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SELF-SIMILARITY AND GROWTH KINETICS DRIVEN BY SURFACE FREE ENERGY REDUCTION

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Abstract—We consider a configuration of interfaces (area S) moving under the driving force of interfacial free energy reduction in a large volume V. The time dependence of the linear scale $l = V/S$ of the configuration is deduced for systems with a single or multicomponent order parameter, conserved or non-conserved, by use of the hypothesis of statistical self-similarity: specifically, we assume that statistical parameters that are invariant under uniform magnification are also independent of time and that local equilibrium of the intersection angles of interfaces holds along lines of intersections (if any). This hypothesis, together with the scaling characteristics of interface velocities in the system under consideration, is sufficient to yield the result $l(t) \sim t^n$ with $n > 0$; in particular, we show that $n = 1/2$ for curvature driven growth and $n = 1/3$ for diffusion limited coarsening. We conclude that these values are independent of many of the approximations and restrictions that characterize specific models (e.g. over-simplifications of geometry, mean field approximations, small volume fraction of precipitates). Free energy functional models that exhibit the above growth laws are also discussed.

Résumé—On considère une configuration d'interfaces (domaine S) en mouvement comme force motrice de la réduction de l'énergie libre d'interface dans un grand volume V. La dépendance temporelle de l'échelle linéaire $l = V/S$ de la configuration est déduite pour des systèmes avec un paramètre d'ordre à une ou à plusieurs composantes, conservé ou non conservé, en utilisant l'hypothèse de l'autosimilitude statistique: on considère que les paramètres statistiques, invariants par un agrandissement uniforme sont aussi indépendants du temps et que l'équilibre local des angles d'intersection des interfaces se maintient le long des lignes d'intersection (s'il en existe). Cette hypothèse, ajoutée aux caractéristiques des vitesses d'interface dans le système considéré, est suffisante pour établir le résultat $l(t) \sim t^n$ avec $n > 0$; en particulier on montre que $n = \frac{1}{2}$ pour une croissance due à la courbure et $n = \frac{1}{3}$ pour le grossissement contrôlé par la diffusion. On conclut que ces valeurs sont indépendantes de beaucoup d'approximations et de restrictions qui caractérisent les modèles particuliers (par exemple simplifications de la géométrie, approximations de champ moyen, faible fraction volumique des précipités). Les modèles fonctionnels d'énergie libre qui présentent les lois do croissance ci-dessus sont également discutés.

Zusammenfassung—Wir betrachten eine Anordnung von Grenzflächen (mit Fläche S), die sich in einem großen Volumen unter der treibenden Kraft einer sich verringernden Grenzflächenenergie bewegt. Die Zeitabhängigkeit des linearen Skala $l = V/S$ der Anordnung wird für Systeme mit einem einzigen oder einem vielkomponentigen Ordnungsparameter mittels der Hypothese der statistischen Selbst-Ähnlichkeit abgeleitet. Insbesondere nehmen wir an, daß statistische Parameter, die unter der einheitlichen Vergrößerung invariant sind, auch von der Zeit abhängig sind, und daß lokales Gleichgewicht des Winkels zweier sich schneidender Grenzflächen entland der Linie der Schnitte (wenn es sie gibt) erhalten bleibt. Diese Hypothese, zusammen mit der Skalierungscharakteristik der Grenzflächengeschwindigkeiten im betrachteten System, reicht aus, das Ergebnis $l(t) \sim t^n$ mit $n > 0$ zu erhalten; insbesondere zeigen wir, daß $n = \frac{1}{2}$ für das durch die Krümmung getriebene Wachstum und $n = \frac{1}{3}$ für die diffusionsbegrenzte Vergröberung gilt. Wir folgern, daß diese Werte von vielen Näherungen und Einschränkungen, die spezifische Modelle charakterisieren (z.B. Vereinfachungen in der Geometrie, Näherung eines mittleren Feldes, kleiner Volumenteil der Ausscheidungen), unabhängig sind. Außerdem werden Modelle für Funktionale der freien Energie, welche die eben geschilderten Wachstumsgesetze aufweisen, diskutiert.

