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Physics 603

HOMEWORK ASSIGNMENT #9

Spring 2014

Due date to be determined.

1. PB 12.4. Note that PB 12.5 (not assigned) follows fairly quickly from 12.4 after transforming to lattice gas variables as in §12.4 and using Eqns. 12.4.4 and 12.4.5.

2. PB 12.14. You are welcome to invoke results from PB 12.4. In part a, find the value of the new factor γ in equilibrium ($L = L$) and then generalize by replacing L with L . In part c, note that s is independent of temperature.

3. Here is the promised Landau theory problem: Analogous to Eq. 12.9.1, let (with $\tilde{a} > 0$)

$$\psi(m; T, B) = -mB + \frac{1}{2}a(T - T_0)m^2 + (1/4)f_4m^4 + (1/6)f_6m^6$$

a) For a first-order phase transition consider $\psi(m; T, 0)$ with $f_6 > 0$ and $f_4 = -|f_4|$. (Note $B=0$ here.)

For the following, write down the equations needed to find the quantities that are sought. You may solve the equations using a math package like Mathematica.

i) Find the critical temperature T_c and the non-zero value of $|m|$ at T_c . (Same pair of equations.)

ii) What is the height of the barrier between this non-zero value of $|m|$ and $m = 0$ (at T_c).

iii) What is the temperature $T_h > T_c$ at which the non-zero solution for m is no longer metastable? (This would be the maximum temperature to which the ordered phase could be superheated.)

b) For a continuous phase transition consider $\psi(m; T, B)$ with $f_4 > 0$ and $f_6 = 0$.

i) At $T = T_c = T_0$, find the exponent δ , where $m \sim B^{1/\delta}$ for small B .

ii) For the susceptibility $\chi = \lim_{B \rightarrow 0} (dm/dB)$, find the exponents γ and γ' just above and below T_0 , respectively. Show that $\gamma = \gamma'$. Also show that the critical amplitude ratio is 2.

4., 5. Qualifier problems: 4) binary alloy, related to Ising model

5) Dieterici gas, related to van der Waals gas

Consider a binary alloy where each site of a lattice is occupied by an atom of type A or B . (A realistic alloy might mix roughly half copper and half zinc to make β -brass.) Let the numbers of the two kinds of atoms be N_A and N_B , with $N_A + N_B = N$. The concentrations are $n_A = N_A/N$ and $n_B = N_B/N$, and the difference is $x = n_A - n_B$. The interaction energies between the neighboring atoms of the types AA, BB, and AB are ε_{AA} , ε_{BB} , and ε_{AB} , correspondingly.

- (a) **[4 points]** For a cubic lattice in three dimensions, how many nearest neighbors does each atom have? In the rest of the problem, denote the number of neighbors as c for generality.
- (b) **[6 points]** Consider the system at a high enough temperature such that the atoms are randomly distributed among the sites. Calculate the average interaction energy U per site under these conditions. First, express U in terms of n_A and n_B , and then obtain $U(x)$.

In the rest of the problem, consider the case $2\varepsilon_{AB} > \varepsilon_{AA} + \varepsilon_{BB}$ and also assume that $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_0$ for simplicity. In this case, sketch a plot of the function $U(x)$ for $-1 \leq x \leq 1$. Indicate locations of the extrema of $U(x)$.

- (c) **[6 points]** Under the same conditions (where the atoms are randomly distributed among the sites), calculate the configurational entropy S per site. Assume that $N_A, N_B \gg 1$, so the Stirling approximation $\ln(N!) \approx N \ln N - N$ can be used. First, express S in terms of n_A and n_B , and then obtain $S(x)$.

Sketch a plot of the function $S(x)$. What are the values of S at $x = \pm 1$? For which value of x is the entropy S maximal?

- (d) **[6 points]** Using the results of Parts (b) and (c), obtain the free energy per site $F(x, T) = U(x) - TS(x)$, where T is the temperature. Notice that $F(x) = F(-x)$ (because of the assumption $\varepsilon_{AA} = \varepsilon_{BB}$), which simplifies consideration.

Sketch $F(x)$ at a high temperature and at a low temperature. Show that, at a high temperature, $F(x)$ has one global minimum as a function of x . Show that, at a low temperature, $F(x)$ has one local maximum surrounded by two minima, excluding the boundaries at $x = \pm 1$.

