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Phase Coarsening in Thin Films

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Phase coarsening (Ostwald ripening) phenomena are ubiquitous in materials growth processes such as thin film formation. The classical theory explaining late-stage phase coarsening phenomena was developed by Lifshitz and Slyozov, and by Wagner in the 1960s. Their theory is valid only for a vanishing volume fraction of the second phase in three dimensions. However, phase coarsening in two-dimensional systems is qualitatively different from that in three dimensions. In this paper, the many-body concept of screening length is reviewed, from which we derive the growth law for a 'screened' phase island, and develop diffusion screening theory for phase coarsening in thin films. The coarsening rate constant, maximum size of phase islands in films, and their size distribution function will be derived from diffusion screening theory. A critical comparison will be provided of prior coarsening concepts and improvements derived from screening approaches.

INTRODUCTION

Phase coarsening, or Ostwald ripening, occurs throughout a range of processing and aging-in-service of many material types.[1] Specifically, phase coarsening is a many-body relaxation phenomenon in aging microstructures driven by the decrease of total interfacial free energy stored within interfaces. Larger phase particles in a microstructure grow during phase coarsening by preferential absorption of atoms or molecules released at the expense of smaller particles, which are further diminished in mass by losing them. Phase coarsening is humorously referred to as 'thermodynamic capitalism', where big entities get bigger and small entities are forced to vanish from the population. The importance of all this from a materials engineering viewpoint is that the physical, chemical, and mechanical properties of multiphase materials reflect their average particle size and particle size distribution (PSD). These microstructural features, in turn, depend sensitively upon the kinetics of phase coarsening.[2]

The earliest quantitative description of late-stage, or steady-state, phase coarsening kinetics in three-dimensional (3D) systems was published in the early 1960s by Lifshitz and Slyozov[3] and by Wagner.[4] Their theoretical treatments of Ostwald ripening, often referred to as 'LSW theory', retain full validity only in the limit of a vanishingly small volume fraction. In fact, strictly speaking, LSW theory describes the behavior of just a single particle 'alone' but interacting with a mean potential field established by the rest of the microstructure. No particle–particle interactions, whatsoever, are considered. LSW theory, nonetheless, correctly predicts a widely observed behavior measured during phase coarsening in numerous 3D two-phase systems, namely, that the time-dependent average particle radius, $\langle R(t)\rangle$, follows the kinetic scaling law,

$$\langle R(t)\rangle^3 - \langle R(0)\rangle^3 = K_{LSW}\, t, \tag{1}$$

where t and K_{LSW}, respectively, are the phase coarsening time and the coarsening rate constant. The growth rate in LSW theory of a spherical particle of radius R placed in the mean chemical potential field established by the microstructure is given by the kinetic equation,

$$\left(\frac{dR}{dt}\right)_{LSW} = \frac{1}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right), \tag{2}$$

where R_c denotes the 'critical' radius of an isolated particle that is conditionally stable at a time t. Conditional stability implies that neither growth nor shrinkage of the particles that have critical size occurs, because their surface potential momentarily exactly matches the mean chemical potential. The match in potential precludes mass transfer to or from the particle, at least until the critical particle itself increases in size, and lowers its potential. Growth causes the previously stable particle to be in an undersaturated environment, and start to shrink. Once shrinkage occurs, the particle's surface potential rises farther, increasing its rate of loss of mass. That sequence eventually causes the particle to shrink ever faster and faster toward extinction. A steady state is reached when all particle sizes, relative to the growing critical particle, form a self-similar distribution that remains time invariant relative to the critical particle. That distribution looks identical at all future times, save for a single scale factor that increases the size of all particles.

