050520 Quiz 8 Polymer Properties

Gibbs Thompson theory (not discussed in class) describes phase separation using the concept of a discrete surface that separates two phases of fixed concentration so that a pseudo-equilibrium can be described using a free energy difference between mixed and phase separated conditions,

$$\Delta G = \Delta H - T\Delta S + \left(S/V\right)\Gamma \qquad (1)$$

where Γ is the energy required to create a surface and the enthalpy, entropy and free energy difference terms are per unit volume. S/V is the surface to volume ratio for phase separated domains, while ΔS is difference in entropy between mixed and phase separated states.

a) Explain the difference between Gibbs-Thompson theory (which was not discussed in class) and the idea of a fluctuation in composition. Include the idea of a noise pattern in random fluctuations compared to a discrete phase separated domain.

b) The S/V term in equation (1) leads to two critical sizes, one where the first derivative of ΔG is 0 and one where ΔG itself is 0. Both Gibbs-Thompson critical sizes are related to the ratio of the surface to bulk energies. How does this compare with the critical size (critical wave vector) seen in spinodal decomposition discussed in class? Hint: The spinodal critical size is related to the relative rates of growth rather than a pseudo-equilibrium point[1].

c) Write a linear *constitutive* equation that describes the relationship between the size of composition fluctuations at wave vector "k", ϕ_k, and the strength of the field driving this fluctuation, $\Psi_k = dG_k/d\phi_k$. By writing this *constitutive* equation what has been implied concerning our understanding of a molecular model for composition fluctuations?

d) Using the definition of the field and the constitutive equation give an expression for the free energy associated with a fluctuation and the mean free energy (kT). Use the latter expression to obtain an expression for the mean square composition fluctuations at wave vector "k", $<\phi_k^2>$.

e) How does the response function, α_k, relate to the scattered intensity in an x-ray or neutron scattering measurement? How does α_k relate to the probability for a fluctuation of wavevector "k".

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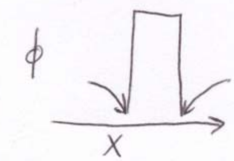
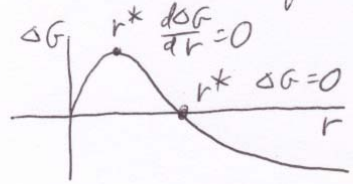
[1] Cahn-Hilliard theory for spinodal decomposition also leads to two critical sizes, one for the maximum growth rate (discussed in class) and one where the growth rate becomes negative at high wavevector or small size.

ANSWERS: **050520 Quiz 8 Polymer Properties**

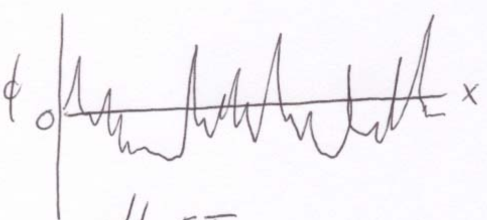
a) GT



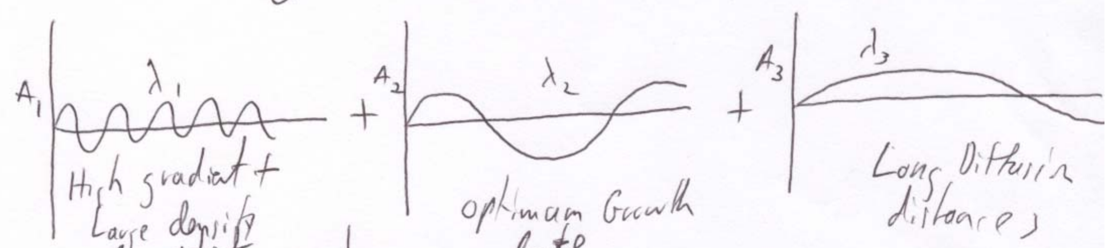
diffusion down a concentration gradient
Discrete Surface described by "r"
Since $S \sim r^2$ & $V \sim r^3$
S/V has units of r^{-1} implying a size

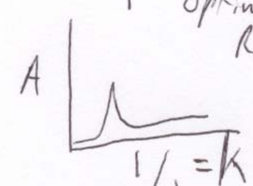


For Composition Fluctuations we consider a noise pattern for composition



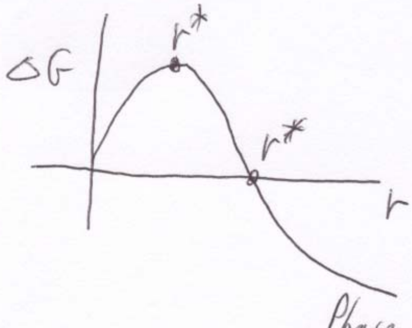
$\Downarrow$ FT





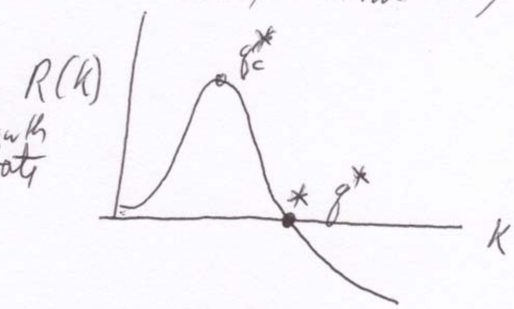
- There is no interface.
- All K's coexist
- Growth Rates differ with "K"

b) GT



Phases Spontaneously Grow at Large sizes

Fluctuation (Density Functional Theory)



$q_c^* = \sqrt{2} q^* \rightarrow$ wavevector where growth becomes negative

q_c^* ↓ maximum Growth Rate

c)

$$\phi_k = \alpha_k \Psi_k$$

This constitutive equation is empirical, that is it just describes the response but does not involve any model or understanding. Nothing has been implied.

d)

$$dG_k = \Psi_k \, d\phi_k$$

$$= \frac{\phi_k}{\alpha_k} \, d\phi_k$$

$$G_k = \frac{1}{\alpha_k} \int \phi_k \, d\phi_k = \frac{\phi_k^2}{2\alpha_k}$$

$$\langle G_k \rangle = kT = \frac{\langle \phi_k^2 \rangle}{2\alpha_k} \qquad \langle \phi_k^2 \rangle = 2\alpha_k kT$$

$k = \frac{q}{2\pi}$

e) $S(k) = \langle \phi_k^2 \rangle = 2KT\alpha_k$

α_k is the "k" dependent part of the scattering

For a Gaussian Polymer α_k is the Debye scattering function for a polymer chain

From the Boltzmann Eqn.

$$p(\phi_k) = \exp\left(-\frac{G_k}{KT}\right) = \exp\left(\frac{-\phi_k^2}{2\alpha_k KT}\right)$$