

## 5

## Thermal properties of phonons

Ref. Chapter 5

Q1: Why do most solids become larger as we increase the temperature?

Q2: Why is foam a good thermal insulator?

Q3: Why is metal cold to touch?

### 5.1. Background

Here we review some basic ideas of quantum mechanics, thermodynamics and statistical physics, which will be used in this chapter.

#### 5.1.1. What are phonons?

Quantum Mechanics tells us that **waves are particles**. Energy  $E = \hbar \omega$  and momentum  $P = \hbar k$

So elastic waves (sound waves) are particles too, and these particles are called phonons.

- The energy of a phonon  $E = \hbar \omega$
- The momentum of a phone  $P = \hbar k$ .

#### 5.1.2. What is temperature?

The rigorous definition of temperature requires knowledge on thermodynamics and thermal equilibrium (which are discussed in Physics 460). Roughly speaking, the temperature ( $T$ ) measures how widely the particles are moving in a system.

At higher  $T$ , atoms move more widely. At lower  $T$ , atoms don't want to move much.

For elastic waves, this means that at higher  $T$ , the amplitude of sound waves are larger (more phonons). At lower  $T$ , the amplitude is smaller (less phonons).

- We have more phonons at high  $T$  and less phonons at low  $T$ .

### 5.2. Planck distribution: how many phonons do we have?

In a solid, there are many different sound waves (with different wavelength and frequencies). In this section, we pick one of these waves (with fixed wavevector and frequency) and try to understand this single mode first. Then, in the next section, we will consider all different modes and add their contributions together.

#### 5.2.1. number of phonons (fixed frequency $\omega$ )

The number of phonon is not a fixed value. If an atom start to oscillate, then we created some phonons. If the oscillation stops, the phonons disappear. Although we cannot determine the number of phonons, at a fixed temperature we know the probably of having  $n$  phonons.

Let's consider a sound wave with a fixed wavevector  $k$  and a fixed frequency  $\omega$  and ask how many phonons we will have in this wave. The probably of having  $n$  phonons here is

$$P(n) \propto \exp\left(-\frac{E_n}{k_B T}\right) \quad (5.1)$$

Here  $k_B = 1.3806503 \times 10^{-23} \text{ J/K}$  is the Boltzmann constant (which is one fundamental physics constant) and  $T$  is absolute temperature. ( $0 \text{ K} = -273 \text{ C}^\circ$ ).  $E_n$  is the energy carried by these  $n$  phonons. Because each phonon carries energy  $\hbar\omega$ ,  $E_n = n \hbar\omega$ . So,

$$P(n) = \frac{1}{Z} \exp\left(-\frac{n \hbar\omega}{k_B T}\right) \quad (5.2)$$

Here  $Z$  is the normalization factor (which is called the partition function).

This  $\exp\left(-\frac{E}{k_B T}\right)$  is known as the Boltzmann factor, which is one fundamental assumption in statistical physics. Here, we will not try to prove this probability. Instead, we will use it as granted (details can be found in Physics 460).

Q: What is this normalization factor  $Z$ ?

A: Total probability is 1. We can use this condition to fix  $Z$ .

$$1 = \sum_{n=0}^{\infty} P(n) = \sum_{n=0}^{\infty} \frac{1}{Z} \exp\left(-\frac{n \hbar\omega}{k_B T}\right) = \frac{1}{Z} \sum_{n=0}^{\infty} \exp\left(-\frac{n \hbar\omega}{k_B T}\right) = \frac{1}{Z} \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \quad (5.3)$$

Here we used the fact that  $1 + x + x^2 + x^3 + \dots = \frac{1}{1-x}$

So we have

$$Z = \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \quad (5.4)$$

Average number of phonons

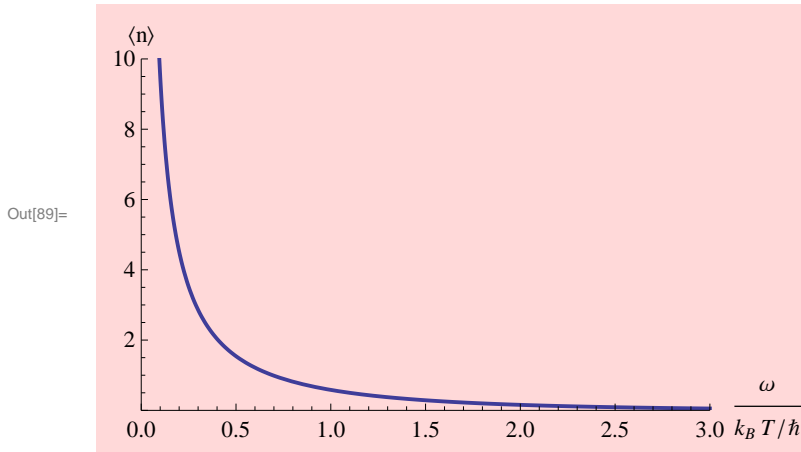
$$\begin{aligned} \langle n \rangle &= \sum_{n=0}^{\infty} n P(n) = \sum_{n=0}^{\infty} \frac{n}{Z} \exp\left(-\frac{n \hbar\omega}{k_B T}\right) = \frac{1}{Z} \sum_{n=0}^{\infty} n \exp\left(-\frac{n \hbar\omega}{k_B T}\right) \\ &= \frac{1}{Z} \frac{k_B T}{\hbar} \sum_{n=0}^{\infty} \frac{d}{d\omega} \exp\left(-\frac{n \hbar\omega}{k_B T}\right) = -\frac{1}{Z} \frac{k_B T}{\hbar} \frac{d}{d\omega} \sum_{n=0}^{\infty} \exp\left(-\frac{n \hbar\omega}{k_B T}\right) \\ &= -\frac{1}{Z} \frac{k_B T}{\hbar} \frac{d}{d\omega} \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \\ &= \frac{1}{Z} \frac{k_B T}{\hbar} \left( \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \right)^2 \exp\left(-\frac{\hbar\omega}{k_B T}\right) \frac{\hbar}{k_B T} \\ &= \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \end{aligned} \quad (5.5)$$

The average phonon number depends on temperature  $T$ , the frequency of the phonons  $\omega$  and some fundamental physics constants  $\hbar$  and  $k_B$ .