In addition, in the derivation of Eq. 2, all length scales are non-dimensionalized through the appropriate capillary length, $l_c = \frac{2\sigma V_m}{R_g T}$, where σ, V_m, R_g and T represent the surface energy, molar volume, universal gas constant, and absolute temperature, respectively. Physical coarsening time is non-dimensionalized through the characteristic diffusion time, $\tau_d = \frac{l_c^2}{DC_0 V_m}$, to yield the dimensionless time, t. Here D and C_0 are, respectively, the matrix interdiffusion coefficient and the equilibrium solute concentration in the matrix at a planar interface with the precipitate phase.[5] Equation 2 indicates that particles larger in radius than the critical size grow, whereas those particles with radii smaller than the critical size shrink. The subtle complication in this analysis is that the critical particle size is itself growing larger as a function of coarsening time, causing each particle eventually to stop growing and start shrinking. Note that this formulation predicts a deterministically-based kinetic equation, devoid of any local attributes of the microstructure.[5] LSW theory importantly also predicts that sparse coarsening systems approach a scale-independent steady-state, and exhibit self-similar, i.e., affine, behavior, in which the PSD—normalized by the average particle size—becomes time invariant and independent of the initial particle size distribution and materials parameters.

The source of disagreement between LSW predictions for the PSD and the observed coarsening rate constant found in real material microstructures arises from the non-zero volume fraction that real systems always entail. A non-zero second phase volume fraction produces local interactions among the particles, an important effect not included in LSW theory. In order to take into account some of the influences of the omnipresent non-zero volume fraction, numerous variants of mean-field coarsening theory have been developed over the past 50 years.[6–12] The present authors recently reviewed the status of theoretical, computational, and experimental studies of phase coarsening,[1,13] following two prior reviews of this field.[14,15] All of these mean-field variants, however, are again valid only at extremely low volume fractions ($V_V \ll 0.1$).[16] Wang et al.[17,18] developed a diffusion screening theory for phase coarsening that remains valid over the range of volume fractions $0 \leq V_V \leq 0.3$ in 3D systems. Marsh and Glicksman[19] introduced an earlier concept of a statistical 'field cell' that acts around each size class of the spherical precipitates undergoing coarsening. They obtained normalized coarsening rates that are in good agreement with data derived from various liquid-phase sintering experiments, particularly in the range $0.3 \leq V_V \leq 0.6$, where the PSDs appear markedly different from experimental ones. Recently, Streitenberger also developed analytical description of phase coarsening at high volume fractions.[20]

Coarsening theories also exist for phase islands developing in 2D systems. Marqusee[21] considered the average influence of a non-zero area fraction surrounding patches, or phase islands, resident on a planar substrate. The microstructure acts as an 'effective medium'. Marqusee introduced the concept of a so-called 'screening length' in 2D systems. Family and his coworkers developed both analytical and numerical approaches for predicting the kinetics of 2D Ostwald ripening.[22,24] Bales and Zangwill carried out kinetic Monte Carlo simulations on the evolution of 2D phase islands.[25] Bartelt et al. used low-energy electron diffraction (LEED) to study Ostwald ripening of 2D phase islands distributed on substrates,[26] and Müller et al. studied coarsening of nanocrystals on thin SiO_2 films.[27] Additional references on phase island coarsening are included in the two review papers.[28,29] Although significant progress has been made in this direction, several issues still remain open. For example, the precise quantitative form of the screening length in two dimensions is lacking, and the development of a theory of phase coarsening from first principles that has general applicability to 2D systems is also missing. In this paper, we will address these open issues.

The organization of this paper is as follows: In "Diffusion Screening Theory in 3D Microstructures", we briefly describe diffusion screening theory in 3D systems. In "Diffusion Screening Theory in 2D Microstructures", a diffusion screening theory in 2D systems is developed. In "Results", the results are given from the pertinent theoretical predictions of diffusion screening theory in 2D systems. Finally, in the "Conclusions", a short summary and status are provided of our findings based on this research.

DIFFUSION SCREENING THEORY IN 3D MICROSTRUCTURES

LSW theory is purely mean-field in character, and plays the role of a limit law in phase coarsening kinetics. That is, in a two-phase alloy taken to the abstract limit of $V_V \to 0$, one recovers LSW theory that ignores *all* particle–particle interactions. In real systems, however, the non-zero volume fraction of particles, $V_V \neq 0$, has substantial effects on the properties of materials. Recently, the authors furthered the development and applied many-body screening theory to diffusion-controlled coarsening in two-phase microstructures, for which a 'diffusion screening' length, R_D, is introduced via the Debye–Hückel theory.[30] This interesting analogy arises solely because electrostatic fields obey the same mathematical field equations as does diffusion. This holds true despite the fact that phase particles are immobile and of continuous size, whereas ions are mobile and quantized!

