

Phonon statistics
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This lecture note is prepared for the lecture of Phys.411/511 (Statistical Thermodynamics). Here I show that the phonon statistics is similar to the photon statistics. We show that using a simple calculation, the chemical potential of phonon as well as photon is zero as is expected.

1. Fundamentals: one-simple harmonics

We consider the partition function of a simple harmonics with the angular frequency ω . In quantum mechanics, the system has discrete energy levels,

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega$$

where $n = 0, 1, 2, \dots$. $\frac{1}{2}\hbar\omega$ is the zero-point energy. For simplicity, hereafter we neglect the zero-point energy. The partition function (in the canonical ensemble) is

$$Z_{C1} = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = (1 - e^{-\beta\hbar\omega})^{-1}$$

The average energy is

$$\begin{aligned} U &= \langle \varepsilon \rangle \\ &= -\frac{\partial}{\partial \beta} \ln Z_{C1} \\ &= \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta\hbar\omega}) \\ &= \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \end{aligned}$$

Note that the chemical potential of phonon is zero like that of photon.

The heat capacity is given by

$$C = \frac{\partial U}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial U}{\partial \beta} = -\frac{1}{k_B T^2} \frac{\partial U}{\partial \beta}$$

or

$$C = k_B (\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

In the high temperature limit $x \ll 1$, where $x = \beta \hbar \omega$,

$$\frac{C}{k_B} \rightarrow 1$$

which is the same as that predicted from the energy partition law; $\frac{1}{2}k_B$ from the kinetic energy and $\frac{1}{2}k_B$ from the potential energy. Note that the Hamiltonian of the simple harmonics is

$$H = \frac{1}{2m} p^2 + \frac{1}{2} m \omega^2 x^2 .$$

We make a plot of C/k_B as a function of $x = \beta \hbar \omega$.

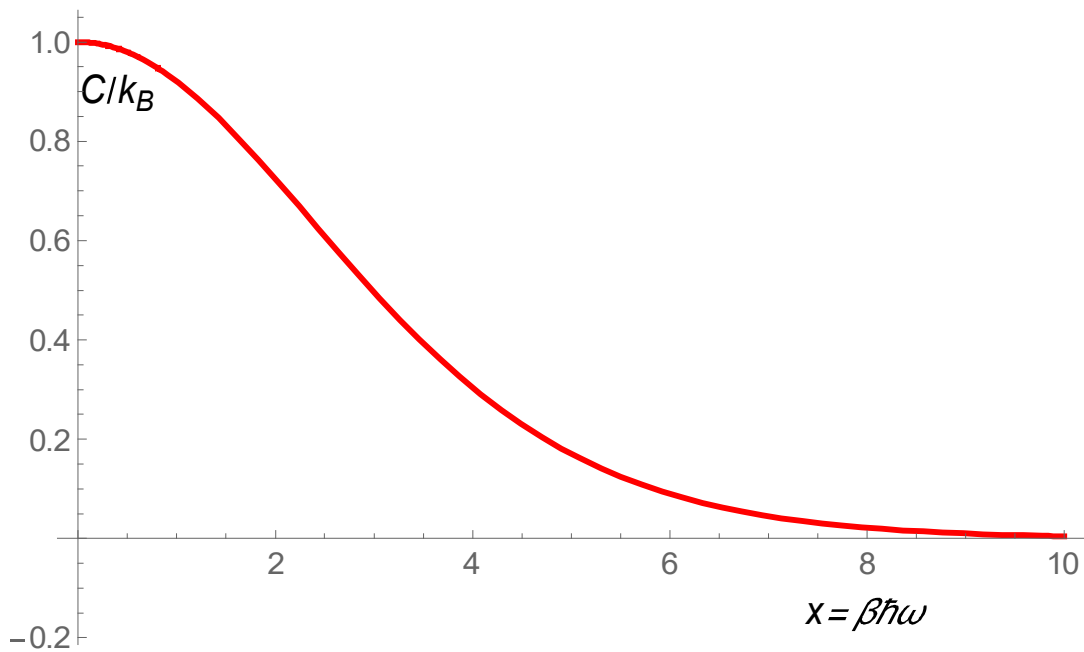


Fig. C/k_B vs $x = \beta \hbar \omega$.

