Soft condensed matter physics, spring 2010
Exercise 4

The answers are to be returned no later than Tue 16.2.2010 at 16:00. The answers are discussed in the exercise session Thu 18.2.2010 at 16:00, room D115.

Phase transitions

1. The phase behavior of a certain liquid mixture can be described by the regular solution model (see Jones, chapter 3), in which the free energy of mixing can be written as

$$\frac{F_{\text{mix}}}{k_b T} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B,$$

where ϕ_A, ϕ_B are volume fractions of constituents A and B. The interaction parameter is being given by $\chi = 600/T$, where T is the temperature in Kelvin. Calculate the following quantities:
a) The temperature at the critical point.
b) The volume fractions of the coexisting compositions at 273 K.
c) The volume fractions on the spinodal line at 273 K.

2. Diffusion in a 1D phase-separating mixture can described by the Cahn-Hilliard equation

$$\frac{\partial \phi}{\partial t} = M f_0'' \frac{\partial^2 \phi}{\partial x^2} - 2M\kappa \frac{\partial^4 \phi}{\partial x^4},$$

where ϕ is volume fraction of one of the constituents, $M f_0''$ is an effective diffusion coefficient D_{eff}, and M, f_0'' and κ are coefficients characteristic to the specific mixture. With the assumption that M, f_0'' and κ are constants, show that one solution for Cahn-Hilliard equation is

$$\phi(x,t) = \phi_0 + A\cos(qx)\exp[-D_{\text{eff}} q^2 (1 + \frac{2\kappa q^2}{f_0''})t].$$

3. The solution for Cahn-Hilliard equation shown in previous problem includes a term called the amplification factor

$$R(q) = -D_{\text{eff}} q^2 (1 + \frac{2\kappa q^2}{f_0''}).$$

Sketch an illustrative figure of $R(q)$ and explain it's physical relevance (see e.g. Jones).

4. A light-scattering experiment is carried out on a phase-separating polymer mixture. Values of intensity are recorded as a function of time at a variety of scattering angles q. The data is shown in table 1.
a) Plot the scattered intensity as a function of time for q=1.21 μm^{-1}. Explain the shape of the curve.
b) Use the data to extract values for the amplification factor, $R(q)$, as a function of scattering wavevector q. *Hint: It is to be expected that* $I(q,t) \propto \exp[2R(q)t]$.
c) How, according to Cahn-Hilliard theory, do you expect $R(q)$ to vary with q? Plot your values of $R(q)$ in a way that tests this this theory and comment on the degree of agreement.
d) Use your graph to estimate a value of the effective diffusion coefficient D_{eff}.

TURN PAPER

5. For some phase transformation having kinetics that obey the Avrami equation

$$y = 1 - \exp(-kt^n),$$

where k and n are time-independent constants and y is the fraction of transformation, the parameter n is known to have a value of 1.7. If after 100 s, the reaction is 50% complete, how long it will take for the transformation to be 99% complete?

Recommended reading on the subjects at hand
Richard A.L. Jones, *Soft Condensed Matter*, chapter 3.
William D. Callister, Jr, *Material science and engineering*, chapter 10.

Table 1: Data from the light-scattering experiment of problem 4.

$Q(\mu m^{-1})$	0.970	1.210	1.460	1.860	2.780	3.000
Time (s)	$\ln(I(Q,t))$					
0.983	−11.920	−12.170	−12.100	−11.900	−10.910	−11.280
1.966	−11.570	−11.610	−11.260	−11.010	−10.430	−10.560
2.950	−11.500	−11.050	−10.700	−10.470	−10.150	−10.190
3.575	−11.210	−10.630	−10.320	−10.100	−10.000	−10.000
4.916	−10.880	−10.250	−9.997	−9.807	−9.898	−9.901
5.899	−10.590	−9.997	−9.693	−9.579	−9.854	−9.872
6.972	−10.390	−9.763	−9.482	−9.455	−9.832	−9.882
7.866	−10.140	−9.529	−9.295	−9.269	−9.810	−9.872
8.849	−9.987	−9.389	−9.178	−9.207	−9.832	−9.941
9.654	−9.755	−9.225	−9.015	−9.083	−9.825	−9.941
10.820	−9.600	−9.061	−8.898	−9.041	−9.847	−9.951
11.710	−9.445	−8.968	−8.827	−8.979	−9.861	−9.990
12.780	−9.290	−8.851	−8.757	−8.938	−9.876	−10.020
13.680	−9.155	−8.734	−8.687	−8.876	−9.876	−10.030
14.750	−9.077	−8.640	−8.594	−8.834	−9.883	−10.050