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \quad (5.6)$$

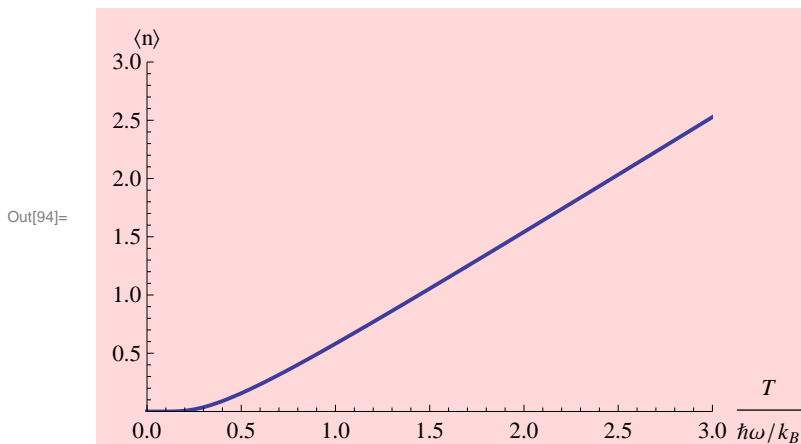
This relation is known as the Planck distribution or the Bose-Einstein distribution.

```
In[89]:= Plot[{{ $\frac{1}{\text{Exp}[x] - 1}$ }}, {x, 0, 3}, PlotRange -> {{0, 3}, {0, 10}},
PlotStyle -> Thick, AxesLabel -> {" $\frac{\omega}{k_B T / \hbar}$ ", "<n>"}, LabelStyle -> Medium]
```



At a fixed temperature  $T$ , low frequency modes have much more phonons than high frequency modes. The phonons with  $\omega < k_B T / \hbar$ , the number of phonon modes at  $\omega > k_B T / \hbar$  is very low. So at very low temperature, we only need to consider acoustic phonons.

