i.e. the volume changes uniformly in all directions.

$$\gamma = -\frac{d\ln\omega_k}{d\ln V} = -\frac{\frac{1}{2}d\ln C}{3\,d\ln a'} = -\frac{1}{6}\frac{a'}{C}\frac{dC}{da'} \approx -\frac{a'}{6}\frac{U'''(a)}{U''(a)} \approx -\frac{a}{6}\frac{U'''(a)}{U''(a)}$$

The Grüneisen constant is non-zero because of the anharmonicity of the interatomic potential.

The above Grüneisen ansatz is often valid for non-phonon problems, as well. E.g., for free electrons or photons. For phonons, $\gamma = 1\sim3$ typically.

Thermal expansion coefficient α

The volume coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \overset{\text{Euler relation}}{=} -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)\left(\frac{\partial P}{\partial T}\right) = \frac{1}{B}\left(\frac{\partial P}{\partial T}\right)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \overset{\checkmark}{=} -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{B}\left(\frac{\partial P}{\partial T}\right)_V$$

B: bulk modulus

If the above Grüneisen ansatz is valid, then $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma}{V} C_V$.

Sum of all inter-atomic potentials

$$F = \overset{\uparrow}{E_{pot}} - k_B T \sum_{modes} \ln Z \qquad Z = \sum_{n=0}^{\infty} \exp\left[\left(-\beta\left(n+\frac{1}{2}\right)\hbar\omega\right)\right] = \frac{\exp(-\frac{1}{2}\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)}$$

$$F = E_{pot} + \sum_{modes} \left\{\frac{1}{2}\hbar\omega + k_B T \ln[1-\exp(-\beta\hbar\omega)]\right\}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial E_{pot}}{\partial V}\right)_T - \sum_{modes} \hbar\left(\frac{\partial \omega}{\partial V}\right)_T \left\{\frac{1}{2} + \frac{\exp(-\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)}\right\} = -\frac{\partial E_{pot}}{\partial V} - \sum_{modes} \hbar \frac{\partial \omega}{\partial V}\left\{\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega)-1}\right\} = -\frac{\partial E_{pot}}{\partial V} - \sum_{modes} \hbar \frac{\partial \omega}{\partial V}\left\{\frac{1}{2} + n(\beta\omega)\right\}$$

$$P = -\frac{\partial E_{pot}}{\partial V} - \sum_{modes} \frac{\hbar(-\gamma)\omega}{V}\left\{\frac{1}{2} + n(\beta\omega)\right\} = -\frac{\partial E_{pot}}{\partial V} + \frac{\gamma}{V} E_{modes} \longrightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{\gamma}{V} C_V$$

Then,

$$\boxed{\alpha = \frac{\gamma}{V}\frac{C_V}{B}}$$ the thermal expansion due to the anharmonicity ($\gamma \propto U'''(a)$).

Phonon Scattering

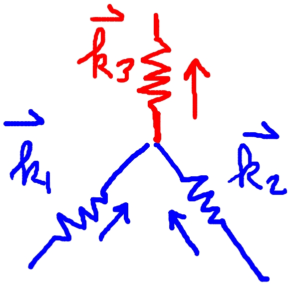
As mentioned above, the anharmonic potential scatter phonons, making them unstable. This leads to the finite thermal conductivity.
Another source of the phonon scattering is due to impurities, defects, and the finite size of the crystal.

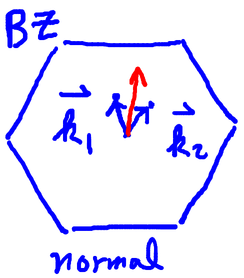
Umklapp scattering

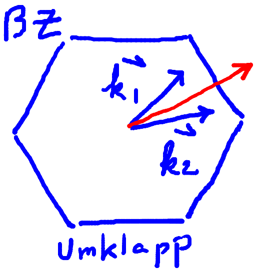
Peierls realized (1954) that not all phonon-phonon scatterings contribute to the finite thermal conductivity. He pointed out the importance of the Umklapp scattering in contrast to the normal scattering.

Recall the conservation of crystal momentum for any scattering process in a crystal: $\sum \vec{k}_f = \sum \vec{k}_i + \vec{G}$. First, let us make sure that all $\vec{k}_i$ and $\vec{k}_f$ values are within a cell. Next, if $\vec{G}$ happens to be 0, then that is a **normal** scattering, while if $\vec{G}$ is not 0, then that is an **Umklapp** (flip-over) scattering.

Note that this distinction depends on how we take a cell! Almost always, that cell is taken to be the first BZ. The following sketch shows a scattering process by which two phonons merge into one phonon. Normal and Umklapp scattering examples are shown.

