

THE UNIVERSITY OF QUEENSLAND
SCHOOL OF MATHEMATICS AND PHYSICS
PHYS3020/3920/7021 – Statistical Mechanics

Module 2 Worksheet: Canonical Ensembles

Module Problem Set Due Monday 5 Sept, 2 pm. Submission portal on Blackboard.

Questions 2, 3, 4, 7, 8 and 9 are for assessment.

1. **[PRACTICE PROBLEM] Bringing water to boil**

Estimate how long it should take to bring a cup of water to boiling temperature in a typical 800 watt microwave oven, assuming that all the energy ends up in the water. (Assume any reasonable initial temperature for the water.)

Hint: Make use of the definition of a calorie from the lecture notes.

2. **[FOR ASSESSMENT] Factorizability of the partition function**

(a) Consider a system of two independent particles, each different, in a thermal contact with a common reservoir at temperature T . The first particle has two permissible orbital states, of energies E_{11} and E_{12} ; similarly, the second particle has permissible energies E_{21} and E_{22} . Write the partition function explicitly, and by explicit algebra factor it in the form of the product of the partition functions of each particle. By doing this you will explicitly demonstrate the factorability property of the partition function, for two independent systems, in this simple example of two particles each of which can be in just two states.

(b) Show that the partition function $Z(\mathbf{1} + \mathbf{2})$ of two independent systems $\mathbf{1}$ and $\mathbf{2}$ in thermal contact at a common temperature T is equal to the product of the partition functions of the separate systems:

$$Z(\mathbf{1} + \mathbf{2}) = Z(\mathbf{1})Z(\mathbf{2}).$$

In other words, do the same as in part (a), but for two generic independent systems, i.e., without assuming that each of them can be in just two states.

3. **[FOR ASSESSMENT] Partition function for a harmonic oscillator**

A one-dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $E_s = s\hbar\omega$, where s is a positive integer or zero. (We omit the zero point energy $\frac{1}{2}\hbar\omega$.)

(a) Find the partition function Z for a harmonic oscillator at temperature T .

(b) Find the thermal average energy U of a harmonic oscillator at temperature T .

(c) Find the partition function and the thermal average energy of a system consisting of two independent harmonic oscillators both oscillating with the same frequency ω .

(d) Generalize the result of (c) to an arbitrary number of harmonic oscillators N . This should give you the same result as in Challenge Problem 1, except that now the derivation is in the canonical formalism.

4. **[FOR ASSESSMENT] A two level system**

Consider a system that has two energy levels, of energies 0 and E , and of multiplicities (degeneracies) g_0 and g_1 .

(a) Find the partition function of the system at temperature T , and the probability of the system to be in a single state with zero energy and in a single state of energy E .

(b) Find the thermal average energy U and the heat capacity C_V of the system, as a function of T . What is the dominant behavior of the energy and heat capacity at very low and at very high temperatures? What is the dominant behaviour of the average energy in the high-temperature limit at very small and very large values of the ratio $r \equiv g_1/g_0$. Sketch the average energy U and the heat capacity C_V as functions of T , for a given ratio of $r \equiv g_1/g_0$ (indicate characteristic scales on the axis). How would these sketches be affected by an increase and decrease of r ?

5. **[PRACTICE PROBLEM] Free energy of a two state system**

- (a) Find an expression for the Helmholtz free energy F as a function of T of a system with two states, one at energy 0 and one at energy E .
- (b) Hence find expressions for the entropy S and the thermal average energy U of the system.

6. **[PRACTICE PROBLEM] One-dimensional gas**

Consider an ideal gas of N particles, each of mass m , confined to a one dimensional line of length L . (Neglect the spin of the particles.)

- (a) Find the thermal average energy of the gas at temperature T .
- (b) What takes the role of quantum concentration in 1D? Define it and write down an explicit expression for the 1D quantum concentration as a function of temperature T .

