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 $\frac{1}{2}k_{\mathrm{B}}T$.

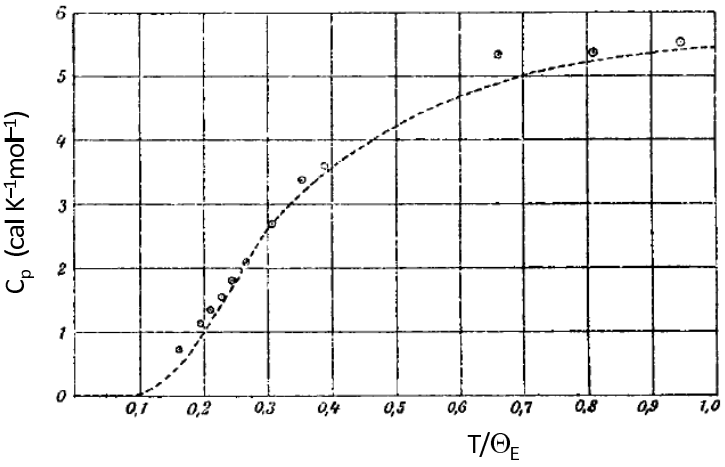
Dulong & Petit's law: The molar heat capacity of a crystal is $3R$ regardless of the substance.

This law represents the classical (high temperature) limit of the heat capacity, which derives from three translational and three vibrational degrees of freedom.

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.

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