The screening length captures the many-body diffusive interactions that set the maximum distance over which particles interact, and beyond which their interactions cease. Debye originally introduced an electrostatic screening distance into his theory of dilute ionic solutions and gas plasmas to ascertain the effect of surrounding ions. The screening distance defines the distance beyond which an ion no longer is affected by the Coulombic potential field of its neighboring ions. The diffusion screening length in phase coarsening is perfectly analogous, but is related to the volume fraction of particles and the moments of the microstructure's PSD, rather than to the ionic concentration. Specifically, the diffusion screening length, R_D, is defined here as,

$$R_D = \frac{1}{\sqrt{3}}\left(\frac{\langle R^3\rangle}{\langle R\rangle}\right)^{1/2} V_V^{-1/2}. \tag{3}$$

Equation 3 shows that the diffusion distance, which sets the collective limit for multiparticle interactions in a microstructure, decreases in inverse proportion to the square-root of the volume fraction.

Moreover, interactions occurring among particles that are located within the diffusion screening distance increase a particle's growth rates as follows,

$$\frac{dR}{dt} = \left(\frac{dR}{dt}\right)_{LSW}\left[\frac{1}{1-\frac{R}{R_D}}\right]. \tag{4}$$

Diffusion screening theory also predicts the following important behaviors for a two-phase coarsened microstructure:

1. The relationship between the dynamically stable maximum-size particle's normalized radius, $\rho_{max} = \frac{R}{R_c}$, and the system's volume fraction is predicted as,

$$\rho_{max} = 1 - \frac{1}{\sqrt{3V_V}} + \sqrt{\frac{1}{3V_V} + \frac{1}{\sqrt{3V_V}} + 1}. \tag{5}$$

2. The scaling law governing the growth of the average particle is similar to Eq. 1, except that K_{LSW} is replaced by the volume-fraction dependent function $K(V_V)$, and the relative coarsening rate, $K(V_V)/K_{LSW}$, now depends explicitly on the volume fraction,

$$\frac{K(V_V)}{K_{LSW}} = \frac{27}{4} \times \left[\frac{2-(1-\sqrt{3V_V})\left(1-\frac{1}{\sqrt{3V_V}}+\sqrt{\frac{1}{3V_V}+\frac{1}{\sqrt{3V_V}}+1}\right)}{\left[1-\frac{1}{\sqrt{3V_V}}+\sqrt{\frac{1}{3V_V}+\frac{1}{\sqrt{3V_V}}+1}\right]^3}\right]\langle\rho\rangle^3. \tag{6}$$

Equation 6 serves to show the direct dependence of the coarsening rate constant at non-zero volume fractions to the square-root of the volume fraction. This square-root dependence provides a key kinetic marker of diffusion screening, and one that has been verified experimentally.[31] The average value of the normalized particle radius, $\langle\rho\rangle$, is weakly dependent on the volume fraction. For an infinitely dilute system, where $\langle\rho\rangle = 1$, which is a well-known result confirmed by calculating the first moment of the PSD derived from LSW theory. Therefore, as $\langle\rho\rangle^3 = 1$, Eq. 6 may be accurately approximated as

$$\frac{K(V_V)}{K_{LSW}} \approx \frac{27}{4} \times \left[\frac{2-(1-\sqrt{3V_V})\left(1-\frac{1}{\sqrt{3V_V}}+\sqrt{\frac{1}{3V_V}+\frac{1}{\sqrt{3V_V}}+1}\right)}{\left[1-\frac{1}{\sqrt{3V_V}}+\sqrt{\frac{1}{3V_V}+\frac{1}{\sqrt{3V_V}}+1}\right]^3}\right]. \tag{7}$$

