1. Consider the behavior of a linear chain of N statistically independent segments depicted in Figure 1. The energetics and degeneracies of the individual segments are described in the figure caption. The chain is at equilibrium under tension f at temperature $k_bT = 1/\beta$.

   When answering the questions below, you might find it convenient to utilize the variables $n_i, 1 \leq i \leq N$, where $n_i = 0$ when the ith segment is any one of its g_0 low energy states, and $n_i = 1$ when the ith segment is any one of its g_1 high energy states. Accordingly, its average value, $\langle n_i \rangle$, is the probability that a particular segment is in a high energy state.

   Further, the energy and length of the chain when it is in a microstate ν are

$$E_\nu = N\epsilon_0 + \triangle\epsilon \sum_{i=1}^{N} n_i$$

   and

$$L_\nu = N\ell_0 - \triangle\ell \sum_{i=1}^{N} n_i,$$

   respectively. Given the degeneracies g_0 and g_1, there are many microstates with the same values for E_ν and L_ν.

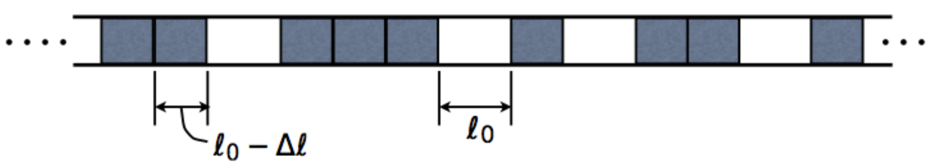


Figure 1: Linear chain with low energy segments (white) and high energy segments (dark). For a low energy segment, there are g_0 microstates, each with energy ϵ_0 and segment length ℓ_0. Similarly, for a high energy segment, there are g_1 microstates each with energy $\epsilon_0 + \triangle\epsilon$ and segment length $\ell_0 - \triangle\ell$.

   By noting that the different n_i's are uncorrelated, the partition function of the chain is found to be

$$Z = (g_0 e^{-\beta\epsilon_0 + \beta f \ell_0} + g_1 e^{-\beta(\epsilon_0 + \triangle\epsilon) + \beta f(\ell_0 - \triangle\ell)})^N.$$

   (a) Evaluate the probability that the ith segment is in one of the higher energy states. Express your answer in terms of $\beta, f, \triangle\epsilon, \triangle\ell$, and $r = g_1/g_0$.

   (b) Evaluate the average length, $\langle L \rangle$. Express your answer in terms of β, f, N and the microscopic variables $\triangle\epsilon, \ell_0, \triangle\ell$, and $r = g_1/g_0$.

   (c) Evaluate the average energy, $\langle E \rangle$. Express your answer in terms of β, f, N and the microscopic variables $\epsilon_0, \triangle\epsilon, \triangle\ell$, and $r = g_1/g_0$.

(d) Evaluate the mean square fluctuation in chain length, $\langle(\delta L)^2\rangle = \langle L^2\rangle - \langle L\rangle^2$. Express your answer in terms of β, f, N and the microscopic variables $\triangle\epsilon, \triangle\ell$, and $r = g_1/g_0$.

(e) Use the result of Part (d) to evaluate $(\partial\langle L\rangle/\partial\beta f)_{\beta,N}$. [**Hint:** a mean square fluctuation can be related to a response of a mean to a change in conjugate field.] Express your answer in terms of β, f, N and the microscopic variables $\triangle\epsilon, \triangle\ell$, and $r = g_1/g_0$.

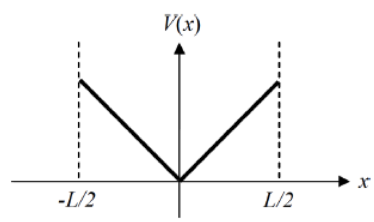
(f) Use the result of Part (e) to evaluate the average chain length, $\langle L\rangle$, for small (but non-zero) tension f. Carry out the evaluation through linear order in f. Express your answer in terms of β, f, N and the microscopic variables $\triangle\epsilon, \ell_0$, and $r = g_1/g_0$.

(g) The heat capacity of the chain under constant tension is $C_f = T(\partial S/\partial T)_{f,N}$, where S stands for the entropy of the chain. Evaluate C_f for the case where tension is small (*i.e.*, through lowest non-trivial order in f). Express your answer in terms of β, f, N and the microscopic variables $\triangle\epsilon, \triangle\ell$, and $r = g_1/g_0$. Check that your result predicts $C_f \to 0$ as $T \to 0$.

2. N classical particles with mass m are confined to a 3D box of size $L \times L \times L$. A special field is applied in the x direction (see figure) and the total potential energy is given by:

$$V(x,y,z) = \begin{cases} \alpha\,|x| & -L/2 \le x,y,z \le L/2 \\ \infty & \text{otherwise} \end{cases}$$

The the system is in contact with a bath at temperature $T = (k_B\beta)^{-1}$.