1. INTRODUCTION

The purpose of this paper is to deduce, from a few general assumptions, the time dependence of the scale l of a configuration of interfaces (e.g. phase, domain or grain boundaries) moving under the driving force of interface free energy reduction. We define l by

$$l = \frac{V}{S} \tag{1}$$

where V is the volume of the system containing a total area S of interface boundary such that the linear dimensions of V are much larger than l. As the interfacial free energy and S decrease, l increases and the structure coarsens. Our treatment is free of many of the simplifications and approximations (e.g. over-simplifications of geometry, mean field approximation, etc.) that characterize specific models of domain or grain growth and coarsening.

Hence our conclusions are independent of these restrictions.

Our basic hypothesis is that after a possible initial transient, statistical self-similarity holds according to which consecutive configurations of the structure are geometrically similar in a statistical sense [1]. Specifically, we assume that any parameter of the structure that is invariant under a uniform magnification is also independent of time, and that local equilibrium of the intersection angles of interfaces holds along lines of intersection (if any). This hypothesis, together with the scaling characteristics of the interface velocities in the system under consideration, is used to obtain an equation of motion for l that yields our result $l(t) \sim t^n$, where $n > 0$ depends on the system.

Our treatment extends previous ones in that it offers a simple comprehensive framework for the analysis of systems with an order parameter that is either a single scalar (no intersecting boundaries) or a multicomponent vector (possible intersecting boundaries) and that is either conserved (as in precipitate coarsening) or non-conserved (as in domain or grain growth). Our scaling argument reduces to that of Allen and Cahn [2] for the case of the coarsening of domains in a system with two types of domains (scalar non-conserved order parameter) and agrees with the results of one of us [1] who based a scaling analysis of growth and coarsening on changes in the volume per particle; the latter treatment is, of course, limited to systems with discrete particles, and requires more assumptions (e.g. no impingement of particles) than the present analysis. The generality of our treatment stems from the provision, in the equation of motion for l, for a general law of boundary migration and the inclusion of terms giving the contribution to dl/dt arising from boundary intersection line migration.

Support for the self-similarity hypothesis is provided by theoretical analyses [3–12], computer simulation results [13–32], and by direct experimental observations [33–35]. In any case, since the hypothesis can be directly checked in both experimental and computer studies of a given system, our analysis provides a framework within which growth laws may be analyzed. Two examples of this approach follow: the first one concerns domain growth in the Potts model (an idealized model of grain growth), extensively studied by Monte Carlo techniques. The kinetic exponent obtained from early studies [14–16] was argued to be a function of the number of states (grain orientations present) and was sensibly below 1/2, for more than two states. Subsequent analysis of the vertices showed that local equilibrium had not been attained and therefore that the scaling regime had not been reached. Recent studies [17–19, 36], in which vertex equilibrium holds, obtain estimates of $n \simeq 1/2$, independent of the number of states, in agreement with the results presented in section 3. The second example is related to coarsening in a binary alloy at critical concentrations (away from the region of validity of the Lifshitz–Slyozov theory). Numerical solutions [27, 28] show

the existence of a self-similar regime and yield an exponent $n \simeq 1/3$. A recent theoretical analysis, however, yields the asymptotic exponent $n = 1/4$ instead [37]. The results that we present in section 4 show that $n = 1/3$ is the only exponent consistent with the self-similarity hypothesis, thus supporting the evidence from the numerical simulations.

