Quiz 7 070521 Polymer Properties

A mean field theory deals with interactions and takes a multi-bodied problem (that is interactions between many sites) and converts it to a single-bodied problem (interactions of individual sites with a mean field). This simplifies calculations. Mean field theories are useful for weak interactions that are effective over short distances and for small magnitude fluctuations. Consider a matrix of n sites that interact. If we consider the order of interactions (binary = 2; ternary = 3) the number of independent permutations, P, for interactions of order "r" is given by $P_r^n = \frac{n!}{(n-r)!(r)!}$ (that is, the number of terms needed to calculate the energy).

- 1) a) Explain how the definition of the Flory interaction parameter, χ , is consistent or inconsistent with the definition of a mean field.
 - b) Is a mean field approach appropriate for a polymer blend in a single phase? Explain.

c) Is a mean field approach appropriate for a polymer blend deep within the spinodal region? Explain.

d) Is a mean field approach appropriate for a polymer blend at the critical temperature? Explain.

e) For a polymer system with 10,000 sites how many terms would an expression for the enthalpy of interaction have relative to the mean field approach if only ternary interactions were considered (use the Sterling approximation from last week, $\ln y! = y \ln(y) - y$ for large y. (Divide the ternary number of terms by the mean field number of terms.)

- 2) The random phase approximation (RPA) describes the relationship between a fluctuation in concentration and an applied field for a binary blend by calculating the net susceptibility from the component susceptibilities. The RPA relies on a mean field assumption.
 - a) Define a field in the RPA analysis.
 - b) Is this field related to the Flory interaction parameter, χ ?
 - c) Can this field be purely entropic in character?
 - d) Define the *internal* field for a binary blend of A and B polymers.

e) Show how the susceptibility of a binary blend is related to the susceptibility of the component parts.

3) In order to understand how equilibrium is reached, in a system governed by thermodynamics, we need to consider in detail the nature of random thermal fluctuations.

a) Explain how fluctuations are involved in phase separation by considering the free energy versus composition above, at, or below the critical temperature.

b) Explain the use of a Fourier decomposition of the spatial distribution of fluctuations in composition to understand fluctuations. Argue why such a decomposition is or is not appropriate.

c) In the spinodal regime phase separation occurs predominantly at a preferred wave number, k. Considering the nature of fluctuations explain why larger fluctuations do not occur.

d) Considering the nature of fluctuations explain why smaller fluctuations do not occur.

e) Hashimoto applies Flory-Huggins theory to the Cahn-Hilliard analysis of spinodal decomposition to determine the growth rate of domains in the spinodal regime. Critique this.

4) It has been observed that a spinodal-like structure is produced in many reacting systems such as when a low molecular weight end reactive oligomer is reacted with a high molecular weight end reactive polymer in a rapid reaction.

a) What is the difference between such a reacting system driven to phase separation and a polymer blend driven to phase separation by a thermal quench to a high or low temperature?

b) Rather than temperature what parameter would be best used to guage the depth of quench for such a system.

c) When would a reacting system undergo nucleation and growth?

d) Why would a reacting system have a lower likelihood of displaying phase ripening (Ostwald ripening of the spinodal structure to spherical domains)?

e) In a thermal system is phase separation reversible?

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1) a) The Flory-Huggins interaction parameter is proportional to an average energy of interaction so it reflects a mean-field. It is applied to all binary interactions in the system. It replaces all higher order interactions with an average interaction parameter. These are all consistent with a mean field.

b) Yes it is appropriate since fluctuations are small and interactions are weak.

c) Deep in the spinodal regime fluctuations are large so the mean-field approach should not be appropriate.

d) At the critical point fluctuations can be very large and can be effective over long distances. The mean-field approach breaks down at the critical point.

2) a) A field is the change in the system free energy with respect to the change in fluctuation.

b) The field could be related to the Flory interaction parameter but is not necessarily related, that is, the cohesiveness of the material is a type of field, the internal field. It is also possible to apply an external field to cause a fluctuation in composition. The part of the external field associated with the chi parameter is $\frac{2kT\phi_k\chi}{V_0}$.

c) The field, as defined in class with no interaction parameter, is entropic.

d) The internal field is the part of the field associated with the cohesiveness of the material and the incompressibility assumption. If the external field only acts on one component then the internal field is wholly responsible for the response of the other component to an applied field.e) As done in class,

3) () Price Decomposition is appropriate heraase the response of the system depends on K. Hik K is appoind by high geodient; Lowk by Long transport & mes. c) Larger Alus heating are opposed by transport C.m. Fr d) Smaller Slaches has an opposed by suddent Cest c) F-H is a men hall though that is good for small fluctuations such as in the single phore. At high guench depthe fluctuation are large so til pickoly wan 4

3) a) Fluctuations probe the free energy plot and allow for the comparison of states. With no fluctuations in composition there would be no phase separation.

4) a) The thermal system is reversible, that is if the system is heated above the critical point it reverts to a single phase and this can be done many times with the same phase separation points. In a reacting system the system is non-reversible. This means that the reacting system is not an equilibrium system, it is a kinetically driven system.

b) Extent of reaction would replace temperature in a reacting system.

c) When the reaction occurs slowly you might expect nucleation and growth. There also might be a phase-diagram like behavior in composition but for the reacting system the rate of reaction governs most aspects.

d) For a reacting system the phase separation is generally locked in due to the increase in molecular weight and crosslinking during reaction. In a crosslinked or entangled system it is kinetically difficult for phase ripening to occur.

e) Phase separation is necessary to have true spinodal behavior. This can occur generally for thermally driven phase separation only.