7. **[FOR ASSESSMENT] Entropy of mixing**

The entropy of a classical ideal gas of N identical particles of mass m (contained in a box of volume V , at temperature T) is given by

$$S(T, N, V) = k_B N \left[\ln \frac{V n_Q}{N} + \frac{5}{2} \right],$$

where $n_Q = (mk_B T / 2\pi\hbar^2)^{3/2}$ is the quantum concentration.

Consider a system consisting of two containers, both of the same volume V , which are separated by a wall and which contain two different ideal gases A and B under the same pressure, at the same temperature, and both with the same number of particles $N_A = N_B \equiv N$. Assume that the masses of the particles of type A and of type B are the same. If the separating wall is removed, the two gases will mix until a new equilibrium is reached. Show that as a result of this, the total entropy of the system increases by an amount of $2k_B N \ln 2$, known as the entropy of mixing.

8. **[FOR ASSESSMENT] Harmonic oscillator in the canonical formalism**

A one-dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $E_s = s\hbar\omega$, where s is a positive integer or zero. (We omit the zero point energy $\frac{1}{2}\hbar\omega$.)

- (a) Find the partition function Z for a harmonic oscillator at temperature $k_B T$ (see Problem 3).
- (b) Show that the free energy is

$$F = k_B T \ln [1 - \exp(-\hbar\omega/k_B T)].$$

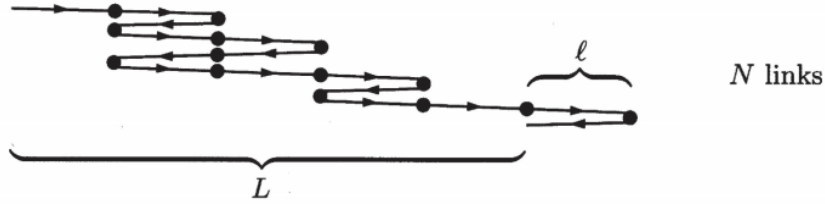
- (c) Hence show that the entropy is

$$S/k_B = \frac{(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]} - \ln [1 - \exp(-\hbar\omega/k_B T)].$$

- (d) Find the thermal average energy of the harmonic oscillator U .
- (e) The heat capacity can be found through either $C_V = (\partial U / \partial T)_V$ or $C_V = T(\partial S / \partial T)_V$. Use the thermodynamic identity $dU = TdS - pdV$ to show that these definitions are equivalent. Use one of these definitions to compute the heat capacity of the system.

9. **[FOR ASSESSMENT] Polymer system (rubber band model)**

Polymers, like rubber, are made of very long molecules, usually tangled up in a configuration that has lots of entropy. A very crude statistical mechanics model of a polymer (or a rubber band) would consist of a chain of a large number N of monomer links each of length l , arranged on a line, with the end of one link connected to the beginning of the next link in the chain. Each link may point either left or right. Different possible orientations of all links may be thought of as defining different microstates of the system. The total length L of the rubber band (defining the macrostate) is the net displacement from the beginning of the first link to the end of the last link.



(a) Find an expression for the entropy of the system in terms of N and N_R , the number of links pointing to the right. Simplify it using Stirling's approximation.

(b) Write down a formula for L in terms of N and N_R . For a one-dimensional system such as this, the length L is analogous to volume V of a three-dimensional system. Similarly, pressure p is replaced by the negative of the tension force, $-\mathcal{F}$, where \mathcal{F} is positive when the rubber band is pulling inward. Using this analogy, rewrite the standard thermodynamic identity $dU = TdS - pdV$, apply it to a process in which $dU = 0$, and then show that the tension force can be found as

$$\mathcal{F} = -T \left(\frac{\partial S}{\partial L} \right)_U.$$

(c) From this expression, calculate the tension in terms of L , T , N , and l .

(d) Simplify the expression for the tension force in the limit when $L \ll Nl$, and show that the tension force is directly proportional to L (Hooke's law), with the "spring constant" equal to $k_B T / Nl^2$. Discuss the dependence of the tension force on temperature. If you increase the temperature of a rubber band with a given tension, does the band tend to expand or contract?