3. The scaled PSD, $f(\rho)$, predicted using diffusion screening theory, may be calculated as

$$f(\rho) = \frac{A}{d\rho/d\tau}\exp\left[\int_0^{\rho}\frac{d\rho}{d\rho/d\tau}\right], \tag{8}$$

where A is the normalization constant. The scaled growth rate, or so-called kinetic growth equation of a particle, $d\rho/d\tau$, can be derived from Eq. 4 in terms of its normalized radius, ρ, through the relationship,

$$\frac{d\rho}{d\tau} = \frac{1}{K_c}\left[\frac{\rho-1}{\rho^2(1-\rho/\rho_D)}\right] - \rho, \tag{9}$$

where $\rho = R/R_c$, $K_c = dR_c^3/3dt$, $\tau = \ln {R_c}^3/3$, and $\rho_D = R_D/R_c$.[13] The PSDs were predicted from diffusion screening theory by numerical solution of Eq. 8 for different volume fractions.In summary, the predictions from 3D diffusion screening theory were tested recently using simulations[17] and experiments in Al-Li alloys.[31,32] These theoretical predictions are in satisfactory agreement with both careful computational and experimental work. In the present article, we develop diffusion screening theory for 2D systems, including phase coarsening and precipitate aging in thin films and on surfaces.

DIFFUSION SCREENING THEORY IN 2D MICROSTRUCTURES

We analyze a two phase system consisting of polydisperse circular phase islands in a 2D film. The sizes of 2D phase islands are described by the distribution $f(R,t)$, defined here as the total number of phase islands per unit area at time t, having radii between R and $R+dR$. The normalization of $f(R,t)$ is based on the total number of phase islands per unit area, that is,

$$\int_0^\infty f(R,t)dR = N_S, \tag{10}$$

where N_S is the number density of phase islands. With this normalization, the area fraction ϕ_S is defined as

$$\phi_S \equiv \pi \int_0^\infty R^2 f(R,t)dR, \tag{11}$$

hence

$$\phi_S = \pi N_S \langle R^2 \rangle, \tag{12}$$

where $\langle R^2 \rangle$ is the average of the square of the island radii.

Marqusee was the first to model the effects of non-zero volume fraction on phase coarsening kinetics in 2D systems.[21] The emission of solute from dissolving phase islands, or its absorption by growing ones was modeled mathematically using a balanced distribution of point *sources* and *sinks* of solute in the two-phase medium. Marqusee proposed that the steady-state concentration filed, $C(r)$, satisfies[21]

$$[\nabla^2 - R_S^{-2}]\delta C(r) = 0, \tag{13}$$

where $\delta C(r) = C(r) - \bar{C}$. The quantity R_S plays the role of screening length as does R_D in 3D coarsening. See again Eq. 3. Now R_S is treated as a parameter, which is constant when ϕ_S is specified. We derive an expression for R_S in a manner different from that used by Marqusee. $C(r)$ is subject to the following boundary conditions:

(1) the concentration at infinity has the bulk value

$$C(r)\big|_{r=\infty} = \bar{C}; \tag{14}$$

(2) at the surface,

$$C(r)\big|_{r=R} = C_{eq}(R), \tag{15}$$

where $C_{eq}(R)$ is the local equilibrium concentration associated with a circular phase island of radius R. The solution to Eq. 13 is

$$C(r) = \bar{C} + [C_{eq}(R) - \bar{C}]\left[\frac{K_0(r/R_S)}{K_0(R/R_S)}\right], \tag{16}$$

where K_0 is the zeroth-order modified Bessel function of the second kind. The local flux into the droplet at the origin is

$$J = 2\pi R D \nabla c|_R = 2\pi D \frac{R}{R_S}\left[\frac{K_1(R/R_S)}{K_0(R/R_S)}\right][\bar{C} - C_{eq}(R)], \tag{17}$$

where K_1 is the first-order modified Bessel function of the second kind. Using mass balance one can obtain the growth law for 2D diffusion-limited growth

$$\frac{dR}{dt} = \frac{D\Omega_S}{R_S}\left[\frac{K_1(R/R_S)}{K_0(R/R_S)}\right][\bar{C} - C_{eq}(R)], \tag{18}$$

