Physics 408 – Final Exam   Name_____

You are graded on your work, with partial credit where it is deserved.

Please give clear, well-organized solutions.

1. Consider the coexistence curve separating two different phases of a single substance (e.g., liquid and vapor). The phases are related by a first order phase transition, with a latent heat $L = T\Delta s$. Here Δs is the entropy change per particle (with the change of phase), and Δv is the corresponding volume change.

(a) (5) Using the Euler equation $E = TS - PV + \mu N$, plus the equation for dE that defines T, P, and μ, obtain a simple equation involving $SdT - VdP + Nd\mu$ in a single phase. (Here the variables have their usual meanings: energy, temperature, entropy, pressure, volume, chemical potential. and number of particles.)

(b) (5) Let the two phases be labeled 1 and 2, with chemical potentials μ_1 and μ_2. What is the relation between $d\mu_1$ and $d\mu_2$ along the coexistence curve? Explain clearly why this relation must hold.

(c) (5) Use the results of parts (a) and (b) to obtain the Clausius-Clapeyron equation for $\dfrac{dP}{dT}$ along the coexistence curve (which can also be called the phase boundary) in terms of $\Delta s = s_1 - s_2$ and $\Delta v = v_1 - v_2$.

(d) (5) Explain two different reasons why the slope can be negative for P versus T along a coexistence curve. For each of these two possibilities, give an example of a substance that has this property, and explain why it has this property.

(e) (5) Now consider the coexistence curve for a liquid and a vapor. Treat the vapor as an ideal gas, with a volume per particle $v_{gas} = V / N$. Also assume $v_{liq} \ll v_{gas}$, where v_{liq} is the volume per particle in the liquid.

Show that $P = Ce^{-L/kT}$ along the coexistence curve, where C is a constant.

2. Suppose that the electrons in a 2-dimensional system (for example, a very thin metallic film) can be treated as an ideal quantum gas.

(a) (6) Let p be the magnitude of an electron momentum allowed by the periodic boundary conditions. Also let $D(p)$ be the density of states in momentum space, defined by

$$D(p)dp = \text{number of electron states in } dp \text{ at } p .$$

Using the facts that (i) the area (in momentum space) in dp at p is $2\pi p\, dp$, (ii) the area per momentum is h^2 / A (where h is Planck's constant and A is the area of the system), and (iii) an electron has 2 spin states, calculate $D(p)$.

(b) (6) For nonrelativistic electrons, calculate $D(\varepsilon)$, the usual density of states as a function of energy, which is defined by

$$D(\varepsilon)d\varepsilon = \text{number of electron states in } d\varepsilon \text{ at } \varepsilon .$$

[Hint: You should find that $D(\varepsilon)$ is a constant (in the present case of nonrelativistic particles in 2 dimensions).]

(c) (6) Using $D(\varepsilon)$ and the Fermi-Dirac distribution function $\dfrac{1}{e^{(\varepsilon-\mu)/kT}+1}$, write down the expression (i.e., an integral over ε) for the energy E of the system as a function of the temperature T.

(d) (7) It turns out that the change in the chemical potential with temperature is given by $dD(\varepsilon)/d\varepsilon$, and is zero in the present case.* I.e., $\mu(T)=\varepsilon_F$ at all temperatures in the present case.

Using this fact, and assuming that $T \ll T_F$, obtain an approximate expression for C_A, the heat capacity at constant area.**

Show that C_A is equal to $\text{constant} \times T^n$, while at the same time determining n.

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* Except for a mathematical triviality which we can ignore, due to the fact that $D(\varepsilon)=0$ for $\varepsilon < 0$, giving a discontinuity in this function and thus a nonzero derivative at $\varepsilon = 0$.

** C_A can be treated in the same way as C_V, the heat capacity at constant volume in 3 dimensions.

3. Let us model a long molecule as a 1-dimensional solid with a length L. The phonon energies (at low frequency) are related to the momenta by $\varepsilon(p) = v_s p$, where v_s is the sound velocity and $\varepsilon = \hbar\omega = h\nu$.

