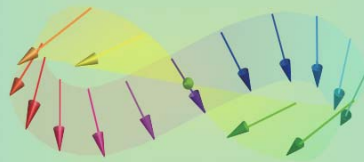


# Introductory Nanotechnology ~ Basic Condensed Matter Physics ~



Atsufumi Hirohata

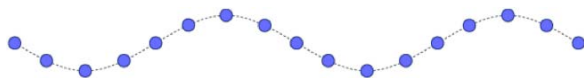
*Department of Electronics*

THE UNIVERSITY of York



## Quick Review over the Last Lecture

Waves :

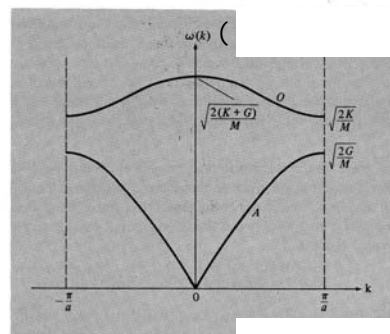


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Wave modes :



( )

Photon : ( ), phonon : ( )



## Contents of Introductory Nanotechnology

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First half of the course :

Basic condensed matter physics

1. Why *solids* are *solid* ?
2. What is the *most common atom* on the earth ?
3. How does an electron travel in a material ?
4. How does lattices vibrate thermally ?
5. What is a *semi-conductor* ?
6. How does an electron tunnel through a barrier ?
7. Why does a magnet attract / retract ?
8. What happens at interfaces ?

Second half of the course :

Introduction to nanotechnology (nano-fabrication / application)

### How Does Lattices Vibrate Thermally ?

- Specific heat
- Einstein model
- Debye model



## Imagine You Are on a Beach in Summer ...

When you walk on a beach ...



Water : difficult to be warmed up / cooled down.



## Specific Heat Capacity

In order to compare :

Thermal energy required to increase temperature of a unit-volume material

(1 mole at constant volume)

Molecule	Material	$c_{V,\text{mol}}$ [J/mol·K]
1-atom	He	12.5
	Ar	12.5
2-atom	H <sub>2</sub>	20.4
	CO	20.8
	HCl	21.0
3-atom	H <sub>2</sub> S	26.9
	SO <sub>2</sub>	32.3
Many-atom (>3)	CH <sub>4</sub>	27.0
	C <sub>2</sub> H <sub>2</sub>	33.1

$c_{V,\text{mol}}$  increases with increasing numbers of atoms in a molecule.

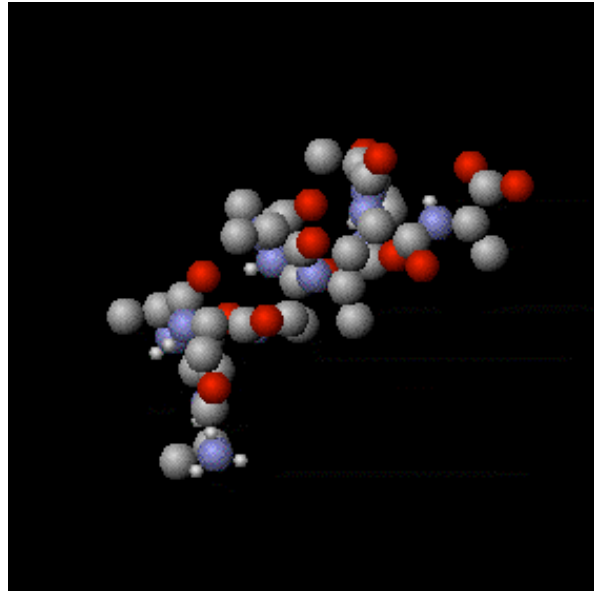
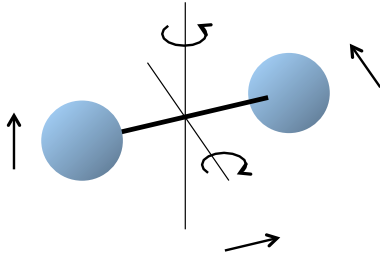
→ increases with increasing numbers of degree of freedom.



## Thermal Fluctuation in a Molecule

At finite temperature :

Atoms in a molecule vibrates (translation and rotation).

