

**Preliminary Examination: Thermodynamics and Statistical Mechanics**

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**Instructions:**

- The exam consists of 10 short-answer problems (10 points each).
- Where possible, show all work; partial credit will be given if merited.
- Personal notes on two sides of an 8×11 page are allowed.
- Total time: 3 hours.

**P1.** A system containing  $N$  particles confined to a container with volume  $V$  is in equilibrium at a temperature  $T$ . The partition function is given by

$$Z = \left( \alpha V T^{\frac{7}{2}} \right)^N$$

where  $\alpha$  is a constant. Use this information to determine the pressure exerted on the walls of the container as a function of  $N$ ,  $T$ , and  $V$ . Comment on how your result differs, if it does, from the corresponding result for an ideal gas. If you see no difference, comment on whether this means that the system under consideration is an ideal gas.

**P2.** A cup of hot coffee at 80 °C is mixed together with two cups of cold coffee at 40 °C at constant pressure in an insulated container. The specific heat for coffee at constant pressure is known to be 4.2 J-g<sup>-1</sup>-deg<sup>-1</sup> at room temperature and one atmosphere. Determine the resultant temperature of the mixture. Make any reasonable approximations you need to obtain your result.

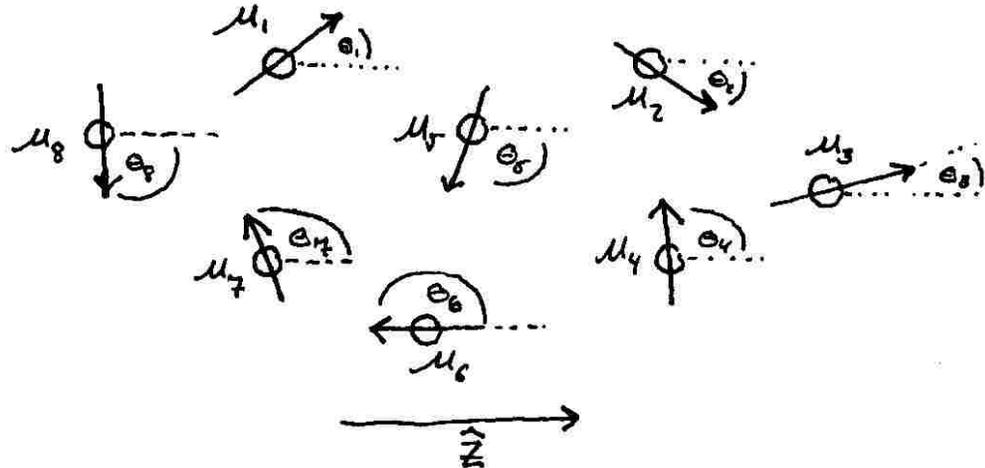
**P3.** The non-interacting fermi gas is a useful model for understanding the electronic properties of a metal. Suppose that the chemical potential (fermi energy) for electrons in the conduction band of a certain metal is 4.000 eV at room temperature. Sketch a graph of the corresponding fermi-dirac distribution function at room temperature ( $T \simeq 300$  K) as a function of energy  $\varepsilon$ , from 3.900 eV <  $\varepsilon$  < 4.100 eV. Also show on your graph, for comparison, the shape of the distribution function at  $T = 0$  K.

**P4.** The partition function for a system of  $N$  distinguishable, noninteracting, freely orientable classical magnetic dipoles, each having a magnetic moment  $\mu$ , in the presence of a constant uniform magnetic field  $\vec{B} = B_0 \hat{z}$ , is given by

$$Z = \sum_{\theta_1, \theta_2, \theta_3, \dots, \theta_N} e^{\beta \mu B_0 (\cos \theta_1 + \cos \theta_2 + \cos \theta_3 + \dots + \cos \theta_N)}$$

