Lecture 13 Heat Capacities of Solids 23 Oct 2008

C_V is calculated $C_V = \partial E / \partial T$

C_P is measured and subject to atmospheric pressure

$C_P - C_V$ = (exact expression at end of Ch. 5 Mandl)

C_P Measurements

At room T, most solids follow $C_P \sim 3nNk$
where n = # atoms per molecule
N = # molecules in the solid
k = Boltzmann constant

Dulong - Petit's Rule: For a monatomic molecule, $n=1$,
for 1 mole $C_P \sim 3N_0 k = 3R = 24.93\ \text{J K}^{-1}\text{mol}^{-1}$

p. 148 Mandl Table

Follows Rule		Exceptions		
Element	C_P	Element	C_P	
Al	24.4	S	22.7	$\text{J K}^{-1}\text{mol}^{-1}$
Au	25.4	Si	19.9	
Cu	24.5	C(diamond)	6.1	

The classical limit of vibrational energy explains this rule.
In non-metals, there are 3 independent vibrations:
3kT equipartition theory

$E_{vib} = 3NkT$ = vibration energy of N atoms

$$C_V^{vib} = \frac{\partial E_{vib}}{\partial T} = 3Nk = 3nNK$$

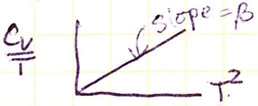
Diamond is an exception to the rule.

Temperature dependence is not explained by this rule.

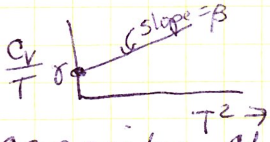
$$\lim_{T \to 0} C_V = 0$$

$C_V \propto T^3$ $C_P \propto T^3$ for non-metals p. 149

$C_P = \beta T^3$ non-metals



$C_P = \beta T^3 + \gamma T$ metals



We are not considering heat capacity of conduction electrons because we need to have the fermi-dirac statistics from the end of the course.

Calculation of Vibrational Heat Capacity

- The number of degrees of freedom are the number of vibrational states
- Theorem of Classical Mechanics

For any system with proper 'normal' coordinates, you can write the vibrational energy as the sum of simple, small angle, harmonic oscillator energies

$$E_{vib} = \sum_{\alpha=1}^{3N} \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2 q_\alpha^2}{2} \right)$$

p_α - canonical 'normal' momentum
q_α - normal coordinate

$$p_\alpha = \frac{\partial \mathcal{L}}{\partial \dot{q}_\alpha} \qquad \mathcal{L} = \text{Lagrangian}$$

Classically, the amplitude can be anything, the $E_{c\alpha}$ become infinite.

- Energy of radiation in cavity is also a sum but over infinite degrees of freedom of the electromagnetic field.

Quantum mechanics energy of one simple harmonic oscillator

$$\epsilon_\alpha = \hbar\omega_\alpha (n_\alpha + 1/2) \qquad \hbar\omega \text{ is very small}$$

$$E = \lim_{N \to \infty} \sum_{\alpha=1}^{3N} \epsilon_\alpha = \lim_{N \to \infty} \sum_{\alpha=1}^{3N} \hbar\omega_\alpha (n_\alpha + 1/2)$$

To Solve:

Ⓐ Apply partition function to system and heat bath.

system -	one harmonic oscillator	ω_α one mode
heat bath -	the rest of the oscillators	3N normal modes

Ⓑ Canonical Partition Function: $Z = \sum_r e^{-E_r/KT}$

Ⓒ Probability of a particular microstate: $p_r = \frac{e^{-E_r/KT}}{Z}$

Ⓓ Non-degenerate quantum state:

$$Z_\alpha = \sum_{n_\alpha=0}^{\infty} e^{-\hbar\omega_\alpha(n_\alpha+1/2)/KT} = e^{-\hbar\omega_\alpha/2KT}\left[1 + e^{-\hbar\omega_\alpha/KT} + e^{-2\hbar\omega_\alpha/KT} + \dots\right]$$

$$e^{-\hbar\omega_\alpha/2KT}(1 + x + x^2 + \dots) = \left(\frac{1}{1-x}\right) e^{-\hbar\omega_\alpha/2KT}$$

trick to calculate the sum:

$$S = 1 + x + x^2 + \dots$$

$$Sx = x + x^2 + x^3 + \dots$$

$$S - Sx = 1 \longrightarrow S = \frac{1}{1-x}$$ only works when $x < 1$

Lecture 13 continued... Heat Capacities of Solids

Partition function is:

$$Z_\alpha = \frac{e^{-\beta\hbar\omega_\alpha/2}}{1-e^{-\beta\hbar\omega_\alpha}}$$

Ⓔ Can find the average energy of a SHO in equilibrium with a heat bath from the partition function.