One possible limitation of our analysis is the neglect of thermal fluctuations. The growth process itself originates from an amplification of the thermal fluctuations present in the initial state. Furthermore, thermal fluctuations continue to be present during the whole growth process. They become increasingly important as one approaches a critical point. In the present case, however, we take the view that for sufficiently long times (after a quench to a temperature well below any critical temperature), the system reaches local equilibrium at the interfaces. In this regime, there is only one length scale in the system (the scale l); all the remaining length scales (including the width of the interfaces) become effectively irrelevant. We feel that this view is justified on the basis of experimental and computational evidence previously cited. There are also calculations in simple models [38] which indicate that thermal fluctuations do not modify the exponent in the growth law but only non-universal amplitudes.

A second possible limitation is our assumption of local equilibrium at any intersection lines between domain boundaries. Local equilibrium seems plausible since for sufficiently large l, the corresponding interface velocities are small and hence there is sufficient time for the equilibration of the interface intersection angles. It is conceivable, however, that there are systems in which the coordinates of these lines have to be treated explicitly and their equations of motion derived [39]. The only case, to our knowledge, where such an analysis has been carried out was in the case of the clock model [40]. In that case, a dimensional analysis of the equations of motion of the vortices led to the same growth exponent as obtained from the equation of motion for the interfaces.

Finally we mention that plausible necessary conditions for the self-similarity hypothesis to hold are the following: (1) the initial state of the system is spatially uniform in a statistical sense on a sufficiently large scale; (2) the law of boundary motion is such that the ratio of the velocities of any two boundary elements is invariant under uniform magnification (otherwise the geometry of configurations would be expected to change with time). Condition (2) holds (for large l) for the laws of boundary motion we shall consider.

2. DERIVATION OF THE KINETIC GROWTH LAW FROM THE SELF-SIMILARITY HYPOTHESIS

In this section, we will develop an expression for l as a function of time and a parameter β that describes the scaling properties of the boundary velocities; values of β for various processes or mechanisms of boundary migration are discussed in the following sections.

Let v_n be the local velocity of an element of boundary along the normal directed away from the nearest center of curvature and let K be the sum of the principal curvatures, the latter chosen to be positive if the normal points away from the corresponding center of curvature and negative otherwise. Then since the displacement of an element of boundary dS by a distance δn along the normal produces an area change $\delta(dS) = K\delta n(dS)$, we have the following expression for the rate of change of S

$$\frac{dS}{dt} = \int K v_n dS + \dot{S}_e, \qquad (2)$$

where the integration is conducted over all boundaries and $\dot{S}_e$ is the total rate of area creation at boundary intersection lines or edges (if any) due to extensions of boundaries along their tangent planes when the edges move.

To calculate $\dot{S}_e$, we define at each point of an edge

$$\omega = \sum_i \tau_i \qquad (3)$$

where τ_i is a unit vector that is normal to the edge in the local tangent plane of the ith intersecting boundary and directed away from the boundary (i.e. in the direction of the boundary extension); the sum in equation (3) is conducted over all boundaries intersecting at the edge. Then defining v_e to be the velocity of an element dl of edge, normal to the edge, we have

$$\dot{S}_e = \int v_e \cdot \omega \, dl \qquad (4)$$

where the integration is over all edges. Note that $\dot{S}_e = 0$ when all the intersection angles at an intersection line are equal, since then $\omega = 0$.

Differentiating $l = V/S$ and using equations (2) and (4), we obtain

$$\frac{dl}{dt} = -\frac{l^2}{V}\left[\int K v_n dS + \int v_e \cdot \omega \, dl\right]. \qquad (5)$$

Now suppose that under a uniform magnification of the linear dimensions of the structure by λ, v_n changes by the factor λ^β. Then v_e will change by the same factor because of the assumption of local equilibrium at the edges, and ω will remain at the correct equilibrium value. Hence we may write

$$\frac{dl}{dt} = \Gamma l^\beta \qquad (6)$$

where

$$\Gamma = -\frac{l^{2-\beta}}{V}\left[\int K v_n dS + \int v_e \cdot \omega \, dl\right] \qquad (7)$$

is invariant under uniform magnification; it follows form the statistical self-similarity hypothesis, that Γ is also independent of time in the self-similar regime so that equation (6) may be integrated to yield (for $\beta < 1$) our principal result

$$l(t)^{1-\beta} - l(t_0)^{1-\beta} = (1 - \beta)\Gamma(t - t_0) \qquad (8)$$

where t_0 is some initial time in the self-similar regime.

