

Lecture 13: continuation of understanding thermal properties of materials via phonons

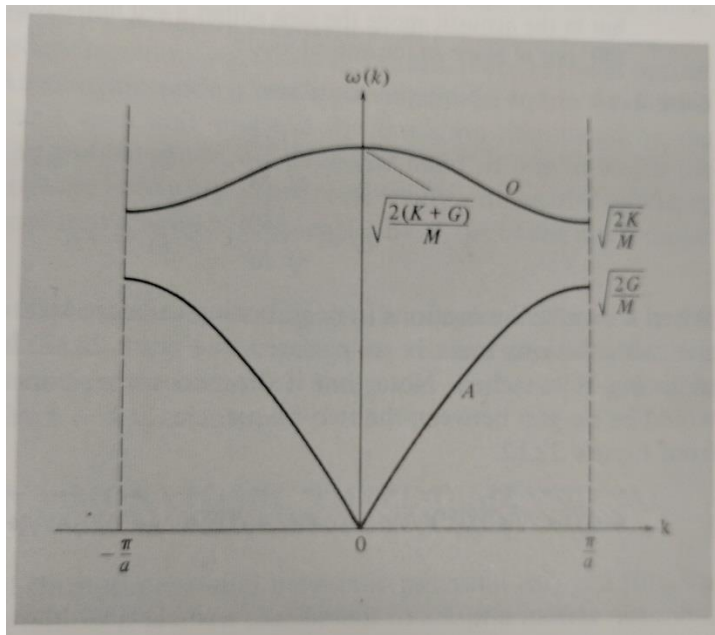
- **Review:**
 - Debye model for heat capacity
 - Density of states
 - Temperature dependence of heat capacity at high and low temperature
- Einstein model for heat capacity
- Anharmonic effects
- Thermal conductivity

Overview

Chapter 5 focuses on using quantized vibration of the atomic lattice to understand thermal properties of materials—how they raise their temperature in response to an energy input, how they expand with temperature, and how they respond to a temperature gradient. These are all very applicable and concrete concepts, but it is also challenging because this chapter uses prerequisites from quantum mechanics and statistical mechanics.

Review

In the previous chapter, we derived dispersion relations between the frequency and wavevector of waves in a crystalline solid, where the crystal is modeled as atoms on springs. We learned that there are acoustic phonons and optical phonons with longitudinal and transverse versions of both. Optical phonons only happen if there are more than one atoms per basis. We also learned that phonons have a group velocity given by $v_g = \partial\omega/\partial k$, which is itself a function of wavevector because the dispersions are not perfectly linear.



The derivation of the dispersion relations was purely classical, because there is nothing explicitly quantum mechanical about a bunch of masses connected by springs. However, atoms are quantum mechanical particles, and one way that their quantum nature comes into play is via quantization of

momentum. By considering periodic boundary conditions for the system of masses on a spring and saying that there are N masses in total and the total length of the spring is L, we get that K can take on the values $0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm N\pi/L$

Thus, the k-axis of the dispersion relation is not continuous, but consists of N equally spaced 'bins' separated by $\Delta K = 2\pi/L$. As a corollary, the frequencies of the phonons can only take on certain values, based on the permissible values of K—these are the 'normal modes'.

Phonons are bosons, so each bin defined by a value of (K, ω) can hold 0, 1, 2, 3, 4 or however many particles. The specific occupation number of each bin will **depend on the temperature**, and the expectation value is given by the Planck distribution.

$$\langle n \rangle_{\omega} = \frac{1}{e^{-\hbar\omega/k_B T} - 1}$$

Colloquially, we say that at higher temperature, atoms vibrate around more. The Planck distribution quantifies that statement: at higher temperature a 'normal mode' of a specific frequency has a higher expected occupation number, meaning that there are **more quanta** of atomic lattice vibrations at that frequency.

Our first application of this concept is towards calculating **heat capacity**, which is a temperature-dependent materials property that tells you how much you can raise the temperature of that solid by having it absorb a certain amount of energy.

The heat capacity at **constant volume**, defined as $c_V = \left(\frac{\partial U}{\partial T}\right)_V$ where U is the total internal energy.

$$U = \sum_K \sum_p \langle n_{K,p} \rangle \hbar\omega_{K,p} = \sum_K \sum_p \frac{\hbar\omega_{K,p}}{e^{\hbar\omega_{K,p}/k_B T} - 1}$$

Where the sum over K adds up all of the 'momentum bins' and the sum over p adds up all the 'polarizations' (longitudinal, transverse, and all of the acoustic and optical phonons).

