Statistical Mechanics

Part I (Warm-up)

1. Part I: Starting from the first and second law of thermodynamics, show that

   (a) the maximum work that can be extracted from a system in a process at constant temperature is equal in magnitude to the change in its Helmholtz free energy.

   (b) the maximum non-expansion work that can be extracted from a system in a process at constant temperature and pressure is equal in magnitude to the change in its Gibbs free energy.

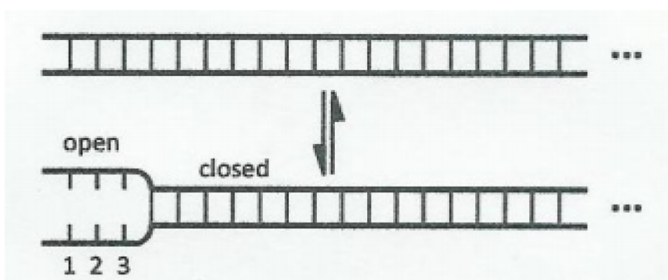
   Part II: Consider a system consisting of two particles, each of which can be in any one of three quantum states of respective energies 0, ε, and 3ε. The system is in contact with a heat reservoir at temperature T. Ignore the spin degrees of freedom

   (a) Write an expression for the partition function Z if the particles obey classical Boltzman statistics and are considered distinguishable.

   (b) What is Z if the particles obey Bose-Einstein statistics?

   (c) What is Z if the particles obey Fermi-Dirac statistics?

2. DNA can be modeled as two parallel polymer strands with links between the strands called base pairs. Each base pair can be in a closed state with energy 0 or in an open state with energy $\varepsilon > 0$.



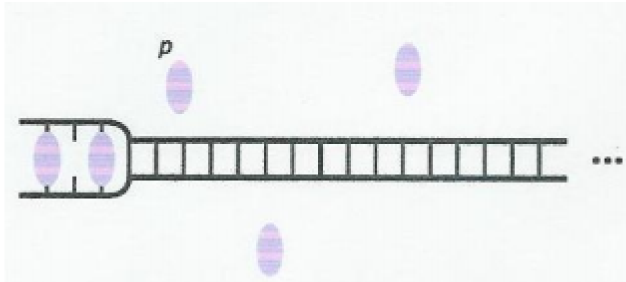
   Consider a DNA molecule with N base pairs in thermal equilibrium at temperature T, as shown. Thermal fluctuations can cause each base pair to open, leading to separation of the two strands. Assume that the two strands are tethered together at the right end such that the molecule can open only from the left end, and only in sequential order (i.e. base pairs can open only if $1, 2.., s-1$ to the left of it are already open.)

   (a) Show that the partition function Z for this system is given by the following expression

$$Z = \frac{1 - \exp\left(-\frac{(N+1)\varepsilon}{k_B T}\right)}{1 - \exp\left(\frac{-\varepsilon}{k_B T}\right)} \tag{1}$$

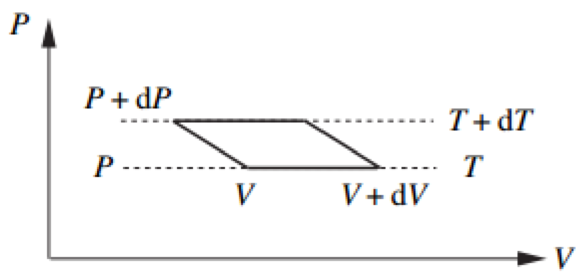
   (b) In the limit that $N \to \infty$ determine the mean number $\langle n \rangle$ of open base pairs.

   (c) Evaluate $\langle n \rangle$ from part (b) in the limit (i) $T \to 0$ and (ii) $T \to \infty$



(d) Next, consider the same DNA molecule now surrounded by a protein p at concentration c. Protein p can bind to the DNA only at a site that is open as shown.
Assume each protein p can occupy no more than one base pair. The chemical potential for p is $\mu = \Delta + k_B T \ln\left(\frac{c}{c_0}\right)$, where c_0 and Δ are constants ($c_0 > 0$). Write down a closed form expression for the Grand canonical ensemble for this system, in the limit that $N \to \infty$

3. Photon gas Carnot cycle: the aim of this problem is to obtain the black-body radiation relation, $E(T,V) \propto VT^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.