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In[94]:= Plot[{{ $\frac{1}{\text{Exp}[1/x] - 1}$ }}, {x, 0, 3}, PlotRange -> {{0, 3}, {0, 3}},
PlotStyle -> Thick, AxesLabel -> {" $\frac{T}{\hbar \omega / k_B}$ ", "<n>"}, LabelStyle -> Medium]
```



For a fixed frequency, the number of phonons reduce as  $T$  goes down.

At high  $T$ ,

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \approx \frac{k_B}{\hbar \omega} T - \frac{1}{2} \quad (5.7)$$

At low  $T$ ,

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \approx \exp\left(-\frac{\hbar \omega}{k_B T}\right) \quad (5.8)$$

### 5.2.2. Energy carried by phonons (fixed frequency $\omega$ )

One phonon has energy  $\hbar\omega$ , so the average energy carried by these sound waves are

$$\langle E \rangle = \langle n \rangle \hbar \omega = \hbar \omega \langle n \rangle = \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad (5.9)$$

### 5.2.3. History of the Planck distribution or the Bose-Einstein distribution.

This distribution was firstly discovered by Planck in the study of black-body radiation. There, Planck studies the energy carried by light, which is another type of wave (electromagnetic waves) very similar to sound waves. At that time, before the quantum mechanics is established, people consider light as classical waves. If one assumes that light is a classical wave, one find that the energy carried by these waves (light) is infinite at any temperature, which is obviously wrong. This infinite energy problem is known as the ultraviolet catastrophe. Eventually, it is Planck who pointed out that if we view light as particles (photons) with each particle carrying energy  $\hbar\omega$ , then all the problems are solve. This discovery, as well as many other progresses, eventually led to the discovery of the quantum physics.

In fact, the distribution Planck discovered is valid for any waves, not limited to light. For sound waves and phonons, the same physics law applies and the number of phonons follow exactly the same distribution.

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad (5.10)$$

Later, Bose and Einstein discovered that for any bosonic particles, the average number of particles is

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1} \quad (5.11)$$

where  $\epsilon$  is the energy of this particle and  $\mu$  is the chemical potential. The Planck distribution is a special case of the Bose-Einstein distribution, where  $\mu$  is 0.

(Photons and phonons are both bosonic particles (bosons), so they obey the Bose-Einstein distribution.)

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## 5.3. Total number of phonon modes, total energy and heat capacity

In the last section, we proved that for a sound mode with frequency  $\omega$ , the energy carried by this sound wave is

$$\langle E_\omega \rangle = \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1}$$

In a solid, there are many different sound modes (with different frequencies). What is the total energy carried by all these sound modes?

$$E = \sum_i \langle E_{\omega_i} \rangle \quad (5.12)$$

where  $\sum_i$  sums over all the different phonon modes. This sum can be rewrite in terms of an integral over frequency  $\omega$

### 5.3.1. Density of states (DOS)

The density of states (DOS) is a function of frequency  $\omega$ , which measure the number of sound modes per interval of frequency (or energy).

The number of states (modes) in the frequency range between  $\omega$  and  $\omega+d\omega$  is:

$$dN = D(\omega) d\omega \quad (5.13)$$

where  $D(\omega)$  is the DOS.

Total number of phonon modes:

$$N = \int_0^\infty dN = \int_0^\infty d\omega D(\omega) d\omega \quad (5.14)$$

We can separate  $D(\omega)$  into the sum of  $D_p(\omega)$

$$D(\omega) = \sum_p D_p(\omega) = D_{LA}(\omega) + D_{LT}(\omega) + \dots \quad (5.15)$$

where  $p$  indicates different phonon branches (also known as polarizations).

### 5.3.2. Total number of phonon modes

Q: How many different phonon modes we have?

A: The total number of phonon modes in one branch (LA, LO, ...) coincides with the number of unit cells.

