Linear stability analysis of phase separation in nanoscale systems

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Abstract

A linear stability analysis of the early stages of spinodal decomposition in nanospheres has been performed. The dominant decomposition mode is described in terms of a stability map, which defines regions of the fastest growing composition modulation in a space of particle radius and k_m, where k_m is the most unstable mode in the bulk system. It is shown that at sufficiently small particle size the first unstable mode is the non-radially symmetric first-order spherical harmonic. The analysis is extended to the case of nanowires and the interplay between decomposition along the wire length vs. radial and angular perturbations is discussed.
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1. Introduction

In recent years, the study of nanoscale systems has become a major research topic within the materials science and physics communities. Although most studies have focused on the processing and unique properties of nanowires and nanoparticles, a number of experiments and simulations have demonstrated that phase equilibria at small sizes can differ in significant ways from the bulk counterpart. McHale et al. [1] have shown that in alumina the equilibrium phase changes from the corundum structure to a defected spinel as the particle size is decreased, and a similar surface energy-dictated crossover has been observed in zirconia [2] and TiO$_2$ [3]. It has long been established that the melting point of metallic nanoparticles is a function of particle size and is lower than the bulk melting point [4–9]. In contrast, for nanosize metal particles embedded in an insoluble matrix material, experiment [10–15] and theory [16] have shown that the melting temperature is typically increased. Transmission electron microscopy (TEM) studies of phase equilibria in binary alloy nanoparticles [17,18], most notably the In–Sn and Bi–Sn study of Allen

and Jesser [18], have shown that the liquidus line is depressed from the bulk phase diagram and an increase in solubility in the solid is observed. In a molecular dynamics and Monte Carlo investigation of roughly five nanometer radius particles in a model Cu–Pb system [19], Hoyt [20] has demonstrated that the phenomenon of surface segregation can lead to a decrease in the slope of the liquidus line. A classical thermodynamic treatment of solubility in nanoparticles can be found in a series of papers by Shirinyan and co-workers [21–23]. Similar to the melting point depression observed in isolated nanoparticles, Monte Carlo simulation studies by Yang et al. [24,25] found that the transition temperature of the disordered to the $L1_0$ ordered phase in Fe–Pt decreases with decreasing particle size, and a similar decrease in T_c was found from both experiment [26] and simulation [27] in Cu$_3$Au. In contrast, Chatterjee et al. [28] found increased stability of the $L1_2$ ordered phase with decreasing particle size in the Cu–Au–Ag ternary.

A handful of previous studies have examined spinodal decomposition in nanoparticles. Barnes et al. [29] used scattering experiments and molecular dynamics simulations to investigate the droplet sizes below which the phase separation reaction can be suppressed in mixed polymer systems. Using Mossbauer spectroscopy, Petrov et al. [30] noted increased kinetics of phase separation in 27 nm Fe–

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Cr particles and Gornostyrev et al. [31] solved the Cahn–Hilliard equation for the case of surface directed spinodal decomposition in nanograin-sized systems. In an atomistic simulation study of spinodal decomposition in a cylindrical nanopore, Gelb and Gubbins [32] found that domain growth followed a power law at short times, but transitioned to a slower growth mode when the size of the plug shaped domains exceeded the pore radius. In a recent high-resolution TEM study of particular relevance to the present work, Braidy and Botton [33] fabricated nanospheres of Au coated with Pt and monitored the change in structure with annealing time. The authors found that the initial concentric sphere configuration transformed to an equilibrium state consisting of two lobes of Au rich and Pt rich phases separated by a flat interface. In 2001, Johnson [34] performed a detailed theoretical analysis of spinodal decomposition in nanoparticles, including the effect of elastic strains, and numerically solved the diffusion equation for the growth of radially symmetric concentration and stress profiles. Johnson also determined that below a critical radius, R_c, the linear instability does not occur. The result (neglecting elastic effects) given by $R_c = 4.49\sqrt{\kappa/f''}$, where κ is the gradient energy coefficient and f'' is the second derivative of the homogeneous free energy with respect to composition, agrees with an earlier treatment by Nauman et al. [35].

