1. **Isobaric ensemble** — A piston of macroscopic mass $M$ encloses, under gravity, a fluid in a cylinder of area $A$. The whole system (piston plus fluid) is immersed in a thermal bath at temperature $T$. The full Hamiltonian of the system includes, in addition of the fluid Hamiltonian $H_N$, the potential and kinetic energies of the piston due to its one-dimensional motion along the vertical direction.

(a) Show that the average of an operator involving only the fluid may be written as

$$\langle \mathcal{O} \rangle = \frac{\int dV e^{-\beta PV} \int d\Gamma \mathcal{O} e^{-\beta H_N(\Gamma)}}{Q(\beta, P, N)}$$

where $\Gamma$ refers to all of the fluid’s degrees of freedom. Precisely define $P$. Give the integral expression for the isobaric partition function $Q(\beta, P, N)$.

(b) Use the saddle-point method to relate the logarithms of $Q(\beta, P, N)$ and the canonical partition function $Z(\beta, V, N)$; derive from it the relation between the Gibbs free energy, $G(\beta, P, N) = -\beta^{-1} \ln Q(\beta, P, N)$, and the Helmholtz free energy.

(c) Find the entropy and the mean volume $\langle V \rangle = \langle V \rangle$ in the isobaric ensemble in terms of the thermodynamic derivatives of $G(\beta, P, N)$.

(d) Derive the relation between the isothermal compressibility $\kappa_T = -V^{-1} \left( \partial V / \partial P \right)_{T,N}$ and the variation in volume fluctuation, $\langle (V - \bar{V})^2 \rangle$.

(e) Find the distribution of volumes, $P(V)$, for $V$ near $\bar{V}$. Express the result in terms of $\bar{V}$ and $\kappa_T$.

2. **Anharmonic Oscillator** — A system is composed of $N$ identical classical oscillators, each of mass $m$, defined on a one-dimensional lattice. Assume that the potential for the oscillators has the form $U(x) = \varepsilon_0 |x/a|^n$. Find the average thermal energy at temperature $T$. Note that the harmonic oscillator corresponds to the case $n = 2$.

3. **Surface fluctuation** — The figure below illustrates a simple model of the surface of a two-dimensional ‘solid’ confined to a square lattice. The two ends of the surface are $N$ lattice sites apart, with $N \gg 1$. The surface energy is proportional to the surface length, with energy $\varepsilon > 0$ per lattice length. The surface height can change by at most one lattice length at a time. (Overhangs are forbidden, so that outward-pointing surface normals never point downward.)
Thus the surface can be modeled by a Hamiltonian
\[ H = \varepsilon \sum_{i=1}^{N} (1 + \sigma_i^2), \]
where \( \sigma_i = +1, 0, \) or \( -1 \) depending on whether the \( i \)th ‘column’ contains a step up, no step, or step down, respectively.

(a) Find the partition function of the surface at temperature \( T \).
(b) Sketch the temperature dependence of the free energy \( F(T) \) of the surface. Interpret your result physically in the limit \( k_B T \ll \varepsilon \) and \( k_B T \gg \varepsilon \).
(c) Find the total length of the surface (including all the up and down steps) as a function of the temperature and sketch its temperature dependence.

4. **Polymer Elasticity** — Consider a model polymer consisted of \( N + 1 \) monomers connected by \( N \) freely jointed links, each of fixed length \( a \). One end of a polymer is fixed, say at the origin, and a force \( f \) is applied to the monomer at the other end.

(a) Show that the Hamiltonian of the system is (up to an additive constant) given by
\[ \mathcal{H} = -\sum_{i=1}^{N} f \cdot a_i, \]
where \( a_i = r_i - r_{i-1} \) denotes the orientation of the \( i \)th link, \( r_j \) being the position vector of the \( j \)th monomer.
(b) Compute the partition function \( Z(T, f) \) and obtain the free energy to order \( f^2 \).
(c) Show that the average end-to-end distance \( R(f) \) of the polymer is given by \( R = \langle \sum_{i=1}^{N} a_i \rangle \), and find \( R \) to leading order in \( f \) using the result of part (b). Explain the physical origin of the spring-like elastic behavior of this system.

