Preliminary Examination: Thermodynamics and Statistical Mechanics

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Instructions:

- This exam consists of 10 problems with 10 points each.
- Read all 10 problems before you begin to solve any problem, and solve the problems that seem easiest to you first. Spend your time wisely. If you are stuck on one problem, move on to the next one, and come back to it if you have time after you have solved all other problems.
- Show necessary intermediate steps in each solution. Partial credit will be given if merited.
- No textbook, personal notes or external help may be used other than what is provided by the proctor.
- This exam takes 3 hours.

Potentially Useful Information:

Physical constants and symbols:

k_B	Boltzmann's constant
$\hbar$	Planck's constant h divided by 2π

Formulas and relations:

$$\int_0^\infty x^{2n} e^{-\alpha x^2}\,\mathrm{d}x = \left(-\frac{\partial}{\partial\alpha}\right)^n \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \qquad \text{if } \mathrm{Re}(\alpha) > 0$$

$$\int_0^\infty x^{2n+1} e^{-\alpha x^2}\,\mathrm{d}x = \left(-\frac{\partial}{\partial\alpha}\right)^n \frac{1}{2\alpha} \qquad \text{if } \mathrm{Re}(\alpha) > 0$$

$$\ln N! \approx N \ln N - N \qquad \text{if } N \gg 1$$

$$1 + x + x^2 + \cdots + x^N = \frac{1 - x^{N+1}}{1 - x}$$

Problem 1: A gas of $N \gg 1$ non-interacting, non-relativistic, spin-1/2 fermions of mass m and temperature $T = 0$ is confined to a macroscopic volume V. Find the total energy of the gas.

Problem 2: The vibration motion of a solid containing N atoms is sometimes modeled as that of a collection of $3N$ independent harmonic oscillators, each of the same natural frequency ω. Starting from the partition function

$$Z = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^{3N}$$

with $\beta = 1/k_B T$, obtain an expression for the entropy of such a system, and determine the heat capacity C of the system in the limit that $T \to \infty$.

Problem 3: A liquid of initial temperature $2T$ is placed in contact with the environment at constant temperature T and pressure P. What is the change in the total entropy of the liquid and the environment when the liquid spontaneously cools down to T? Assume that the heat capacity of the liquid at constant pressure C_P is temperature independent.

Problem 4: A dilute gas consisting of N hydrogen atoms is at temperature T and pressure P. A fraction of the atoms combine to form diatomic hydrogen. For N_s single atoms and N_d diatomic molecules, the Gibbs free energy of the gas is

$$G = N_s k_B T \ln \left(\frac{N_s}{N_s + N_d} \frac{P}{P_s^0} \right) + N_d k_B T \ln \left(\frac{N_d}{N_s + N_d} \frac{P}{P_d^0} \right) - N_d \Delta.$$

Here Δ is the binding energy of the hydrogen molecule, and P_s^0 and P_d^0 are functions of only temperature. Find the relation between N_s and N_d when the full equilibrium is reached.

Problem 5: Assume that the atoms in a solid are confined in one direction by a one-dimensional potential of the form

$$V(x) = ax^2 - bx^3 + \cdots ,$$

where a and b are two constants with b being small in some appropriate sense, and x is the small displacement of the atom from its equilibrium position. Use this model to show that the expansion of the solid is proportional to the temperature T and the anharmonicity coefficient b. Assume the temperature is high enough that the summation over quantum states can be replaced by a phase space integral.

Problem 6: Calculate the translational part of the partition function of a single free particle of mass m confined to a container of volume V at temperature T. Show that the result has the suggestive form of the ratio of the container volume V to another volume characteristic of the particle at temperature T which involves Planck's constant h and the mass of the particle.

Problem 7: Blackbody radiation may be considered as a three-dimensional photon gas in equilibrium at a temperature T. Show that the energy per unit volume of this radiation is proportional to T^4.

Problem 8: One model for the adsorption of gas atoms on a metal surface approximates the surface to be a corregated muffin-tin potential. A gas atom can lower its energy by sitting in one of the potential minima which are the adhesion sites on the surface each with a binding energy Δ. Ignore all other interactions. Show that the free energy of exactly $N \gg 1$ atoms adsorbed to a metal surface with $M > N$ adhesion sites is

$$F = -N\Delta + Mk_\mathrm{B}T[(1-y)\ln(1-y) + y\ln y],$$

where $y = N/M$.

Problem 9: The Gibbs free energy for a gas consisting of N diatomic molecules is given by

$$G = -Nk_\mathrm{B}T\ln\left[\frac{k_\mathrm{B}T}{P}\left(\frac{mk_\mathrm{B}T}{2\pi\hbar^2}\right)^{3/2}\left(\frac{2Ik_\mathrm{B}T}{\hbar^2}\right)\right],$$

where m and I are the mass and the moment of inertia of the molecule, respectively, and P and T are the pressure and temperature of the gas. Suppose that the gas cools down from T to $T/2$ at constant pressure. Find the change in the enthalpy of the gas, and determine how much heat is released to the surroundings in the cooling process.

Problem 10: Calculate the entropy of a collection of $N \gg 1$ non-interacting distinguishable two-level systems with an energy gap Δ. Assume that the whole system is in equilibrium with an environment of temperature T.