Statistical Mechanics and Thermodynamics of Simple Systems

Handout 7

Equipartition Theorem

This theorem applies to classical systems with continuous energy levels.

Let the energy E of a particular system be given by $E = \alpha x^2$, where α is a positive constant and x is some dynamical variable. Let us also assume that x could in principle take any value with equal probability. The probability $P(x)$ for the system to have a particular energy αx^2 is proportional to the Boltzmann factor $\mathrm{e}^{-\beta \alpha x^2}$, so that after normalizing we have

$$P(x) = \frac{\mathrm{e}^{-\beta \alpha x^2}}{\int_{-\infty}^{\infty} \mathrm{e}^{-\beta \alpha x^2}\,\mathrm{d}x}, \tag{1}$$

and the mean energy is

$$\langle E \rangle = \int_{-\infty}^{\infty} E\, P(x)\,\mathrm{d}x = \frac{\int_{-\infty}^{\infty} \alpha x^2 \mathrm{e}^{-\beta \alpha x^2}\,\mathrm{d}x}{\int_{-\infty}^{\infty} \mathrm{e}^{-\beta \alpha x^2}\,\mathrm{d}x} = \frac{1}{2\beta} = \frac{1}{2}k_{\mathrm{B}}T. \tag{2}$$

We can easily extend this treatment to the case where the energy contains a sum of n independent quadratic terms: $\langle E \rangle = n \times \frac{1}{2}k_{\mathrm{B}}T$. This result is expressed as

> the **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, the mean energy of the system is given by $\frac{1}{2}nk_{\mathrm{B}}T$.

The equipartition theorem expresses the fact that energy is 'equally partitioned' between all the separate modes of the system, each mode having a mean energy of precisely $\frac{1}{2}k_{\mathrm{B}}T$.

Examples

- **Ideal monatomic gas**

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

$$\rightarrow \langle E \rangle = U = \frac{3}{2}k_{\mathrm{B}}T \quad \text{per atom} \tag{3}$$

- **Simple harmonic oscillator in 1D**

$$E = \frac{1}{2}kx^2 + \frac{1}{2}m\dot{x}^2$$

$$\rightarrow U = k_{\mathrm{B}}T \quad \text{per atom} \tag{4}$$

- **Heat capacity of a 3D solid:** Solid contains N atoms in total. Assume that for each atom the bond strength is same along the x, y and z directions, and that the amplitude of oscillations is small compared to inter-atomic distances.

$$E = \sum_{i=1}^{N} \frac{1}{2}k_i(x_i^2 + y_i^2 + z_i^2) + \frac{1}{2}m_i(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

$$\rightarrow U = 3Nk_{\mathrm{B}}T \quad \text{per atom} \tag{5}$$

Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_{\mathrm{B}} = 3R$ per mole — **Dulong & Petit's law**.

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 $E_n = (n + \frac{1}{2})\hbar\omega$. The partition function is

$$Z = Z^{3N}(1), \tag{6}$$

where,

$$
\begin{aligned}
Z(1) &= \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \\
&= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} x^n \qquad [x = e^{-\beta\hbar\omega}] \\
&= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \tag{7}
\end{aligned}
$$

Here we have used the sum of an infinite geometric series, $\sum_{n=0}^{\infty} x^n = 1/(1-x)$. Hence, the internal energy is

$$U = \{n(\omega) + \frac{1}{2}\}\hbar\omega, \quad \text{where } n(\omega) = \langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}. \tag{8}$$

The expression for $n(\omega)$ defines the **Planck distribution**, which gives the mean number of energy quanta in each harmonic oscillator at temperature T (the same expression applies to Black-body radiation). The heat capacity is

$$C_V = 3Nk_B(\Theta_E/T)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}, \tag{9}$$