It is convenient to replace the sum over K with an integral, because adjacent values of K are so close together that it is almost a continuum.

$$U = \sum_p \int_0^{\infty} d\omega D_p(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

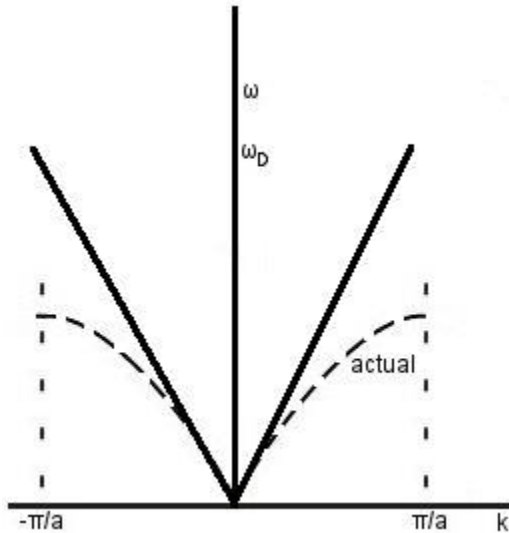
Where $D_p(\omega)$ is the **density of states**—the number of phonon modes between frequency ω and $\omega + d\omega$ of polarization p. Densities of states are encountered in various contexts in solid state physics, and they are used to enumerate the number of quantum states available to be occupied by various particles. The units are (number of states)/energy. The problem of finding heat capacity has thus become a problem of finding the density of states.

The density of states in **three dimensions** has the general expression: $D(\omega) = \frac{K^2 V}{2\pi^2} \frac{dK}{d\omega}$

If the dispersion of all phonon branches in a material is calculated, then the density of states can be derived. However, for ease of analytical calculations, we make approximations for the dispersion.

The first approximation we considered is the **Debye model**, which approximates a solid as only having acoustic phonons with a **single** (not k-dependent) group velocity and a cutoff frequency ω_D

$$\omega \equiv vK$$



Putting this all together with the generic expression for density of states in 3D, we get:

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

This integral can only be solved analytically in the limit of very low and very high temperature. It is customary to make the following substitutions:

$$x \equiv \frac{\hbar\omega}{k_B T}$$

$$x_D \equiv \hbar\omega_D/k_B T \equiv \theta/T$$

θ is defined as the Debye temperature (the temperature equivalent of the Debye frequency). It is given by:

$$\theta = \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3}$$

Notice that the only intrinsic material's dependent parameter in the Debye temperature is the phonon propagation velocity, which is basically the speed of sound.

The general expression for the heat capacity (temperature derivative of U) after these substitutions are made is:

$$C_V = 9Nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

And a graphical form is shown below.

In the limit of low temperature, the upper bound of the integral is set to go to infinity. In the high temperature limit, the exponents are Taylor expanded and only leading order terms are kept at the end.

Low temperature limit: $C_V \approx \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta}\right)^3$

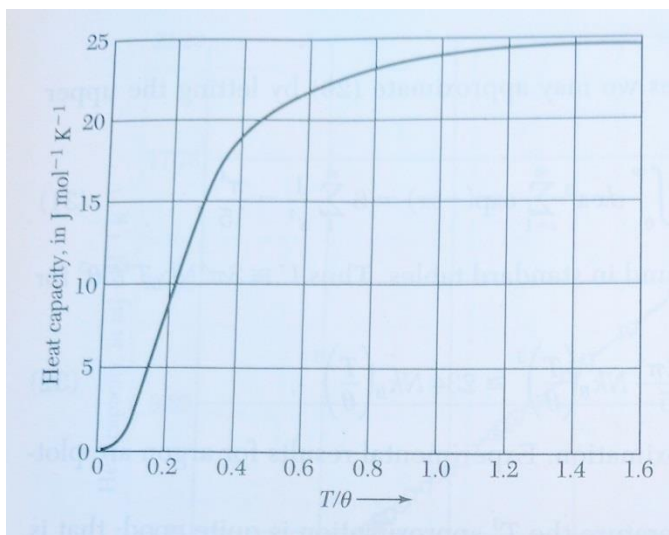
This gives a molar heat capacity of $1944 \left(\frac{T}{\theta}\right)^3 \text{ J/K}$

This T^3 behavior is supported by experiments.

High temperature limit: $C_V \approx 3Nk_B$

This gives a molar heat capacity of 24.9 J/K in the high temperature limit.

This is the heat capacity expected for a classical gas. The crossover from 'quantum' to 'classical' behavior for the phonon gas happens around the Debye temperature.



Example: If one mole of material absorbs 1 joule of energy, what will its temperature be raised to?