The previous discussions of spinodal decomposition in nanospheres by Johnson and Nauman et al. focused solely on radially symmetric concentration profiles. However, as evidenced by the two-lobe structure observed in the aforementioned Au–Pt experiment, other non-symmetric modes may play the dominant role in the initial decomposition. Therefore the purpose of the present work is to perform a linear stability analysis of the Cahn–Hilliard equation in a spherical geometry while retaining a complete set of spherical harmonics in the description of the concentration field. The results are plotted as a stability map which delineates, in a space of k_m, the fastest growing wavenumber, vs. the particle size, regions where a particular spherical harmonic is dominant. It is shown that the critical radius below which no instability occurs is considerably smaller than the prediction based only on radially symmetric concentration perturbations. In addition, the effect of elastic strain energy is examined and it is shown that, although the stress and strain fields are functions of the particle size, the linear stability is affected only through a constant shift of f'' a result identical to the original treatment of Cahn. Finally, the stability analysis is extended to the case of nanowires, and the competition between instability along the wire axis vs. instability in the radial direction is explored.

2. Spinodal decomposition in nanospheres

The linear stability analysis starts with a general expression [36,37] for the total free energy of the system expressed as an integral over the volume V

$$F = \int_V \left[f(c) + \frac{1}{2}(E_{ij} - e\delta_{ij})C_{ijkl}(E_{kl} - e\delta_{kl}) + \kappa \mid \nabla c \mid^2 \right] dV \tag{1}$$

Here $f(c)$ is the free energy per unit volume of a homogeneous system of composition c and κ is the gradient energy coefficient. The average composition of the nanoparticle is given by c_o. It is important to note that, in general, additional terms involving the surface free energy of the nanoparticle should be included in the free energy expression. However, we make the following simplifying assumptions: the surface stress f, and the interfacial free energy are independent of composition. As shown by Johnson, under these conditions the stability of the system with respect to composition fluctuations is unaffected by the surface terms.

In Eq. (1) the second term in brackets represents the elastic strain energy, where the C_{ijkl} are components of the compliance tensor, E_{kl} is the total (or measured) strains and e, a function of concentration, is the strain due to composition variations with no change in stress. The solution to the strain and displacement fields for an arbitrary concentration profile in a sphere is quite involved and, for clarity, the discussion is postponed until the next section. Below we investigate linear spinodal decomposition for the case of equal size atoms.

The kinetics of spinodal decomposition are governed by the following diffusion equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot M \nabla \frac{\delta F}{\delta c} \tag{2}$$

where M is a concentration dependent mobility. Let ζ denote the difference in concentration from the average, that is $\zeta = c - c_o$. Then, to examine linear stability the functional derivative appearing in the diffusion equation is evaluated, expanded in a Taylor series about $\zeta = 0$ and truncated at only linear terms in ζ. The result reads

$$\frac{\partial \zeta}{\partial t} = M_o f'' \nabla^2 u - 2M_o \kappa \nabla^4 u \tag{3}$$

where f'', the second derivative of the free energy with respect to concentration, and M_o are evaluated at $\zeta = 0$ and the gradient energy coefficient is assumed to be composition independent.

The spherical symmetry of the nanoparticles problem suggests trial solutions to Eq. (3) given by:

$$\zeta(\theta, \phi, r, t) = e^{\alpha t} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{i=1}^{\infty} Y_{lm}(\theta, \phi) g(\beta_i r) \tag{4}$$

Here $Y_{lm}(\theta, \phi)$ are spherical harmonics (the angular portion of solutions to Laplace's equation in spherical coordinates) of degree l and order m, θ and ϕ are the colatitude angle and the azimuthal angle, respectively, g is a function to be determined and, as described below, the β_i parameters scale the radial dimension such that solute is conserved. The parameter α determines the stability; if $\alpha > 0$ for a particular set of l, m, i, then that mode will be unstable and will grow exponentially with time.