We also make a plot of C/k_B as a function of $x = \frac{1}{\beta\hbar\omega}$

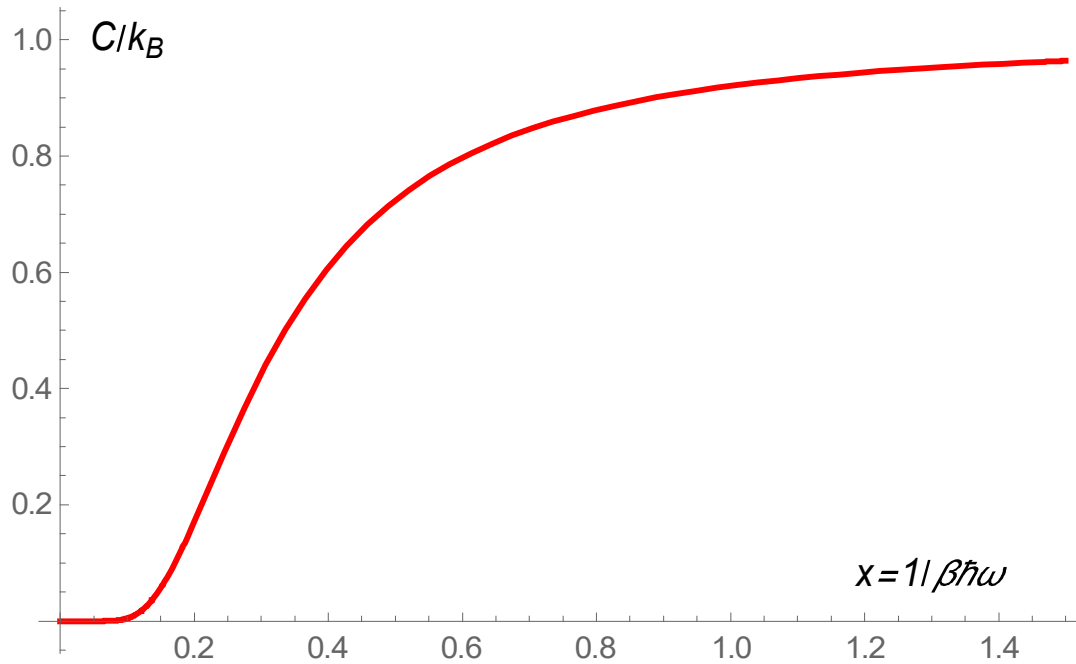


Fig. C/k_B vs $x = 1/(\beta\hbar\omega)$.

2. General case; many-mode system

We now consider the system with many modes (denoted by $|\mathbf{k}\rangle$ with angular frequency ω_k).

The partition function of this system is

$$\begin{aligned} Z_C &= Z_{C1}(\mathbf{k}_1)Z_{C1}(\mathbf{k}_2)Z_{C1}(\mathbf{k}_3)\dots\dots\dots \\ &= \prod_{\mathbf{k}} Z_{C1}(\mathbf{k}) \\ &= \prod_{\mathbf{k}} \frac{e^{\frac{\beta\hbar\omega_k}{2}}}{e^{\beta\hbar\omega_k} - 1} \end{aligned}$$

and

$$\begin{aligned} \ln Z_C &= \sum_{\mathbf{k}} \ln[e^{\frac{\beta\hbar\omega_k}{2}} (1 - e^{-\beta\hbar\omega_k})^{-1}] \\ &= \sum_{\mathbf{k}} \left[-\frac{\beta\hbar\omega_k}{2} + \ln(1 - e^{-\beta\hbar\omega_k})^{-1} \right] \end{aligned}$$

where

$$\begin{aligned} Z_{C1}(\mathbf{k}) &= e^{-\frac{\beta\hbar\omega_k}{2}} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_k} \\ &= e^{-\frac{\beta\hbar\omega_k}{2}} (1 - e^{-\beta\hbar\omega_k})^{-1} \end{aligned}$$

We neglect the zero-point energy term in $\ln Z_C$. Thus we have

$$\ln Z_C = \sum_k \ln(1 - e^{-\beta\hbar\omega_k})^{-1}$$

The Helmholtz free energy is

$$F = -k_B T \ln Z_C = k_B T \sum_k \ln(1 - e^{-\beta\hbar\omega_k})$$

The internal energy is

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta} \ln Z_C \\ &= \frac{\partial}{\partial\beta} \sum_k \ln(1 - e^{-\beta\hbar\omega_k}) \\ &= \sum_k \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \end{aligned}$$

Here we introduce the density of states $D(\omega)$. The number of states is $D(\omega)d\omega$ for $\omega - \omega + d\omega$.

