Classical Equipartition Theorem

Consider a system with $f$ degrees of freedom - Eq. p3
1. $f$ generalized coordinates
2. $f$ generalized momenta

\[ P(\mathbf{q}, \mathbf{p}) \, dq \, dp = \text{probability that the system} \]
lies within the infinitesimal phase space volume $dq \, dp \text{ located at } \mathbf{q}, \mathbf{p}$

\[ = \frac{e^{-\beta H} \, dq \, dp}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H} \, dq \, dp} \]

$H = \text{Hamiltonian - often}$

\[ = \text{total energy} \]

\[ = K + U \]

kinetic potential

Usually

\[ K = \sum_{i=1}^{f} \frac{1}{2} \mathbf{p}_i \cdot \mathbf{p}_i \]

\[ U = U(\mathbf{q}) \]

So averages over $dq$ and $dp$ can be factored

If $U$ is only a function of $\mathbf{q}$ and $E$ only of $\mathbf{q}$

\[ \overline{u} = \frac{\int \mathbf{u}(\mathbf{q}) \, e^{-\beta K} \, dq}{\int e^{-\beta K} \, dq} \]

\[ \overline{\mathbf{u}} = \frac{\int \mathbf{u}(\mathbf{q}) \, e^{-\beta K} \, dq}{\int e^{-\beta K} \, dq} \]

(1) Have already seen that $\overline{\mathbf{u}}(\mathbf{q}) = \mathbf{e}_i = \mathbf{p}_i$

\[ \text{that} \overline{e}_i = \frac{1}{kT} \]

(2) What if $U = \sum \alpha_i \mathbf{q}_i$ (sum of quadratic terms)

\[ \mathbf{u}_i = \alpha_i \mathbf{q}_i \]

what is $\overline{\mathbf{u}}_i$?

\[ \overline{\mathbf{u}}_i = \frac{\int \mathbf{u}_i \, e^{-\beta \mathbf{u}_i} \, dq_i}{\int e^{-\beta \mathbf{u}_i} \, dq_i} \]

since all other factors cancel

\[ \mathbf{u}_i = \alpha_i \mathbf{q}_i \]

and let $y = \beta \mathbf{q}_i \circ \mathbf{d}y = \beta \mathbf{d}y$

\[ \overline{\mathbf{u}}_i = -\frac{1}{2\beta} \left( \frac{1}{\beta} \int e^{-\beta \mathbf{u}_i} \, dq_i \right) = -\frac{1}{2\beta} \frac{1}{\beta} \int e^{-\beta \mathbf{u}_i} \, dq_i = -\frac{1}{2\beta} \left( \frac{1}{\beta} \right) = \frac{1}{2\beta} \]

\[ \overline{\mathbf{u}}_i = \frac{1}{2} kT \]

So each square term in $H \Rightarrow \frac{1}{2} kT$ to $E$
Apply this theorem to a crystalline solid with $N$ atoms vibrating harmonically

$$H = \frac{3N}{2m} \left( \frac{P_i^2}{2m} + \frac{\hbar}{\beta} q_i^2 \right)$$

$- 6N$ squared terms

$$E = \left( \frac{1}{2} kT \right) \times 6N = 3NkT = 3\nu RT$$

$$C_V = 3\nu R \quad \text{or} \quad c_V = \frac{C_V}{V} = 3R$$

molar heat capacity at const. vol.

"Law of Dulong and Petit" $\frac{C_V}{R} = 3$

Approx. obeyed by many solids, but also sig. deviat.

Sulfur $\frac{C_P}{R} = 2.7 \quad (< \frac{C_V}{R})$ Diamond $\frac{C_P}{R} = 0.73 \ll 3$

To explain this, Einstein (1907) proposed a simple model for quantized vibrations of solids (phonon gas)

On average each atom moves in a potential of the form

$$\phi = \phi_0$$

$q = \text{displacement from equilibrium position}$

potential energy $U(193) = U^0 + \frac{1}{2} \sum_{i=1}^{3N} \hbar \omega_i q_i^2$ (normal)

So the total energy of a state of the system is the sum of the energies of the $3N$ independent normal mode oscillations

$$E = \text{The energy of one harmonic oscillator w/ frequency } \omega$$

$$E = (n + \frac{1}{2}) \hbar \omega \quad \omega = \sqrt{\frac{\hbar m}{\kappa}}$$