where Ω_S is the molar area of the phase (a material constant proportional to $V_m^{\frac{2}{3}}$). Dynamic equilibrium with the bulk continuous phase that forms the thin film requires local equilibrium concentration at the interface of an island of radius R as determined from the Gibbs–Thomson effect,

$$C_{eq}(R) = C_0\left(1 + \frac{l_S}{R}\right), \tag{19}$$

where, $l_S = \frac{2\sigma\Omega_S}{R_g T}$ is the characteristic capillary length in 2D systems as l_c is in 3D systems.The droplet with a critical radius, R_c, has zero growth rate, i.e., $dR/dt = 0$ in accord with Eq. 18, when $C_{eq}(R_c) = \bar{C}$. A droplet with the critical radius instantaneously neither grows nor shrinks. Substituting Eq. 19 into Eq. 18, and then applying the definition of the critical radius, yields the kinetic law in 2D. After some algebraic manipulation one finds

$$\frac{dR}{dt} = \frac{DC_0 l_S \Omega_S}{R_S}\left[\frac{K_1(R/R_S)}{K_0(R/R_S)}\right]\left[\frac{1}{R_c} - \frac{1}{R}\right]. \tag{20}$$

Equation 20 may be non-dimensionalized as follows: (1) All length scales including R, R_c, and R_S in Eq. 20 are non-dimensionalized through the appropriate capillary length, l_S. (2) Physical time t in Eq. 20 is non-dimensionalized through the characteristic diffusion time, $\tau_S = \frac{l_S^2}{DC_0\Omega_S}$, to yield the dimensionless time, t. Finally, the non-dimensionalized kinetic equation, Eq. 20, becomes

$$\frac{dR}{dt} = \frac{1}{R_S}\frac{K_1(R/R_S)}{K_0(R/R_S)}\left[\frac{1}{R_c} - \frac{1}{R}\right]. \tag{21}$$

In order to compare with the kinetic equation, Eq. 2, derived from LSW theory, Eq. 21 is re-organized as

$$\frac{dR}{dt} = P\left(\frac{dR}{dt}\right)_{LSW}, \tag{22}$$

indicating that P is a function only of the ratio of the island radius to the diffusion screening distance, R/R_S.

$$P = \frac{R}{R_S}\left[\frac{K_1(R/R_S)}{K_0(R/R_S)}\right]. \tag{23}$$

Equation 22 shows that the growth rate of 2D islands equals the factor P times the growth rate of 3D particles in LSW theory. However, the prefactor P is the more complicated function of R/R_S shown in Eq. 23.

RESULTS

Growth Law in Thin Films at Small Area Fractions

When ϕ_s is extremely small, but not zero, R_S is large, and R/R_S is much smaller than unity. Standard rational approximations for the modified Bessel functions with small arguments are well known,[33] namely

$$K_0(x) \approx -\ln(x); \quad and \qquad K_1(x) \approx \frac{1}{x}. \tag{24}$$

The kinetic equation for coarsening in thin films, Eq. 22, may be found for small island coverage (i.e., large screening distances, R_S, using Eq. 24 as approximations for the Bessel functions. This procedure yields

$$\frac{dR}{dt} = \frac{1}{|\ln(R_S/R)|}\left(\frac{dR}{dt}\right)_{LSW}. \tag{25}$$

Hayakawa and Family[22] also considered many-body effects during 2D Ostwald ripening by using Green's function responses for solutions to the diffusion equation.[23] Their kinetic law is identical to Eq. 25, which is derived by a different field theoretic method. This check also reveals that the result, Eq. 21, is consistent and more accurate, and may be applied to a broader range of island area fractions in thin films. However, the growth law found by Hayakawa and Family has validity only at low area fractions. Figure 1 shows little difference between our prefactor, P, in Eq. 22 and that for Hayakawa and Family at low area fractions, where $\phi_S < 0.01$. Figure 1 also shows that when the island area fraction of precipitates is larger, viz., $\phi_S > 0.01$, the growth laws derived from both formulas remain similar. The kinetic equation, Eq. 22, however, is more accurate than that of Hayakawa and Family, Eq. 25, and remains useful in the important range of phase island area fractions, $\phi_S > 0.1$.

