PHY2201 Summary Sheet 17

Einstein solid – crystal of N atoms, each free to perform SHM about its equilibrium position in x, y and z directions.

Classical equipartition theorem (PHY1002) – in thermal equilibrium at temperature T, ensemble will possess a mean internal energy U given by

$$U = \frac{k_{\mathrm{B}}T}{2}\nu$$

With ν being the number of degrees of freedom, i.e. the number of squared terms appearing in the expression for the total internal energy when expressed in generalized co-ordinates of position and velocity q and $\dot{q}$.

e.g. point particle of mass m moving in 3-D

$$E = \mathrm{KE} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2$$

Hence $\nu = 3$

e.g. classical harmonic oscillator of mass m, spring constant k in 3-D,

$$E = \mathrm{KE} + \mathrm{PE} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}ky^2 + \frac{1}{2}m\dot{z}^2 + \frac{1}{2}kz^2$$

i.e. $\nu = 6$

Hence classically, $U = 3Nk_{\mathrm{B}}T$ for the solid and

$$c_{\mathrm{v}} = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_{\mathrm{B}}$$

(Dulong-Petit law 1822), predicts that c_{v} is independent of T. However, experimentally it is found that $c_{\mathrm{v}} \to 0$ as $T \to 0$.

Einstein (1907): quantize the allowed energies of each of the N harmonic oscillators, such that $\varepsilon_i = (i+1/2)\hbar\omega$, with $\omega = \sqrt{k/m}$ being the natural frequency of the oscillator. Hence, for <u>each oscillator</u>

$$Z = \sum_{i=0}^{\infty} \exp(-\varepsilon_i / k_B T) = \sum_{i=0}^{\infty} \exp(-(i+1/2)\hbar\omega / k_B T)$$

Define the Einstein temperature $\theta_E = \hbar\omega/k_B$

$$Z = \sum_{i=0}^{\infty} \exp(-(i+1/2)\theta_E/T) = \exp(-\theta_E/2T) \sum_{i=0}^{\infty} \exp(-i\,\theta_E/T)$$

Summation on RHS is a convergent geometric series, first term a = 1, common ration r = $\exp(-\theta_E/T)$. The sum tends to $a/(1-r)$ as the number of terms tends to ∞ (e.g. Stroud Engineering Mathematics Programme 13), hence

$$Z = \frac{\exp(-\theta_E/2T)}{1-\exp(-\theta_E/T)}$$

Hence (exercise)

$$U = 3Nk_B T^2 \frac{\partial \ln Z}{\partial T} = 3Nk_B\theta_E\left(\frac{1}{2} + \frac{1}{\exp(\theta_E/T)-1}\right)$$

Hence (exercise)

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B\theta_E \frac{d}{dT}\left(\frac{1}{2} + \frac{1}{\exp(\theta_E/T)-1}\right)$$

$$\boxed{c_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{(\exp(\theta_E/T)-1)^2}}$$

As $T \to \infty$ $\exp(\theta_E/T) \to 1 + \theta_E/T$, hence $c_v \to 3Nk_B$ i.e. tends to the classical result for high T.

As $T \to 0$ $\exp(\theta_E/T) - 1 \to \exp(\theta_E/T)$ hence $c_v \to (\theta_E/T)^2 / \exp(\theta_E/T) \to 0$ (because $\exp(x)$ diverges more rapidly than x^n for any finite n.