STATISTICAL MECHANICS : Mid-term exam (take-home exam) (Fall 2009)

For this take-home exam, feel free to consult any text book. But, DO NOT work together or ask your senior fellows. Each person must submit his/her own work by 12:00 pm at sharp October 21st. For delayed submission, 10 points will be deducted every hour. Since partial credit will be given, make sure to show all your work and to present it in a *neat* and *organized* fashion. Try to communicate well. I will NOT even bother to grade if the organization of your work or handwriting is messy. Please, take this exam seriously !!!

1 (20 pt) A simple model for the motion of particles through a nanowire consists of a one-dimensional ideal gas of N particles moving in a periodic potential. Let the Hamiltonian for one particle with coordinate x and momentum p be

$$\mathcal{H} = \frac{p^2}{2m} + \frac{kL^2}{4\pi^2}\left[1 - \cos\left(\frac{2\pi x}{L}\right)\right] \tag{1}$$

where m is the mass of the particle, k is a constant, and L is the length of the one-dimensional "box" or unit cell.

(a) Calculate the change in the Helmholtz free energy per particle required to change the length of the "box" from L_1 to L_2. Express your answer in terms of the zeroth order modified Bessel function

$$I_0(x) = \frac{1}{\pi}\int_0^{\pi} d\theta e^{\pm x\cos\theta} \tag{2}$$

(b) Calculate the equation of state by determining the one-dimensional "pressure" P. Do you obtain an ideal-gas equation of state? Why or why not? You might find the following properties of modified Bessel functions useful:

$$\frac{dI_\nu(x)}{dx} = \frac{1}{2}\left[I_{\nu+1}(x) + I_{\nu-1}(x)\right] \tag{3}$$

$$I_\nu(x) = I_{-\nu}(x) \tag{4}$$

2. (20 pt) Consider a system of N distinguishable non-interacting spins in a magnetic field H. Each spin has a magnetic moment of size μ, and each can point either parallel or antiparallel to the field. Thus, the energy of a particular state of the whole spin system is

$$E_\nu = -\sum_{i=1}^{N} n_i \mu H, \tag{5}$$

where $n_i\mu$ is the magnetic moment in the direction of the field with $n_i = \pm 1$.

(a) Determine the internal energy of this system as a function of β, H, and N by employing an ensemble characterized by these variable.

(b) Determine the entropy of this system as a function of β, H, and N.

(c) Determine the behavior of the energy and entropy for this system as $T \to 0$.

(d) Determine the average total magnetization ($\langle M \rangle = \langle \sum_{i=1}^{N} \mu n_i \rangle$) as a function of β, H, and N.

(e) Determine the magnetic susceptibility $\langle (\delta M)^2 \rangle$.

(f) Derive the behavior of $\langle M \rangle$ and $\langle (\delta M)^2 \rangle$ in the limit of $T \to 0$.

3. (20 pt) (a) Consider a region within a fluid described by the van der Waals equation $\beta p = \rho/(1 - b\rho) - \beta a \rho^2$, where $\rho = \langle N \rangle / V$. The volume of the region is L^3. Due to the spontaneous fluctuations in the system, the instantaneous value of the density in that region can differ from its average by an amount of $\delta\rho$. Determine, as a function of β, ρ, a, b, and L^3, the typical relative size of these fluctuations; that is, evaluate $\langle (\delta\rho)^2 \rangle^{1/2}/\rho$. Demonstrate that when one considers observations of a macroscopic system (i.e., the size of the region becomes macroscopic, $L^3 \to \infty$) the relative fluctuations become negligible.

(b) A fluid is at its critical point when $(\partial \beta p / \partial \rho)_\beta = (\partial^2 \beta p / \partial \rho^2)_\beta = 0$. Determine the critical point density and temperature for the fluid obeying the van der Waals equation. That is, compute β_c and ρ_c as a function of a and b.

(c) Focus attention on a subvolume of size L^3 in the fluid. Suppose L^3 is 100 times the space filling volume of a molecule - that is, $L^3 \approx 100b$. For this region in the fluid, compute the relative size of the density fluctuations when $\rho = \rho_c$, and the temperature is 10% above the critical temperature. Repeat this calculation for temperature 0,.1% and 0.001% from the critical temperature.

(d) Light that we can observe with our eyes has wavelengths of the order of 100 nm. Fluctuations in density cause changes in the index of refraction, and those changes produce scattering of light. Therefore, if a region of fluid 100 nm across contains significant density fluctuations, we will visually observe these fluctuations. On the basis of the type of calculation performed in part (b), determine how close fluctuations become optically observable. The phenomenon of long wavelength density fluctuations in a fluid approaching the critical point is known as critical opalescence. (Note: You will need to estimate the size of b, and to do this you should note that the typical diameter of a small molecule is around 5 Å.)