where $\Theta_E = \hbar\omega/k_B$.
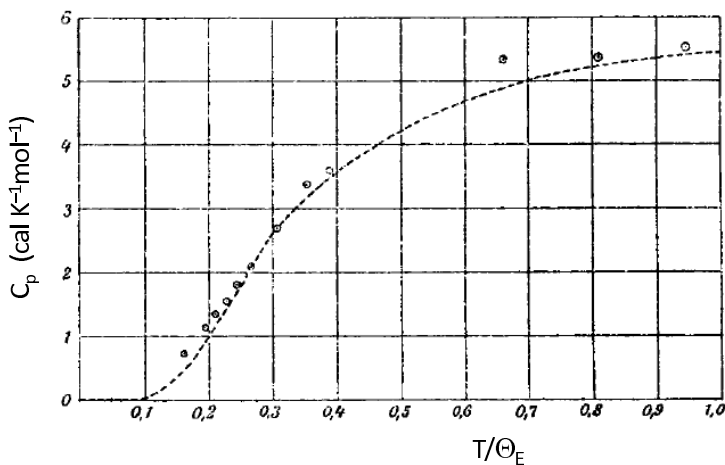
The molar heat capacity C_p ($\approx C_V$) of diamond (data points) compared with the curve calculated from the Einstein model eqn (9) with $\Theta_E = 1325$ K. Note the units: 1 calorie (cal) $= 4.2$ J, so $3R = 5.94\,\mathrm{cal\,K^{-1}mol^{-1}}$. The deviation from the theoretical curve at low temperature 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.

Gas of heteronuclear diatomic molecules

We restrict ourselves to heteronuclear diatomic molecules (i.e. both atoms that make up the molecule are different, e.g. CO, HD). Homonuclear diatomic molecules (e.g. H_2, N_2, O_2) have additional quantum mechanical constraints imposed on them by exchange symmetry.

We assume that the translational, rotational and vibrational motions are independent, which is valid providing the characteristic energy scales of each degree of freedom are distinct. With this assumption, one can write

$$Z = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}, \tag{10}$$

and hence $U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}}$. Consider each degree of freedom in turn:

- From the equipartition theorem, $U_{\text{trans}} = \frac{3}{2}RT$ per mole, so $C_V^{\text{trans}} = \frac{3}{2}R$.

- Treat the vib. part as N SHOs. This means that eqn (9) applies but with N instead of $3N$ in the prefactor. When $T \gg \Theta_E$, $C_V^{\text{vib}} \to R$ per mole.

- Treat the rot. motion as a rigid rotor. The energy levels are quantized:

$$E_l = \frac{\hbar^2}{2I}l(l+1), \qquad (I = \mu R^2), \tag{11}$$

  where l is an integer ($l \geq 0$), I is the moment of inertia of the molecule, $\mu = m_1 m_2/(m_1 + m_2)$ is its reduced mass, and R is the separation of the atoms. Each energy level is $(2l+1)$-fold degenerate, so that the single-molecule partition function is

$$
\begin{aligned}
Z_{\text{rot}}(1) &= \sum_{l=0}^{\infty} (2l+1) e^{-\beta \frac{\hbar^2}{2I} l(l+1)} \\
&= 1 + 3e^{-2\frac{\Theta_{\text{rot}}}{T}} + 5e^{-6\frac{\Theta_{\text{rot}}}{T}} + \ldots, \tag{12}
\end{aligned}
$$

  where $\Theta_{\text{rot}} = \hbar^2/(2Ik_B)$. When $T \gg \Theta_{\text{rot}}$,

$$Z_{\text{rot}}(1) \approx \int_0^{\infty} (2l+1) e^{-\frac{\Theta_{\text{rot}}}{T} l(l+1)} \, dl = \frac{T}{\Theta_{\text{rot}}}, \tag{13}$$

  Hence, $C_V^{\text{rot}} \to R$ per mole.
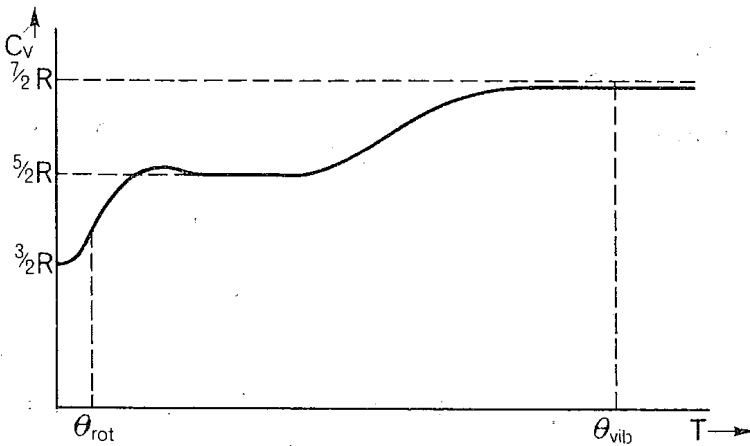
The molar heat capacity C_V of an ideal gas of heteronuclear diatomic molecules.