When $l(t) \gg l(t_0)$

$$l(t) = [(1 - \beta)\Gamma t]^n \qquad (9)$$

where $n = 1/(1 - \beta)$.

The sign of dl/dt follows from the inequality for the spontaneous change of the total interfacial free energy F_s

$$\frac{dF_s}{dt} = \frac{d}{dt}(\bar{\sigma}S) = \bar{\sigma}\frac{dS}{dt} < 0 \qquad (10)$$

where $\bar{\sigma}$ is the average of the interfacial free energy per unit area σ given by

$$\bar{\sigma} = \frac{1}{S}\int \sigma \, dS \qquad (11)$$

since $\bar{\sigma}$ is evidently invariant under uniform magnification, it is independent of time, according to our hypothesis. We conclude from equation (10) that $dS/dt < 0$ and hence from equation (1) that $dl/dt > 0$.

Clearly the preceding development may be carried out in two dimensions by replacing V by the total area A of the system, S by the total length L of boundary and using the definition $l = A/L$. The result is again an equation of the form of equation (6), with solutions given by equations (8) and (9) with Γ independent of time.

3. CURVATURE DRIVEN GROWTH

We proceed now to determine the value of β for different growth mechanisms. A case that has been extensively treated in the literature and that can be analyzed in terms of the self-similarity hypothesis presented in the previous sections is that of curvature driven growth [2, 7–9, 41] which includes the curvature driven models of grain growth [1, 14, 19, 41–45]. In this case one either assumes or deduces that the velocity of a given element of boundary is proportional to the thermodynamic driving force per unit area. It then follows (with M for the mobility) that [46]

$$v_n = -M\left[\frac{K_1}{\kappa_1} + \frac{K_2}{\kappa_2}\right] \qquad (12)$$

where the K_i are the two principal curvatures of the interface and the κ_i are defined in terms of the surface tension and are independent of scale. We therefore have from equation (12) that $\beta = -1$ and $n = 1/2$. This conclusion depends only on the self-similarity hypothesis and equation (12), and does not require the usual oversimplifications of geometry that characterize specific models [44, 45]; these models do make predictions, however, about the coefficient in the growth law that we cannot make.

The parabolic growth law ($n = 1/2$) is a fairly well established result for models in which no intersection lines are present. If edges are present, support for this conclusion is provided by numerical solutions to the equation of motion (12) (for an isotropic surface free energy) for an array of interfaces and intersection points, the latter assumed to be in local equilibrium

[26, 47, 48]. The same exponent has been obtained for domain growth in the Potts model. Computer simulations of that model have shown the existence of statistical self-similarity for sufficiently long times and obtained $\beta = -1$ [17–19]. Finally, the parabolic law is supported by some, but not all, experimental studies of grain growth [49–51].

The simplest free energy functional model for which equation (12) (for the particular case of an isotropic surface free energy) may be derived concerns a purely relaxational dynamics for a single, scalar, non-conserved order parameter (model A [52]). Let $\psi(r, t)$ be the order parameter. The equation of motion is

$$\partial_t \psi(r, t) = -L \frac{\delta \mathcal{F}[\psi]}{\delta \psi(r, t)} \qquad (13)$$

in the absence of random noise. $\mathcal{F}[\psi]$ is the Ginzburg–Landau free energy functional

$$\mathcal{F}[\psi] = \int dV \left[\frac{1}{2} |\nabla \psi|^2 - \frac{r}{2} \psi^2 + \frac{u}{4} \psi^4 \right] \qquad (14)$$

with r and u positive, phenomenological coefficients. There are two coexisting, homogeneous, equilibrium states with $\psi_{\pm} = \pm \sqrt{r/u}$.