4 (20 pt) (a) Show that for an ideal gas of structureless fermions, the pressure is given by

$$\beta p = \frac{1}{\lambda^3} f_{5/2}(z) \tag{6}$$

where $z = e^{\beta\mu}$,

$$\lambda = (2\pi\beta\hbar^2/m)^{1/2} \tag{7}$$

m is the mass of the particle,

$$\begin{aligned} f_{5/2}(z) &= \frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 \log\left(1 + z e^{-x^2}\right) \\ &= \sum_{l=1}^{\infty} (-1)^{l+1} z^l / l^{5/2}, \end{aligned} \tag{8}$$

and the chemical potential is related to the average density,

$$\rho = \langle N \rangle / V, \tag{9}$$

by

$$\rho\lambda^3 = f_{3/2}(z) = \sum_{l=1}^{\infty} (-1)^{l+1} z^l / l^{3/2} \tag{10}$$

(b) Similarly, show that the internal energy, $\langle E \rangle$, obeys the relation

$$\langle E \rangle = \frac{3}{2} pV \tag{11}$$

[(c)-(f)] For high temperature and/or low density regime ($\rho\lambda^3 \ll 1$),

(c) Show that

$$z = \rho\lambda^3 + (\rho\lambda^3)^2 / 2\sqrt{2} + \cdots \tag{12}$$

(d) Use the result in (c) together with the Fermi distribution for $\langle n_p \rangle$ to deduce the Maxwell-Boltzmann distribution

$$n_p \approx \rho\lambda^3 e^{-\beta\epsilon_p} \tag{13}$$

where p stands for momentum and $\epsilon_p = p^2/2m$.

(e) Show that the thermal wavelength, λ, can be viewed as an average De Broglie wavelength since $\lambda \sim h/\langle |p| \rangle$.

(f) Show that

$$\beta p/\rho = 1 + \rho\lambda^3/2^{5/2} + \cdots \tag{14}$$

Why does a finite value of $\rho\lambda^3$ leads to deviations from the classical ideal gas law? Why should you expect the quantum deviations to vanish when $\rho\lambda^3 \to 0$?

[(g)-(h)] For low temperature and/or high density ($\rho\lambda^3 \gg 1$).

(g) By obtaining the asymptotic behavior of the integral representation $f_{3/2}(z) = (4/\sqrt{\pi}) \int_0^\infty dx x^2 (z^{-1} e^{x^2} + 1)^{-1}$ for low temperature and/or high density, show that

$$\rho\lambda^3 = f_{3/2}(z) \approx (\log z)^{3/2} 4/3\sqrt{\pi} \tag{15}$$

hence

$$z \approx e^{\beta\epsilon_F} \tag{16}$$

where $\epsilon_F = (\hbar^2/2m)(6\pi^2\rho)^{2/3}$. Estimate the Fermi energy ϵ_F of a typical metal, say Cu, in eV unit. Note that 1Hatree is 27.2 eV and discuss whether the low temperature and/or high density approximation ($\rho\lambda^3 \gg 1$) is a good approximation for Cu at a standard condition (1 atm, 25^oC).

(h) Show that

$$p = \frac{2\epsilon_F \rho}{5} \left[1 + \mathcal{O}(k_B^2 T^2/\epsilon_F^2)\right] \tag{17}$$

Hence the pressure does not vanish at $T = 0$. Why?

5. (20 pt) Consider a dilute gas made up of molecules which have a permanent electric dipole moment μ. The energy E of a molecule in an electric field $\mathcal{E}$ pointing in the z direction can be written

$$E = E_{trans} + E_{rot} - \mu \cdot \mathcal{E} \tag{18}$$

where $\mathcal{E}$ and dipole μ make an angle θ. Treat the diples as classical rods with moment of inertia I. Then

$$E_{rot} = \frac{I}{2}(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) \tag{19}$$

Assume that the canonical partition function for the gas can be written

$$Q = \frac{q^N}{N!} \tag{20}$$

where the partition function for a single molecule is $q = q_{trans} q_{rot}$.

(a) Show that

$$q_{rot} = \frac{2I \sinh \beta \mathcal{E} \mu}{\hbar^2 \beta^2 \mathcal{E} \mu} \tag{21}$$

(b) Show that the polarization, P, satisfies

$$P = \frac{N}{V} \langle \mu \cos \theta \rangle = \frac{N}{V} \left(\mu \coth \beta \mu \mathcal{E} - \frac{k_B T}{\mathcal{E}} \right) \tag{22}$$

(c) Show that in the weak-field limit ($\mu \mathcal{E} / k_B T \ll 1$) the dielectric constant ϵ, given by

$$\epsilon \mathcal{E} = \epsilon_0 \mathcal{E} + P \tag{23}$$

satisfies

$$\epsilon = \epsilon_0 + \frac{N \beta \mu^2}{3V} \tag{24}$$