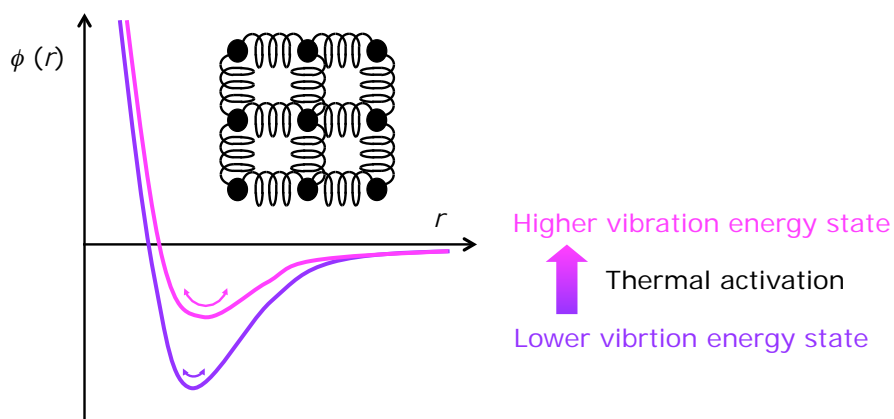


\* <http://www.wikipedia.org>



## Amplitude of Lattice Vibration

Amplitude increases with increasing temperature :





## Specific Heat 1 - Classical Model for Ideal Gas

Equal volume specific heat :

$$c_V = \left( \frac{\partial U}{\partial T} \right)_V$$

According to Dulong-Petit empirical law,

$$c_V = 6 \text{ [cal/mol} \cdot \text{K]} = 25.1 \text{ [J/mol} \cdot \text{K]} \quad (T \approx RT)$$



In order to explain this law, L. Boltzmann introduced classical thermodynamics :

Average kinetic energy for a particle in a vacuum is written as follows in 3D

$$E_K = 3 \cdot \frac{k_B T}{2}$$

For 1 mole ( $N_0$  : Avogadro constant),

$$E_{K, \text{mol}} = \frac{3N_0 k_B T}{2} \equiv \frac{3RT}{2}$$

where  $R = N_0 k_B$  : gas constant, and  $E_{K, \text{mol}}$  equals to internal energy of ideal gas.

\* <http://www.wikipedia.org>



## Specific Heat 1 - Classical Model for a Crystal Lattice

For a crystal lattice, each atom at a lattice point have potential energy of

$$E_{U, \text{mol}} = \frac{3N_0 k_B T}{2} \equiv \frac{3RT}{2}$$

Therefore, internal energy of 1 mol solid crystal is written as

$$U_{\text{mol}} = E_{K, \text{mol}} + E_{U, \text{mol}} = 3RT$$

By substituting  $R = 1.99 \text{ cal/mol} \cdot \text{K}$ ,

$$c_{V, \text{mol}} = \left( \frac{\partial U_{\text{mol}}}{\partial T} \right)_V = 3R = 5.96 \text{ [cal/mol} \cdot \text{K]}$$

This agrees very well with Dulong-Petit empirical law.

However, about 1900,

J. Dewar found that specific heat approaches 0 at low temperature.



\* <http://www.wikipedia.org>



## Specific Heat 2 - Einstein Model 1

In a crystal lattice as a harmonic oscillator, energy is expressed as

$$E_n = \frac{h\nu_E}{2} + nh\nu_E \quad (n = 0, 1, 2, \dots)$$

Einstein assumed that  $\nu$  is constant for all the same atoms in the oscillator.

Now, the numbers of the oscillators with energy of  $E_0, E_1, E_2, \dots$  are assumed to be  $N_0, N_1, N_2, \dots$ , respectively, and these numbers to follow the Maxwell-Boltzmann distribution.

$$\frac{N_n}{N_0} = \exp\left(-\frac{E_n - E_0}{k_B T}\right) = \exp\left(-\frac{nh\nu_E}{k_B T}\right)$$

In order to calculate average energy  $\langle E \rangle$  of an oscillator, probability for  $E_n$  is

$$\frac{N_n}{\sum_n N_n} \therefore \langle E_n \rangle = \sum_n E_n \left( \frac{N_n}{\sum_n N_n} \right) = \frac{1}{2} h\nu_E + \frac{\sum_n nh\nu_E \exp\left(-\frac{nh\nu_E}{k_B T}\right)}{\sum_n \exp\left(-\frac{nh\nu_E}{k_B T}\right)}$$



## Specific Heat 2 - Einstein Model 2

Substituting  $x = -h\nu_E / k_B T$ , the second term in the right part becomes

$$\begin{aligned} h\nu_E \sum_n n \exp(nx) / \sum_n \exp(nx) &= h\nu_E \frac{e^x + 2e^{2x} + \dots}{1 + e^x + e^{2x} + \dots} \\ &= h\nu_E \frac{d}{dx} \log(1 + e^x + e^{2x} + \dots) = h\nu_E \frac{d}{dx} \log \frac{1}{1 - e^x} = h\nu_E \frac{1}{e^{-x} - 1} \end{aligned}$$