(a) Express the work done, W, in the above cycle, in terms of dV and dP
(b) Express the heat absorbed, Q, in expanding the gas along an isotherm, in terms of P, dV, and an appropriate derivative of $E(T,V)$.
(c) Using the efficiency of the Carnot cycle, relate the above expressions for W and Q to T and dT.
(d) Observations indicate that the pressure of the photon gas is given by $P = AT^4$,where $A = \pi^2 k_B^4/45(\hbar c)^3$ is a constant. Use this information to obtain $E(T,V)$, assuming $E(T,0) = 0$.
(e) Find the relation describing the adiabatic paths in the above cycle.

4. Gas in a potential: A gas consisting of N identical classically moving but indistingushable particles is confined inside a cylinder of length $L = a - b$ and cross section area $A = \pi r^2$ defined, in Cartesian coordinates, by

$$b < z < a, \qquad x^2 + y^2 < R^2 \tag{2}$$

Particles do not interact with each other and the motion of each is governed by the Hamiltonian

$$H = \frac{\vec{p}^2}{2m} + Kz \tag{3}$$

where K is a constant. Use units in which $k_B = 1$. The has is in equilibrium

(a) Calculate the partition function of the gas.

(b) Determine the pressure p_a of the gas on the wall at $z = a$.

(c) Determine the pressire p_b of the gas on the wall at $z = b$.

(d) Compare the pressure at p_a and p_b in the limit $KL >> T$. Explain.

(e) What is the root mean square, $\vec{v^2}(z)$ of a particle velocity at a given coordinate z.

Part II

1. Squeezed chain: A rubber band is modeled as a single chain of N massless links of fixed length a. The chain is placed inside a narrow tube that restricts each link to point parallel or anti-parallel to the tube.

   (a) Ignoring any interactions amongst the links, give the number of configurations of the chain, $\Omega(L, N)$, where L is the end-to-end length of the chain.

   (b) Use Stirling's approximation to express the result for entropy as a function of N and $x = L/(Na)$.

   The tube is now uniformly squeezed such that stretched configurations are energetically favored. For this problem, assume a simplified form of this energy that depends inversely on the local link density, such that the energy of a uniformly stretched state is

   $$E(L, N) = -\frac{\sigma}{2} L \times \frac{L}{N} = -\frac{\sigma a^2}{2} N x^2 \tag{4}$$

   (Use this formula for energy for all states of given L and N in the remainder of this problem.)

   (c) Calculate the free energy $F(T, L, N)$, and the force $J(T, L, N)$ acting on the end points of the chain. (The work done on expanding the chain is $dW = JdL$)

   (d) Sketch the isotherms $J(x, T)$ at high and low temperatures, and identify the temperature T_c when the behavior changes

   (e) What is the condition for stability of the chain? What portion of the above isotherms are inherently unstable

   (f) Using the form for J obtained in part (c), find an expression for the unforced ($J = 0$) chain length that is valid as T approaches T_c from below.

2. Boson magnetism: Consider a gas of non-interacting spin 1 bosons, each subject to a Hamiltonian

   $$H(\vec{p}, s_z) = \frac{\vec{p}^2}{2m} - \mu_0 s_z B \tag{5}$$

   where $\mu_0 = e\hbar/mc$, and s_z takes three possible values of $(-1, 0, +1)$. The orbital effect $\vec{p} \to \vec{p} - e\vec{A}$, has been ignored.

   (a) In a grand canonical ensemble of chemical potential μ, what are the occupancy numbers $\{\langle n_+(\vec{k})\rangle, \langle n_0(\vec{k})\rangle, \langle n_-(\vec{k})\rangle\}$, of one-particle states of wavenumber $\vec{k} = \vec{p}/\hbar$?

(b) Calculate the average total numbers $\{N_+, N_0, N_-\}$, of bosons with the three possible values of s_z in terms of the functions $f_m^+(z)$ where

$$f_m^+(z) = \frac{1}{\Gamma(m)} \int_0^\infty \frac{x^{m-1}}{z^{-1}e^x - 1} dx \tag{6}$$

(c) Write down the expression for the magnetization $M(T, \mu) = \mu_0(N_+ - N_-)$, and by expanding the result for small B find the zero field susceptibility $\chi(T, \mu) = \partial M/\partial B|_{B=0}$.

