Quick Review over the Last Lecture

Waves:

Wave modes:

Photon: ( ), phonon: ( )
Contents of Introductory Nanotechnology

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 ...

Very hot on sand !

Comfortable in water !

Water : difficult to be warmed up / cooled down.

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**Specific Heat Capacity**

In order to compare :

Thermal energy required to increase temperature of a unit-volume material (1 mole at constant volume)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Material</th>
<th>(c_{V,\text{mol}}) [J/mol(\cdot)K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-atom</td>
<td>He</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>12.5</td>
</tr>
<tr>
<td>2-atom</td>
<td>(H_2)</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>20.8</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>21.0</td>
</tr>
<tr>
<td>3-atom</td>
<td>(H_2S)</td>
<td>26.9</td>
</tr>
<tr>
<td></td>
<td>(SO_2)</td>
<td>32.3</td>
</tr>
<tr>
<td>Many-atom (&gt;3)</td>
<td>(CH_4)</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>(C_2H_2)</td>
<td>33.1</td>
</tr>
</tbody>
</table>

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

\(\rightarrow\) 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:

Higher vibration energy state
Lower vibration energy state
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 \((N_0 : \text{Avogadro constant})\),

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

where \(R = N_0 k_B : \text{gas constant}, \) 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:

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

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

\[ E_n = \frac{h\nu_E}{2} + nh\nu_E \quad (n = 0, 1, 2, \ldots) \]

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

Now, the numbers of the oscillators with energy of \( E_0, E_1, E_2, \ldots \) are assumed to be \( N_0, N_1, N_2, \ldots \), 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

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

Specific Heat 2 - Einstein Model 2

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

\[
h\nu_E \sum_n n \exp(nx) / \sum_n \exp(nx) = h\nu_E \frac{e^x + 2e^{2x} + \ldots}{1 + e^x + e^{2x} + \ldots} = h\nu_E \frac{d}{dx} \log(1 + e^x + e^{2x} + \ldots) = h\nu_E \frac{d}{dx} \log \left( \frac{1}{1 - e^x} \right) = h\nu_E \frac{1}{e^{-x} - 1}
\]

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, \( E_n = nh\nu_E \) \( \implies \langle nh\nu_E \rangle = h\nu_E \langle n \rangle \)

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

→ Planck distribution

\[
\langle n \rangle = k_B T / h\nu_E \quad \text{(high temperature } h\nu_E < k_B T) \]

\[
\langle n \rangle = \exp(-h\nu_E/k_B T) \quad \text{(low temperature } h\nu_E > k_B T) \]
Average energy of an oscillator can be modified as
\[ \langle E \rangle = h\nu_E/2 + (n)h\nu_E \]
\[ \therefore \langle E \rangle = h\nu_E/2 + k_BT = k_BT \quad \text{(high temperature } h\nu_E \ll k_BT) \]
→ Energy only depends on \( T \) (= classical model).
\[ \therefore \langle E \rangle = h\nu_E/2 + h\nu_E \exp(-h\nu_E/k_BT) \quad \text{(low temperature } h\nu_E >> k_BT) \]

For 1 mol 3D harmonic oscillator,
\[ U_{\text{mol}} = 3N_0\langle E \rangle = \frac{3}{2}N_0h\nu_E + 3N_0h\nu_E \frac{1}{\exp(h\nu_E/k_BT)-1} \]

Thus, equal volume specific heat is
\[ c_{V,\text{mol}} = \left( \frac{\partial U_{\text{mol}}}{\partial T} \right)_V = 3R \frac{h
u_E}{k_BT} \left[ \exp(h\nu_E/k_BT) \right]^{-1} \left[ \exp(h\nu_E/k_BT)-1 \right]^2 \]

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
\[ h\nu_E = k_BT \Theta_E \]
→ Einstein temperature

With using Einstein temperature, equal volume heat is rewritten as
\[ c_{V,\text{mol}} = 3R \left( \frac{\Theta_E}{T} \right)^2 \exp\left( \frac{\Theta_E}{T} \right) \left[ \exp\left( \frac{\Theta_E}{T} \right) - 1 \right] \]
\[ f_E = x^2e^x(e^x-1)^2 \]
→ \( f_E(x) \) : Einstein function

For high temperature \( (T > \Theta_E) \),
\[ f_E(x) = 1 \quad \therefore c_{V,\text{mol}} = 3R \]
→ Agrees with Dulong-Petit empirical law

For low temperature \( (T << \Theta_E) \),
\[ c_{V,\text{mol}} \propto \exp(-\Theta_E/T) \]

With decreasing temperature, Einstein model decrease faster than measurement.

Specific Heat 2 - Einstein Model 5

In Einstein model, discrete energy levels are assumed:

\[ E_3 = \left( 3 + \frac{1}{2} \right) \hbar \nu_E \quad n = 3 \]
\[ E_2 = \left( 2 + \frac{1}{2} \right) \hbar \nu_E \quad n = 2 \]
\[ E_1 = \left( 1 + \frac{1}{2} \right) \hbar \nu_E \quad n = 1 \]
\[ E_0 = \frac{1}{2} \hbar \nu_E \quad n = 0 \]

For low temperature \((T << \Theta_v)\), 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.

\[ \rightarrow \text{Departure from experiment at low temperature} \]

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.
\[ \rightarrow \text{follows Planck distribution with energy of } E = h \nu = \hbar \omega \]

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

\[ n_i = g_i \langle n \rangle = \frac{g_i}{\exp(h\omega_i/k_B T) - 1} \leq \frac{g(\omega) d\omega}{\exp(h\omega/k_B T) - 1} \]

\[ \rightarrow \omega \text{ is treated as a continuous function} \]

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

\[ g(\omega) d\omega = \frac{V}{(2\pi)^3} 4\pi k^2 dk \]

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:

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

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

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

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

$\omega_D$ : Debye angular frequency

Therefore, Debye temperature is defined as

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

Specific Heat 3 - Debye Model 3

Now, numbers of states can be rewritten as

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

By neglecting the zero point energy, total internal energy is

$$\langle E \rangle = \langle n \rangle h\omega = \frac{1}{\exp(h\omega/k_BT)-1} g(\omega) d\omega$$

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

Therefore, equal volume specific heat is calculated to be

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

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

$$\left( x = \frac{h\omega}{k_B T}, \Theta_D = \frac{h\omega_D}{k_B}, R = Nk_B = N_0(k_B) \right)$$
Specific Heat 3 - Debye Model 4

For high temperature \((\Theta_D << T)\),

\[
c_{V, \text{mol}} = 9R \left( \frac{T}{\Theta_D} \right)^3 \frac{1}{3} \left( \frac{\Theta_D}{T} \right)^3 = 3R
\]

\[
\equiv \frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4 (1 + x)}{(x + x^2/2 + \ldots)^2} \approx \frac{x^4}{x^2} = x^2
\]

→ Agrees with Dulong-Petit empirical law

For low temperature \((T << \Theta_D)\),

\[
c_{V, \text{mol}} = \frac{12\pi^4 R}{5} \left( \frac{T}{\Theta_D} \right)^3 = 464.5 \left( \frac{T}{\Theta_D} \right)^3 \text{[cal/mol·K]} \propto T^3
\]

\[
\equiv \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \approx \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}
\]

→ Agrees with experiment