Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Late-stage two-dimensional coarsening of circular clusters

A. J. Ardell
Department of Materials Science and Engineering, University of California, Los Angeles, California 90024
(Received 15 August 1989)

The size distribution of circular clusters resulting from a computer simulation of the late stages of phase separation in two dimensions was recently reported by Rogers and Desai [Phys. Rev. B **39**, 11956 (1989)]. The distribution that evolved was considerably broader than that predicted by an analytical version of the Lifshitz-Slyozov theory of late-stage coarsening in two dimensions. The results of the numerical analysis are compared with an older version of the two-dimensional theory which includes the effect of diffusive correlations among nearest-neighbor clusters; the correlations are related to the volume (area) fraction of clusters. The size distribution predicted by the older theory is in much better agreement with the numerical data. The implications of this agreement for the late-stage coarsening of three-dimensional clusters are discussed.

Rogers and Desai[1] recently published the results of a numerical study of the kinetics of phase separation in two dimensions. Several off-critical compositions were investigated in a system with a symmetrical phase diagram. The focal point of their work was domain growth and scaling behavior in the late stages of decomposition. Scaling was best satisfied for the initial composition C_0 farthest from the critical composition C_c ($=0.5$). Under these circumstances the growth rate of the circular clusters, characterized by an average radius $\langle R_c \rangle$, increased with time t according to $\langle R_c \rangle \propto t^n$, while the average number of clusters per unit area, N, decreased with t according to $N \propto t^{-2n}$, with $n \sim 0.29$.

Rogers and Desai compared this late-stage coarsening behavior with that predicted by a two-dimensional version of the Lifshitz-Slyozov[2] (LS) theory of coarsening. Since the classical LS theory was formulated for a three-dimensional array of clusters, Rogers and Desai were obliged to derive the corresponding equations for the two-dimensional problem. This requires an analytical solution to the problem of steady-state diffusion to a circular cluster in the center of an infinite plane, and it is easy to show that the flux at the interface of such a cluster is zero. To circumvent this difficulty, Rogers and Desai employed an asymptotic analysis of the diffusion equation, from which they proceeded to show that the LS theory in two dimensions predicts $n = \frac{1}{3}$, with a scaled, time-independent, cluster size distribution given by

$$f(x) = cx^2 \left[1 - \frac{2x}{3}\right]^{-28/9} \left[1 + \frac{x}{3}\right]^{-17/9} \exp\left[\frac{-2/3}{1 - 2x/3}\right]; \quad x < \tfrac{3}{2}, \tag{1}$$

where $x = R/R^*$, R is the radius of an individual cluster, $R^* = R^*(t)$ is a cluster of critical size which is neither growing nor shrinking at time t, and c is a normalization constant.

One important result of their computer simulation was that the normalized cluster probability function produced by the numerical analysis was considerably broader than that predicted by Eq. (1). They attributed the discrepancy to correlations among neighboring clusters.

Many years ago I analyzed the problem of two-dimensional coarsening[3] with the intent of predicting the average growth rate of cylindrical fibers in directionally solidified eutectic alloys. My solutions to the two-dimensional coarsening problem included "correlations" among clusters, and in this sense were more comprehensive than the solution of Rogers and Desai. The principal purpose of this Comment is to compare the distribution obtained from their computer simulation with the predictions of my model.

Diffusive correlations arise through the effect of the cluster volume fraction (or area fraction) and the manner in which this influences the diffusion fields around individual clusters. I chose a particularly simple model of the diffusion geometry; i.e., that of steady-state diffusion between concentric cylinders of radii R and R'. The radius R' of the outer cylinder was taken as $R + \langle l \rangle/2$, where $\langle l \rangle$

is the mean free distance between a cluster and its nearest neighbors. So long as R' is finite, steady-state solutions to the diffusion problem are well behaved and predict nonzero fluxes at the interface of the inner cylinder. The flux is proportional to the concentration gradient, given by

$$\left.\frac{dC}{dr}\right|_{r=R} = \frac{C_{R'} - C_R}{R \ln(R'/R)}, \tag{2}$$

where r is a spatial coordinate and C_R and $C_{R'}$ are the concentrations at R and R', respectively.

The volume fraction Q enters the problem through the geometrical relationship between R, R', and $\langle l \rangle$. Using an expression for $\langle l \rangle$ derived by Bansal and Ardell[4] the ratio R'/R becomes

$$\frac{R'}{R} = 1 + \frac{1}{\eta x}, \tag{3}$$

where

$$\eta = \frac{4Q^{1/2}}{e^{4Q}\Gamma(\frac{1}{2}, 4Q)} \tag{4}$$

and

$$\Gamma(\tfrac{1}{2}, 4Q) = \int_{4Q}^{\infty} y^{-1/2} e^{-y} dy. \tag{5}$$

The calculation of Bansal and Ardell is accurate to $Q \sim 0.5$, which covers most physically realistic dispersions. The difficulty in the limit of zero area fraction is that $R' \to \infty$ as $Q \to 0$, so that (2) is always zero.

