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.

Unless otherwise noted, commonly used symbols are defined as follows:

\begin{align*}
P & : \text{ Pressure} \\
T & : \text{ Absolute Temperature} \\
k & : \text{ Boltzmann’s constant} \\
h & : \text{ Planck’s constant divided by } 2\pi \\
\beta & : (kT)^{-1} \\
S & : \text{ Entropy} \\
V & : \text{ Volume} \\
g & : 9.8 \text{ m/s}^2
\end{align*}

Useful Relations:

\begin{align*}
\int_{-\infty}^{\infty} dx e^{-\alpha x^2} &= \sqrt{\frac{\pi}{\alpha}}; \ \text{Re} \ \alpha > 0 \\
\int_0^\infty dx x^\nu e^{-\beta x} &= \frac{\Gamma (\nu + 1)}{\beta^{\nu+1}} \\
\Gamma (\nu + 1) &= \nu \Gamma (\nu) \\
\sum_{m=0}^{N} x^m &= \frac{1 - x^{(N+1)}}{1 - x} ; \ |x| < 1. \\
\ln N! &\sim N \ln N - N
\end{align*}
The partition function for a gas of $N$ noninteracting indistinguishable free particles of mass $m$ in a vessel of fixed volume $V$ and temperature $T$ is given by

$$
Z_0 = \frac{1}{N!} \left[ \frac{1}{(2\pi \hbar^2)^3} \int dp_x dp_y dp_z \int dx dy dz \exp \left( -\beta \frac{p^2}{2m} \right) \right]^N = \frac{V^N}{N!} \left( \frac{mkT}{2\pi \hbar^2} \right)^{3N/2}.
$$

Suppose now that the vessel is a tall vertical column with area $A$ and height $h$, so that $V = Ah$. For the following three problems, consider the case that $h$ is large enough that gravitational effects are important.
**P1.** Show that when gravity is included, the partition function for the noninteracting gas,

\[ Z(z_1, z_2) = \left( \frac{\exp(-\beta mgz_1) - \exp(-\beta mgz_2)}{\beta mg h} \right)^N Z_0, \]

is modified so that \( Z_0 \) is multiplied by an additional factor having to do with the gravitational potential energy. Here \( z_1 \) is the elevation of the bottom of the column, and \( z_2 = z_1 + h \) is the location of the top of the column.

**P2.** Starting with \( Z(z_1, z_2) \) above, derive expressions for the gas pressure at the bottom and the top of the column respectively. If the gas under consideration is \( \text{Xe} \), and the pressure at the bottom of the column is 1.00 atm, what is the pressure at the top of the column at an elevation \( h = 3000 \) m, assuming ideal gas behavior at room temperature? The molecular weight of \( \text{Xe} \) is 54 g/mole.

**P3.** Derive an expression for the heat capacity at constant volume in the two limiting cases; \( h << kT/mg \), and \( h >> kT/mg \).
A solenoid of length $\ell$, and radius $r$, with a winding density (number of turns per unit length) $\eta$, carries a current $I$. The core of the solenoid is comprised of a solid having a permeability $\mu$ that is greater than the permeability of free space $\mu_0$. The free energy at constant $I$ and $T$ is given by

$$F = -\left(\frac{1}{2}\mu_0 I^2 + \sigma T \ln \frac{T}{T_0}\right)V$$

where the constant $\sigma$ is the heat capacity per unit volume of the core, $T_0$ is a constant, and $V = \pi r^2 \ell$ is the volume.

**P4.** The core can be withdrawn from the solenoid by sliding it along the cylindrical axis. What is the minimum work that must be performed to completely withdraw the core at constant $I$ and $T$?

**P5.** The permeability $\mu = \mu_0 (1 + \chi)$ is determined by a linear susceptibility

$$\chi = \frac{C}{T}$$

that is inversely proportional to temperature with a Curie constant $C$. Show that the entropy of the solenoid/core system is given by

$$S = V \left[\sigma \left(1 + \ln \frac{T}{T_0}\right) - \left\{ \begin{array}{ll}
\frac{1}{2} \frac{\mu_0 \chi^2 I^2}{T} & \text{(core within solenoid)} \\
0 & \text{(core withdrawn)} \end{array} \right. \right]$$

**P6.** Suppose that the core is withdrawn adiabatically and reversibly, while the current $I$ is held constant. If the initial temperature of the core is $T_1$, what is the final temperature $T_2$ after it has been withdrawn?
One model for the adsorption of gas atoms on a metal surface considers the surface to be a corrugated muffin-tin potential, as shown in the figure. Gas atoms can lower their energy by sitting in the potential minima, which serve as a set of identical adhesion sites, each with a binding energy $\Delta$. Interactions between the adsorbed atoms can be ignored, except for the constraint that each site may be occupied by only one atom.

P7. Show that the entropy of a metal surface with $M$ adhesion sites and $N$ adsorbed atoms in equilibrium at a temperature $T$ is given by

$$S = k \left[ M \ln \left( \frac{M}{M-N} \right) - N \ln \left( \frac{N}{M-N} \right) \right].$$

Assume that $N$, $M$, and $M-N$, are each much larger than 1.

P8. Show that the chemical potential of a metal surface with $M$ adhesion sites and $N$ adsorbed atoms in equilibrium at a temperature $T$ is given by

$$\mu = -\Delta - kT \ln \left( \frac{M-N}{N} \right).$$

P9. Now consider a metal surface in which the $M$ adhesion sites are comprised of equal populations of sites of two different types, $A$ and $B$, having binding energies $\Delta_A$ and $\Delta_B$, respectively. If the total number of adsorbed atoms is one half of the total number of sites, i.e. $N = \frac{1}{2} M$, what is the occupation of each type of site as a function of the temperature $T$ and the difference in binding energy $\delta = \Delta_A - \Delta_B$?
P10. A potential well admits of only two bound states, a ground state having energy \( \varepsilon_0 = \frac{1}{2} \hbar \omega_0 \) and an excited state with energy \( \varepsilon_1 = \frac{3}{2} \hbar \omega_0 \). The potential well is occupied by exactly \( N \) noninteracting indistinguishable bosons, and is in equilibrium with the surroundings at a temperature \( T \). Show that for large enough \( N \), the energy of the system is given by

\[
U \sim \frac{1}{2} N \hbar \omega_0 + \frac{\hbar \omega_0}{e^{\beta \hbar \omega} - 1}
\]