Preliminary Exam: Statistical Mechanics, Tuesday January 12, 2016. 9:00-12:00

Answer a total of any **THREE** out of the four questions.
For your answers you can use either the blue books or individual sheets of paper.
If you use the blue books, put the solution to each problem in a separate book.
If you use the sheets of paper, use different sets of sheets for each problem and sequentially number each page of each set.
Be sure to put your name on each book and on each sheet of paper that you submit.
If you submit solutions to more than three problems, only the first three problems as listed on the exam will be graded.

**Some Possibly Useful Information**

\[
\ln N! \approx N \ln N - N \quad \text{as} \quad N \to \infty
\]

\[
\int_{-\infty}^{+\infty} dx \, \exp(-\alpha x^2 + \beta x) = \sqrt{\frac{\pi}{\alpha}} \exp\left(\frac{\beta^2}{4\alpha}\right) \quad \text{with Re}(\alpha) > 0
\]

\[
\int_{0}^{\infty} dx \, x \exp(-\alpha x^2) = \frac{1}{2\alpha}
\]
**Problem 1**

Suppose we have a material with the equation of state \( p = \frac{\alpha T}{V^2} \), where \( \alpha \) is a constant. The heat capacity of this material at constant volume is linear in temperature, \( C_V = A(V)T \).

(a) Using Maxwell’s thermodynamic relations or otherwise construct an expression for \( \left( \frac{\partial S}{\partial V} \right)_T \).

(b) In fact, the coefficient \( A(V) \) must not depend on the volume \( V \). Prove this.

(c) Find \( S(V, T) \) assuming the value \( S(T_0, V_0) = S_0 \).

(d) Find the heat capacity at constant pressure \( C_p = T \left( \frac{\partial S}{\partial T} \right)_p \).

**Problem 2**

Helium atoms can be adsorbed on a graphite surface and the resulting system can be modeled as an ideal gas at temperature \( T \), free to move on the graphite surface, with energy \( E = \frac{p^2}{2M} - \epsilon \) where \( \epsilon > 0 \) is the magnitude of binding energy per He atom of mass \( M \).

(a) Write down the canonical (classical) partition function \( Z(N_a, T, A) \) for the He atoms on this surface. Here \( N_a \) is the number of adsorbed (indistinguishable) Helium atoms and \( A \) is the area of the graphite surface. Obtain a closed expression for \( Z \) defining any new variables you use.

(b) Calculate the chemical potential for the adsorbed atoms.

(c) Suppose we have He gas above the graphite surface. Find the relevant chemical potential for this gas in terms of its pressure and other relevant thermodynamical variables. You may use the ideal gas law for pressure here.

(d) Obtain the equilibrium density of He atoms adsorbed on graphite.
Problem 3

Consider a system of indistinguishable particles whose states can be specified in the following way.

(i) There are single particle states, labeled by an index $i$ with energy $\epsilon_i$, which will be degenerate ($\epsilon_i$ may have the same value for several values of $i$) for particles with non-zero spin $s$.

(ii) Each multi-particle state corresponds to a set of occupation numbers $\{n_i\}$, where $n_i$ counts the number of particles occupying the $i$th single-particle state and has values from 0 to $M$. Each distinct set of occupation numbers corresponds to a distinct state.

Answer the following questions:

a) Which values of $M$ would give a Fermi-Dirac distribution, and which a Bose-Einstein distribution?

b) From now on, assume any finite value for $M$, i.e., a more general case than the two in part (a). Show that the grand partition function takes the following form

$$Z = \prod_i \frac{1 - q_i^{M+1}}{1 - q_i}.$$ 

What is $q_i$? Determine the expectation value $\langle N \rangle$ for the total number of particles, the expectation value $\langle n_i \rangle$ for the number of particles in state $i$, and the expectation value $\langle E \rangle$ for the total energy of the system. (You do not need to evaluate the sums.)

c) Now take the single-particle energies to be $\epsilon_i = \frac{\vec{p}_i^2}{2m}$ and change the sum into an integral over energies:

$$\sum_i \rightarrow g \int_0^\infty d\epsilon D(\epsilon)$$

for a 3-dimensional volume, which has the form of a cube with side of length $L$. What is $g$, and what is the form of the energy density $D(\epsilon)$? Now the total energy $\langle E \rangle$ can be expressed as

$$\langle E \rangle = T^\alpha f(z).$$

What is the value of $\alpha$? (Note that $f(z)$ is in the form of an integral which you do not need to evaluate. Here $T$ is the temperature.)
Problem 4

Consider a gas of $N$ classical point particles of mass $m$, which interact through a two-body potential of the form

$$\Phi(r_{ij}) = a r_{ij}^{-\nu},$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $a$ is positive, and $\nu$ is a positive integer. If this gas occupies a volume $V$ at temperature $T$,

a) show that its canonical partition function $Z(T, V, N)$ is a homogeneous function, in the sense that

$$Z(\alpha T, \alpha^{-\frac{3}{\nu}} V, N) = \alpha^{3N(\frac{1}{2} - \frac{1}{\nu})} Z(T, V, N),$$

where $\alpha$ is an arbitrary scaling factor;

b) show that its Helmholtz free energy $F(T, V, N)$ obeys the relation

$$T \left( \frac{\partial F}{\partial T} \right)_V - \frac{3}{\nu} V \left( \frac{\partial F}{\partial V} \right)_T = F - 3 \left( \frac{1}{2} - \frac{1}{\nu} \right) N k_B T$$

by using the homogeneity property from part (a) and differentiation with respect to $\alpha$.

c) show, using part (b), that the internal energy can be expressed as

$$U = ypV + xNk_B T.$$

What are $x$ and $y$?

*Hint:* Remember that the Helmholtz free energy is expressed as $F = -k_B T \ln Z$ and as $F = U - TS$. 