Through the use of the Gibbs-Thomson equation, the development of the two-dimensional LS theory is straightforward. The significant results in the context of this discussion are that the normalized distribution of cluster sizes takes the general scaling form[5]

$$f(x) = \frac{-2x^2}{dx^3/d\tau} \exp\left[\int_0^x \frac{2u^2 du}{du^3/d\tau}\right], \tag{6}$$

where

$$\frac{dx^3}{d\tau} = \frac{(x-1)\zeta}{\ln(1 + 1/\eta x)} - x^3, \tag{7}$$

$\tau = 3 \ln R^*$, and

$$\zeta = \frac{x_m^3}{(2x_m - 3)(1 + \eta x_m)}, \tag{8}$$

where x_m is the maximum allowed value of x [Eq. (6) is valid only for $x < x_m$]. The cutoff particle size x_m satisfies the equation

$$(1 + \eta x_m) \ln\left(1 + \frac{1}{\eta x_m}\right) = \frac{x_m - 1}{2x_m - 3}. \tag{9}$$

The theory also predicts that $R^* \propto (t/\zeta)^n$, with $n = \frac{1}{3}$, for all values of Q.

In the limit $Q = 0$, the case treated by Rogers and Desai, $\eta = 0$, $x_m = \frac{3}{2}$ from (9), $\zeta \to \infty$ from (8), and the ratio $\zeta/\ln(1 + 1/\eta x) \to 2(\frac{3}{2})^3$. Equation (7) is thus simplified, enabling the straightforward integration of (6), which for $x < x_m$ becomes

$$f(x) = (\tfrac{2}{3})^3 x^2 \left(1 - \frac{2x}{3}\right)^{-28/9} \left(1 + \frac{x}{3}\right)^{-17/9} \times \exp\left(\frac{-4x/9}{1 - 2x/3}\right). \tag{10}$$

Equations (10) and (1) appear to differ in the argument of the exponential function, but they are in fact identical,[6] with $c = (\frac{2}{3})^3 e^{2/3}$. We note that Eq. (10) is obtained without recourse to special mathematical approximations. Interestingly, however, it applies to a physically meaningless static dispersion because $\zeta \to \infty$, hence the rate of cluster growth becomes zero. Nevertheless, for any physically meaningful nonzero value of Q the solutions are perfectly well behaved. For example, for $Q = 0.001$, which is a very dilute dispersion, $\zeta \sim 15$.

We now turn to the distribution measured numerically by Rogers and Desai for the "composition" $\psi_0 = 0.4$. Since $\psi_0 = (C_c - C_0)/(C_c - C_e)$, where C_e is the equilibrium concentration (the concentration at the coexistence curve), and $Q = (C_0 - C_e)/(1 - 2C_e)$, we have $Q = (1 - \psi_0)/2$ in general, so that $Q = 0.3$ for $\psi_0 = 0.4$. Equation (6) was evaluated numerically for $Q = 0.3$ for comparison with the results of Rogers and Desai; the function $f(x)$ was transformed to $f_0(x')$ for this purpose[7] (in general $x' = x/\langle x \rangle$, and for $Q = 0.3$ $\langle x \rangle = 1.023$, cf. $\langle x \rangle = 1.0665$ for $Q = 0$), and the results for the longest time investigated by Rogers and Desai (a dimensionless time of 5000) are shown in Fig. 1. The numerical distribution is somewhat narrower and more sharply peaked than the theoretical distribution, although the differences are not really evident except in the vicinity of the peak. It is important to note, however, that the experimental distribution is still evolving towards its eventual scaling form, broadening with increasing time. Therefore, the agreement between theory and experiment in Fig. 1 can only be expected to improve for simulations run to yet later stages.

The implications of the favorable comparison in Fig. 1

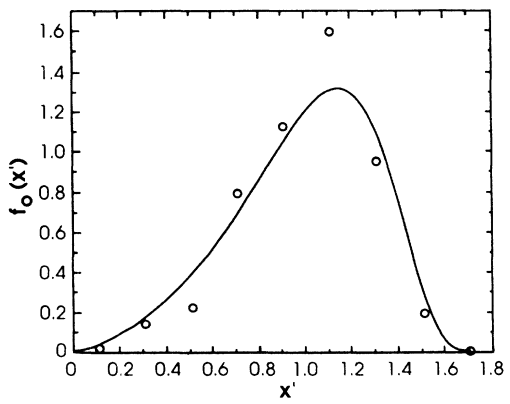

FIG. 1. Comparison of the distribution of sizes of circular clusters obtained numerically after a reduced time of 5000 (open circles), with the distribution predicted by the theory of two-dimensional late-stage coarsening for a cluster volume fraction of 0.3.

are quite significant because my model emphasizes the role of local diffusive correlations. The growth of an individual cluster in this model is determined only by the way its nearest neighbors influence the composition in its immediate vicinity. More distant neighbors, which influence the diffusion fields in other theories of two-dimensional[8,9] and three-dimensional coarsening,[10] are assumed here to have no effect. The comparison in Fig. 1 suggests that models which include far-field diffusion may be inappropriate, no matter how rigorously they are formulated. Some newly reported experimental results[11] provide additional support for this idea.

