

IF/UFRJ
Statistical Mechanics - 2024/1 – Raimundo

Problem Set #2 – The Microcanonical Ensemble

18/3/2024

1. Consider N practically uncoupled harmonic oscillators in the microcanonical ensemble. The total energy of the system is

$$E = \frac{1}{2}N\hbar\omega + M\hbar\omega \quad (1)$$

where ω is the common angular frequency of all oscillators, and M is an integer.

- (a) Show that the number of states with energy E is given by

$$\Omega(M, N) = \frac{(M + N - 1)!}{M!(N - 1)!}, \quad \text{with} \quad M = \frac{E}{\hbar\omega} - \frac{1}{2}N. \quad (2)$$

The arguments leading to the above result must be laid out in detail.

- (b) Assuming $N, M \gg 1$, show that the energy is expressed in terms of the temperature as

$$E = N\hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_B T} - 1} \right]. \quad (3)$$

Sketch $E/N\hbar\omega$ as a function of $k_B T/\hbar\omega$, and discuss in detail the behaviour at high and low temperatures.

- (c) Show that the chemical potential is given by

$$\mu = k_B T \ln [2 \sinh(\hbar\omega/2k_B T)]. \quad (4)$$

Sketch $\mu/\hbar\omega$ as a function of $k_B T/\hbar\omega$, and discuss in detail the behaviour at high and low temperatures.

2. N non-interacting particles of mass m occupy a d -dimensional box of volume $V \equiv L^d$, where L is its linear size. Assume the energy-momentum relation (dispersion relation) for each particle is given by $\varepsilon = ap^s$, where

$$p \equiv |\mathbf{p}| \equiv \left[\sum_{\nu=1}^d p_{\nu}^2 \right]^{1/2}. \quad (1)$$

- Obtain the number of classical single-particle states with energy less than E , and the density of states.
 - Obtain the density of quantum states for a single particle. Comment.
 - From your result in (a), and assuming the maximum energy of each particle is independently limited to E/N , obtain an approximate expression for the number of classical N -particle states with energy less than E . Is this approximation necessary if $s = 2$?
 - Use the result of the previous item to express the energy E in terms of the temperature, and to derive the equation of state for this classical ideal gas. Discuss the approximation used in the previous item in the light of your final result.
3. *Optional.* A fluid is contained in a box made up of insulating walls and a movable piston; see Fig. 1. When a weight w is placed on the piston, the system reaches

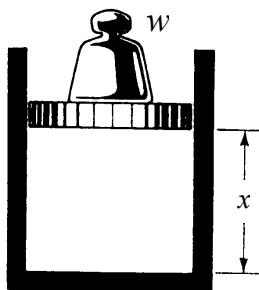


Figure 1: Problem 3: the volume of the weight is much smaller than that of the container.

equilibrium with the fluid occupying a volume $V = Ax$, where A is the cross-sectional area of the piston and x is its height. Consider the whole system (piston and weight) as isolated, and denote by $\Omega(E, V)$ the number of states of the fluid with total energy E and volume V .

- When the whole system has energy E' , what is the relation between the number of states of the whole system and the number of states of the fluid?

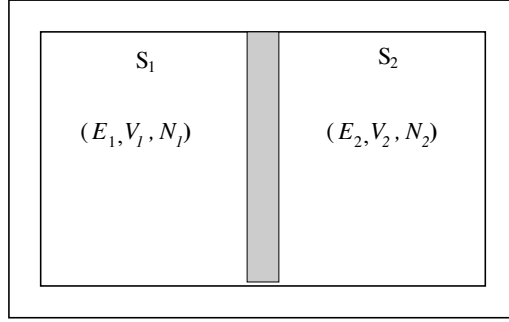


Figure 2: Two subsystems, S_1 and S_2 separated by a partition.

- (b) Use the condition of maximum entropy to show that the pressure of the fluid may be given by

$$P = \frac{(\partial S / \partial V)_E}{(\partial S / \partial E)_V} = - \left(\frac{\partial E}{\partial V} \right)_S. \quad (1)$$

- (c) Assume the fluid is an ideal gas, whose entropy is given by Eq. (2.4.16) of the LN. Use the result of the previous item to show that the equation of state is $P = (2/3)E/V$.
4. A system of N independent particles is such that each one of them can be in either of two energy levels, $\pm \epsilon_0$.
- (a) Determine the number of states with energy $E = M\epsilon_0$, $M = -N, -N + 1, \dots, N$
- (b) Obtain the system temperature as a function of E . Comment.
- (c) Make a sketch of $S(E)$ and of $T(E)$; consider both regions $E > 0$ and $E < 0$. Comment.
- (d) Obtain the heat capacity, $C \equiv dE/dT$, and make a sketch of $C(T)$. Discuss the behaviour at low and high temperatures.
5. Consider two ideal gases initially occupying each side of a container, separated by an insulating, fixed, and impenetrable partition; see Fig. 2. On the left hand side there are N_1 molecules of mass m_1 occupying a volume V_1 at a temperature T ; on the right hand side there are N_2 molecules of mass m_2 occupying a volume V_2 at the same temperature T of the left hand side.
- (a) Write down an expression for the entropy of each gas, in terms of N_i , V_i , m_i , $i = 1, 2$, and T , before the partition is removed.

- (b) The partition is removed. Write down an expression for the total entropy, S_T , in terms of N_i , $V \equiv V_1 + V_2$, m_i , $i = 1, 2$, and T , after equilibrium is reached.
- (c) Define the *entropy of mixing* as

$$\Delta S \equiv S_T - (S_1 + S_2), \quad (1)$$

and show that if the gases have the same densities, one has

$$\Delta S = k_B \left[N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right], \quad (2)$$

which is positive, as expected (Why?).

- (d) Now assume the molecules are identical. Show that even in this case one has $\Delta S > 0$.
- (e) The result in (5d) is obviously *wrong*, and is known as *The Gibbs Paradox*: one should have $\Delta S = 0$, since this particular mixing is a reversible process. Indeed, by repositioning the partition in the same position, one recovers the initial state, before mixing. In order to correct this, first show that (2) can be written as

$$\Delta S \approx k_B [\ln(N_1 + N_2)! - \ln N_1! - \ln N_2!]. \quad (3)$$

This suggests that the number of states is overestimated by a factor $N!$, due to the indistinguishability of the particles. Hence, in going from one-particle states to N -particle states, one must divide the outcome by $N!$. Show that by incorporating this factor in the number of states leads to: (i) an extensive entropy, and (ii) zero entropy of mixing for identical molecules.