Then U can be expressed by

$$U = \int D(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} d\omega$$

The heat capacity is obtained as

$$\begin{aligned}
C &= \frac{\partial U}{\partial T} \\
&= -\frac{1}{k_B T^2} \frac{\partial U}{\partial \beta} \\
&= k_B \int D(\omega) \frac{(\beta \hbar \omega)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} d\omega
\end{aligned}$$

2. The lattice vibrations and normal modes

We consider the system consisting of N unit cells. Suppose that there is one atom per unit cell. There are $3N$ modes, since there are three polarizations (one longitudinal and two transverse modes). The density of states is defined by $D(\omega)$. $D(\omega)d\omega$ is the number of normal modes with the angular frequency between ω and $\omega + d\omega$. The total number of modes is N for each polarization

$$\int_0^{\infty} D(\omega) d\omega = N$$

So we get the expression of the partition function as

$$\ln Z_C = -\int_0^{\infty} \ln(1 - e^{-\beta \hbar \omega}) D(\omega) d\omega$$

The mean energy is

$$U = -\frac{\partial \ln Z_C}{\partial \beta} = \int_0^{\infty} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} D(\omega) d\omega.$$

The heat capacity at constant volume

$$C_V = \frac{\partial U}{\partial T} = -k_B \beta^2 \frac{\partial U}{\partial \beta} = k_B \int_0^{\infty} \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} (\beta \hbar \omega)^2 D(\omega) d\omega.$$

The Helmholtz free energy F is

$$\begin{aligned}
F &= -k_B T \ln Z_C \\
&= k_B T \int_0^{\infty} \ln(1 - e^{-\beta \hbar \omega}) D(\omega) d\omega
\end{aligned}$$

The entropy S is

$$\begin{aligned}
 S &= \frac{U}{T} - \frac{F}{T} \\
 &= \frac{1}{T} \int_0^{\infty} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} D(\omega) d\omega - k_B \int_0^{\infty} \ln(1 - e^{-\beta\hbar\omega}) D(\omega) d\omega \} \\
 &= k_B \int_0^{\infty} \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega}) \right] D(\omega) d\omega
 \end{aligned}$$

3. Debye model

The density of state is expressed by

$$D(\omega)d\omega = \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

for each polarization (one longitudinal mode and two transverse modes). We assume that

$$\omega = vk$$

Then we have

$$D(\omega)d\omega = \frac{V}{(2\pi)^3 v^3} 4\pi\omega^2 d\omega = \frac{V}{2\pi^2 v^3} \omega^2 d\omega$$