It is potentially of interest to compare the results of Rogers and Desai with the predictions of two other recent theories of two-dimensional coarsening.[8,9] Unfortunately, such a comparison is not warranted for the theory of Zheng and Gunton[9] because the authors themselves doubt its applicability for values of Q exceeding 0.01. The predictions of the theory of Marqusee,[8] on the other hand, are more relevant. A comparison of my distribution function[3] with his for $Q=0.4$ shows fair agreement, and it is likely that this is also the case for $Q=0.3$. The fair agreement at these rather large values of Q must be fortuitous, however, because for $Q=0.1$ and 0.01 in his Fig. 1 it is evident that the distributions are already much narrower than those of my theory. In fact, Marqusee's distribution for $Q=0.01$ is much more sharply peaked than that predicted by Eqs. (1) and (10) for $Q=0$. This is no doubt related to the small values of the particle-size cutoffs in Marqusee's theory, which fall below the theoretical limit of $x/\langle x\rangle=1.5/1.0665=1.4065$ for $Q=0$ at a finite area fraction of ~ 0.14 (see his Fig. 2). Marqusee's theory is therefore inconsistent with Eqs. (1) and (10) in the limit $Q\rightarrow 0$; no attempt has been made to uncover the reasons for this discrepancy.

There is no example of the late-stage coarsening behavior of precipitates (three-dimensional clusters) in alloys that agrees with all the predictions of the various theories of this phenomenon. This is partly because precipitates in solids are often surrounded by strain fields which sometimes cause them to interact elastically, and partly because their shapes are not always spherical. However, Cu-Co alloys containing spherical Co-rich precipitates and Al-Li alloys containing spherical Al_3Li precipitates are possible exceptions. Co precipitates have a relatively large elastic misfit with the bulk matrix, but their volume fraction is quite small (Q rarely exceeds 0.04) so that elastic interactions are very weak. The volume fraction of Al_3Li precipitates can be quite large (up to $Q\sim 0.5$), but the precipitates are nearly misfit-free, and therefore provide perhaps the most ideal cluster for testing the various theories of coarsening in three dimensions.

My two-dimensional model was a straightforward extension of an earlier theory,[12] formulated for three-dimensional behavior, which is generally disfavored because of its *ad hoc* introduction of an outer cutoff limit in the diffusion geometry. However, if the two-dimensional model provides an accurate description of late-stage coarsening, as implied by the agreement in Fig. 1, the original theory could be equally valid for describing late-stage coarsening behavior in three dimensions. This has been shown[13] to be the case for the best data available on the kinetics of particle growth and particle size distributions in Cu-Co alloys. It is also true for the growth kinetics in the more concentrated Al-Li alloys, but for this alloy the particle size distributions are in better agreement with a theory derived by Davies, Nash, and Stevens,[14] which includes the effect of physical encounters among nearest-neighbor clusters.

I am grateful to R. C. Desai for bringing his recent work to my attention and for a stimulating discussion which eventually led me to dredge up the memory of my old work; it had been essentially forgotten not only by the world at large, but also by me. I also thank him for alerting me to the existence of the theories of Marqusee, and Zheng and Gunton. Thanks are due to J. Zhang for helping with the calculations.

---

[1]T. M. Rogers and R. C. Desai, Phys. Rev. B **39**, 11956 (1989).

[2]I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1959).

[3]A. J. Ardell, Metall. Trans. **3**, 1395 (1972).

[4]P. P. Bansal and A. J. Ardell, Metallography **5**, 97 (1972).

[5]There are misprints in the counterparts of Eqs. (6) and (7) in my paper (Ref. 3), Eqs. (11) and (19), respectively. The upper limit of the integral in (19) should be u, not u_m, and the left-hand side of (11) should be $du^3/d\tau$, not $du/d\tau$.

[6]R. C. Desai (personal communication).

[7]Rogers and Desai made the corresponding, and necessary, transformation, but did not explicitly point out the difference between $f(x)$ and $f_0(x')$, namely, $f_0(x')=\langle x\rangle f(x)$.

[8]J. Marqusee, J. Chem. Phys. **81**, 976 (1984).

[9]Q. Zheng and J. D. Gunton, Phys. Rev. A **39**, 4848 (1989).

[10]See P. W. Voorhees, J. Stat. Phys. **38**, 231 (1985), and Y. Enomoto, M. Tokuyama, and K. Kawasaki, Acta Metall. **34**, 2119 (1986), for discussions of recent three-dimensional theories.

[11]D. J. Chellman and A. J. Ardell, in *Materials Architecture,* edited by J. B. Bilde-Sørensen, N. Hansen, D. Juul Jensen, T. Leffers, H. Lilholt, and O. B. Pedersen (Risø National Laboratory, Roskilde, Denmark, 1989), p. 295.

[12]A. J. Ardell, Acta Metall. **20**, 61 (1972).

[13]A. J. Ardell, in *Phase Transformations 1987,* edited by G. W. Lorimer (The Institute of Metals, London, 1988), p. 485.

[14]C. K. L. Davies, P. Nash, and R. N. Stevens, Acta Metall. **28**, 179 (1980).