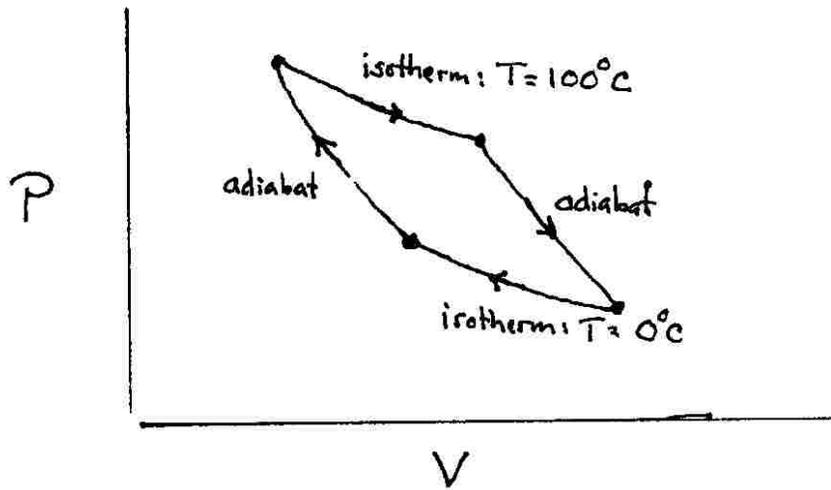
where  $\theta_i$  is the angle that the  $i^{\text{th}}$  magnetic dipole makes with the  $z$  axis and  $\beta = (kT)^{-1}$ . We are neglecting the effect of the induced magnetic field. Obtain an expression for the average magnetic moment of the system. Sketch the magnetization as a function of temperature.

Useful integral:  $\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \exp(\beta \mu B_0 \cos \theta) = 4\pi \frac{\sinh(\beta \mu B_0)}{\beta \mu B_0}$ .



**P5.** Hidden away in a government laboratory in Albuquerque NM is a cylinder containing the last existing sample of an experimental fluid manufactured in the late 1950s and code-named "fluid-X". The cylinder is fitted with a frictionless piston so that fluid-X can be expanded and contracted over a cycle that consists of two reversible isotherms alternating with two reversible adiabats, as shown in the figure below. The temperatures of the isotherms are  $0^\circ\text{C}$  and  $100^\circ\text{C}$ , respectively. After one complete cycle, it is found that the ratio of the net work performed on the surroundings to the heat absorbed during the expansion at  $100^\circ\text{C}$  is given by  $\eta = 0.27$ . An Albuquerque newspaper has recently reported that one of the laboratory's objectives at their new nanofabrication facility is to use modern techniques in computational chemistry and self-assembly to design and manufacture a fluid for which this ratio is higher than 0.27, for exactly the same cycle.

What is the significance of  $\eta$ ? Is it thermodynamically possible to make a fluid for which  $\eta$  is higher than that of fluid-X for the same cycle? Is it possible to make a fluid for which  $\eta$  is lower? Discuss the reasons why or why not for both cases.



**P6.** A system consists of  $N$  very small beads each having a mass  $m$  that are free to slide on a stiff horizontal wire of length  $L$ . Collisions of the beads with one another and with the ends of the wire bring the system into equilibrium with the surroundings at a temperature  $T$ . When the wire is at an elevation  $h$ , the partition function  $Z$  and its associated free energy  $A$  are as follows:

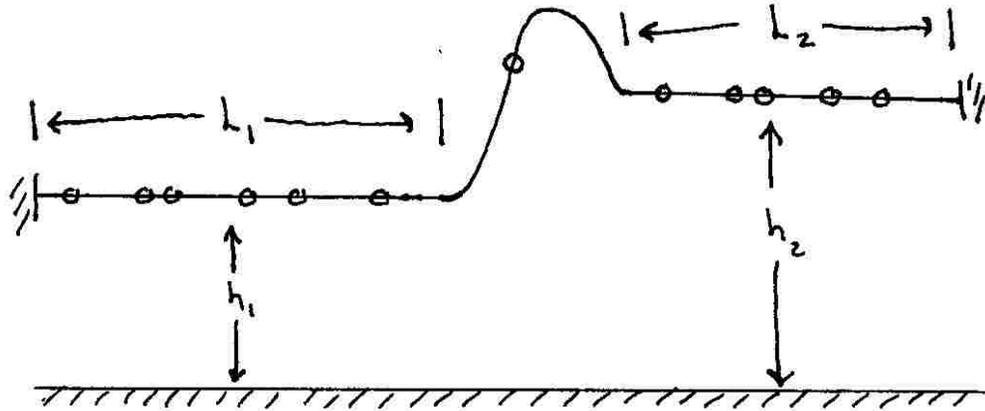
$$Z = \frac{\left(\sqrt{mkT/2\pi\hbar^2} L e^{-\beta mgh}\right)^N}{N!};$$

$$A \sim Nmgh - kT \left(N \ln \frac{L}{N} + N\right) - \frac{N}{2} kT \ln (mkT/2\pi\hbar^2).$$