- (e) **[6 points]** A system tends to minimize its free energy F , subject to externally imposed constraints. A binary alloy with a given x may stay in the uniform state, where the atoms are randomly distributed among the sites, which is called the *mixed* state. However, it may also become unstable with respect to spontaneous segregation into two phases with different values of x , if such a segregation decreases the free energy F . This state is called *unmixed*.

Using $F(x)$ derived in Part (d), show that the uniform mixed state is stable at high temperatures, but becomes unstable below a certain temperature T_* . Determine T_* and the value of x where this instability occurs.

Hint: The system remains stable as long as $d^2F/dx^2 > 0$ for all x . Determine at what T and x this condition becomes violated.

- (f) [**6 points**] For $T < T_*$, the free energy $F(x)$ has two minima at x_1 and x_2 . Obtain an equation for $x_1(T)$ and $x_2(T)$. This is a transcendental equation, so you don't need to solve it explicitly for x .

Consider in turn what happens to the binary alloy with a given value x if $x < x_1(T)$, if $x_1(T) < x < x_2(T)$, and if $x_2(T) < x$. Would the state of the binary alloy be mixed or unmixed in these cases? For the unmixed state, what are the values of x in the two phases?

What are the limiting values of $x_1(T)$ and $x_2(T)$ in the limit $T \rightarrow 0$? Describe the ground state of a binary alloy at $T = 0$. Does this state minimize the interaction energy U , given that $\varepsilon_0 < \varepsilon_{AB}$?

- (g) [**6 points**] For a given x , show that the binary alloy is in the mixed state for $T > T_c(x)$ and in the unmixed state for $T < T_c(x)$. Calculate $T_c(x)$ and sketch it. Indicate the areas corresponding to the mixed and unmixed states on this sketch. Show that T_* is the maximal value of T_c .

Hint: To obtain $T_c(x)$ use the results of Part (f). $T_c(x)$ is obtained from the same equation as $x_1(T)$ and $x_2(T)$.

5.

Problem I.

To go beyond the ideal gas model and introduce interactions between gas atoms/molecules, the best known approach is the van der Waals model, which includes a repulsive volume exclusion and a short-range attraction. A variant of this model has the equation of state

$$P(V_m - b) = RT \exp\left(-\frac{a}{RTV_m}\right) \quad (1)$$

where V_m is the molar volume. For simplicity we consider one mole of gas throughout this problem, so hereafter call V_m simply V . In the figure below, plotted in terms of dimensionless pressure and volume to be defined below, are a family of isotherms of this equation. At high temperatures the isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$ is always positive while at low temperatures there is a range of volumes for which $\kappa_T < 0$, rendering the system unstable.

- (a) **points** Explain physically why the system is unstable when $\kappa_T < 0$. On the figure draw with a solid curve $\kappa_T = \infty$, i.e. the phase boundary between the regions where $\kappa_T < 0$ and $\kappa_T > 0$.
- (b) **points** At the top of this curve is the critical point (V_c, P_c) , intersected by the critical isotherm at critical temperature T_c . Write the two equations [involving the first and the second derivative of $P(V)$] that determine this point and solve them to show $V_c = 2b$ and $T_c = a/4bR$. (If you encounter algebra problems with this process, just proceed with the given values of V_c and T_c .) Then find P_c .
- (c) **points** Find $P_c V_c / RT_c$ for this so-called Dieterici equation of state and evaluate it using your calculator. For the van der Waals equation of state, this dimensionless combination is $3/8$. Which accounts better for the experimental value 0.29 for noble gases?
- (d) i) **points** Rewrite the equation of state in terms of dimensionless variables $v = V/V_c$, $p = P/P_c$, and $t = T/T_c$. What is the significance of this equation?
 ii) **points** For $V = V_c$ and for T slightly larger than T_c , find κ_T to leading order in $1/\tau$, where $\tau \equiv t - 1$.
- (e) **points** i) On the isotherm given by the thick line on the graph, perform a Maxwell construction and state the two values of v that coexist for that temperature. ii) Indicate (roughly) on the graph with a dashed line the region in which 2-phase liquid-gas coexistence occurs. iii) Draw a rough sketch of the P vs. T phase diagram, indicating with a dashed curve this same phase boundary and the critical point.

