Phys 971 Stat Mech: Homework 7

due 12/13/2013

1

Consider the adsorption of gas molecules to a surface. In the gas phase we will treat the molecules as an ideal gas with fixed chemical potential μ. We will treat the surface as a 2D square lattice (coordination number $z = 4$) with N binding sites. There is a binding energy $-\epsilon$ for the binding of each molecule to the surface. In addition, there is a favorable interaction energy $-\epsilon'$ between adsorbed molecules on adjacent binding sites. Each binding site can be occupied by zero or one molecule. Derive an equation for the surface coverage $\theta = N_{\text{bound}}/N$ of the bound molecules in the mean-field approximation. Sketch graphical solutions to this equation for the cases $\mu < \mu_c$ when the lattice is sparsely populated and $\mu > \mu_c$ when the gas phase is sufficiently concentrated that a condensed phase has appeared on the lattice.

2

Pathria 12.13 (11.13 in version 2) Consider a two-component solution of N_A atoms of type A and N_B atoms of type B, which are supposed to be randomly distributed over $N(= N_A + N_B)$ sites of a single lattice. Denoting the energies of the nearest-neighbor pairs AA, BB, and AB by ϵ_{11}, ϵ_{22}, and ϵ_{12}, respectively, write down the free energy of the system in the Bragg-Williams approximation* and evaluate the chemical potentials μ_A and μ_B of the two components. Next, show that if $\epsilon = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}) < 0$ (i.e. if the atoms of the same species display greater affinity to be neighborly), then for temperatures below a critical temperature T_c, which is given by the expression $q|\epsilon|/2k_B$**, the solution separates out into two phases of unequal relative concentrations.

   *This is the mean field approximation discussed in lecture. **Here q is the lattice coordination number. [My solution differs from the one given by Pathria (above) by a factor of 2. –JS]

3

Pathria 12.20 (11.20 in version 2): Consider a system with a modified expression for the Landau free energy, namely

$$\psi_h(t, m) = -hm + q(t) + r(t)m^2 + s(t)m^4 + u(t)m^6,$$

with $u(t)$ a fixed positive constant. Minimize ψ with respect to the variable m and examine the spontaneous magnetization m_0 as a function of the parameters r and s. In particular, show the following*
   (a) For $r > 0$ and $s > -(3ur)^{1/2}$, $m_0 = 0$ is the only real solution.

(b) For $r > 0$ and $-(4ur)^{1/2} < s \leq -(3ur)^{1/2}$, $m_0 = 0$ or $\pm m_1$, where $m_1^2 = ((s^2 - 3ur)^{1/2} - s)/3u$. However, the minimum of ψ at $m_0 = 0$ is lower than the minima at $m_0 = \pm m_1$, so the ultimate equilibrium value of m_0 is 0.

(c) For $r > 0$ and $s = -(4ur)^{1/2}$, $m_0 = 0$ or $\pm(r/u)^{1/4}$. Now the minimum of ψ at $m_0 = 0$ is of the same height as the ones at $m_0 = \pm(r/u)^{1/4}$, so a nonzero spontaneous magnetization is as likely to occur as the zero one.

(d) For $r > 0$ and $s < -(4ur)^{1/2}$, $m_0 = \pm m_1$ — which implies a *first-order* phase transition (because the two possible states available here differ by a *finite* amount in m). The line $s = -(4ur)^{1/2}$, with r positive, is generally referred to as a "line of first-order phase transitions."

(e) For $r = 0$ and $s < 0$, $m_0 = \pm(2|s|/3u)^{1/2}$.

(f) For $r < 0$, $m_0 = \pm m_1$ for all s. As $r \to 0$, $m_1 \to 0$ if s is positive.

(g) For $r = 0$ and $s > 0$, $m_0 = 0$ is the only solution. Combining this result with (f), we conclude that the line $r = 0$, with s positive, is a "line of second-order phase transitions," for the two states available here differ by a *vanishing* amount in m.

The lines of first-order phase transitions and second-order transitions meet at the point $(r = 0, s = 0)$, which is commonly referred to as a *tricritical point*.

* To fix ideas, it is helpful to use the (r, s)-plane as our "parameter space."

4

In class we looked at a simplified model of diffusion by calculating the properties of a random walk on a 1D lattice. Here we will consider the more realistic case of 3D diffusion in continuous space. We will treat the diffusive process as a series of moves separated by a fixed time interval Δt. For each move, the particle displacement is normally distributed

$$P_1(\boldsymbol{x}) = \frac{1}{(2\pi)^{3/2}b^3}e^{-\boldsymbol{x}^2/2b^2} \tag{1}$$

where b is a parameter describing the step size.

a) Calculate the mean squared displacement $\langle(\boldsymbol{x}(t) - \boldsymbol{x}(0))^2\rangle$ after a time $t = N\Delta t$ where $\boldsymbol{x}(t) = \sum_{i=1}^{N} \boldsymbol{x}_i$.

b) Show that the diffusion process is scale invariant at timescales longer than the microscopic collision time. To do this calculate the probability distribution for the displacement after N steps

$$P_N(\boldsymbol{R}) = \left\langle \delta\left(\boldsymbol{R} - \sum_{i=1}^{N} \boldsymbol{x}_i\right)\right\rangle \tag{2}$$

where δ is the Dirac delta function and each of the x_i are distributed according to Eq. 1. Show that this distribution is equivalent to a random walk of $N' = N/\lambda$ steps of size $b' = b\lambda^{1/2}$ where λ is an arbitrary scale factor.

5

Pathria 15.8 (14.11 in version 2): Integrate equation (15.3.14) to obtain

$$\boldsymbol{r}(t) = \boldsymbol{v}(0)\tau(1 - e^{-t/\tau}) + \tau \int_0^t (1 - e^{(u-t)/\tau})\boldsymbol{A}(u)du,$$

so that $\boldsymbol{r}(0) = 0$. Taking the square of this expression and making use of the autocorrelation function $K_A(s)$, derive formula (15.3.31) for $\langle r^2(t)\rangle$.