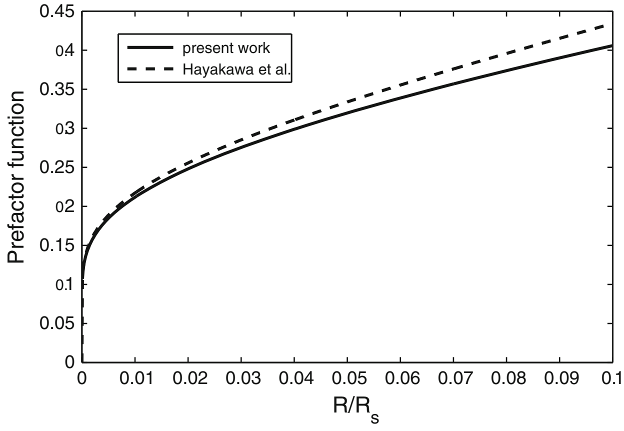

Fig. 1. Comparison of growth laws from our work, Eq. 22 (solid line), and the Hayakawa and Family result, Eq. 25 (dashed line).

Maximum Normalized Radius, Coarsening Rate, and PSD

The dimensionless growth rate of a phase island can be expressed using Eq. 21, by inserting the normalized island radius, $\rho = R/R_c$.

$$\frac{d\rho}{d\tau} = \frac{1}{K^\star}\frac{(\rho-1)}{\rho\rho_S}\left[\frac{K_1(\rho/\rho_S)}{K_0(\rho/\rho_S)}\right] - \rho, \tag{26}$$

where the constant $K^\star$ is defined as,

$$K^\star = \frac{1}{3}\frac{d(R_c)^3}{dt}. \tag{27}$$

Here, the normalized time scale, τ, and dimensionless screening length, ρ_S, are defined, respectively, as

$$\tau = \frac{1}{3}\ln(R_c)^3, \tag{28}$$

and

$$\rho_S = \frac{R_S}{R_c}. \tag{29}$$

Lifshitz and Slyozov[3] showed many years ago that steady-state solutions to the continuity equation governing the PSDs for coarsening in 3D are possible if and only if $K^\star$ is constant. The value of $K^\star$ can be determined by applying a stability condition, based on mass conservation in ρ space, which guarantees a self-similar distribution. Specifically, Lifshitz and Slyozov showed that to maintain a self-similar (affine) distribution of particle sizes indefinitely, two conditions must be satisfied *simultaneously* at the largest normalized particle size, ρ_{max}. To insure mass conservation in ρ-space, the following must hold:

$$(1)\ \left(\frac{d\rho}{d\tau}\right)_{\rho=\rho_{max}} = 0, \quad and \quad (2)\ \left\{\frac{d}{d\rho}\left(\frac{d\rho}{d\tau}\right)\right\}_{\rho=\rho_{max}} = 0. \tag{30}$$

Application of these stability conditions lead to the following two equations,

$$K^\star = \frac{(\rho_{max}-1)}{\rho_{max}^2}\frac{1}{\rho_S}\left[\frac{K_1(\rho_{max}/\rho_S)}{K_0(\rho_{max}/\rho_S)}\right], \tag{31}$$

and

$$\frac{1}{\rho_S}\left[\frac{K_1^2(\zeta)}{K_0^2(\zeta)}-1\right]\rho_{max}^2-\left[\frac{1}{\rho_S}\frac{K_1^2(\zeta)}{K_0^2(\zeta)}+2\frac{K_1(\zeta)}{K_0(\zeta)}-\frac{1}{\rho_S}\right]\rho_{max}+3\frac{K_1(\zeta)}{K_0(\zeta)}=0, \qquad (32)$$

where $\zeta = \rho_{max}/\rho_S$.

