NATIONAL UNIVERSITY OF SINGAPORE

PC2230 Thermodynamics and Statistical Mechanics

(Semester II: AY 2021-22)

Time Allowed: 2 Hours

INSTRUCTIONS TO STUDENTS

1. Please write your student number only. Do not write your name.
2. This assessment paper contains 4 questions, each with 4 sub-questions a to d. It comprises 3 printed pages.
3. Students are required to answer ALL questions. The answers to questions are to be written on the answer books.
4. Students should write the answers for each question on a new page.
5. This is a CLOSED BOOK examination.
6. Students are allowed to bring in an A4-sized (both sides) sheet of notes.
7. Nonprogrammable calculators are allowed.
8. Each sub-question carries equal weight of 6.25 marks.

1. Consider two Einstein solids A and B in thermal equilibrium. The system A consists of a single oscillator, while the solid system B consists of N oscillators, which is assumed to be large and serves as a reservoir for system A. All the oscillators have the same energy units ϵ. The combined system A and B has a total q units with a total energy $U = \epsilon q$.

a. Give the multiplicity Ω_A of system A when the energy of system A is ϵn, here n is a non-negative integer. Also, give the multiplicity Ω_B of the reservoir, maintaining the total energy units of combined system to be q.

b. All the microstates of the combined system as a microcanonical ensemble are equal probable. Based on this assumption, and using the result in part a, write down an exact expression for the probability $p(n)$ that the system A is in the microstate n, irrespective of the microstates of system B.

c. When both N and q are much larger than n, show that the probability of system A in microstate n is given by $\ln p(n) \approx -n \ln\left(1 + \frac{N}{q}\right) + \text{const}$, where the const may depend on N and q but not n.

d. What is the temperature T_A of system A based on the result in c? What is the temperature T_B of system B?

2. The van der Waals equation for non-ideal gas is $\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$, where P is pressure, V is volume, N is the number of particles, T is temperature, and a and b are two constants.

a. Draw qualitatively three isothermal curves in the P-V diagram with one above the critical temperature T_c, one exactly at the critical temperature, and one below the critical temperature.

b. For the curve below the critical temperature, explain the Maxwell construction, and state the principle used for the construction. Detail math is not needed.

c. State the two conditions that determine the critical point (V_c, P_c, T_c). Use the conditions to determine the critical volume, pressure, and temperature in terms of the constants a and b.

d. The isothermal curve below T_c in parts a and b, represents a phase transition from liquid to gas phase when volume increases. Discuss how to determine the latent heat L when liquid is transformed into a gas at a particular fixed pressure and temperature.

3. Consider an atom that has three energy levels, $-\epsilon$, 0, and $+\epsilon$. We assume the atom is in thermal equilibrium with a reservoir at temperature T.

a. Using canonical ensemble, calculate the partition function Z.

b. Calculate the Helmholtz free energy F.

c. Determine the entropy s from the free energy in part b for a single atom.

d. Instead of using the canonical ensemble, consider the microcanonical ensemble with N atoms. Here we assume N is large. Like an Einstein solid, each atom is assumed distinguishable. Determine the multiplicity Ω, and show that the entropy from the Boltzmann principle agrees with that in part c, i.e., $S = Ns$.

4. This question concerns blackbody radiation or thermal photon gas.

a. Each mode of electromagnetic field in a cavity is a quantum harmonic oscillator with energy units ϵ. The energy of the oscillator is given by $E(n) = n\epsilon$ in the microstate $n = 0,1,2,\cdots$. Compute the partition Z in canonical ensemble.

b. In a cavity, it is not one single oscillator, but a continuum of distribution of oscillators with different energy units. $g(\epsilon)d\epsilon$ gives the number of oscillators between ϵ and $\epsilon + d\epsilon$. Here, $g(\epsilon) = bV\epsilon^2$, where V is the volume of the cavity, and ϵ is the energy unit of the oscillator, b is some constant. Use this information and the result of part a to compute the total Helmholtz free energy F of the thermal photon gas at temperature T. You can use the integral $\int_0^\infty x^2 \ln(1 - e^{-x})\, dx = -\frac{\pi^4}{45}$.

c. Compute the internal energy U of the system, using the result in part b.

d. From the thermodynamic identity, prove that the pressure of thermal photon gas is given by $P = \frac{1}{3}\frac{U}{V}$.

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