

Homework 6 Advanced Thermodynamics Due Monday October 4, 2021

Inguva PK, Walker PJ, Yeu HW, Zhu K, Haslam AJ, Matar OK, *Continuum-scale modelling of polymer blends using the Cahn–Hilliard equation: transport and thermodynamics* Soft Matter **17** 5645-5665 (2021) consider the use of a variety of equations of state in the framework of the Cahn-Hilliard theory for spinodal decomposition to simulate phase separation. Inguva goes through a detailed review of the Cahn-Hilliard theory.

- a) Inguva, in Figure 1, shows the phase diagram for a system that follows the Hildebrandt, Margules, or Flory-Huggins models. Explain how the binodal, spinodal and critical points can be calculated if you have an expression for the free energy G . How are they defined in terms of the molar free energy per kT or RT , g ? If you wanted an expression for the distance from the binodal or for the distance from the spinodal, i.e. the quench depth that drives phase separation, what expression would you use?
- b) Inguva on page 5647 lists three tunable components that control spinodal decomposition, the energy gradient parameter (*contribution to the free energy due to the presence of a composition gradient*), the mobility coefficient (*related to the diffusion coefficient and the second derivative in composition of the change in free energy on mixing, i.e. the distance from the spinodal line, this is a negative term since transport occurs against a concentration gradient for spinodal decomposition*) and the change in Gibbs free energy on mixing. Compare these components with those for nucleation and growth. What components control the rate of phase growth for nucleation and growth. How do they compare with those governing spinodal decomposition?
- c) On page 5648 Inguva mentions the relationship between Cahn-Hilliard theory and an expression for the interfacial tension in a phase separated system where the interface is governed by the change in free energy on mixing, equation (14). What are the units of κ from equation (14)? Does this agree with the units you obtain from a unit analysis of equations (9), (18) and (19)? Combine equations (19) and (14) and write a definition in your own words for the surface tension for this phase separated system.
- d) Cahn-Hilliard theory results in an “apparent” or “effective” diffusion coefficient, equation (23) that depends on the diffusion coefficient (that might be given by the Stokes Einstein equation $D = kT/(\zeta)$ where ζ is the drag coefficient) and the distance from the spinodal condition. The apparent diffusion coefficient is an experimentally observed parameter as shown by Hashimoto T, Kumaki J, Kawai H, *Time-Resolved Light Scattering Studies on Kinetics of Phase Separation and Phase Dissolution of Polymer Blends. 1. Kinetics of Phase Separation of a Binary Mixture of Polystyrene and Poly(vinylmethyl ether) Macromolecules* **16** 641-648 (1983). The mobility is just the diffusion coefficient, so the apparent diffusion coefficient divided by the distance from the spinodal. In the spinodal regime what is the sign of the apparent diffusion coefficient? How does this make sense? You need to give the classical definition of the diffusion coefficient and a sketch of the concentration profile for spinodal decomposition.
- e) Hashimoto used light scattering to study spinodal decomposition. He found that a preferred size associated with a peak in the scattering is seen. How is the peak size and the minimum size for phase separation related to the three components of part b)?