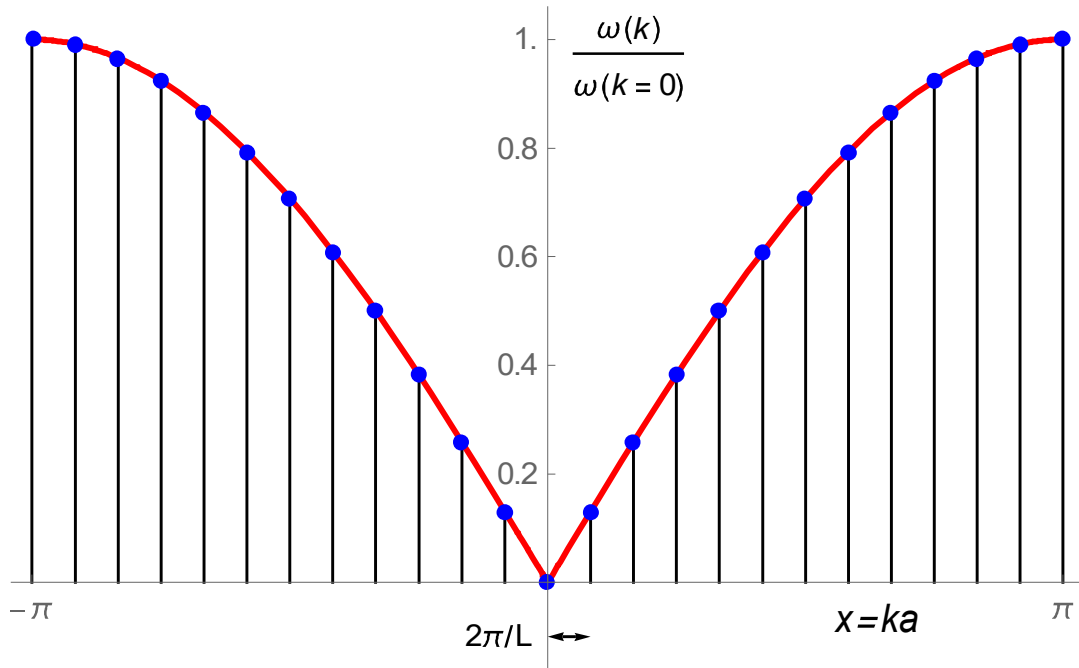


Fig. Quantized energy level for the phonon. The phonon dispersion relation.

The total number of states are N , where N is the number of unit cell. We introduce a Debye angular frequency (cut-off) ω_D .

$$\int_0^{\omega_D} D(\omega) d\omega = N$$

or

$$\int_0^{\omega_D} \frac{V}{2\pi^2 v^3} \omega^2 d\omega = \frac{V}{2\pi^2 v^3} \frac{\omega_D^3}{3} = \frac{V \omega_D^3}{6\pi^2 v^3} = N$$

or

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

The Debye temperature is defined by

$$\hbar \omega_D = k_B \Theta_D.$$

$$\begin{aligned}
C_V &= k_B \int_0^{\omega_D} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} (\beta\hbar\omega)^2 D(\omega) d\omega \\
&= k_B \frac{V}{2\pi^2 (v\beta\hbar)^3} \int_0^{\omega_D} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} (\beta\hbar\omega)^4 d(\beta\hbar\omega) \\
&= k_B \frac{V}{2\pi^2 (v\beta\hbar)^3} \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \\
&= 3Nk_B \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\end{aligned}$$

where $x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\Theta}{T}$. We note that

$$\frac{V}{2\pi^2 (v\beta\hbar)^3} = \frac{3N}{\omega_D^3} \frac{2\pi^2 v^3}{2\pi^2 (v\beta\hbar)^3} = \frac{3N}{\omega_D^3} \frac{1}{(\beta\hbar)^3} = 3N \left(\frac{T}{\Theta}\right)^3$$

since

$$\frac{V\omega_D^3}{6\pi^2 v^3} = N.$$

Then we have the final result for the heat capacity with 3 polarization (1 longitudinal and 2 transverse modes),

$$\begin{aligned}
C_V &= 3 \times 3Nk_B \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \\
&= 3Nk_B \left[3 \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \right] \\
&= 3Nk_B f_D \left(\frac{T}{\Theta}\right)
\end{aligned}$$

Here we introduce the Debye function as

$$f_D\left(\frac{T}{\Theta}\right) = 3\left(\frac{T}{\Theta}\right)^3 \int_0^{T/\Theta} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$f_D(y) = \frac{3}{y^3} \int_0^y \frac{x^4 e^x}{(e^x - 1)^2} dx$$

The integrand $\frac{x^4 e^x}{(e^x - 1)^2}$ can be approximated as

$$\frac{x^4 e^x}{(e^x - 1)^2} = x^2 - \frac{x^4}{12} + \dots$$

in the vicinity of $x \approx 0$ (in the limit of high temperature). We note that

$$f_D(y=0) = 1,$$

leading to the heat capacity at high temperature limit ($y \approx 0$)

$$C_V = 3Nk_B$$

This means that the heat capacity for $N = N_A$ is $3R$, which is so-called **Dulong-Petit law**.

At low temperatures ($y \rightarrow \infty$)

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}$$

leading to

$$C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta}\right)^3$$

((Note))

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = 4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{4\pi^4}{15}$$

This is known as the Debye T^3 law.