To find the behaviour of $\chi(T, n)$ where $n = N/V$ is the total density, proceed as follows:

(d) For $B = 0$, find the high temperature expansion for $z(\beta, n) = e^{\beta\mu}$, correct to second order in n. Hence obtain the first correction from quantum statistics to $\chi(T, n)$ at high temperatures.

(e) Find the temperature $T_c(n, B = 0)$, of Bose-Einstein condensation. What happens to $\chi(T, n)$ on approaching $T_c(n)$ from the high temperature side?

(f) What is the chemical potential μ for $T < T_c(n)$, at a small but finite value of B? Which one-particle state has a macroscopic occupation number?

(g) Using the result in (f), find the spontaneous magnetization,

$$\bar{M}(T, n) = \lim_{B \to 0} M(T, n, B). \tag{7}$$

3. Exciton dissociation in a semiconductor: By shining an intense laser beam on a semiconductor, one can create a metastable collection of electrons (charge $-e$, and effective mass m_e) and holes (charge $+e$, and effective mass m_h) in the bulk. The oppositely charged particles may pair up (as in a hydrogen atom) to form a gas of excitons, or they may dissociate into a plasma. We shall examine a much simplified model of this process.

   (a) Calculate the free energy of a gas composed of N_e electrons and N_h holes, at temperature T, treating them as classical non-interacting particles of masses m_e and m_h

   (b) By pairing into an excition, the electron hole pair lowers its energy by ε. [The binding energy of a hydrogen-like exciton is $\varepsilon \approx me^4/(2\hbar^2\epsilon^2)$, where ϵ is the dielectric constant, and $m^{-1} = m_e^{-1} + m_h^{-1}$.] Calculate the free energy of a gas of N_p excitons, treating them as classical non-interacting particles of mass $m = m_e + m_h$.]

   (c) Calculate the chemical potentials μ_e, μ_h, and μ_p of the electron, hole, and exciton states, respectively.

   (d) Express the equilibrium condition between excitons and electron/holes in terms of their chemical potentials.

   (e) At a high temperature T, find the density n_p of excitons, as a function of the total density of excitations $n \approx n_e + n_h$.

4. The Clausius-Clapeyron equation describes the variation of boiling point with pressure. It is usually derived from the condition that the chemical potentials of the gas and liquid phases are the same at coexistence. For an alternative derivation, consider a Carnot engine using one mole of water. At the source (P, T) the latent heat L is supplied converting water to steam. There is a volume increase V associated with this process. The pressure is adiabatically decreased to $P - dP$. At the sink $(P - dP, T - dT)$ steam is condensed back to water.

(a) Show that the work output of the engine is $W = VdP + \mathcal{O}(dP^2)$. Hence obtain the Clausius-Clapeyron equation

$$\left.\frac{dP}{dT}\right|_{boiling} = \frac{L}{TV} \tag{8}$$

(b) What is wrong with the following argument: "The heat Q_H supplied at the source to convert one mole of water to steam is $L(T)$. At the sink $(L, T - dT)$ is supplied to condense one mole of steam to water. The difference $dTdL/dT$ must equal the work $W = VdP$, equal to LdT/T from Eq. (1). Hence $dL/dT = L/T$, implying that L is proportional to T!"

(c) Assume that L is approximately temperature-independent, and that the volume change is dominated by the volume of steam treated as an ideal gas, that is, $V = Nk_BT/P$.

(d) A hurricane works somewhat like the engine described above. Water evaporates at the warm surface of the ocean, steam rises up in the atmosphere, and condenses to water at the higher and cooler altitudes. The Coriolis force converts the upward suction of the air to spiral motion. (Using ice and boiling water, you can create a little storm in a tea cup.) Typical values of warm ocean surface and high altitude temperatures are 80°F and −12°F, respectively. The warm water surface layer must be at least 200 feet thick to provide sufficient water vapor, as the hurricane needs to condense about 90 million tons of water vapor per hour to maintain itself. Estimate the maximum possible efficiency, and power output, of such a hurricane. (The latent heat of vaporization of water is about 2.3×10^6 J kg^{-1}.)