Chapter 3.2: Canonical Examples

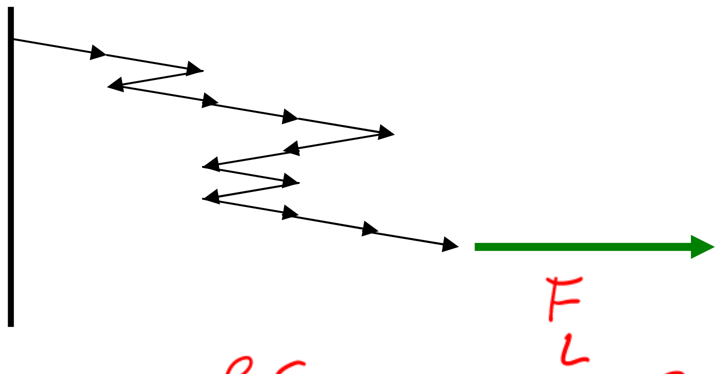
Comparison overview

Microcanonical ensemble large isolated systems	**Canonical ensemble** systems of any size at fixed T
E given (and const.)	T given (and const.)
calculate $\Omega(E, V, N, \dots)$	calculate $Z = \sum_r e^{-\beta E_r}$
determine $S = k_B \ln \Omega(E, V, N)$	determine $F = -k_B T \ln Z (T, V, N, \dots)$
take derivatives/expectation values	take derivatives/expectation values
$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$ or $\beta = \frac{\partial \ln \Omega}{\partial E}$	$E = -\frac{\partial \ln Z}{\partial \beta}$
$p = \frac{1}{T}\left(\frac{\partial S}{\partial V}\right)_E$ $\quad F_\alpha = \frac{1}{T}\left(\frac{\partial S}{\partial \alpha}\right)_{E,\text{rest}}$	$p = -\left(\frac{\partial F}{\partial V}\right)_T$ $\quad F_\alpha = -\left(\frac{\partial F}{\partial \alpha}\right)_T$

Example: Polymer with N segments

Simplification: each segment can point left or right   two states $r = \pm$

$r = \{r_1, r_2, \ldots r_N\} = \{+ + - + + + - - + - + + + \}$



Energy

$\mathcal{E}(\{r_j\}) = \mathcal{E}(r_1) + \mathcal{E}(r_2) + \ldots \mathcal{E}(r_N)$

$\mathcal{E}(r_j) = r_j F_L \cdot d \qquad r_j = \pm 1$

$$Z = \sum_{\{r_j\}} e^{-\beta \mathcal{E}} = \sum_{\{r_j\}} e^{-\beta \mathcal{E}(r_1)} e^{-\beta \mathcal{E}(r_2)} \cdots e^{-\beta \mathcal{E}(r_N)} = (Z_1)^N$$

$$Z_1 = \sum_{r=\pm} e^{-\beta \mathcal{E}(r)} = e^{\beta F_L d} + e^{-\beta F_L d} = 2\cosh(\beta F_L d)$$

$$Z = (2\cosh \beta F_L d)^N$$

Force and temperature are given. Calculate length as expectation value:

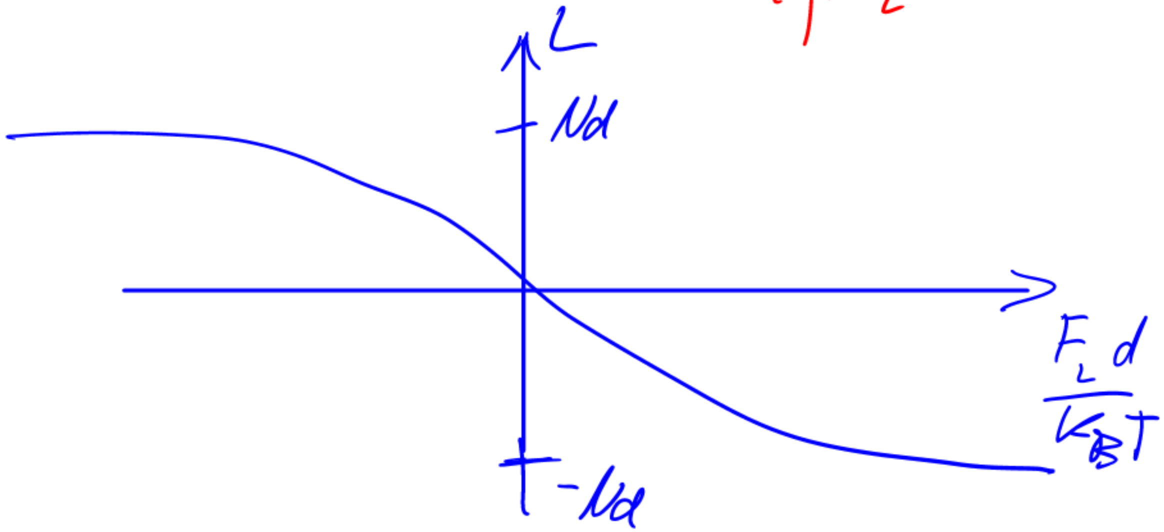
$$l_r = \pm d$$

$$L = N\langle l \rangle = N \sum_r P_r l_r = N\left(\frac{d e^{-\beta F_L d}}{Z_1} - \frac{d e^{\beta F_L d}}{Z_1}\right)$$

$$= Nd \frac{-2 \sinh \beta F_L d}{2 \cosh \beta F_L d} = -Nd \tanh \frac{F_L d}{k_B T}$$

before:

$$F_L = \frac{k_B T}{2d} \ln \frac{Nd - L}{Nd + L}$$



Def. 3.3:

For independent and distinguishable particles the partition function is $Z = (Z_1)^N$, where the Free Energy $Z_1 = \sum_r e^{-\beta \varepsilon_r}$ is the single particle partition function for the degrees of freedom of one particle.

$$\mathcal{E}_{tot}(\{r_j\}) = \mathcal{E}(r_1) + \mathcal{E}(r_2) + \dots \mathcal{E}(r_N)$$

if total energy is a sum of individual energies, then the degrees of freedom are called independent

Addition of energies and energy shifts

generally for two degrees of freedoms r_a, r_b

if $\varepsilon_{tot}(r_a, r_b) = \varepsilon_a(r_a) + \varepsilon_b(r_b)$:

$$Z = \sum_{r_a r_b} e^{-\beta \varepsilon_{tot}} = \sum_{r_a} e^{-\beta \varepsilon_a(r_a)} \sum_{r_b} e^{-\beta \varepsilon_b(r_b)} = Z_a Z_b$$

$$P_{r_a, r_b} = \frac{e^{-\beta \varepsilon_a} e^{-\beta \varepsilon_b}}{Z_a Z_b} = P_{r_a} P_{r_b}$$

$$F_{tot} = -k_B T \ln Z = F_a + F_b$$

$$E_{tot} = E_a + E_b$$

$$S_{tot} = S_a + S_b$$

Shift of ground state energy

$$\varepsilon_r' = \varepsilon_r + \varepsilon_0$$

$$Z' = \sum_r e^{-\beta \varepsilon_r'} = \sum_r e^{-\beta(\varepsilon_r + \varepsilon_0)} = e^{-\beta \varepsilon_0} Z$$

$$F' = -k_B T \ln Z' = -k_B T \ln Z + \underline{\cancel{\beta} \varepsilon_0 \cdot \cancel{k_B T}} = F + \varepsilon_0$$

$$E' = E + \varepsilon_0$$

$$S' = S$$

$$P_r' = \frac{e^{-\beta \varepsilon_r'}}{Z'} = \frac{\cancel{e^{-\beta \varepsilon_0}}}{\cancel{e^{-\beta \varepsilon_0}}} \frac{e^{-\beta \varepsilon_r}}{Z} = P_r$$