050527 Quiz 9 Polymer Properties

The random phase approximation can be used to describe the free energy of a polymer blend. For example Mueller¹ gives:

(i) In the vicinity of the critical point, the variation of the composition can be treated as a small parameter. Expanding the spatial variation of the composition in a Fourier-basis, $\phi(\mathbf{q}) = \phi_A(\mathbf{q}) = -\phi_B(\mathbf{q})$ for $q \neq 0$, and only considering terms to quadratic order, one derives the random phase (RPA) approximation for the free energy per molecule:²⁶

$$\frac{F_{\text{RPA}}[\phi(\mathbf{q})]}{T\Phi V} = \frac{1}{2} \sum_{\mathbf{q}} \phi(\mathbf{q}) \left\{ \frac{1}{\phi g(\mathbf{q})} + \frac{1}{(1-\phi)g(\mathbf{q})} \right\} \phi(-\mathbf{q}) - \frac{1}{2} \sum_{\mathbf{q}} \phi(\mathbf{q}) 2\chi N \phi(-\mathbf{q}) , \quad (3)$$

where the Debye function g characterizes the single chain structure factor of a Gaussian chain

$$g(\mathbf{q}) = \frac{12}{q^2 R_e^2} \left(\exp\left[-q^2 R_e^2/6\right] - 1 + q^2 R_e^2/6 \right) \,. \tag{4}$$

The first two terms in Eq.(3) represent the conformational entropies of the two polymer species, the last term is the energy of mixing.

where Φ in the first term is the number density of chains and T is kT.

a) Use $\phi_k = \alpha_k \psi_k$ and $\psi_k = dF/d\phi_k$ to show the similarity between Mueller's equation (3) and the RPA equation derived in class (with $\alpha_{kA} = g(q)$ and $\alpha_{kB} = g(q)$). (First give the RPA equation from class; then convert to F thorugh substitution and an integral; then comment on the comparison.)

b) Using the internal field $\underline{\psi}_{\underline{k}}$ show how an expression for α_k^0 for a binary blend can be obtained. (That is, derive the athermal part of the RPA equation of part "a".)

c) Write a pseudo-equilibrium expression for the free energy of a phase separating polymer blend (including an expression for the surface energy) as a function of the domain size "r" using the Flory-Huggins Equation.

d) Use this expression to show that the critical phase size, r_c , is proportional to the phase size at zero free energy, r^* .

e) How do the free energy expressions in parts "a" and "c" relate to or compare with the Ginzburg-Landau functional for free energy given in class:

$$G_{GL}(\phi(r)) = \int (g(\phi(r)) + \beta(\nabla\phi)^2) dr^3$$

¹ http://www.cond-mat.physik.uni-mainz.de/~mueller/mueller.pdf

a)
$$RPA$$

 $\frac{1}{\varkappa_{K}^{o}} = \frac{1}{\varkappa_{K}} + \frac{1}{\varkappa_{Kg}} - \frac{2\pi k^{2}}{V_{o}}$
 $\frac{1}{\varkappa_{K}^{o}} = \frac{4}{\varkappa_{K}} = \frac{4\pi}{4\kappa_{g}} + \frac{1}{\varkappa_{Kg}} + \frac{1}{\varkappa_{v}} + \frac{1}{4\kappa_{g}} + \frac{1}{4\kappa_{g}}$

c)
$$\frac{\Delta G}{k_{T}} = \frac{4\pi}{3} \left(\frac{4\pi}{2} \ln \frac{4\pi}{2} + \frac{4\pi}{2} \ln \frac{4\pi}{2} + \frac{4\pi}{2} \ln \frac{4\pi}{2} + 4\pi \ln \frac{2}{2} \right) + 4\pi r^{2} \right)$$
when $\Delta G = 0$

$$r^{+} = \frac{3}{\left(\frac{4\pi}{2\pi} + \frac{4\pi}{2\pi} + \frac$$