#### Why does the total number of phonons coincides with the number of unit cells?

Let's use a simple example to demonstrate this. Consider a 1D chain of atoms (assuming that there is one atom per unit cell). The atoms are labeled by an integer  $s = 1, 2, 3 \dots N$ .

#### Periodic boundary condition

Sound waves on this lattice can be written as

$$u_s = \mathcal{A} \exp(-i \omega t) \exp(i k a s) \quad (5.16)$$

where  $u_s$  is the deformation of the site  $s$ ,  $\mathcal{A}$  is the amplitude,  $\omega$  is the frequency,  $k$  is the wavevector and  $a$  is the lattice constant.

Periodic boundary condition means  $u_s = u_{s+N}$

$$u_{s+N} = \mathcal{A} \exp(-i \omega t) \exp[i k a (s + N)] = \mathcal{A} \exp(-i \omega t) \exp(i k a s) \exp(i k a N) = u_s \exp(i k a N) \quad (5.17)$$

Therefore,  $\exp(i k a N) = 1$ , so  $k a N = 2 \pi n$  where  $n$  is an integer. So

$$k = \frac{2 \pi n}{a N} = \frac{2 \pi n}{L} \quad (5.18)$$

where,  $a N = L$  is just the length of the system.

Notice here that  $k$  and  $k + 2 \pi/a$  gives exactly the same wave,

$$\exp\left[i \left(k + \frac{2 \pi}{a}\right) a s\right] = \exp(i k a s + i 2 \pi s) = \exp(i k a s) \exp(i 2 \pi s) = \exp(i k a s) \quad (5.19)$$

So we will only need to consider  $-\pi/a < k \leq \pi/a$ .

Therefore, all the possible values of  $k$  are

$$k = 0, \pm \frac{2 \pi}{L}, \pm \frac{4 \pi}{L}, \pm \frac{6 \pi}{L} \dots \frac{N \pi}{L} \quad (5.20)$$

There are  $N$  possible values of  $k$ , so we have  $N$  phonon modes. This number  $N$  is the number of unit cells.

#### Uncertainty relation and the thermal dynamic limit

Q: In the k-space, how far is the separation between two allowed phonon modes?

A:  $2\pi/L$ , since  $k = 2 \pi n/L$

This result can also be understood using the uncertainty relation. For a system with size  $L$ , phonons are confined in the real space, so we know the position of the phonon with uncertainty  $L$ . Quantum mechanics tells us that if we know the position with uncertainty  $L$ , the uncertainty of momentum  $\Delta P$  shall be  $2 \pi \hbar/L$ . So each quantum state will occupy a region of  $2 \pi \hbar/L$  in the momentum space. We also know that the momentum  $P$  and the wave-vector  $k$  are the same quantity, up to a factor of  $\hbar$ . So this means that in the k-space, each phonon mode shall occupy a region with size  $2\pi/L$ . In other words, two phonon modes will be separated by  $2\pi/L$ .

In the thermal dynamic limit ( $L \rightarrow \infty$ ), the spacing between two phonon modes  $2 \pi/L \rightarrow 0$ , so we can treat the momentum  $k$  as a continuous variable.

#### Fixed boundary condition (see our textbook)

#### Total number of phonons in a d-dimensional crystal.

In a d-dimensional crystal with  $n$  atoms per cell, there will be  $d n$  phonon modes [ $d$  acoustic and  $d(n - 1)$  optical]. Each phonon branch have  $N$  phonon modes. So the total number of phonon modes is  $d n N$ .

The total number of degrees of freedom is:  $d \times \text{number of atoms} = d n N$ .

the total number of degrees of freedom=the total number of phonon modes.

### 5.3.3. Total energy

Total energy is

$$U = \int_0^{\infty} d\omega D(\omega) \langle E_{\omega} \rangle = \int_0^{\infty} d\omega D(\omega) \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad (5.21)$$

So the only thing we need to know here is the function of  $D(\omega)$  (the density of states).

### 5.3.4. Heat capacity

How many energy do we need to increase the temperature of the system by 1 degree?

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (5.22)$$

## 5.4. Einstein model (optical phonon modes)

### 5.4.1. Assumptions

For an optical branch, the phonon band is often very flat ( $\omega$  is almost a constant). So we can assume that

- all the phonon modes (for this optical branch) have the same energy  $\omega_0$

So the density of states

$$D(\omega) = N \delta(\omega - \omega_0) \quad (5.23)$$

where  $\delta(x)$  is a delta function.

### 5.4.2. Total number of phonon modes

$$\int_0^{\infty} d\omega D(\omega) = \int_0^{\infty} d\omega N \delta(\omega - \omega_0) = N \quad (5.24)$$