Following the LSW steady-state stability argument,[3] the normalized PSD, $f(\rho, \tau)$, satisfies the following continuity equation,

$$\frac{\partial f(\rho,\tau)}{\partial \tau}+\frac{\partial}{\partial \rho}\left[\frac{d\rho}{d\tau}f(\rho,\tau)\right]=0. \qquad (33)$$

In the late stages of thin film phase coarsening, the hypothesis of statistical self-similarity can be used. The PSD achieves an affine form in that $f(\rho, \tau)$ may be recast in the product form

$$f(\rho,\tau)=F_0(\rho)\cdot H(\tau). \qquad (34)$$

Here $F_0(\rho)$ is the time-independent, normalized, probability density, or PSD. $H(\tau)$ is the explicit, time-dependence of the PSD that specifies the microstructure's temporal behavior.

Substituting Eq. 34 into Eq. 33, and separating the variables ρ and τ in Eq. 33, yields a pair of separable ordinary differential equations in time and space, namely:

$$\frac{H'(\tau)}{H(\tau)}=-\lambda, \qquad (35)$$

and

$$\frac{d}{d\rho}\left(\frac{d\rho}{d\tau}\right)+\frac{1}{F_0(\rho)}\frac{d\rho}{d\tau}\left(\frac{dF_0(\rho)}{d\rho}\right)=\lambda. \qquad (36)$$

Here λ is the separation constant, or eigenvalue. The general solution to Eq. 36 is

$$F_0(\rho)=\frac{A_S}{d\rho/d\tau}\exp\left[\int_0^\rho \frac{1}{d\rho/d\tau}d\rho\right], \qquad (37)$$

where A_S is the norm, which is determined by the condition of unit probability for the total phase island population,

$$\int_0^\infty F_0(\rho)d\rho = 1. \qquad (38)$$

As shown in Eqs. 37, and 38, the normalized PSD can be obtained from Eq. 37, provided that the growth rate of the normalized radius, $d\rho/d\tau$, is known.

The rate constant $K^\star$ appearing in the growth rate equation, Eq. 26 must be found before one attempts to calculate the PSD from Eq. 37. The steady-state kinetic coarsening equation may be expressed using the definition of $K^\star$ in terms of the critical radius, as shown in Eq. 27,

$$R_c^3(t)-R_c^3(0)=3K^\star t \qquad (39)$$

Here $R_c(0)$ defined the critical phase island radius for some arbitrary initial time, $t = 0$ in the steady state. It is, however, easier both experimentally and computationally to determine the average radius, $\langle R\rangle$, and thus implement the kinetic coarsening equation in terms of average radius rather than critical radius. From the definition of the normalized radius, ρ, there exists a relationship between average and critical radius, specifically,

$$\langle\rho\rangle = \langle R\rangle/R^* = \int_0^{\rho_{max}} \rho F_0(\rho)d\rho. \qquad (40)$$

Substituting the the relationship between average and critical radius, Eq. 40, into Eq. 39, yields the kinetic coarsening equation in terms of the average radius,

$$\langle R(t)\rangle^3-\langle R(0)\rangle^3=3K(\phi_S)t, \qquad (41)$$

where

$$K(\phi_S)=3K^\star\langle\rho\rangle^3. \qquad (42)$$

$\langle R(0)\rangle$ is the average radius at $t = 0$, and $K(\phi_S)$ is the coarsening rate constant for a thin film with area fraction ϕ_S.

In addition, one also needs the PSD scaled by average radius $G_S(R/\langle R\rangle)$. The PSD in Eq. 37 is scaled by the critical radius. However, most PSDs derived from experiments are scaled by the average radius. According to the definitions of the average radius and critical radius, one easily obtains the PSD scaled by average radius,

$$G_S(R/\langle R\rangle)=\langle\rho\rangle F_0(\langle\rho\rangle R/\langle R\rangle). \qquad (43)$$

Comparison of Diffusion Screening Lengths

Diffusion screening lengths were first introduced arbitrarily to remove the divergence of the field solution for the diffusion equation at steady state. We have already derived the diffusion screening length for 3D phase coarsening, shown in Eq. 3, using the analogy of the electrostatic Debye length for a dilute ionic solution.

