CLASS WORK evaluation on 1/3 FEB, 2023

# Experiment 3
# Specific heat of Solids

1. METHOD

(a) **(Dulong-Petit distribution Law)**

Molar specific heat is the energy that must be added to 1 kmole of solid whose volume is fixed to raise its temperature by 1 K. The internal energy of solid recides in the vibrations of its constituent particles.

According to classical physics a harmonic oscillator in a system in thermal equilibrium at temperature $T$ has an average energy $kT$ (it has two degrees of freedom $2 \times \frac{1}{2}kT$). An atom can be represented by three harmonic oscillators corresponding to the three spatial dimensions, thus each atom in a solid should have $3kT$ energy.

Dulong-Petit assumed that a system of $N_A$ atoms shall have the total internal energy $E = N_A\, 3kT$ and hence a specific heat $C_v = \left(\frac{\partial E}{\partial T}\right)_V = 3R$.

(b) **(Einstein distribution Law)**

Einstein discerned that the assumption of Planck for the average energy as

$$\bar{\epsilon} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

**but $\nu$ with specific value** $\nu_E$. The density of states that Einstein assumed

$$G(\nu)d\nu = fN_A\delta(\nu - \nu_E)d\nu$$

such that $\int G(\nu)d\nu = \int fN_A\delta(\nu - \nu_E)d\nu = fN_A$. The total internal energy is

$$U_E = \int \bar{\epsilon}(\nu)G(\nu)d\nu = 3\;N_A\;\bar{\epsilon}(\nu_E) = 3N_A\;\frac{h\nu_E}{e^{h\nu_E/kT} - 1}$$

and hence a specific heat $C_v = \left(\frac{\partial U_E}{\partial T}\right)_V$

$$\frac{C_v}{3R} = \left(\frac{h\nu_E}{kT}\right)^2 \frac{e^{h\nu_E/kT}}{(e^{h\nu_E/kT} - 1)^2} = \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

where Einsteins Temperature is $\theta_E = \frac{h\nu_E}{k}$.

(c) **(Debye distribution Law)**

Debye assumed (as opposed to Einstein who assumed every atom to be independent oscillator), the solid as a continuous elastic body and all atoms sharing an elastic standing wave known as phonon. Debye asserted that a phonon gas obeys the same statistics as that of a photon (radiation) gas in thermal equilibrium. He assumed that there is a density of states (dos)

$$G(\nu)d\nu = \frac{4\pi V_0}{c^3}\nu^2 d\nu$$

and modified them by taking one longitudinal and two transverse polarised waves and modified the dos

$$G(\nu)d\nu = 4\pi V_0\left(\frac{1}{c_l^3}+\frac{1}{c_t^3}\right)\nu^2 d\nu = 9N_A\left(\frac{\nu}{\nu_D}\right)^2\frac{d\nu}{\nu_D}$$

**where $\nu_D$ is the Debye cut off frequency when** $\int_0^{\nu_D} G(\nu)d\nu = fN_A$ ( taking one longitudinal and two transverse polarised waves). The average energy is $\bar{\epsilon} = \frac{h\nu}{e^{\frac{h\nu}{kT}}-1}$ and deduced the total internal energy as

$$U_D = \int_0^{\nu_D}\bar{\epsilon}\,G(\nu)d\nu = \int_0^{\nu_{cut}}\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}\left(4\pi V_0\left(\frac{1}{c_l^3}+\frac{1}{c_t^3}\right)\nu^2\right)d\nu = \frac{9N_A}{{\nu_D}^3}\int_0^{\nu_D}\frac{h\nu^3}{e^{\frac{h\nu}{kT}}-1}d\nu$$

and hence a specific heat

$$\frac{C_v}{3R} = \int_0^{\nu_D}\left(\frac{3\nu^2}{\nu_D^3}\right)\left(\frac{h\nu}{kT}\right)^2\frac{e^{\frac{h\nu}{kT}}}{(e^{\frac{h\nu}{kT}}-1)^2}d\nu = \frac{-3(\theta_D/T)}{e^{\theta_D/T}-1}+\frac{12}{(\theta_D/T)^3}\int_0^{\theta_D/T}\frac{(\theta_D/T)^3}{e^{\theta_D/T}-1}d\left(\frac{\theta_D}{T}\right)$$

where Debyes Temperature is $\theta_D = \frac{h\nu_D}{k}$.

2. CODING AND PLOTS

   (a) **(Figure 1; Density of State)**
   *Plot* $G(\frac{\nu}{\nu_x})$ *versus* $(\nu/\nu_x)$ *where* $x$ *represents both for* $Debye$ *and* $Einsteins$ *cases*

   (b) **(Figure 2:** $C_v/3R$ **versus** $T/\theta$**)**

   *(a) Plot the value of* $C_v/3R$ *versus* $T/\theta$ *for Dulong Petit where* $\theta$ *is an arbitrary constant.*

   *(b) Overlay the plot with* $C_v/3R$ *versus* $T/\theta_E$ *where* $\theta_E = h\nu_E/k$

   *(c) Overlay this value of* $C_v/3R$ *versus* $T/\theta_D$ *where* $\theta_D = h\nu_D/k$

   *(d) differentiate the expression of* $U_E$ *and* $U_D$ *with respect to* $T$ *in the program, plot the same and compare with your* $C_v/3R$ *plot. Use same colour as in (b) and (c) but dash dots to represent the corresponding results*

   **(Note)** : *You may use the range of* $T/\theta$, $T/\theta_E$ *and* $T/\theta_D$ *from* 0 *to* 2.

3. APPLICATIONS

   (a) `https://lampx.tugraz.at/~hadley/ss1/phonons/table/dosdebye.html`