One way to derive a kinematic equation for the interfaces from the model defined by equations (13) and (14) [2, 10, 11] involves first finding a one-dimensional stationary solution, say in the z direction, such that $\psi_{st}(z = \pm \infty) = \psi_{\pm}$. From equations (13) and (14), one obtains

$$0 = -\frac{d^2 \psi_{st}}{dz^2} - r\psi_{st} + u\psi_{st}^3. \qquad (15)$$

For long enough times, the system will consist of large domains separated by thin interfaces. A new system of orthogonal coordinates $\{u_1(r, t), u_2(r, t), u_3(r, t)\}$ is introduced where $u_1(r, t) = 0$ defines the position of the interfaces. For gently curved interfaces and when the order parameter well inside the domains has reached the equilibrium value, the following quasi-stationary form is then assumed as a solution of equation (13): $\psi(r, t) \simeq \psi_{st}[u_1(r, t)]$. This assumption can be shown to yield

$$v_n = -LK \qquad (16)$$

where $K = K_1 + K_2$. (From this law and certain approximations, a scaling solution for the dynamic structure factor has also been derived [9].)

4. COARSENING IN A BINARY ALLOY

We consider here the late stages of evolution of a binary alloy quenched into the coexistence region of its phase diagram. The analysis that follows applies both to dilute and concentrated alloys and hence extends previous results [1] for the dilute case.

Let us denote by A and B the two coexisting phases in bulk equilibrium at the quench temperature T, and $c_A^{(0)}$ and $c_B^{(0)}$ the corresponding equilibrium concentrations of one of the two species. As the system

evolves after the quench, the structure coarsens and the system is divided into large regions in which the concentration field approaches its bulk equilibrium value. These regions are separated by thin interfaces. Let $c_A(r, t)$ and $c_B(r, t)$ be the concentration fields of one of two species in phases A and B respectively. For sufficiently long times, diffusion (assumed isotropic) will be described by Fick's law in both phases

$$\partial_t c_A(r, t) = D_A \nabla^2 c_A(r, t)$$
$$\partial_t c_B(r, t) = D_B \nabla^2 c_B(r, t) \qquad (17)$$

where D_A and D_B are the diffusion coefficients in the phases A and B respectively. In the same regime of time, the interfaces will be only gently curved. As a consequence, $|(c^1 - c^{(0)})/c_A^{(0)} - c_B^{(0)})| \ll 1$, where $c^1 - c^{(0)}$ is the difference between the concentration at the interface and the equilibrium concentration for either phase. We may then use the quasistationary approximation in which the concentration fields, assumed to be in a steady-state at any given instant, are given by

$$\nabla^2 c_A(r, t) = 0, \qquad (18)$$

and

$$\nabla^2 c_B(r, t) = 0. \qquad (19)$$

The equations for the concentration fields must be supplemented with appropriate boundary conditions at the interfaces separating the phases. First, conservation of mass in an infinitely thin interface implies that

$$\Delta c v_n = [-D_A \nabla c_A + D_B \nabla c_B] \cdot \hat{n} \qquad (20)$$

where Δc is the local discontinuity in the concentration fields at the interface and v_n is the local normal velocity. The unit normal $\hat{n}$ is oriented from the B phase into the A phase.

We further assume that for a given point P at the interface, the concentration of both phases has the local equilibrium value c_A^1 and c_B^1. If stresses are ignored, these values should each obey the scaling relation

$$c^{1\lambda}(\lambda r) - c^{(0)} = \frac{1}{\lambda} [c^1(r) - c^{(0)}] \qquad (21)$$

where $c^{1\lambda}(\lambda r)$ is the concentration at the point P^λ into which P is mapped by uniform magnification of the original system by the scale factor λ. Equation (21) applies at both sides of the A–B interface.