High temperature: $c_{V,molar} = 24.9 \text{ J/K}$

$$\frac{1\text{J}}{\Delta T} = 24.9 \rightarrow \Delta T = 0.04\text{K}$$

Low temperature (starting at 0K): $c_{V,molar} = 1944 \left(\frac{T}{\theta}\right)^3 \text{ J/K}$

We need to know what material we are talking about, and it is better if we consider an insulator or a semiconductor such that electrons do not contribute to heat capacity. Consider silicon with a Debye temperature of 645K.

We solve this problem by integrating the heat capacity wrt to temperature (opposite procedure of getting heat capacity from derivative of energy)

$$\frac{1944}{645^3} \int_0^{T_F} T^3 = 1J$$

T_F is the final temperature that is reached.

After integrating and solving for the final temperature we get: $T_F = 27K = \Delta T$

Thus the intuition we get is that at lower temperature, a solid's temperature will change **more** if it absorbs the same amount of energy because its heat capacity is smaller.

Einstein model of density of states

The Einstein model is much simpler than the Debye model. It considers N oscillators of the same frequency (ω_0). Whereas the Debye model approximated all phonons as being acoustic, the Einstein model approximates all of them as being optical.

This gives a density of states $D(\omega) = 3N\delta(\omega - \omega_0)$

The total internal thermal energy is given by:

$$U = N\langle n \rangle \hbar \omega$$

As we derived in the previous lecture, $\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$ which is also the planck distribution applicable to a gas of photons in thermal equilibrium

This gives $U = \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1}$ and we can get the heat capacity by taking a temperature derivative

$$c_V = \frac{3N(\hbar\omega_0)^2 e^{\hbar\omega_0/k_B T}}{k_B T^2 (e^{\hbar\omega_0/k_B T} - 1)^2}$$

Using the substitution $x \equiv \hbar\omega_0/k_B T$ this gives:

$$c_V = \frac{3Nk_B x^2 e^x}{(e^x - 1)^2}$$

In the limit of high temperature this is approximately

$$c_V \approx \frac{3Nk_B x^2 (1 + x)}{x^2} \approx 3Nk_B$$

Which is the same result as for a classical gas and the same as for the debye model.

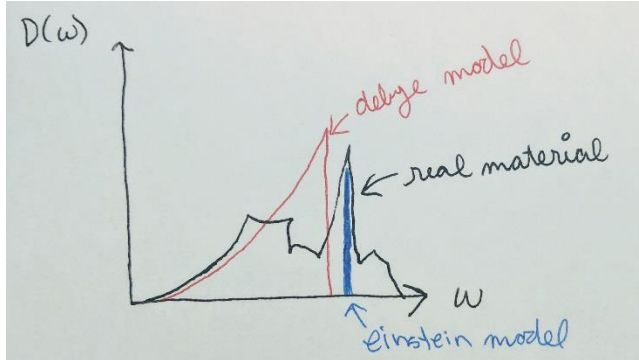
In the limit of low temperature, $e^{\hbar\omega_0/k_B T} \gg 1$ so $(e^{\hbar\omega_0/k_B T} - 1) \approx e^{\hbar\omega_0/k_B T}$

Thus, $c_V \approx 3Nk_B (\hbar\omega_0/k_B T)^2 e^{-\hbar\omega_0/k_B T}$

This exponential temperature dependence of heat capacity at low temperature is **not consistent** with experiments, so the Einstein model is not a good description for this aspect of physical systems.

However, the Einstein model is used in other contexts in solid state physics because it is a good approximation of the optical part of the phonon spectrum.

To summarize, we have thus far considered two approximations to the real phonon density of states for the purpose of calculating heat capacity.



Thermal expansion

Question: why does heat expand most material?

Answer: Colloquially, people often say that heat expands materials because there is more thermal energy and atoms vibrate around more.

But this does not square with the mathematical description of lattice vibrations that we have been using thus far, which is a harmonic oscillator potential. A classical harmonic oscillator with more average energy would simply exhibit further deviations from its equilibrium position, but it would do this **symmetrically** in both directions. Thus, we would not expect atoms in general to move further apart from their neighbor if they were really in a perfect harmonic oscillator potential.

But this is a shortcoming of the model we have been using, and we saw when we calculated the potential energy landscape for atoms in a van der waals solid or an ionic solid that these potentials are actually **asymmetric** when you move further away from the minimum position. It is easier to pull atoms apart than to push them together.

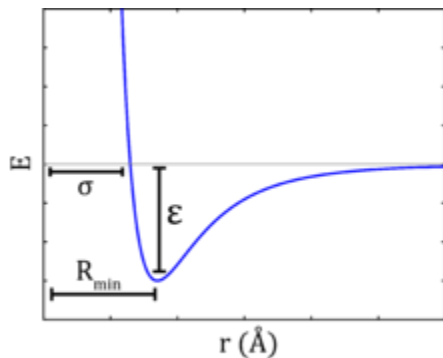


Figure: Lennard-Jones potential for van der waals solid,

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

We can approximate a real potential by a polynomial expansion to order higher than x^2 . Use the variable x to denote atomic separation from their equilibrium position.

$$U(x) = cx^2 - gx^3 - fx^4$$

Where c , g , and f are all positive.