5. **DNA denaturation bubble** — An DNA bubble refers to the localized opening of a contiguous segments of the DNA double helix. It may occur to relieve torsional strain applied to the double helix, or upon raising the temperature close to the melting temperature where the double helix dissociates (or “denatures”). A naive model for the energy of a DNA bubble of \( L \) open bases starting from the \( i \)th base is
\[ H_i = \sum_{j=i}^{i+L-1} \varepsilon_j \]
where \( \varepsilon_j \) is the energy cost of opening the \( j \)th base pair, and \( 1 \leq i \leq N - L + 1 \) are the possible bubble positions in a DNA sequence of \( N \) total bases; see Figure.

It turns out that \( \varepsilon_j \) can take on two possible values, \( \varepsilon_j = 0 \) if the \( j \)th base pairing is an A/T, and \( \varepsilon_j = \Delta \varepsilon > 0 \) if it is G/C. In the following, consider the bubble to be large (i.e., \( L \gg 1 \)), and embedded in an even much longer DNA sequence (i.e., \( N \gg L \)), with an average composition of 50% A/T and 50% G/C.
Find the probability $p_L(n)$ that a bubble of length $L$ has $n$ G/C pairings and $L - n$ A/T pairings. Write down the density of states $\Omega(E, L, N)$ in terms of the number of G/C pairs $n_i$ for a bubble starting at position $i$. Treating $n_i$ as a random variable drawn according to the probability $p_L(n)$ independently for each $i$, write down an expression for $\Omega(E, L, N)$. [This is known as the “annealed approximation”.] Apply Stirling’s formula ($\ln(n!) \approx n \ln(n) - n$ for $n \gg 1$) to show that the entropy function has the asymptotic form

$$S(E, L, N)/k_B = \ln N - L f(E/E_0)$$

where $E_0 \equiv \Delta \varepsilon \cdot L$ is the maximum allowed energy of the bubble.

(b) Plot $S/k_B$ vs. $E$ in the interval $0 \leq E \leq E_0$ for $N = 10^4$ and $L = 10, 30, 100$ (all on the same plot). Show that for some combinations of $N$ and $L$’s, there can be an energy value $E_c$ below which $S < 0$. Sketch how $E_c$ depends on $N$ and $L$.

(c) At a given temperature $T$, explain how the “graphical method” of Legendre Transform can be used to find the average energy $\overline{E}(T)$ and the Helmholtz energy $F(T) = E - TS$ from the shape of $S$ found in (b). What is the value of $S$ as $T \to \infty$? What does this result mean physically?

(d) Directly compute the partition function $Z(T, L, N)$ from $p_L(n)$ and $H$, again using the annealed approximation. Find $\overline{E}(T)$ and $S(T)$ from $Z$. Recompute $S(E)$ by using your expression for $S(T)$ and inverting your expression for $\overline{E}(T)$. Compare your result to that obtained in (a).

(e) From your expression for $S(T, L, N)$ above, show that the bubble length $L$ must be below a critical value $L_c(N, T)$ to ensure that $S > 0$ at a given temperature $T > 0$. For $\Delta \varepsilon = 1$ kcal/mole, $T = 300^\circ K$, and $N = 10^4$, find $L_c$.

(f) Alternatively, for given $L$ and $N$, the temperature $T$ must be above a critical value $T_c(L, N)$ for $S > 0$. Illustrate the relation between $T_c(L, N)$ and the critical energy value $E_c(L, N)$ obtained in (b) by using the graphical construction of (c).

(g) Clearly for $T < T_c$ or for $L > L_c$, something went wrong with the annealed approximation since physically $S$ cannot be negative. Can you identify what is responsible for the break down of this approximation at low temperature or large $L$? You may continue to take the limits $L \gg 1$ and $N \gg L$ as valid. [Hint: Consider what it means when a system has $S = 0$ at a finite temperature. (Quantum mechanics is not relevant at the temperature scale we discuss here.)]

Note: This system is a simple realization of the so-called “Random Energy Model” widely used to describe heterogeneous systems including the “spin glass” and proteins.