(a) Calculate the canonical partition function for $N = 1$. How would your answer change for N indistinguishable non-interacting particles confined to the box?

(b) Calculate the average energy and heat capacity for N identical particles. What is the relative fluctuations in energy? Show that it scales as $N^{-1/2}$.

(c) Calculate the pressure that the particles exert on the walls of the box. [**Hint:** use the relation $V = L^3$.] Additionally, define the low and high temperature limit and estimate the pressure at these two limits? Explain the results qualitatively.

(d) Set $\alpha = 0$ (Taylor expand) and show that your result from (1) reduces to the ideal gas partition function - $\frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$.

(e) Calculate the grand canonical partition function for $\alpha = 0$. Use the relation: $\sum_N a^N/N! = \exp(a)$. Derive the equation of state of the ideal gas using this ensemble.

3. Consider a one-dimensional harmonic oscillator in a heat bath at temperature T. The Hamiltonian for the oscillator is

$$H(x,p) = p^2/2m + m\omega^2 x^2/2$$

where x is the oscillator coordinate, p is the conjugate momentum, m is a mass, and ω is a frequency. The stationary solutions of Schrödinger's equation give the energy levels $(n + 1/2)\hbar\omega$, with $n = 0, 1, 2, ...$

(a) Determine the average energy of the oscillator as a function of temperature T.

(b) Determine the average energy of the oscillator as a function of T when T is large, *i.e.*, when $\beta\hbar\omega \ll 1$. In this regime, the spacing between energy levels is small compared to the thermal uncertainty of energy.

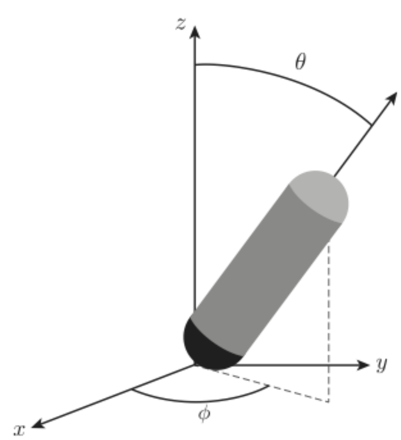
(c) In the classical limit, x and p are variables (not operators) for which a microstate is specified by the pair of variables (x,p) and the average energy is

$$\langle H \rangle = \frac{\int dx \int dp H(x,p) \exp\left[-\beta H(x,p)\right]}{\int dx \int dp \exp\left[-\beta H(x,p)\right]}$$

Use this formula to evaluate the average energy of the oscillator and compare it with that obtained in Part (b). The two results should be the same, illustrating that a classical description is correct when the thermal uncertainties are large compared to energy level spacing.

4. Please do questions 3.15 and 4.26 in *IMSM*.

5. Consider a rigid rod (perhaps a nanocrystal or an inflexible linear molecule) moving in three dimensions.



Equilibrium statistics of the rod's orientation are independent of its center-of-mass position. Here we will focus exclusively on rotational fluctuations, *i.e.*, variations in the polar and azimuthal angles, θ and ϕ, in a laboratory reference frame. Specifically, you will calculate averages and partition functions through summations of the form

$$\sum_{\nu}(...) \to \int_{-1}^{1} d(\cos\theta) \int_{0}^{2\pi} d\phi(...)$$

These rotations are biased by an external field (perhaps an electric field) that encourages alignment of the rod's long axis along the z-direction,

$$u(\theta, \phi) = -\epsilon \cos\theta,$$

where ϵ is a positive constant.

(a) Calculate the canonical partition function q_{rot} for orientational fluctuations at a temperature T.

(b) Differentiate q_{rot} to obtain the average degree of alignment, $\langle\cos\theta\rangle$, as well as the average energy $\langle u\rangle$. Using a computer, plot $\langle u\rangle/\epsilon$ as a function of $k_B T/\epsilon$.

(c) Determine the asymptotic behavior of $\langle u\rangle$ at high temperature. Specifically, identify the leading order term in an expansion of $\langle u\rangle$ in powers of $\beta\epsilon$.

(d) Determine the asymptotic behavior of $\langle u\rangle$ at low temperature. To do so, it is sufficient to recognize that $e^{-\beta\epsilon}$ is very small in this limit and may be neglected in quantities like $e^{\beta\epsilon} + e^{-\beta\epsilon}$.

(e) Make a plot of $\langle u\rangle/\epsilon$ as a function of $k_b T/\epsilon$ that includes the limiting behaviors you determined in parts (c) and (d).

(f) Calculate the heat capacity C_{rot}, as well as the variance $\langle\delta u^2\rangle$ of energy fluctuations. (Do not worry about contributions to C_{rot} from kinetic energy fluctuations.)

(g) Differentiate the asymptotic expansions from parts (c) and (d) to determine limiting behaviors of the heat capacity C_{rot}.

(h) Explain the limiting values of C_{rot} at high and low temperature. In one case you should be able to appeal to the classical limit, and in the other case you should consider the magnitudes of fluctuations in potential energy.