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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 $n = 0, 1, 2, ..., \frac{1}{2}\hbar\omega$ is the zero-point energy. For simplicity, hereafter we neglect the zeropoint 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

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

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 $x = \beta \hbar \omega$,

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

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

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

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



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



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

2. General case; many-mode system

We now consider the system with many modes (denoted by $|k\rangle$ with angular frequency ω_k). The partition function of this system is

$$Z_{C} = Z_{C1}(k_{1})Z_{C1}(k_{2})Z_{C1}(k_{3}).....$$
$$= \prod_{k} Z_{C1}(k)$$
$$= \prod_{k} \frac{e^{\frac{\beta h \omega_{k}}{2}}}{e^{\beta h \omega_{k}} - 1}$$

and

$$\ln Z_C = \sum_k \ln \left[e^{-\frac{\beta\hbar\omega_k}{2}} (1 - e^{-\beta\hbar\omega_k})^{-1} \right]$$
$$= \sum_k \left[-\frac{\beta\hbar\omega_k}{2} + \ln(1 - e^{-\beta\hbar\omega_k})^{-1} \right]$$

where

$$Z_{C1}(\boldsymbol{k}) = e^{-\frac{\beta\hbar\omega_{\boldsymbol{k}}}{2}} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_{\boldsymbol{k}}}$$
$$= e^{-\frac{\beta\hbar\omega_{\boldsymbol{k}}}{2}} (1 - e^{-\beta\hbar\omega_{\boldsymbol{k}}})^{-1}$$

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

$$U = -\frac{\partial}{\partial\beta} \ln Z_{C}$$
$$= \frac{\partial}{\partial\beta} \sum_{k} \ln(1 - e^{-\beta\hbar\omega_{k}})$$
$$= \sum_{k} \frac{\hbar\omega_{k}}{e^{\beta\hbar\omega_{k}} - 1}$$

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

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

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 $D(\omega) \cdot D(\omega)d\omega$ 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

$$\ln Z_{c} = -\int_{0}^{\infty} \ln(1 - e^{-\beta\hbar\omega_{r}}) D(\omega) d\omega$$

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

$$C_{V} = \frac{\partial U}{\partial T} = -k_{B}\beta^{2}\frac{\partial E}{\partial \beta} = k_{B}\int_{0}^{\infty} \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^{2}}(\beta\hbar\omega)^{2}D(\omega)d\omega.$$

The Helmholtz free energy F is

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

The entropy S is

$$S = \frac{U}{T} - \frac{F}{T}$$

= $\frac{1}{T} \int_{0}^{\infty} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} D(\omega) d\omega - k_{B} \int_{0}^{\infty} \ln(1 - e^{-\beta \hbar \omega}) D(\omega) d\omega] \}$
= $k_{B} \int_{0}^{\infty} \left[\frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} - \ln(1 - e^{-\beta \hbar \omega}) \right] D(\omega) d\omega$

3. Debye model

The density of state is expressed by

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

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

$$\omega = vk$$

Then we have



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

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

The Debye temperature is defined by

$$\begin{split} \hbar\omega_{D} &= k_{B}\Theta_{D}.\\ C_{V} &= k_{B}\int_{0}^{\omega_{D}} \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^{2}} (\beta\hbar\omega)^{2} D(\omega) d\omega\\ &= k_{B} \frac{V}{2\pi^{2}(\nu\beta\hbar)^{3}} \int_{0}^{\omega_{D}} \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^{2}} (\beta\hbar\omega)^{4} d(\beta\hbar\omega)\\ &= k_{B} \frac{V}{2\pi^{2}(\nu\beta\hbar)^{3}} \int_{0}^{\Theta/T} \frac{x^{4}e^{x}}{\left(e^{x} - 1\right)^{2}} dx\\ &= 3Nk_{B} \left(\frac{T}{\Theta}\right)^{3} \int_{0}^{\Theta/T} \frac{x^{4}e^{x}}{\left(e^{x} - 1\right)^{2}} dx \end{split}$$