$$\bar{\mathcal{E}}_\alpha = -\frac{\partial \ln Z_\alpha}{\partial\beta} = \frac{-1}{Z_\alpha}\frac{\partial Z_\alpha}{\partial\beta}$$

$$\frac{\partial Z_\alpha}{\partial\beta} = e^{-\beta\hbar\omega_\alpha/2}\frac{(-\hbar\omega_\alpha e^{-\beta\hbar\omega_\alpha})}{(1-e^{-\beta\hbar\omega_\alpha})^2} + \frac{e^{-\beta\hbar\omega_\alpha/2}(-\frac{1}{2}\hbar\omega_\alpha)}{(1-e^{-\beta\hbar\omega_\alpha})}$$

$$\frac{1}{Z_\alpha} = (1-e^{-\beta\hbar\omega_\alpha})e^{+\beta\hbar\omega_\alpha/2}$$

$$\bar{\mathcal{E}}_\alpha = -\frac{1}{Z_\alpha}\frac{\partial Z_\alpha}{\partial\beta} = \frac{\hbar\omega_\alpha e^{-\beta\hbar\omega_\alpha}}{(1-e^{-\beta\hbar\omega_\alpha})} + \tfrac{1}{2}\hbar\omega_\alpha$$

$$\boxed{\bar{\mathcal{E}}_\alpha = \frac{\hbar\omega_\alpha}{(e^{\beta\hbar\omega_\alpha}-1)} + \frac{1}{2}\hbar\omega_\alpha}$$

* This is an extremely important relation to know

demominator depends on T

no temperature dependence
never non-zero energy
but this term doesn't contribute to heat capacity

Ⓕ Can obtain the Dulroy-Petit Rule from the classical limit

(Can Neglect the zero-point energy)

But $\displaystyle\lim_{\hbar\to 0}\bar{\mathcal{E}}_\alpha = \lim_{\hbar\to 0}\left\{\frac{\hbar\omega_\alpha}{e^{\beta\hbar\omega_\alpha}-1} + \frac{\hbar\omega_\alpha}{2}\right\} = \lim_{\hbar\to 0}\left(\frac{kT\left(\frac{\hbar\omega_\alpha}{kT}\right)}{e^{(\hbar\omega_\alpha/kT)}-1}\right)$

$\displaystyle\lim_{\hbar\to 0}\bar{\mathcal{E}}_\alpha = kT\left(\frac{x}{e^x-1}\right)$ where $x \ll 1$ at any temperature
$e^x \sim 1+x$

$$\lim_{\hbar\to 0}\bar{\mathcal{E}}_\alpha \approx kT\left(\frac{x}{1+x-1}\right) = kT$$

If it is classical, there are 3 oscillators $\bar{\mathcal{E}}_\alpha = 3kT$ Dulroy-Petit Rule
Deviations imply that $\frac{\hbar\omega}{kT} \not\ll 1$

Ⓖ Exact expression

$$\overline{E} = \sum_{\alpha=1}^{3N} \overline{\varepsilon}_\alpha = \sum_{\alpha=1}^{3N}\left(\frac{\hbar\omega_\alpha}{e^{\hbar\omega_\alpha/KT}-1} + \frac{1}{2}\hbar\omega_\alpha\right)$$

Ⓗ Can get the heat capacity from $\overline{E}$

$$C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \sum_{\alpha=1}^{3N} k \left(\frac{\hbar\omega_\alpha}{KT}\right)^2 \frac{e^{\hbar\omega_\alpha/KT}}{(e^{\hbar\omega_\alpha/KT}-1)^2}$$

$$\underset{\substack{\uparrow \\ J/K}}{C_V} = \underset{\substack{\uparrow \\ J/K}}{K} \sum_{\alpha=1}^{3N} \underbrace{\left(\frac{\hbar\omega_\alpha}{KT}\right)^2 \frac{e^{\hbar\omega_\alpha/KT}}{(e^{\hbar\omega_\alpha/KT}-1)^2}}_{\text{dimensionless terms in the sum}}$$

heat capacity is energy per unit temperature

Ⓘ Classical result, simplification of the C_v sum

If $\frac{\hbar\omega_\alpha}{KT} << T$ for all α's

$$C_V = K\sum_{\alpha=1}^{3N} \frac{x_\alpha^2 e^{x_\alpha}}{(e^{x_\alpha}-1)^2} = k\sum_{\alpha=1}^{3N} 1 = 3Nk$$

again Dulroy-Petit rule by SHO when $\hbar\omega_\alpha/KT << 1$

Aluminum - works @ RoomTemperature   Carbon-deviates because $\hbar\omega_\alpha/KT$ is not << 1

Ⓙ Einstein's Model

It is a formidable task to find the ω_α's for 3N unknowns.

Einstein says $\omega_\alpha = \omega_E$ for all α

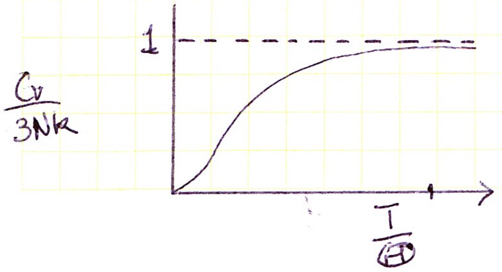
$$C_V = \frac{k(3N)\left(\frac{\hbar\omega_E}{KT}\right)^2 e^{\hbar\omega_E/KT}}{(e^{\hbar\omega_E/KT}-1)^2}$$

Einstein was able to calculate ω_E for an elastic solid.

$\Theta_E = \frac{\hbar\omega_E}{k}$ = Einstein temperature, a characteristic of the solid.

$$C_V = \frac{3Nk\left(\frac{\Theta_E}{T}\right)^2 e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}$$

$\lim_{T\to 0} C_V = 0$ $\lim_{T\to\infty} C_V = 3Nk$ approaches asymptotically



For one mole of solid $\frac{C_v}{3Rk}$

Deviations $C_v << 3R$ for Carbon