Equations (18) to (21) are sufficient to determine β. Thus consider some distribution of interfaces such that the concentration at each point of the interface is given by the local equilibrium value. In the quasi-stationary approximation, this suffices to determine the solution $c_A(r, t)$ and $c_B(t, t)$ in a finite system of any spatial dimension. Furthermore, the concentration $c(r, t)$ at any point is determined by the interfaces within some screening length d_s; we expect d_s to be of the order of l for the assumed statistically uniform system. Therefore the boundary conditions on the external surface of the system will influence the

concentration only to a depth $\sim l$, which we have assumed negligible compared to the linear dimensions of the system.

In the scaled up system, the fields

$$c_i^\lambda(\lambda r, t) = c_i^{(0)} + \frac{1}{\lambda}\left[c_i(r, t) - c_i^{(0)}\right] \quad i = A, B \quad (22)$$

satisfy the Laplace equation and the new boundary conditions as required by equation (21). The conservation of mass in the scaled up system requires

$$\Delta c^\lambda v_n^\lambda = [-D_A \nabla_{\lambda r} c_A^\lambda + D_B \nabla_{\lambda r} c_B^\lambda] \cdot \hat{n} \quad (23)$$

where Δc^λ is the local discontinuity in the concentration fields across the interface. Inserting equation (22) we obtain

$$\Delta c^\lambda v_n^\lambda = \left[-D_A \frac{1}{\lambda} \nabla \frac{1}{\lambda} c_A + D_B \frac{1}{\lambda} \nabla \frac{1}{\lambda} c_B\right] \cdot \hat{n}. \quad (24)$$

The quantity Δc^λ has two contributions: $\Delta c^{(0)} = c_A^{(0)} - c_B^{(0)}$ which is a constant independent of scale, and another contribution that scales as described by equation (21). We thus can write $\Delta c^\lambda = \Delta c^{(0)} + A/\lambda$ where A is a constant. The second term is, in fact, a correction that will be negligible for sufficiently large λ (or long times). Comparing equation (20) and (24) we find $v_n^\lambda = v_n \lambda^{-2}$ or $\beta = -2$. We conclude from equation (9) that the growth law for the linear scale of the system is

$$l(t)^3 - l(t_0)^3 = 3\Gamma(t - t_0) \quad (25)$$

or for long times $n = 1/3$. Again this result is independent of the usual restrictive assumptions of a dilute solution, a small volume fraction of the precipitate, a spherical geometry of precipitate particles, and a mean field approximation.

The result was first derived by Lifshitz and Slozov [4] and Wagner [5] in the case of a very dilute alloy (the former authors did not assume self-similarity, rather they were able to derive a scaling solution for the original set of equations, valid for very small supersaturations and in the mean field approximation). The same scaling behavior is implicit in other analyses (Binder [6]; Kawasaki and Ohta [11], also within the quasistationary approximation.) The growth law given in equation (25) has been recently observed experimentally in a MnCu alloy well inside the unstable region [34]. It has also been recently obtained in several numerical solutions of coarsening [53, 54] and in numerical solutions or computer simulations of the following semimacroscopic models for spinodal decomposition: the kinetic Ising model with a conserved order parameter, the Langevin equation for model B and cell dynamical systems [22–30].

5. NON-CONSERVED ORDER PARAMETER COUPLED TO A CONSERVED DENSITY

There are many systems in which the order parameter that describes the transition does not satisfy any conservation law but is coupled to some other density

which does. Several examples of these systems can be found in ordering processes in monolayers adsorbed on a substrate. The adsorbed species can form ordered structures in certain regions of the temperature–coverage phase diagram [55].

In the case of a physisorbed system, there is no global conservation of atoms of the adsorbed species so that growth proceeds simply by reduction of the interface length. Since the order parameter has usually a degeneracy larger than two, intersection points are present during the growth process. Provided that the interaction points are in local equilibrium, the analysis presented above applies and the growth law would be the same as in the purely curvature driven case.