Because total number of phonon mode in a phonon branch is the number of unit cells. The coefficient  $N$  in the DOS is just the number of unit cells.

### 5.4.3. Total energy

$$U = N \frac{\hbar \omega_0}{\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1} \quad (5.25)$$

We can get the same results using

$$U = \int_0^{\infty} d\omega D(\omega) \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} = \int_0^{\infty} d\omega N \delta(\omega - \omega_0) \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} = N \frac{\hbar \omega_0}{\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1} \quad (5.26)$$

### 5.4.4. Heat capacity

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = N \frac{d}{dT} \frac{\hbar \omega_0}{\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1} = N \frac{\hbar \omega_0}{\left[ \exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1 \right]^2} \exp\left(\frac{\hbar \omega_0}{k_B T}\right) \frac{\hbar \omega_0}{k_B T^2} = N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{\exp\left(\frac{\hbar \omega_0}{k_B T}\right)}{\left[ \exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1 \right]^2} \quad (5.27)$$

### 5.4.5. Heat capacity at low temperatures ( $T \rightarrow 0$ )

At small  $T$ ,  $\exp\left(\frac{\hbar \omega_0}{k_B T}\right) \gg 1$ , so  $\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1 \approx \exp\left(\frac{\hbar \omega_0}{k_B T}\right)$ .

$$C_V = N k_B \frac{\exp\left(\frac{\hbar \omega_0}{k_B T}\right)}{\left[\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1\right]^2} \left(\frac{\hbar \omega_0}{k_B T}\right)^2 \approx N k_B \frac{\exp\left(\frac{\hbar \omega_0}{k_B T}\right)}{\left[\exp\left(\frac{\hbar \omega_0}{k_B T}\right)\right]^2} \left(\frac{\hbar \omega_0}{k_B T}\right)^2 = N k_B \left(\frac{\hbar \omega_0}{k_B T}\right)^2 \exp\left(-\frac{\hbar \omega_0}{k_B T}\right) \quad (5.28)$$

When  $T$  is reduced to zero,  $C_V$  decreases very fast to zero, as  $\exp\left(-\frac{\hbar \omega_0}{k_B T}\right)$ .

This result agrees with the third law of thermal dynamics:  $C_V = 0$  at  $T = 0$ .

#### 5.4.6. Heat capacity at high temperature ( $T \rightarrow \infty$ )

At high  $T$ ,  $\exp\left(\frac{\hbar \omega_0}{k_B T}\right) \approx 1 + \frac{\hbar \omega_0}{k_B T}$ , so

$$C_V = N k_B \frac{\exp\left(\frac{\hbar \omega_0}{k_B T}\right)}{\left[\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1\right]^2} \left(\frac{\hbar \omega_0}{k_B T}\right)^2 \approx N k_B \frac{1}{\left[\frac{\hbar \omega_0}{k_B T}\right]^2} \left(\frac{\hbar \omega_0}{k_B T}\right)^2 = N k_B \quad (5.29)$$

This result agrees with the heat capacity of an ideal gas,  $C_V = \text{number of modes} \times k_B$ .

## 5.5. Debye model (acoustic phonon modes)

### 5.5.1. Assumptions

- Linear dispersion  $\omega = v k$
- The frequency of the phonons must satisfy  $0 \leq \omega \leq \omega_D$ , where the maximum frequency  $\omega_D$  is called the Debye frequency.

### 5.5.2. Density of states

Q: How many modes do we have inside some region in the P-space?

A: We know that this number must be proportional to the size of the region  $\Omega$ :

$$N_\Omega \propto \int_\Omega d^3 P \quad (5.30)$$

Q: What is the coefficient here?

A: We know the uncertainty relation. If we know the size of the system ( $V$ ), the uncertainty in momentum is  $(2\pi\hbar)^d/V$ . This means that one quantum state will occupy a region of size  $(2\pi\hbar)^d/V$  in the momentum space. So the number of modes

$$N = \int \frac{d^3 p}{(2\pi\hbar)^3/V} = V \int \frac{d^3 k}{(2\pi)^3} = V \int \frac{4\pi k^2 dk}{(2\pi)^3} = V \int \frac{k^2 dk}{2\pi^2} \quad (5.31)$$

If  $\omega = v k$

$$N = V \int \frac{k^2 dk}{2\pi^2} = V \int \frac{\omega^2}{2\pi^2 v^3} d\omega \quad (5.32)$$

Compare with  $N = \int D(\omega) d\omega$ . We find that

$$D(\omega) = V \frac{\omega^2}{2\pi^2 v^3} \quad (5.33)$$

And please also keep in your mind that we assumed  $0 \leq \omega \leq \omega_D$

Total number of modes

$$N = \int_0^{\omega_D} D(\omega) d\omega = V \int_0^{\omega_D} \frac{\omega^2}{2\pi^2 v^3} d\omega = V \frac{\omega_D^3}{6\pi^2 v^3} \quad (5.34)$$

So

$$\omega_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3} v = \left(\frac{6\pi^2}{V_C}\right)^{1/3} v \quad (5.35)$$