$n = \text{quantum number } 0, 1, 2, ...$ $\# \text{ of phonons}

$$E_r = \sum_{i=1}^{3N} (n_i + \frac{1}{2}) \hbar \omega_i$$

with $U_0 = 0$

$$Z = \sum_r e^{-\beta E_r} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \ldots \sum_{n_{3N}=0}^{\infty} e^{-\beta \sum_{i=1}^{3N} (n_i + \frac{1}{2}) \hbar \omega_i}$$

This factors into a product of independent terms

$$Z = \prod_{i=1}^{3N} \sum_{n_i=0}^{\infty} e^{-\beta (n_i + \frac{1}{2}) \hbar \omega_i} = \frac{1}{\prod_{i=1}^{3N} e^{-\beta \hbar \omega_i}}$$

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad x = e^{-\beta \hbar \omega_i}$$
For simplicity, Einstein assumed all $w_i = w$ so

$$z = \exp\left(-\frac{3N}{2} \beta \frac{w}{k}\right) \left(1 - \exp(-\beta \frac{w}{k})\right)^{-3N}$$

$$\ln z = -\frac{3N}{2} \beta \frac{w}{k} - 3N \ln (1 - \exp(-\beta \frac{w}{k}))$$

$$E = -\frac{2N \ln z}{3 \beta} = \frac{3N \frac{w}{k}}{} + \frac{3N \frac{w}{k}}{\exp(\beta \frac{w}{k}) - 1}$$

c{C} \{ \begin{array}{l}
\quad \rightarrow 0 \text{ at low } T \\
\quad \rightarrow 3NkT \text{ at high } T
\end{array}\}

Einstein temperature $\theta_E = \frac{hw}{k}$

$$E = E_0 + 3Nk\theta_E / (\exp(\theta_E / T) - 1) \quad (C_V = \frac{\delta E}{\delta T})$$

$$C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E / T)}{(\exp(\theta_E / T) - 1)^2}$$

strong $T$ dependence

at high $T$, $\theta_E / T \ll 1$, $C_V \rightarrow 3vR$
all vibrational modes are fully excited

at low $T$, $\theta_E / T \gg 1$, $C_V \rightarrow 3vR \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E / T}$

no contribution to heat capacity \rightarrow 0 \quad \text{all vibrational modes forced into ground state}

Einstein model unrealistic, but it gave the correct qualitative explanation for deviations from $\gamma$-law if Dulong-Petit $\rightarrow \theta_E / T \gg 1$ means vibrational modes are too stiff to be excited
-behaves like a rigid bond
Canonical Partition Function $Z$

Some useful properties of $Z$:

1. For two (or more) weakly interacting distinguishable systems (e.g., a binary mixture)

$$E_{rs} = E_r^{(1)} + E_s^{(2)} \quad \text{(state energy is additive)}$$

so

$$Z = \sum_{rs} e^{-\beta E_{rs}} = \sum_r e^{-\beta E_r^{(1)}} \sum_s e^{-\beta E_s^{(2)}} = Z^{(1)} Z^{(2)}$$

$$Z = Z^{(1)} Z^{(2)} \quad \text{factors into a product}$$

2. For system containing $N$ weakly interacting indistinguishable particles

$$E_r = \sum_{i=1}^N E_i, \quad E_i = \text{energy of particle } i$$

$$Z = \sum_r e^{-\beta E_r} = \sum_{\{E_i\}} e^{-\beta E_i} = \sum_{\{E_i\}} \prod_{i=1}^N e^{-\beta E_i} \quad \text{ok if "particles" are distinguishable}$$

Now a state is defined by a set of $E_i$ values - if the labels are swapped around without changing the actual values of $E_i$, we still have the same state. To simplify the counting, we ignore this complication and let each $E_i$ take on all possible values, but then we divide by $N!$ to correct (approximately - this is not valid at low $T$ where quantum statistics matters) for over counting. So we get

$$Z \approx \frac{1}{N!} \left( \sum_i e^{-\beta E_i} \right) \left( \sum_i e^{-\beta E_i} \right) \cdots \left( \sum_i e^{-\beta E_i} \right)$$

$$Z = \frac{Z_1^N}{N!} \quad Z_1 = \frac{Z e^{-\beta E_i}}{e_i} \quad \text{a single molecule partition function}$$