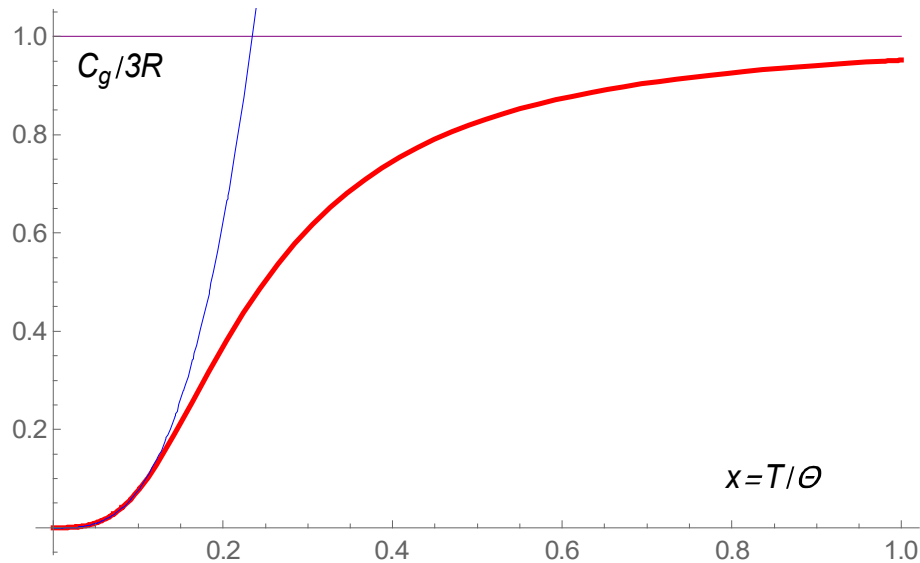


Fig. Plot of $C/(3R)$ vs T/Θ . The low temperature behavior [$C/(3R) \propto (T/\Theta)^3$] is denoted by the blue line.

Table of the Debye temperature

Li 344	Be 1440	Debye temperature in Kelvin (estimated at low temperature)										B ...	C 2230 (diamond)	N ...	O ...	F ...	Ne 75
Na 158	Mg 400											Al 428	Si 645	P ...	S ...	Cl ...	Ar 92
K 91	Ca 230	Sc 360	Ti 420	V 380	Cr 630	Mn 410	Fe 470	Co 445	Ni 450	Cu 343	Zn 327	Ga 320	Ge 374	As 282	Se 90	Br ...	Kr 72
Rb 56	Sr 147	Y 280	Zr 291	Nb 275	Mo 450	Tc ...	Ru 600	Rh 480	Pd 274	Ag 225	Cd 209	In 108	Sn 200	Sb 211	Te 153	I ...	Xe 64
Cs 38	Ba 110	La 142	Hf 252	Ta 240	W 400	Re 430	Os 500	Ir 420	Pt 240	Au 165	Hg 71.9	Tl 78.5	Pb 105	Bi 119	Po ...	At ...	Rn 64

4. Approach for the evaluation of U

We calculate the internal energy using the formula as

$$U = \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} D(\omega) d\omega = \frac{3\hbar V}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega$$

where

$$D(\omega) d\omega = \frac{V}{(2\pi)^3 v^3} 4\pi\omega^2 d\omega = \frac{V}{2\pi^2 v^3} \omega^2 d\omega$$

$$\int_0^{\omega_D} \frac{V}{2\pi^2 v^3} \omega^2 d\omega = \frac{V}{2\pi^2 v^3} \frac{\omega_D^3}{3} = N$$

or

$$N = \frac{V\omega_D^3}{6\pi^2 v^3}$$

We note that

$$U = \frac{3\hbar V}{2\pi^2 v^3} \frac{1}{(\beta\hbar)^4} \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx$$

and

$$\begin{aligned} \frac{U}{N} &= \frac{6\pi^2 v^3}{V\omega_D^3} \frac{3\hbar V}{2\pi^2 v^3} \frac{1}{(\beta\hbar)^4} \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx \\ &= 9k_B T \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx \end{aligned}$$

or

$$U = 9Nk_B T \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^3}{e^x - 1} dx$$