Marquesee[21] produced a numerical plot for the ratio $\langle R\rangle/R_S$ versus ϕ_S for the diffusion screening lengths in 2D phase coarsening. Carlow et al.[34] used a two-parameter function in the form $\langle R\rangle/R_S = b\phi_S^a$, attempting to fit Marquesee's numerical result, and obtain an approximation relationship for the diffusion screening length

$$R_S \approx \frac{\langle R\rangle}{2\phi_S^{3/4}}. \qquad (44)$$

We approximate the average first-nearest neighbor distance as the screening length, which is written as

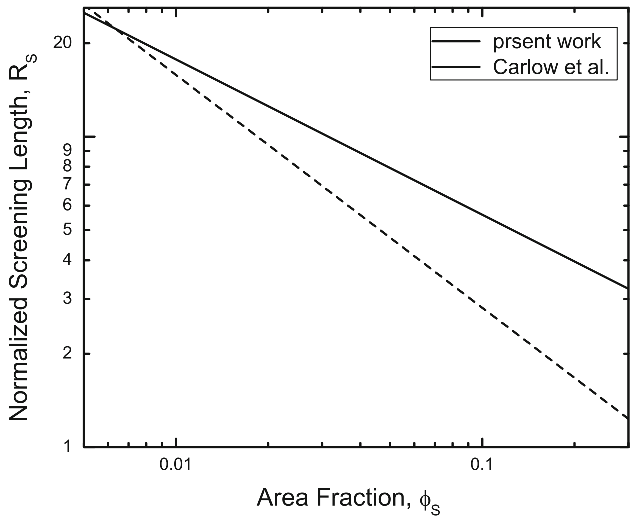

Fig. 2. Comparison of dependence of screening lengths on area fractions from our current work, Eq. 45 (solid line), and the Carlow et al. work, Eq. 44 (dashed line).

$$R_S = \frac{\sqrt{\pi}\langle R\rangle}{\sqrt{\phi_S}}. \tag{45}$$

Figure 2 shows the comparison of screening lengths proposed by the authors and Carlow et al. When the area fractions, $\phi_S \leq 0.01$, screening lengths derived from both formulas, Eqs. 44 and 45 are similar. When the area fractions, $\phi_S > 0.01$, screening lengths derived from both formulas start to deviate from each other.

CONCLUSION

We approximate phase coarsening among phase islands dispersed in thin films as a mesoscopic distribution of diffusion sources and sinks. Poisson's equation in 2D (Eq. 13) describes the concentration field and provides a framework for the screened diffusion field, in analogy with screening that occurs in 3D. The effective screening interaction in thin film microstructures among a population of circular phase islands provides a kinetic equation for the coarsening of precipitates. Screening interactions increase the coarsening rate and alter the shape of the PSD for a specified area coverage. The standard continuity equation in 2D size space is used to describe the PSD, which completes a consistent diffusion screening theory phase coarsening in films.

Several additional conclusions can be drawn on the basis of this study:

(1) The diffusion screening length among phase islands is proportional to $\phi_S^{-1/2}$, a result which may now be tested by experiments. By contrast, Carlow et al.[34] approximated this interaction as $\phi_S^{-3/4}$. Direct experimental tests are suggested to adjudicate these alternative scaling laws.

(2) Equation 32 permits calculation of how interactions among phase islands influence the width of the PSD. Stronger interactions reduce the height and broaden the PSD. Equation 32 also predicts how the maximum allowed island radius depends on the normalized screening length, ρ_S. Because the normalized screening length depends on the area fraction (*c.f.* Eq. 45), the maximum allowed radius should also vary with the area fraction. Again, this effect should be subject to direct experimental checks.

(3) Growth rates derived from the present microstructure theory at low area fraction correctly recover the earlier results by Hayakawa and Family. This suggests that the current screening approach captures essential features of the many-body interactions during diffusion-limited 2D coarsening. In addition, Eq. 31 shows that the coarsening rate constant changes with the maximum allowed island radius and the normalized screening length, both of which change with area coverage of the second phase.

(4) The PSD for 2D phase coarsening can be obtained by numerical solution to Eq. 37 with substitution of growth rate, Eq. 26. The constant $K^{\star}$ in the growth rate, Eq. 26, can be determined from Eq. 31. In summary, diffusion screening theory as developed here may be applied to explain the growth kinetics and phase coarsening of dispersed droplets in thin films.

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