Here,  $V$  is the volume of the system,  $N$  is the number of unit cells and  $v$  is the sound velocity.  $V/N$  is just the size of a unit cell  $V_C$ .

We can also define Debye wavevector  $k_D$  as

$$k_D = \omega_D/v = \left(6\pi^2 \frac{N}{V}\right)^{1/3} \quad (5.36)$$

### 5.5.3. Total energy

$$U = 3 \int_0^{\omega_D} d\omega D(\omega) \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad (5.37)$$

The factor 3 here is because there are three acoustic phonon branches (2 transverse and 1 longitudinal). In a real solid, these three modes have different velocities, so their DOS and  $\omega_D$  are different. But here, we assume these three modes are the same sound velocity for simplicity.

define  $x = \frac{\hbar \omega}{k_B T}$  and  $x_D = \frac{\hbar \omega_D}{k_B T}$ .

$$U = 3V \int_0^{\omega_D} d\omega \frac{\omega^2}{2\pi^2 v^3} \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} = \frac{3V \hbar}{2\pi^2 v^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^{x_D} dx \frac{x^3}{\exp(x) - 1} \quad (5.38)$$

If we define Debye temperature,

$$\theta = \frac{\hbar \omega_D}{k_B} = \frac{\hbar v}{k_B} \left(6\pi^2 \frac{N}{V}\right)^{1/3} \quad (5.39)$$

$$U = \frac{3V}{2\pi^2 v^3 \hbar^3} (k_B T)^4 \int_0^{x_D} dx \frac{x^3}{\exp(x) - 1} = 9N \left(\frac{V/N}{6\pi^2 v^3 \hbar^3}\right) k_B T \int_0^{x_D} dx \frac{x^3}{\exp(x) - 1} = 9N k_B T \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx \frac{x^3}{\exp(x) - 1} \quad (5.40)$$

### 5.5.4. Heat capacity

$$C_V = \frac{\partial U}{\partial T} = 3V \int_0^{\omega_D} d\omega \frac{\omega^2}{2\pi^2 v^3} \frac{d}{dT} \frac{\hbar \omega}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} = \quad (5.41)$$

$$3V \int_0^{\omega_D} d\omega \frac{\omega^2}{2\pi^2 v^3} \frac{\hbar \omega}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right]^2} \exp\left(\frac{\hbar \omega}{k_B T}\right) \frac{\hbar \omega}{k_B T^2} = 3V \frac{\hbar^2}{k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4}{2\pi^2 v^3} \frac{1}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right]^2} \exp\left(\frac{\hbar \omega}{k_B T}\right)$$

define  $x = \frac{\hbar \omega}{k_B T}$  and  $x_D = \frac{\hbar \omega_D}{k_B T}$ .

$$C_V = 3V \frac{\hbar^2}{k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4}{2\pi^2 v^3} \frac{1}{\left[\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right]^2} \exp\left(\frac{\hbar \omega}{k_B T}\right) = 3V \frac{\hbar^2}{2\pi^2 v^3 k_B T^2} \left(\frac{k_B T}{\hbar}\right)^5 \int_0^{x_D} dx x^4 \frac{e^x}{(e^x - 1)^2} = \quad (5.42)$$

$$3V \frac{k_B}{2\pi^2 v^3} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{x_D} dx x^4 \frac{e^x}{(e^x - 1)^2} = 9N k_B \frac{T^3}{6\pi^2 \frac{N}{V} \left(\frac{\hbar v}{k_B}\right)^3} \int_0^{x_D} dx x^4 \frac{e^x}{(e^x - 1)^2} = 9N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx x^4 \frac{e^x}{(e^x - 1)^2}$$

### 5.5.5. Heat capacity at low T

At low  $T$ , we can set the upper limit of the integral to  $\infty$

$$C_V = 9N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx x^4 \frac{e^x}{(e^x - 1)^2} \approx 9N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\infty} dx x^4 \frac{e^x}{(e^x - 1)^2} = 9N k_B \left(\frac{T}{\theta}\right)^3 \frac{4\pi^4}{15} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \quad (5.43)$$

At low temperature, the heat capacity is  $C_V \sim T^3$  (from acoustic phonons)



This result agrees with the third law of thermal dynamics:  $C_V = 0$  at  $T = 0$ .

### 5.5.6. Heat capacity at high T

At high  $T$ ,  $x$  is small, so  $e^x \approx 1 + x$

$$C_V = 9 N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx x^4 \frac{e^x}{(e^x - 1)^2} \approx 9 N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx x^4 \frac{1}{x^2} = 9 N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx x^2 = 9 N k_B \left(\frac{T}{\theta}\right)^3 \frac{1}{3} \left(\frac{\theta}{T}\right)^3 = 3 N k_B \quad (5.44)$$

This results agrees with the heat capacity of an ideal gas,  $C_V = \text{number of modes} \times k_B$ .

## 5.6. Total heat capacity (acoustic modes+optical modes)

### 5.6.1. Low T

At small T, acoustic phonons have