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

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

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),

$$C_{V} = 3 \times 3Nk_{B} \left(\frac{T}{\Theta}\right)^{3} \int_{0}^{\Theta/T} \frac{x^{4}e^{x}}{\left(e^{x}-1\right)^{2}} dx$$
$$= 3Nk_{B} \left[3\left(\frac{T}{\Theta}\right)^{3} \int_{0}^{\Theta/T} \frac{x^{4}e^{x}}{\left(e^{x}-1\right)^{2}} dx\right]$$
$$= 3Nk_{B} f_{D} \left(\frac{T}{\Theta}\right)$$

Here we introduce the Debye function as

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

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

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

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 3*R*, which is so-called Dulong-Petit law.

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

$$\int_{0}^{\infty} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx = \frac{4\pi^4}{15}$$

leading to

$$C_{V} = \frac{12\pi^{4}}{5} N k_{B} \left(\frac{T}{\Theta}\right)^{3}$$

((Note))

$$\int_{0}^{\infty} \frac{x^{4} e^{x}}{\left(e^{x} - 1\right)^{2}} dx = 4 \int_{0}^{\infty} \frac{x^{3}}{e^{x} - 1} dx = \frac{4\pi^{4}}{15}$$

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)											C 2230 (diamond)	N 	0 	F 	Ne 75
Na 158	Mg 400						Al 428	Si 645	Р 	S 	C1 	Ar 92					
К	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
91	230	360	420	380	630	410	470	445	450	343	327	320	374	282	90		72
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
56	147	280	291	275	450		600	480	274	225	209	108	200	211	153		64
Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	T1	Pb	Bi	Ро	At	Rn
38	110	142	252	240	400	430	500	420	240	165	71.9	78.5	105	119			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

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

$$\int_{0}^{\omega_{D}} \frac{V}{2\pi^{2} c_{s}^{3}} \omega^{2} d\omega = \frac{V}{2\pi^{2} c_{s}^{3}} \frac{\omega_{D}^{3}}{3} = N$$

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

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

or

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

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

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

and the corresponding heat capacity is

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

where

$$\int_{0}^{\infty} \frac{x^{3}}{e^{x}-1} dx = \frac{\pi^{4}}{5}.$$

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

$$U = 9Nk_BT\left(\frac{T}{\Theta}\right)^{3} \int_{0}^{\Theta/T} x^2 dx = 3Nk_BT$$

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

5. 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

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

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:

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

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

$$C = 3Nk_B(\beta\hbar\omega)^2 e^{-\beta\hbar\omega} = 3Nk_B(\frac{\Theta_E}{T})^2 e^{-\frac{\Theta_E}{T}}$$

In the limit of high temperature limit

$$C = 3Nk_{B}$$

for $T >> \Theta_E$

for $T \ll \Theta_{F}$

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 3*R*, 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 3*R* 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 = 3.61Å (conventional cell). The number density is

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

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

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

APPENDIX Prof. Debye in Cornell University

https://en.wikipedia.org/wiki/Peter_Debye

In 1939 Debye traveled to the United States to deliver the Baker Lectures at Cornell University in Ithaca, New York. After leaving Germany in early 1940, Debye became a professor at Cornell, chaired the chemistry department for 10 years, and became a member of Alpha Chi Sigma. In 1946 he became an American citizen. Unlike the European phase of his life, where he moved from city to city every few years, in the United States Debye remained at Cornell for the remainder of his career. He retired in 1952, but continued research until his death. Much of Debye's work at Cornell concerned the use of light-scattering techniques (derived from his X-ray scattering work of years earlier) to determine the size and molecular weight of polymer

molecules. This started as a result of his research during World War II on synthetic rubber, but was extended to proteins and other macromolecules. In April 1966, Debye suffered a heart attack, and in November of that year a second one proved fatal. He is buried in the Pleasant Grove Cemetery (Ithaca, New York, USA).