We calculate the expectation value of the displacement using the Boltzmann distribution function

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x e^{-\beta U(x)}}{\int_{-\infty}^{\infty} dx e^{-\beta U(x)}}$$

As before, $\beta = 1/k_B T$. The term $e^{-\beta U(x)}$ represents the **probability** of being at a particular position x at a given temperature (think of an Arrhenius equation in which high-energy processes are exponentially suppressed at low temperature). The denominator is thus a normalization factor which sums up all of the thermal probabilities for an atom to have every possible deviation from its equilibrium position at a particular position. The numerator determines the mean deviation at a particular temperature by weighing each deviation by its probability.

For small deviations x , we can expand the exponential, after first pulling out the e^{cx^2} term which we can integrate

$$\int_{-\infty}^{\infty} dx x e^{-\beta U(x)} \approx \int_{-\infty}^{\infty} dx e^{-\beta cx^2} x (1 + g\beta x^3 + f\beta x^4) = \int_{-\infty}^{\infty} dx e^{-\beta cx^2} (x + g\beta x^4 + f\beta x^5)$$

Integrals of the form $\int_{-\infty}^{\infty} x^n e^{-ax^2}$ have known solutions and are zero for **odd** functions of x

$$\text{Thus } \int_{-\infty}^{\infty} dx x e^{-\beta U(x)} \approx \frac{3\pi^{1/2}}{4} \frac{g}{c^{5/2}} \frac{1}{\beta^{3/2}}$$

$$\text{Similarly, } \int_{-\infty}^{\infty} dx e^{-\beta U(x)} \approx \int_{-\infty}^{\infty} dx e^{-\beta cx^2} = \left(\frac{\pi}{\beta c}\right)^{1/2}$$

Putting it together:

$$\langle x \rangle \approx \frac{3g}{4c^2} k_B T$$

According to this derivation, the mean atomic displacement grows linearly with temperature, which indicates that the thermal expansion coefficient (usually called α) is independent of temperature. This is only really true **above the Debye temperature**, and a more careful definition is needed to get the full temperature dependence.

Note that we have just calculated **linear** thermal expansion, and often, we want to work with **volume** thermal expansion. For an isotropic solid, the coefficient of volumetric thermal expansion is 3 times the linear thermal expansion coefficient.

Example:

The coefficient of **linear** thermal expansion for **copper** (whose Debye temperature is close to room temperature) is $17 \times 10^{-6} K^{-1}$ at room temperature

That means that a copper pot used to boil water will experience a change in linear dimension $\frac{\Delta L}{L} = 17 \times 10^{-4}$ as it is heated up (using $\Delta T = 100K$). That means that if you start out with a pot of radius 10cm, by the time the water is boiling, the radius is 10 cm and 170 microns. Thermal expansion of solids tends to be **very small**, but it needs to be taken into account when designing engineering structures like railroads and bridges.

Sketch of quantum treatment of thermal expansion

The derivation above is intuitive, but it is only physically correct when the phonons in a material behave like a classical gas, above the Debye temperature.

At an arbitrary temperature, we are seeking the thermal expansion coefficient α at constant pressure. We are assuming an isotropic material such that the volume thermal expansion coefficient is 3x the linear thermal expansion coefficient.

$$\alpha = \frac{1}{l} \left(\frac{\partial l}{\partial T} \right)_P = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P$$

The bulk modulus of a material is the volume contraction in response to hydrostatic (equal on all sides) compression:

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T$$

Plugging in the bulk modulus above and noting chain rule

$$\alpha = \frac{1}{3B} \left(\frac{\partial P}{\partial T} \right)_V$$

The goal is to now express the derivative in terms of thermodynamic quantities. **Pressure is the volume derivative of the Helmholtz free energy, $F=U-TS$**

$$P = -\frac{\partial}{\partial V} \left[U - T \int_0^T \frac{dT'}{T'} \frac{\partial}{\partial T'} U(T', V) \right]$$

We have previously derived expressions for internal energy U in terms of the occupation numbers, so the quantum derivation of thermal expansion will involve using those again.

In the end, we get that α is proportional to the heat capacity and has the following temperature dependence:

Low temperature: $\alpha \sim T^3$

High temperature (well above the Debye temperature): $\alpha \sim \text{const}$ (which we got with a classical argument)