$$C_V^{(A)} = \frac{4 \pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \quad (5.45)$$

Optical phonons have

$$C_V^{(O)} = N k_B \left(\frac{\hbar \omega_0}{k_B T}\right)^2 \exp\left(-\frac{\hbar \omega_0}{k_B T}\right) \quad (5.46)$$

At small  $x$  ( $x \ll 1$ ),

$$\exp\left(\frac{1}{x}\right) \ll x^n \ll x \ll x^{1/n} \ll \frac{1}{\ln x} \quad (5.47)$$

So at small T,  $C_V^{(A)} \gg C_V^{(O)}$ , and therefore the total heat capacity is dominated by the acoustic modes and we can ignore the optical modes.

$$C_V \approx C_V^{(A)} = \frac{12 \pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3 \quad (5.48)$$

The Debye temperature  $\theta$  depends on the properties of the material, which is determined by fitting experimental data.

### 5.6.2. High T

At high T, each acoustic phonon branch contributes  $N k_B$  to  $C_V$ . Each optical phonon branch also contributes  $N k_B$  to  $C_V$  (Debye model and Einstein model give the same result).

Therefore, the total heat capacity is

$$C_V = (\text{number of phonon branches}) \times N k_B = d n N k_B \quad (5.49)$$

where  $d$  is the dimensionality,  $n$  is the number atom per unit cell,  $N$  is the number of unit cell. Notice that  $n N$  is the total number of atoms in the system.

$$C_V = d k_B \times (\text{total number of atoms}) \quad (5.50)$$

This result agrees with the heat capacity of an ideal gas.

## 5.7. A real solid

In a real solid,  $D(\omega)$  is a complicated function, which is not even a smooth function. But at small  $\omega$ , very typically, the DOS agrees with the Debye model [ $D(\omega) \propto \omega^2$ ].

The heat capacity for most insulators is  $C_V \sim T^3$ , in good agreement with Debye model. For conductors, the low temperature heat capacity is dominated by electrons instead of phonons, so we will typically see  $C_V \sim T$ , instead of  $T^3$ .

## 5.8. Thermal expansion

In the discussions above (and in chapter 3 and 4), we assume that the atoms in a solid are connected by perfect springs with  $E = C \Delta L^2 / 2$ . But in reality, the potential energy (as a function of the distance between two particles) is not a quadratic function.

When we study heat capacity, phonon modes etc., this approximation is pretty good and can provide us with correct results. However, if we want to study some other topics (e.g. thermal expansion, scattering between phonons), this approximation will not be able to provide the correct physics. It misses two important physics:

- Phonon scatterings: for perfect  $\Delta L^2$  potentials, there is no interaction between phonons. Phonons never collide with each other. When they collide, they just cross each other, as if there is no other phonon. In a real solid, where the bond between two atoms are not perfect springs, there are phonon scatterings.
- Thermal expansion: for perfect springs, the length of the spring (separation between neighboring atoms) never changes, when we rise or reduce the temperature. But in a real solid, this length changes. Typically, it increases as  $T$  increases. In other words, very typically, the size of a solid increases when we raise  $T$  (for some solids, the volume reduces at higher  $T$ ), this is known as thermal expansion.

### 5.8.1. A cartoon picture

Consider the potential energy between two atoms  $U(r)$  where  $r$  is the separation. Here, the first figure shows the potential of a perfect spring and the second figure shows the Lennard-Jones potential, which can be used to describe the interaction between two atoms in some solids.

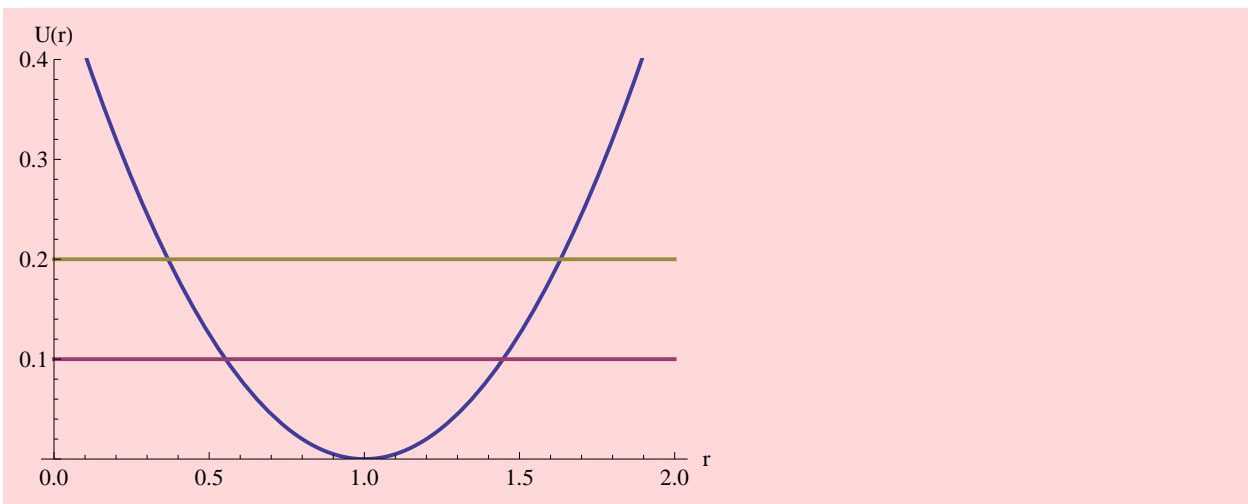
- If  $U(r - r_0) = U(r_0 - r)$ , as shown in the first figure below, oscillations with larger amplitudes (higher energy) have the same average distance  $\langle r \rangle = r_0$  as oscillations with smaller amplitudes (lower energy).
- If  $U(r - r_0) \neq U(r_0 - r)$ , as shown in the second figure below, oscillations with larger amplitudes (higher energy) have larger average separation  $\langle r \rangle$ .

We know that at higher  $T$ , the amplitudes of oscillations increase. So higher  $T$  means larger separation.

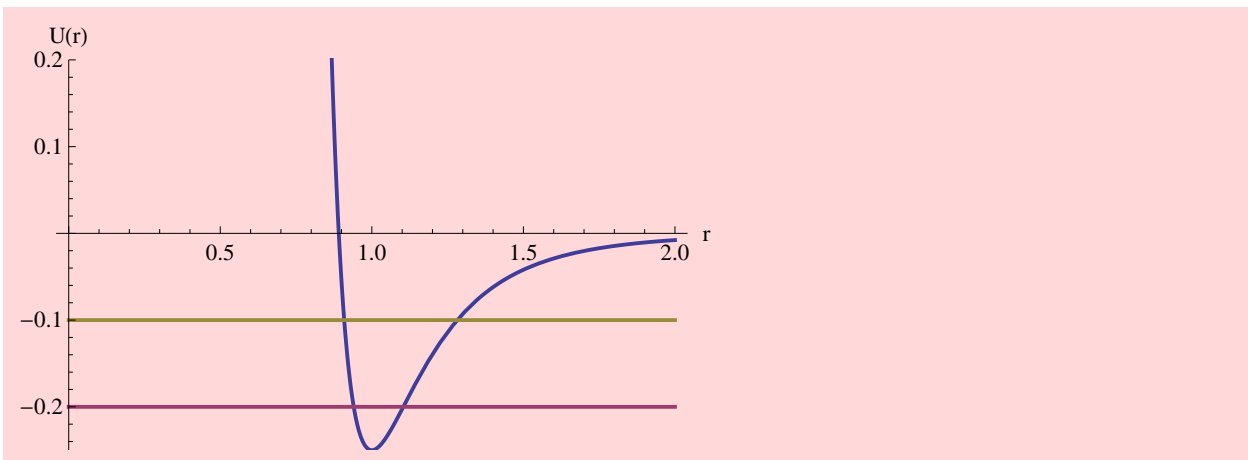
In[103]:=