For the low temperature limit ($T \ll \Theta$)

$$U = 9Nk_B T \left(\frac{T}{\Theta} \right)^3 \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{3\pi^4}{5} Nk_B T \left(\frac{T}{\Theta} \right)^3$$

and the corresponding heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta} \right)^3$$

where

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{5}.$$

For the low temperature limit ($T \gg \Theta$)

$$U = 9Nk_B T \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} x^2 dx = 3Nk_B T$$

and the corresponding heat capacity is

$$C = \frac{\partial U}{\partial T} = 3Nk_B$$

Debye Model of Heat Capacity of Solids

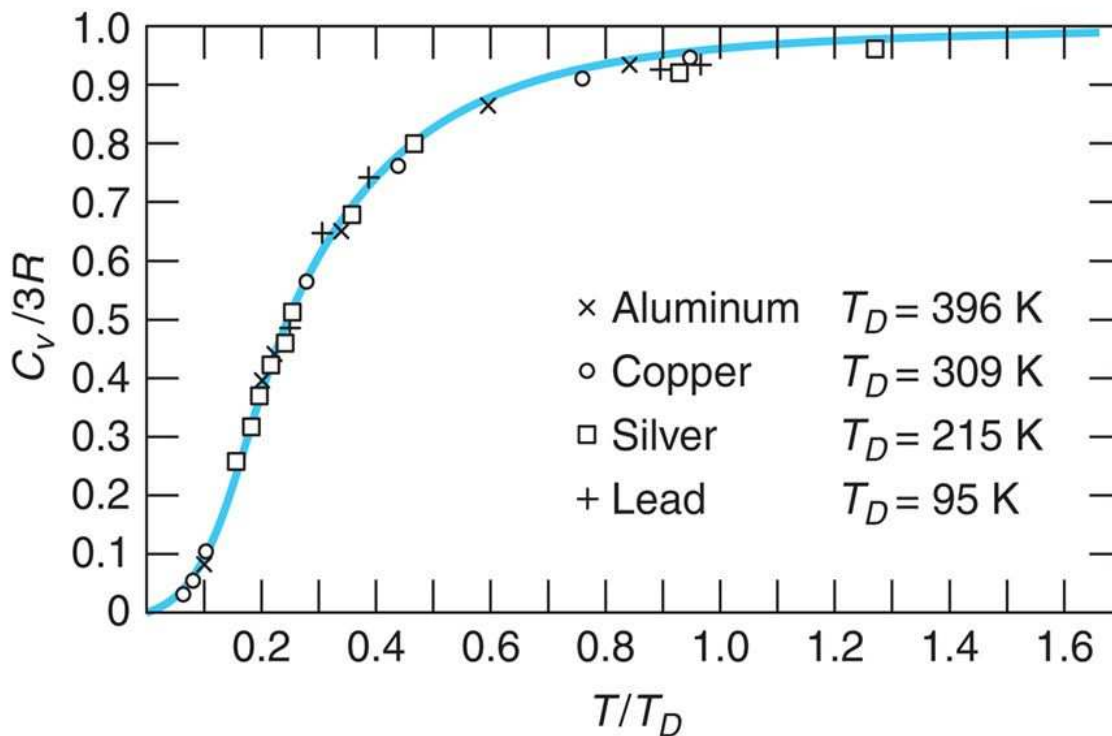


Fig. Scaling plot of $C/3R$ as a function of T/Θ for Al, Cu, Ag, and Pb.

http://images.slideplayer.com/25/7784675/slides/slide_63.jpg

5. Chemical potential

We calculate the chemical potential for phonon as follows. I want to show that the chemical potential is equal to zero just like photon.

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

or

$$\ln \Theta = \ln \frac{\hbar v}{k_B} + \frac{1}{3} \ln(6\pi^2 N) - \frac{1}{3} \ln V$$

$$\frac{d\Theta}{\Theta} = -\frac{1}{3} \frac{dV}{V}$$

The Helmholtz free energy is

$$F = k_B T \int_0^{\omega_D} \ln(1 - e^{-\beta \hbar \omega}) D(\omega) d\omega$$

with the density of states (Debye model)

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

F can be written as

$$\begin{aligned} F &= -k_B T \ln Z \\ &= k_B T \int_0^{\omega_D} \ln(1 - e^{-\beta \hbar \omega}) \frac{V}{2\pi^2 v^3} \omega^2 d\omega \\ &= k_B T \frac{V}{2\pi^2 v^3} \frac{1}{\beta^3 \hbar^3} \int_0^{\Theta/T} \ln(1 - e^{-x}) x^2 dx \\ &= 3Nk_B T \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \ln(1 - e^{-x}) x^2 dx \end{aligned}$$

where $x = \beta \hbar \omega$. When $y = \frac{\Theta}{T}$,

$$\begin{aligned} \int_0^{\Theta/T} \ln(1 - e^{-x}) x^2 dx &= \int_0^y \ln(1 - e^{-x}) x^2 dx \\ &= \frac{y^3}{3} \ln(1 - e^{-y}) - \frac{1}{3} \int_0^y \frac{x^3}{e^x - 1} dx \\ &= \frac{y^3}{3} [\ln(1 - e^{-y}) - D(y)] \end{aligned}$$