Therefore, average energy of an oscillator is

$$\langle E \rangle = \frac{1}{2} h\nu_E + h\nu_E \frac{1}{\exp(h\nu_E/k_B T) - 1}$$

→ Energy of a phonon

By neglecting zero point energy,  $\frac{1}{2} h\nu_E$

Also, assuming,  $E_n = nh\nu_E \quad \therefore \langle nh\nu_E \rangle = h\nu_E \langle n \rangle$

$$\langle n \rangle = \frac{1}{\exp(h\nu_E/k_B T) - 1}$$

→ Planck distribution

$$\langle n \rangle \approx k_B T / h\nu_E \quad (\text{high temperature } h\nu_E \ll k_B T)$$

$$\langle n \rangle \approx \exp(-h\nu_E/k_B T) \quad (\text{low temperature } h\nu_E \gg k_B T)$$



## Specific Heat 2 - Einstein Model 3

Average energy of an oscillator can be modified as

$$\langle E \rangle = h\nu_E/2 + \langle n \rangle h\nu_E$$

$$\therefore \langle E \rangle \approx h\nu_E/2 + k_B T \approx k_B T \quad (\text{high temperature } h\nu_E \ll k_B T)$$

→ Energy only depends on  $T$  (= classical model).

$$\therefore \langle E \rangle \approx h\nu_E/2 + h\nu_E \exp(-h\nu_E/k_B T) \quad (\text{low temperature } h\nu_E \gg k_B T)$$

For 1 mol 3D harmonic oscillator,

$$U_{\text{mol}} = 3N_0 \langle E \rangle = \frac{3}{2} N_0 h\nu_E + 3N_0 h\nu_E \frac{1}{\exp(h\nu_E/k_B T) - 1}$$

Thus, equal volume specific heat is

$$c_{V, \text{mol}} = \left( \frac{\partial U_{\text{mol}}}{\partial T} \right)_V = 3R \left( \frac{h\nu_E}{k_B T} \right)^2 \frac{\exp(h\nu_E/k_B T)}{[\exp(h\nu_E/k_B T) - 1]^2}$$

Since  $\nu_E$  depends on materials, both  $c_{V, \text{mol}}$  and  $h\nu_E$  depends on materials.

Accordingly, characteristic temperature  $\Theta_E$  for  $h\nu_E$  is introduced as

$$h\nu_E \equiv k_B \Theta_E$$

→ Einstein temperature



## Specific Heat 2 - Einstein Model 4

With using Einstein temperature, equal volume heat is rewritten as

$$c_{V, \text{mol}} = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2} \equiv 3R f_E \left( \frac{\Theta_E}{T} \right)$$

$$f_E = x^2 e^x (e^x - 1)^{-2}$$

→  $f_E(x)$  : Einstein function

For high temperature ( $T > \Theta_E$ ),

$$f_E(x) \approx 1 \quad \therefore c_{V, \text{mol}} \approx 3R$$

→ Agrees with Dulong-Petit empirical law

For low temperature ( $T \ll \Theta_E$ ),

$$c_{V, \text{mol}} \propto \exp(-\Theta_E/T)$$

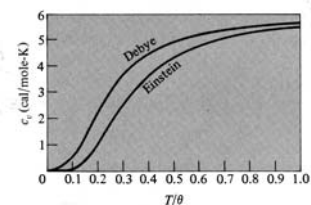
With decreasing temperature,

Einstein model decrease

faster than measurement.

**Figure 23.5**

A comparison of the Debye and Einstein approximations to the specific heat of an insulating crystal.  $\Theta$  is either the Debye or the Einstein temperature, depending on which curve is being examined. Both curves are normalized to approach the Dulong and Petit value of 5.96 cal/mole-K at high temperatures. In fitting to a solid with an  $m$ -ion basis, the Einstein curve should be given  $m - 1$  times the weight of the Debye one. (From J. de Launay, *op. cit.*; see Table 23.2.)





## Specific Heat 2 - Einstein Model 5

In Einstein model, discrete energy levels are assumed :

$$E_3 = \left(3 + \frac{1}{2}\right) h\nu_E \text{ ————— } n = 3$$

$$E_2 = \left(2 + \frac{1}{2}\right) h\nu_E \text{ ————— } n = 2$$

$$E_1 = \left(1 + \frac{1}{2}\right) h\nu_E \text{ ————— } n = 1$$

$$E_0 = \frac{1}{2} h\nu_E \text{ ————— } n = 0$$

For low temperature ( $T \ll \Theta_E$ ), most of the atoms stay at the zero point energy ( $E_0$ ).