(a) (10) Calculate the density of states $D(\varepsilon)$, defined by

$$D(\varepsilon)d\varepsilon = \text{number of phonon states in } d\varepsilon \text{ at } \varepsilon$$
$$= \text{number of vibrational modes in } d\omega \text{ at } \omega$$
$$= \text{number of momenta in } dp \text{ at } p$$

with the last equation holding because we assume that there is only one (longitudinal) polarization.

[Hint: The number of momenta in dp at p can be obtained through the same kind of reasoning as in Problem 2, part (a), but now in 1 dimension.]

(b) (15) For low temperatures, show that C_L, the heat capacity at constant length, is given by $\text{constant} \times T^{n'}$, while at the same time determining n'. [Hint: Use the Bose-Einstein distribution function, which, if you have forgotten it, has a similar appearance to the Fermi-Dirac distribution function of the preceding problem.]

*** C_L can be treated in the same way as C_V, the heat capacity at constant volume in 3 dimensions.

4. A 2-state system has energies $\varepsilon = 0$ and $\varepsilon = \varepsilon_0$. Calculate the following quantities as functions of the temperature T.

(a) (5) Canonical partition function Z.

(b) (5) Average energy $\langle E \rangle$.

(c) (5) Heat capacity C.

(d) (5) Entropy S. [Recall that the Helmholtz free energy is defined by $F = \langle E \rangle - TS$ and that $F = -kT \ln Z$.]

(e) (5) Now demonstrate that the result for C in part (c) follows from the result for S in part (d), showing all your work.

5. (25) For an adsorbate treated as a 2-dimensional ideal gas, we obtained

$$\mu_{ads} = -kT \ln\left(\frac{z_{ads}}{N_{ads}}\right) \quad , \quad \text{where} \quad z_{ads} = \frac{A}{\lambda_{th}^2} e^{\varepsilon_0/kT}$$

and for a 3-dimensional ideal gas (composed of the same molecules) we obtained

$$\mu_{gas} = -kT \ln\left(\frac{z_{gas}}{N_{gas}}\right) \quad , \quad \text{where} \quad z_{gas} = \frac{V}{\lambda_{th}^3} .$$

(Here each μ is the chemical potential, of course.) Use these results to obtain the isotherm that gives the number N_{ads} of adsorbed molecules as a function of the pressure P in the gas.

I.e., obtain P in terms of N_{ads}, the area A available to the adsorbed molecules, the Boltzmann constant k, the temperature T, the thermal de Broglie wavelength λ_{th}, and the binding energy per adsorbed molecule ε_0.

6. The classical Maxwell distribution $f(\vec{v})$ of molecular velocities $\vec{v}$ has the form

$$\left(\text{probability velocity is in } d^3v \text{ at } \vec{v}\right) \equiv f(\vec{v})d^3v \equiv \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} d^3v.$$

(a) (5) Starting with $f(\vec{v})$, integrate out v_y and v_z to obtain just the distribution $\overline{f}(v_x)$, defined by

$$\left(\text{probability } x\text{-velocity is in } dv_x \text{ at } v_x\right) \equiv \overline{f}(v_x)dv_x.$$

(b) (5) Show that $\overline{f}(v_x)$ is properly normalized to unity. I.e., show that

$$\int_{-\infty}^{\infty} dv_x \, \overline{f}(v_x) = 1.$$

(c) (5) Starting with $f(\vec{v})d^3v$, derive the distribution $\overline{\overline{f}}(\varepsilon)$ of molecular energies ε, defined by

$$(\text{probability } \varepsilon \text{ is in } d\varepsilon \text{ at } \varepsilon) \equiv \overline{\overline{f}}(\varepsilon) \ d\varepsilon.$$

(Here ε is just the translational kinetic energy $\dfrac{1}{2}mv^2$, of course.)

(d) (5) Calculate the average molecular energy $\langle \varepsilon \rangle$.

(e) (5) Calculate the most probable molecular energy ε_{mp}.

7. (5 points extra credit) Discuss what you learned from the 10-minute talks in class about one of the following topics, with some specific details (regarding the relevant thermodynamics and statistical mechanics) covered in these talks: (i) the early universe or (ii) Maxwell's reasoning that led to the distribution of molecular velocities in Problem 6 or (iii) the subject matter of one of the other talks.

Merry Christmas and Happy Holidays!