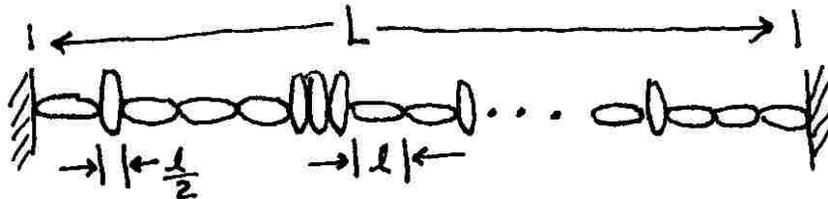
Here  $g$  is the acceleration of gravity and  $\beta = (kT)^{-1}$ . Stirling's approximation for  $\ln(N!)$  was employed in obtaining  $A$  from  $Z$  above. (a) What is the chemical potential of the system?

Suppose that the wire is bent so that a horizontal segment of length  $L_1$  at an elevation  $h_1$  is separated from a horizontal segment of length  $L_2$  at an elevation  $h_2$  by a barrier, as shown in the figure below. It is possible for the beads to slide over the barrier, but they don't often make it over the top. (b) When

equilibrium is reached, what will be the ratio of the bead concentration  $n_1 = N_1/L_1$  in segment 1 to the concentration  $n_2 = N_2/L_2$  in segment 2?



**P7.** A single strand of polymer is composed of  $N \gg 1$  cigar-shaped molecules that are aligned, end-to-end, in a chain, as shown in the figure below. The polymer is confined to one dimension, and is in equilibrium with the surroundings at a temperature  $T$ . The individual molecules may be oriented in one of two distinct positions; either horizontally, or vertically, as shown. When oriented horizontally, each molecule contributes a length  $\ell$  to the overall length of the strand, but when oriented vertically, this contribution is only  $\ell/2$ . The polymer strand is under tension so as to remain a fixed length  $L$ . The energy does not depend on molecular orientation, to a very good approximation. What is the partition function for the polymer strand? What will be the equilibrium length when the tensile force is set to zero?



**P8.** According to the Debye model for the heat capacity of a solid, the vibrational internal energy is given by the integral expression,

$$U = \frac{9V}{8\pi^2 c^3} \int_0^{\omega_0} d\omega \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}$$

where  $c$  is the speed of sound,  $\beta = (kT)^{-1}$ ,  $V$  is the volume, and the upper limit  $\omega_0 = 2c(\pi^2 n)^{1/3}$  on the integral is determined by the cube root of the number of atoms per unit volume,  $n$ . Show that the vibrational contribution to the heat capacity at low-temperatures is proportional to  $T^3$ , and discuss precisely what is meant by a “low” temperature in this system.

**P9.** A dilute gas containing  $N$  molecules of oxygen  $O_2$  is confined to a volume  $V$  and is in equilibrium with the surroundings at a reasonably high temperature  $T$ . The partition function is given by

$$Z = \frac{(q_{\text{trans}} q_{\text{rot}} q_{\text{vib}})^N}{N!}$$

where  $q_{\text{trans}} = V(mkT/2\pi\hbar^2)^{3/2}$  is the single-particle partition function for the translational motion of particles having mass  $m$ , and  $q_{\text{rot}} = 2kTI/\hbar^2$  and  $q_{\text{vib}} = kT/\hbar\omega$  are the single-particle partition functions for the rotational and vibrational degrees of freedom of the  $O_2$  molecule, respectively, where  $I$  is the molecular moment of inertia and  $\omega$  is the vibrational frequency. The electronic degrees of freedom are frozen out. Write down an expression for the Helmholtz free energy and use this to determine the heat capacity at constant volume.

**P10.** A system consisting of a dilute monoatomic gas that is confined to a volume  $V$  contains  $N$  neutral atoms of mass  $m$ . The system is in equilibrium with the surroundings at a temperature  $T$ . The electronic ground state of each atom is three-fold degenerate. The free energy  $A$  for this system is given by

$$A = -kT \ln \frac{(3q)^N}{N!}$$

where  $q = V(mkT/2\pi\hbar^2)^{3/2}$  is the single-particle partition function for translational motion. Suppose now that the gas is subjected to a uniform electric field which doesn't affect the translational motion but has the effect of splitting the ground state of each atom into a triplet, having the energies  $E = 0, \pm\varepsilon$ , respectively. How must the expression for  $A$  be modified so that it gives the free energy of the final equilibrium state that obtains after thermal relaxation at constant volume, temperature, and electric field?