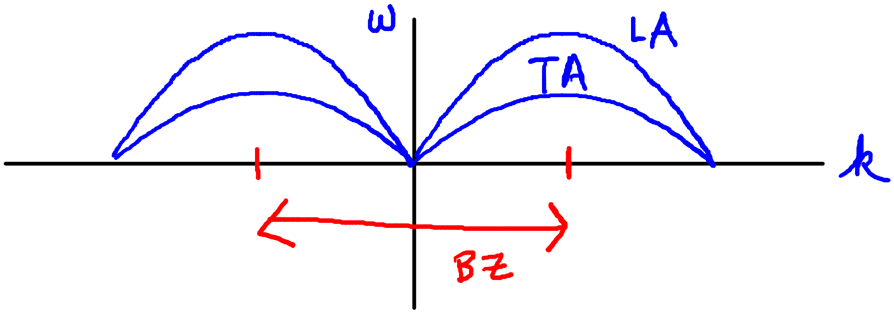




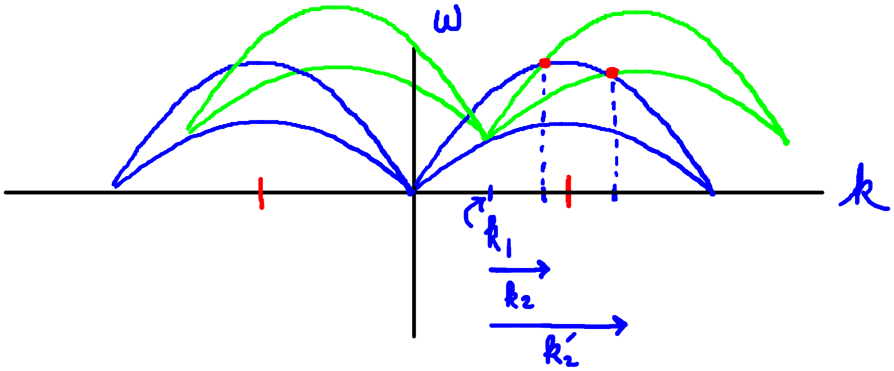


$$\vec{k}_1+\vec{k}_2=\vec{k}_3+\vec{G}$$

Of course, in all of these the total energy should be always conserved. Let us take an example. For instance, consider a monatomic crystal. For simplicity, we consider a high symmetry direction only, where the TA branch is doubly degenerate.



In the following, for a given initial momentum k_1, two momentum values k_2, k_2' make the scattering $k_1 + k_2(\text{or } k_2') \rightarrow k_3 + G$ possible. k_2 gives rise to the normal scattering, while k_2' gives rise to the Umklapp scattering, as $k_1 + k_2$ lies outside the BZ.



Why is the Umklapp scattering important?
With a symmetric cell such as the first BZ, the equilibrium state should be such that the quantity $\vec{J} = \sum_{\vec{k},\sigma} n_{\vec{k},\sigma} \vec{k}$ is zero, where $n_{\vec{k},\sigma}$ is the quantum number for the mode with wave vector $\vec{k}$ and polarization σ. The important point here is that all $\vec{k}$ values are within the BZ and $\vec{J}$ is really zero, not just up to some arbitrary $\vec{G}$. Now, consider a non-equilibrium state of the system where $\vec{J}$ is not zero. Can it relax to the equilibrium state? The answer is no, if all scatterings are normal! **So, with normal phonon-phonon scatterings alone, the thermal conductivity would be infinite!**
Umklapp scatterings however have the ability to reduce $\vec{J}$ to its equilibrium value, zero.

In pure crystals, Umklapp scatterings and the sample size are the two important factors for the thermal conductivity. **At low temperatures, most phonons will have very small wave vectors and thus the Umklapp scattering will become very rare!** This is because only very low energy acoustical phonons are excited at low temperatures.

In impure crystals, scattering of phonons by impurity or defects will be able to change the wave vector of the phonon, contributing to the finite thermal conductivity.

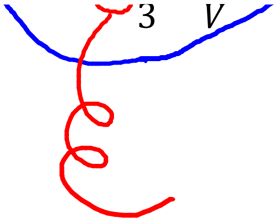
Using the kinetic theory of gas, it can be shown that the heat current due to phonons is given by

$$j_Q = -\frac{1}{3} v l \frac{1}{V} \frac{dE}{dT} \frac{dT}{dz} = -\kappa \frac{dT}{dz}$$

assuming that there is a small temperature gradient applied along the *z* direction (see e.g. Reif; a back of the envelope derivation goes like this. Assuming that volume is nearly constant, $\Delta Q = \Delta E$. So, $j_Q = -v \frac{1}{V} \frac{1}{6} \big(E(z+l) + E(z-l)\big)$ where l is the mean free path and v is the typical speed (sound velocity here). This expression leads to the above expression).

The thermal conductivity

$$\boxed{\kappa = \boxed{-}\frac{1}{3} v l \frac{C}{V}} \longrightarrow \text{heat capacity}$$



Thermal conductivity in an insulator

	Mean free path (l)	Heat Capacity (C)	Thermal conductivity (κ)
High T ($\gg \theta_D$)	Roughly $\propto 1/T$ due to $N_{ph} \propto T$	$N_m k_B$	$\propto \frac{1}{T}$ $\left(\frac{1}{T^x}, x = 1\,..\,2\right)$
Intermediate T	Roughly $\exp\left(\frac{O(\theta_D)}{T}\right)$		$\exp\left(\frac{O(\theta_D)}{T}\right)$
Low T ($\ll \theta_D$)	Sample size, Impurity/Defect length scales	$\propto T^3$	$\propto T^3$