We define the Debye function as

$$D(y) = \frac{1}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx$$

and

$$\begin{aligned} D'(y) &= \frac{1}{y^6} \left[\frac{y^6}{e^y - 1} - 3y^2 \int_0^y \frac{x^3}{e^x - 1} dx \right] \\ &= \frac{1}{e^y - 1} - \frac{3}{y} D(y) \end{aligned}$$

Thus we have

$$\begin{aligned} F &= Nk_B T [\ln(1 - e^{-y}) - D(y)] \\ &= Nk_B T [-y + \ln(e^y - 1) - D(y)] \end{aligned}$$

We note that

$$\frac{1}{\Theta} \left(\frac{\partial \Theta}{\partial V} \right)_T = -\frac{1}{3V}, \quad \left(\frac{\partial y}{\partial V} \right)_T = -\frac{y}{3V}$$

The pressure P is

$$\begin{aligned} P &= - \left(\frac{\partial F}{\partial V} \right)_T \\ &= - \left(\frac{\partial F}{\partial y} \right) \left(\frac{\partial y}{\partial V} \right)_T \\ &= \frac{y}{3V} \left(\frac{\partial F}{\partial y} \right) \end{aligned}$$

Thus we get

$$PV = \frac{1}{3} Nk_B T y \left[\frac{1}{e^y - 1} - D'(y) \right]$$

The internal energy U :

$$\begin{aligned} \ln Z &= -N [\ln(1 - e^{-y}) - D(y)] \\ &= -N [-y + \ln(e^y - 1) - D(y)] \end{aligned}$$

The internal energy is

$$\begin{aligned}
U &= -\frac{\partial}{\partial \beta} \ln Z \\
&= -k_B \Theta \frac{\partial}{\partial y} \ln Z \\
&= Nk_B \Theta \left[\frac{1}{e^y - 1} - D'(y) \right]
\end{aligned}$$

So we get the relation

$$PV = \frac{1}{3}U$$

which is the same form as that for photon. The Gibbs free energy is

$$\begin{aligned}
G &= \mu N \\
&= F + PV \\
&= Nk_B T [-y + \ln(e^y - 1) - D(y)] + \frac{1}{3} Nk_B T y \left[\frac{1}{e^y - 1} - D'(y) \right] \\
&= Nk_B T [-y + \ln(e^y - 1) - D(y)] + \frac{1}{3} y \left[\frac{1}{e^y - 1} - \frac{1}{e^y - 1} + 3D(y) \right] \\
&= Nk_B T [-y + \ln(e^y - 1)] \\
&\simeq Nk_B T (-y + \ln e^y) \\
&= 0
\end{aligned}$$

or

$$\mu = 0$$

where

$$D'(y) = \frac{1}{e^y - 1} - \frac{3}{y} D(y)$$

Note that the chemical potential is equal to zero when $e^y \gg 1$. Since $y = \Theta / T \gg 1$, the chemical potential ($\mu = 0$) holds valid at low temperature region ($T \ll \Theta$).

In summary, it is concluded that the chemical potential is zero and $PV = U / 3$, just like photon.

REFERENCE

A.H. Carter, Classical and Statistical Thermodynamics (Prentice Hall, 2001).

6. Einstein model

We start with

$$Z_C = \prod_{r=1}^{3N} Z_{C1}(r) = \prod_{r=1}^{3N} \frac{e^{-\frac{\beta\hbar\omega_r}{2}}}{1 - e^{-\beta\hbar\omega_r}}$$

Suppose that $\omega_r = \omega$, which is independent of r . This mode is called an optical mode.

$$Z_C = \left(\frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \right)^{3N}$$

Then we have

$$\begin{aligned} \ln Z_C &= -\sum_{r=1}^{3N} \frac{\beta\hbar\omega}{2} - \sum_{r=1}^{3N} \ln(1 - e^{-\beta\hbar\omega_r}) \\ &= -\frac{3N\beta\hbar\omega}{2} - 3N \ln(1 - e^{-\beta\hbar\omega}) \end{aligned}$$

