040528 Quiz 9 Polymer Properties

Spinodal decomposition occurs when a miscible mixture is rapidly quenched deep into the 2-phase region of the phase diagram.

a) Make a sketch of the composition versus position comparing nucleation and growth with spinodal decomposition. Give an equation for the flux, J = dc/dt, which is useful for nucleation and growth and a similar equation that is useful for spinodal decomposition. Explain the reasoning for these two different equations.

b) The "block" model of Leo P. Kadanoff (U Chicago) can be used to describe the free energy change of a binary (A and B) system undergoing spinodal decomposition. Sketch this model and write an expression for the free energy change describing the two terms in general terms.

c) What is the Cahn-Hilliard "linear" approximation? (You will have to convert the Kadanoff summation equation to a Ginzburg-Landau integral functional, consider δG for deviations from $\langle \varphi \rangle$, perform a taylor series expansion and then use the linear approximation.)

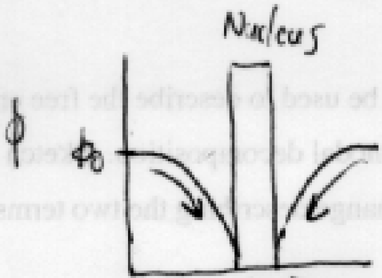
d) What are the advantages (3) of Fourier transforming the Cahn-Hilliard linear-theory expression for the free energy change related to a composition fluctuation. (Explain all terms you use.)

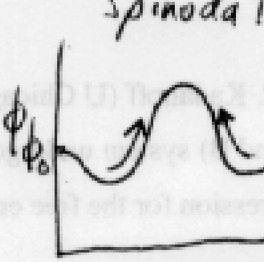
e) Show how the Fourier transform leads to a size dependence to the change in free energy expression and indicate how this expression for free energy change can be used to calculate the scattered intensity as a function of scattering vector and time. (Give the Cahn-Hilliard expression for δG in terms of k, give an expression for the growth rate R(q) and an expression for the scattered intensity following linear growth.)

ANSWERS: 040528 Quiz 9 Polymer Properties

a)

$\phi_0 = \langle \phi \rangle$



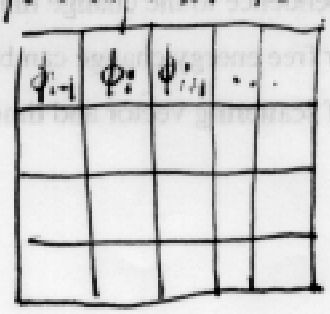


$J_{N\&G} = -D\frac{dc}{dr}$ $\qquad$ $J = -M(\mu_A - \mu_B)$

Transport Down a concentration gradient $\qquad$ Transport Up a concentration gradient

b)

Break a system with fluctuations into blocks smaller than the fluctuations but still large enough for thermodynamics



$$G(\{\phi_i\}) = \sum_i v_B\, g(\phi_i) + \sum_i \beta (\nabla \phi)^2$$

Bulk FE i.e. Flory Huggins expression

Composition Gradient Term

$\langle \nabla\phi \rangle = 0$ so $\langle (\nabla\phi)^2 \rangle$ is used c)

Ginzburg-Landau Functional

$$G(\phi(\underline{r})) = \int \left(g(\phi(r)) + \beta(\nabla\phi)^2 \right) d^3r$$

$$\delta G = G - G_{\phi_0}$$

G at ϕ_0

$$\delta G = \underbrace{\int \left(\frac{\delta g}{\delta \phi}\right)_{\phi_0} \delta\phi \, d^3\underline{r}}_{0} + \frac{1}{2}\int \frac{\delta^2 g}{\delta\phi^2} (\delta\phi)^2 d^3\underline{r} + \int \beta (\nabla \delta\phi)^2 d^3r$$

Linear approximation = Assume derivatives of free energy can be approximated by their values at ϕ_0

$$\delta G = \frac{1}{2}\left(\frac{\partial^2 g}{\partial \phi^2}\right)_{\phi_0} \int (\delta\phi)^2 d^3\underline{r} + \beta \int (\nabla\delta\phi)^2 d^3r$$

d) 1) You need an expression for the scattered intensity as a function of "q", not an expression in terms of "r".

2) r* You need to determine the "mode" of maximum growth under the Cahn-Hilliard theory. Modes are described in terms of inverse space so a Fourier Transform is needed.

3) By Fourier transforming the Cahn-Hilliard equation for the change in free energy the second term results in a size, "q^2" dependence since the del operator is a derivative versus dr and since the Fourier expression for the composition fluctuation is $\delta\varphi(\underline{r}) = V^{-1/2}\sum_k \varphi_k^* \exp ikr$.

e)

$$\delta G = \sum_{k} \left[\left(\frac{\partial^2 g}{\partial \phi^2} \right)_{\phi_0} + \beta k^2 \right] \phi_k^2$$

$$R(q) = M \beta q^2 \left[q^2 + \beta^{-1} \left(\frac{\partial^2 g}{\partial \phi^2} \right)_{\phi_0} \right]$$

$$I(q) = I_0(q) \exp\left(2 R(q) t\right)$$