With increasing temperature, very few atoms are excited to  $E_1$  as compared with the theoretical prediction.

→ Departure from experiment at low temperature



## Specific Heat 3 - Debye Model 1

Debye introduced quantum harmonic oscillators :

Phonon can be produced by lattice vibration and can fill in one energy state.

→ follows Planck distribution with energy of  $E = h\nu = \hbar\omega$

Numbers of particles occupying an energy level  $E_i$ , which is  $g_i$ -fold degenerated at angular frequency of  $\omega_i$  are calculated to be

$$n_i \equiv g_i \langle n \rangle = \frac{g_i}{\exp(\hbar\omega_i/k_B T) - 1} \equiv \frac{g(\omega)d\omega}{\exp(\hbar\omega/k_B T) - 1}$$

→  $\omega$  is treated as a continuous function

Here, the density of states for a phonon is written as

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

For longitudinal / transverse waves,

$$\omega_l = v_l k, \quad \omega_t = v_t k$$

$$\therefore g_l(\omega) = \frac{V\omega_l^2}{2\pi^2} \frac{1}{v_l^3}, \quad g_t(\omega) = \frac{V\omega_t^2}{2\pi^2} \frac{2}{v_t^3}$$





## Specific Heat 3 - Debye Model 2

By using average  $\omega$  and add both longitudinal and transverse waves :

$$g(\omega) = \frac{V\omega^2}{2\pi^2} \left( \frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \equiv C\omega^2 \quad \left( C \equiv \frac{V}{2\pi^2} \left( \frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right)$$

For a  $N$ -atom 3D lattice,  $3N$  modes are allowed :

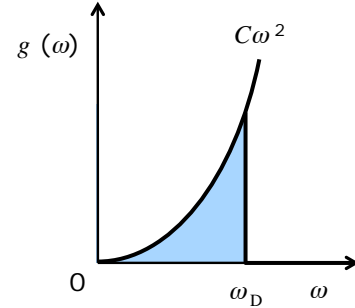
$$\int_0^{\omega_D} C\omega^2 d\omega = \frac{C\omega_D^3}{3} \equiv 3N$$

$$\therefore g(\omega) = \frac{9N\omega^2}{\omega_D^3} \quad 0 \leq \omega \leq \omega_D$$

$\rightarrow \omega_D$  : Debye angular frequency

Therefore, Debye temperature is defined as

$$\Theta_D \equiv \frac{\hbar\omega_D}{k_B}$$



## Specific Heat 3 - Debye Model 3

Now, numbers of states can be rewritten as

$$n = \frac{1}{\exp(\hbar\omega/k_B T) - 1} \frac{9N\omega^2}{\omega_D^3} d\omega$$

By neglecting the zero point energy, total internal energy is

$$\langle E \rangle = \langle n \rangle \hbar\omega = \hbar\omega \frac{1}{\exp(\hbar\omega/k_B T) - 1} g(\omega) d\omega$$

$$\therefore U = \int_0^{\omega_D} \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1} \frac{9N\omega^2}{\omega_D^3} d\omega$$

Therefore, equal volume specific heat is calculated to be

$$c_{V, \text{mol}} = \left( \frac{\partial U}{\partial T} \right)_V = \int_0^{\omega_D} k_B \left( \frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2} \frac{9N\omega^2}{\omega_D^3} d\omega$$

$$\therefore c_{V, \text{mol}} = 9R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\left( x \equiv \frac{\hbar\omega}{k_B T}, \Theta_D \equiv \frac{\hbar\omega_D}{k_B}, R = Nk_B = N_0 k_B \right)$$



## Specific Heat 3 - Debye Model 4

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For high temperature ( $\Theta_D \ll T$ ),

$$c_{V, \text{mol}} \approx 9R \left( \frac{T}{\Theta_D} \right)^3 \frac{1}{3} \left( \frac{\Theta_D}{T} \right)^3 = 3R$$
$$\leftarrow \frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4(1+x)}{(x + x^2/2 + \dots)^2} \approx \frac{x^4}{x^2} = x^2$$

→ Agrees with Dulong-Petit empirical law

For low temperature ( $T \ll \Theta_D$ ),

$$c_{V, \text{mol}} \approx \frac{12\pi^4 R}{5} \left( \frac{T}{\Theta_D} \right)^3 = 464.5 \left( \frac{T}{\Theta_D} \right)^3 \text{ [cal/mol} \cdot \text{K]} \propto T^3$$
$$\leftarrow \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \approx \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}$$

→ Agrees with experiment