Now we neglect the contribution of the zero point energy. Then we have

$$\ln Z_C = -3N \ln(1 - e^{-\beta\hbar\omega})$$

The Helmholtz free energy:

$$F = -3Nk_B T \ln(1 - e^{-\beta\hbar\omega})$$

The average energy:

$$U = -\frac{\partial \ln Z_C}{\partial \beta} = 3N \left(\frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right) = 3N \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right)$$

The heat capacity:

$$C = \frac{\partial U}{\partial T} = -k_B \beta^2 \frac{\partial E}{\partial \beta} = 3Nk_B (\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

We define the Einstein temperature as

$$\beta \hbar \omega = \frac{\Theta_E}{T}$$

In the limit of low temperatures, we have

$$C = 3Nk_B (\beta \hbar \omega)^2 e^{-\beta \hbar \omega} = 3Nk_B \left(\frac{\Theta_E}{T}\right)^2 e^{-\frac{\Theta_E}{T}} \quad \text{for } T \ll \Theta_E$$

In the limit of high temperature limit

$$C = 3Nk_B \quad \text{for } T \gg \Theta_E$$

APPENDIX-I Acoustic and optical branches

We assume that N is the number of unit cells in the system. Each mode has 3 degrees of freedom (1 longitudinal mode and 2 transverse modes). Then the total number of modes is $3 \times N = 3N$.

(a)

In the case of one atom per unit cell, we have $3N$ degree of freedom, with N longitudinal acoustic mode and transverse acoustic mode $2N$

(b)

We consider the number of degrees of freedom of the atoms. With p atoms in the primitive cell and N primitive cells, there are pN atoms. Each atom has three degrees of freedom, one for each of the x, y, z directions, making a total of $3pN$ degrees of freedom for the crystal. The number of allowed k values in a single branch is just N for one Brillouin zone. Thus, the one LA and two TA branches have a total of $3N$ modes. The remaining $(3p - 3) \times N$ degrees of freedom are accommodated by the optical branches.

3 acoustical branches

1 longitudinal acoustical (LA) mode

2 transverse acoustical (TA) mode

$3p - 3$ optical branches

$(p - 1)$ longitudinal optical (LO) mode
 $2(p - 1)$ transverse optical (TO) mode

For $p = 2$, for example, we have 1 LA, 1 LO modes, and 2 TA and 2 TO modes.

APPENDIX-II Dulong-Petit law

https://en.wikipedia.org/wiki/Dulong%E2%80%93Petit_law

The **Dulong–Petit law**, a thermodynamic proposed in 1819 by French physicists Pierre Louis Dulong and Alexis Thérèse Petit, states the classical expression for the molar specific [heat capacity] of certain chemical elements. Experimentally the two scientists had found that the heat capacity per weight (the mass-specific heat capacity) for a number of elements was close to a constant value, *after* it had been multiplied by a number representing the presumed relative atomic weight of the element. These atomic weights had shortly before been suggested by Dalton.

The molar heat capacity of most elements at 25°C is in the range between $2.8 R$ and $3.4 R$. In modern terms, Dulong and Petit found that the heat capacity of a mole of many solid elements is about $3R$, where R is the modern constant called the universal gas constant. Dulong and Petit were unaware of the relationship with R , since this constant had not yet been defined from the later kinetic theory of gases. The value of $3R$ is about 25 joules per kelvin, and Dulong and Petit essentially found that this was the heat capacity of certain solid elements per mole of atoms they contained.

The modern theory of the heat capacity of solids states that it is due to lattice vibrations in the solid and was first derived in crude form from this assumption by Albert Einstein in 1907. The Einstein solid model thus gave for the first time a reason why the Dulong–Petit law should be stated in terms of the classical heat capacities for gases.

APPENDIX-III Evaluation of Debye temperature for Cu

$$\Theta = \frac{\hbar v}{k_B} (6\pi^2 n)^{1/3}$$

Copper has a fcc structure with the lattice constant $a = 3.61\text{\AA}$ (conventional cell). The number density is

$$n = \frac{4}{a^3} = 8.50 \times 10^{22} / \text{cm}^3.$$

When $v = 2.6117 \text{ km/s}$, we have $\Theta = 341.9 \text{ K}$, which in good agreement (ISSP) with the one reported;

$\Theta = 343 \text{ K}$ (Kittel).