```
Plot[{{1/2 (r - 1)^2, .1, .2}, {r, 0, 2}, PlotRange -> {Full, {0, .4}},
      PlotStyle -> Thick, AxesLabel -> {"r", "U(r)"}, LabelStyle -> Medium]
Plot[{{(2^-1/6/r)^12 - (2^-1/6/r)^6, -.2, -.1}, {r, 0, 2}, PlotRange -> {Full, {-.25, .2}},
      PlotStyle -> Thick, AxesLabel -> {"r", "U(r)"}, LabelStyle -> Medium]
```

Out[103]=



Out[104]=



### 5.8.2. Rigorous calculations

Consider a potential:  $U(x) = c x^2 - g x^3 + f x^4$

The probability for the distance to be  $x$  is

$$P \propto \exp\left(-\frac{E}{k_B T}\right) \quad (5.51)$$

So,

$$P(x) = \frac{1}{Z} \exp\left[-\frac{U(x)}{k_B T}\right] \quad (5.52)$$

Again,  $Z$  can be determined by the condition that total  $P$  is unity.

$$1 = \int_{-\infty}^{\infty} dx P(x) = \frac{1}{Z} \int_{-\infty}^{\infty} dx \exp\left[-\frac{U(x)}{k_B T}\right] \quad (5.53)$$

So

$$Z = \int_{-\infty}^{\infty} dx \exp\left[-\frac{U(x)}{k_B T}\right] \quad (5.54)$$

Average distance  $\langle x \rangle$  is

$$\langle x \rangle = \int_{-\infty}^{\infty} dx x P(x) = \frac{1}{Z} \int_{-\infty}^{\infty} dx x \exp\left[-\frac{U(x)}{k_B T}\right] = \frac{\int_{-\infty}^{\infty} dx x \exp\left[-\frac{U(x)}{k_B T}\right]}{\int_{-\infty}^{\infty} dx \exp\left[-\frac{U(x)}{k_B T}\right]} \quad (5.55)$$

$$\exp\left[-\frac{U(x)}{k_B T}\right] = \exp\left[-\frac{c x^2 - g x^3 + f x^4}{k_B T}\right] = \exp\left[-\frac{c x^2}{k_B T}\right] \exp\left[\frac{g x^3 - f x^4}{k_B T}\right] \quad (5.56)$$

At low  $T$ , we know that  $x$  will be small, so  $\exp\left[\frac{g x^3 - f x^4}{k_B T}\right] \approx 1 + \frac{g x^3 - f x^4}{k_B T}$

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} dx x P(x) = \frac{1}{Z} \int_{-\infty}^{\infty} dx x \exp\left[-\frac{U(x)}{k_B T}\right] = \\ &= \frac{\int_{-\infty}^{\infty} dx x \exp\left[-\frac{c x^2}{k_B T}\right] \left(1 + \frac{g x^3 - f x^4}{k_B T}\right)}{\int_{-\infty}^{\infty} dx \exp\left[-\frac{c x^2}{k_B T}\right] \left(1 + \frac{g x^3 - f x^4}{k_B T}\right)} = \frac{\int_{-\infty}^{\infty} dx x \exp\left[-\frac{c x^2}{k_B T}\right] \left(x + \frac{g x^4 - f x^5}{k_B T}\right)}{\int_{-\infty}^{\infty} dx \exp\left[-\frac{c x^2}{k_B T}\right] \left(1 + \frac{g x^3 - f x^4}{k_B T}\right)} = \frac{\frac{3 g \sqrt{\pi}}{4 k_B \left(\frac{c}{k_B T}\right)^{5/2}} T}{\frac{\sqrt{\pi} (4 c^2 - 3 f k_B T)}{4 c k_B \left(\frac{c}{k_B T}\right)^{3/2}} T} = \frac{3 g k_B T}{4 c^2 - 3 f k_B T} \end{aligned} \quad (5.57)$$

At low  $T$ ,

$$\langle x \rangle = \frac{3 g k_B T}{4 c^2 - 3 f k_B T} \approx \frac{3 g}{4 c^2} k_B T \quad (5.58)$$

For a perfect spring,  $\langle x \rangle = 0$  at any temperature. So there is no thermal expansion.

In reality, there are additional terms in the potential energy beyond just  $x^2$ , so  $\langle x \rangle = \frac{3 g}{4 c^2} k_B T$  increases as a linear function of  $T$  at low  $T$  (at high  $T$ , it is more complicated).

Notice that the expansion is controlled by  $g$ , which is the coefficient of the  $x^3$  term. In fact, if there is no  $x^{2n+1}$  term, there is no thermal expansion. This is because these terms breaks the symmetry of  $x \rightarrow -x$ . Without these terms,  $U(x)$  is symmetric under  $x \rightarrow -x$ . As shown in the previous section, there is no thermal expansion.

## 5.9. Thermal conductivity

### 5.9.1. Definitions

Assumes that we have a solid bar. We heat up one of the end, so the two ends will have different temperature. We know the heat (energy) will flow from the “hot” end to the “cold” end.

- Heat current ( $j_U$ ): the energy transmitted across unit area per unit time.  $j_U = \frac{U}{A t}$
- Temperature gradient  $\frac{dT}{dx}$ : the change of temperature per unit length.

Heat current is proportional to the temperature gradient, and the coefficient is known as the thermal conductivity  $K$ :

$$j_U = -K \frac{dT}{dx} \quad (5.59)$$

### 5.9.2. Thermal conductivity

We can consider a solid as a dilute gas of phonons.

$n$ : density of phonons

$\tau$ : average time between two collisions

$v$ : velocity of phonons (sound velocity)

$v_x$ : the x-component of the velocity

For a particle with velocity  $v$ , it will move  $v_x \tau$  along the x axis between two collisions. Its starting position  $x$  has temperature  $T(x)$ , its ending point has temperature  $T(x + v_x \tau)$ . This particle shall carry some energy from  $x$  to  $x + v_x \tau$ . How much energy?

$$U = \frac{C}{N_p} [T(x) - T(x + v_x \tau)] \quad (5.60)$$

Here  $C$  is the heat capacity contributed by all phonons and  $N_p$  is the total number of phonons. For  $N_p$  phonons, we need energy  $C \Delta T$  to increase the temperature of all phonons by  $\Delta T$ . Therefore, so for 1 phonon, we need energy  $\frac{C \Delta T}{N}$  to increase its temperature by  $\Delta T$ .

$\Delta T$  is  $T(x) - T(x + v_x \tau)$ . If  $\tau$  is small,

$$\Delta T = T(x) - T(x + v_x \tau) \approx -\frac{dT}{dx} v_x \tau \quad (5.61)$$

So

$$U = \frac{C}{N_p} [T(x) - T(x + v_x \tau)] = -\frac{C}{N_p} \frac{dT}{dx} v_x \tau \quad (5.62)$$

How many phonons will cross unit area per unit time?  $n v_x$  where  $n$  the density of phonons  $n = N_p/V$

Total energy cross unit area per unit time;

$$j_U = -\left\langle \frac{C}{N_p} \frac{dT}{dx} v_x \tau n v_x \right\rangle = -\frac{C}{N_p} \frac{dT}{dx} \tau \frac{N_p}{V} \langle v_x^2 \rangle = -\frac{C}{V} \frac{dT}{dx} \tau \langle v_x^2 \rangle \quad (5.63)$$

Here  $\langle \dots \rangle$  means average value.

What is  $\langle v_x^2 \rangle$ ? We know that  $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$ . For an isotropic system,  $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$ . So,  $\langle v^2 \rangle = 3 \langle v_x^2 \rangle$

$$j_U = -\frac{C}{V} \frac{dT}{dx} \tau \frac{\langle v^2 \rangle}{3} = -\frac{1}{3} \frac{C}{V} \frac{dT}{dx} \tau v^2 = -\frac{1}{3} \frac{C}{V} v l \frac{dT}{dx} \quad (5.64)$$

In the last step, we defined the mean-free pass  $l = v \tau$ , which is the average distance a phonon travel between two collisions. So

$$K = \frac{1}{3} \frac{C}{V} v l \quad (5.65)$$

### 5.9.3. Thermal insulation

In many cases, we want some good thermal insulating material in order to keep something cool or warm. For example

- Thermos
- Hot water pipes or chilly water pipes
- Keep the heat inside a house during the winter.
- In thermal dynamic experiments, we try to minimize the contribution from the environment.

The insulating capability of a material is measured  $K$ . Smaller  $K$  means better insulating capability.

If we want a good thermal insulating material, we want to minimize  $K$ .

#### How to minimize $K$ ?

$$K = \frac{1}{3} \frac{C}{V} v l \quad (5.66)$$

We shall choose those materials with small  $C$ ,  $v$  and  $l$ .

- $\frac{C}{V} \propto \frac{\text{Number of atoms}}{V} = \frac{M}{V} = \rho$ . So we want the material to have small density.
- $v_l = \sqrt{(B + \frac{4}{3}G)/\rho}$  and  $v_T = \sqrt{G/\rho}$ . So we want soft materials (with smaller elastic constants)
- More impurities will result in smaller  $l$ . So we want materials with lots of impurities in it. Random solids have more impurities than good crystals. So we want random solids.

Soft material with many impurities and low density: like rubber and foam.

**Another option: We can use gas or vacuum.**

- Gas (air) has much smaller  $C$  and  $v$  than solids.
- Vacuum is even better  $C = 0$  and  $v = 0$ .

**5.9.4. Why is metal cold to touch?**

This is because metals have very large  $K$ . In addition to phonons, the electron in a metal can move, which can also carry heat and energy. The motions of electron will give additional contributions to  $K$ , making it very large.