Statistical Mechanics and Thermodynamics of Simple Systems

Handout 9

Equipartition Theorem

Equipartition theorem: If the energy of a classical system is the sum of n quadratic terms, and the system is in contact with a heat reservoir at temperature T, then the mean energy of the system is given by $\frac{1}{2}nk_{\mathrm{B}}T$.

This theorem, which applies to classical systems with continuous energy levels, expresses the fact that energy is 'equally partitioned' between all the separate modes of the system, each mode having a mean energy of precisely $\frac{1}{2}k_{\mathrm{B}}T$.

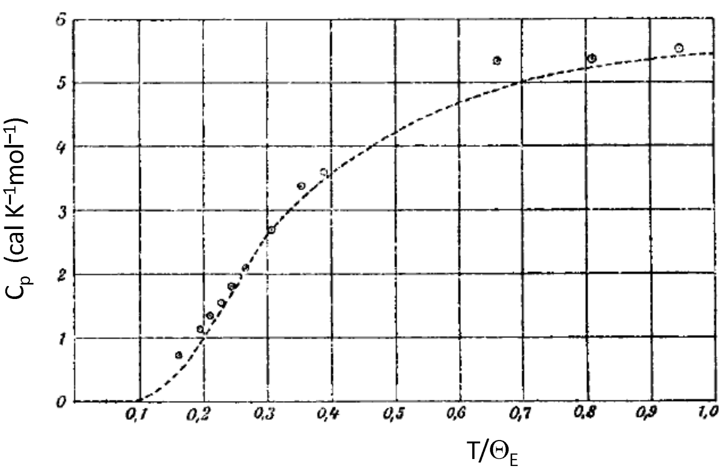
Dulong & Petit's law: The molar heat capacity of a crystal is $3R$ regardless of the substance.

This law represents the classical (high temperature) limit of the heat capacity.

Einstein's model for the heat capacity of a solid. The measured heat capacity of solids deviates below the prediction of Dulong & Petit, and tends to zero as T tends to zero. Einstein assumed that all atoms vibrate at a single angular frequency ω, and treated the system as $3N$ independent, quantized, harmonic oscillators in 3D. Each oscillator has quantized energy levels $E_n = (n + \frac{1}{2})\hbar\omega$. In this model the expression for the molar heat capacity is

$$C_V = 3Nk_{\mathrm{B}}(\Theta_{\mathrm{E}}/T)^2 \frac{\mathrm{e}^{\Theta_{\mathrm{E}}/T}}{(\mathrm{e}^{\Theta_{\mathrm{E}}/T} - 1)^2}, \tag{1}$$

where $\Theta_{\mathrm{E}} = \hbar\omega/k_{\mathrm{B}}$.



The molar heat capacity C_p ($\approx C_V$) of diamond (data points) compared with the curve calculated from the Einstein model eqn (1) with $\Theta_{\mathrm{E}} = 1325\,\mathrm{K}$. Note the units: 1 calorie (cal) = 4.2 J, so $3R = 5.94\,\mathrm{cal\,K^{-1}mol^{-1}}$. The deviation from the theoretical curve at low temperature is due to the assumption that all atoms vibrate at the same frequency, which is not the case in reality. A refinement of the theory by P. Debye gives better agreement at low temperatures. This figure is adapted from Einstein's original paper: A. Einstein, Annalen der Physik, **22** (1907) 180–190.

ATB
Hilary 2013