When the adsorbate is chemisorbed on the surface, the motion of the adatoms proceeds by diffusion. As a consequence, there is, in some cases, a direct coupling between the (nonconserved) order parameter and the (conserved) density of adatoms. The simplest model that includes a coupling between a nonconserved order parameter and a conserved density is the so-called model C of critical dynamics [52]. The model considers two scalar fields $\psi(r, t)$ (not conserved) and $\rho(r, t)$ (conserved). The phenomenological free energy functional which defines the model is

$$\mathscr{F}[\psi, \rho] = \int dV[\tfrac{1}{2}|\nabla\psi|^2 - \tfrac{1}{2}r\psi^2 + \tfrac{1}{4}u\psi^4 + \omega\rho^2 + g\rho\psi^2] \quad (26)$$

with the equations of motion for the fields given by

$$\partial_t \psi(r, t) = -\Gamma_1 \frac{\partial \mathscr{F}}{\delta\psi(r, t)} \quad (27)$$

and

$$\partial_t \rho(r, t) = \Gamma_2 \nabla^2 \frac{\delta \mathscr{F}}{\delta\rho(r, t)} \quad (28)$$

in the absence of random noise.

Following the same procedure outlined in section 3, one seeks a one dimensional stationary solution with the appropriate boundary conditions of the equations

$$\frac{\delta \mathscr{F}}{\delta\psi(r, t)} = -\nabla^2\psi_{st} - r\psi_{st} + u\psi_{st}^3 + 2g\rho_{st}\psi_{st} = 0 \quad (29)$$

and

$$\nabla^2 \frac{\delta \mathscr{F}}{\delta\rho(r, t)} = \nabla^2[2\omega\rho_{st} + g\psi_{st}^2] = 0. \quad (30)$$

Consider a planar interface normal to the z direction with boundary conditions $\psi_{st}(z = \pm\infty) = \psi_\pm$ and $\rho_{st}(z = \pm\infty) = \rho_\pm$; $\psi_\pm$ and $\rho_\pm$ are the spatially homogeneous solutions to equations (29) and (30). The stationary solution $\psi_{st}(z)$ is constant almost everywhere (and equal to the field $\psi_\pm$) except in the thin interfacial region; similarly $\rho_s(z)$ is constant except in the interfacial region where there may be an excess (or defect) density. Note however that, in this model, the equilibrium densities of both ordered phases, obtained by minimization of (26) are equal ($\rho_+ = \rho_-$). Hence no long range transport is needed when the interfaces move and the growth law is

determined by the equation of motion for the field $\psi(r, t)$ and is given by $n = 1/2$.

The situation just described may occur in ordering processes in chemisorbed systems in which all the coexisting phases have the same density of adsorbed atoms. As mentioned above, a multicomponent order parameter is usually needed to describe the different ordered phases; intersection points are present during the growth process. If these intersection points are in local equilibrium at all times, our results would apply. Systems which would fall in this category are, for example, O/W(110) at coverage $\theta = 0.5$ (experimental evidence [35] suggests that $n \simeq 0.28$; recent computer simulations on a model with the same degeneracy give $n = 1/2$ [31]), H/Fe at $\theta = 2/3$ (numerical simulations on a model for H/Fe give a lower exponent $n \simeq 0.20 - 0.30$ [32]).

In a more general situation, however, the different phases will have different densities (for example O/W(110) at coverage $\theta = 0.25$ [35]) and the model given in equation (26) has to be generalized accordingly. In particular, one must allow for long range diffusion in each of the phases. In this case, the growth process will involve long range transport and the analysis given in section 4 is expected to apply at sufficiently long times (when growth is limited by diffusion only).

Note added in proof—If anisotropies of boundary properties are significant, the statistical self-similarity hypothesis must refer to the arrangement of crystal orientations as well as the configuration of interfaces. Note, separately, that equation (25) can easily be shown to hold if diffusion in the phases is anisotropic. Note finally that l in equation (1) can be estimated by direct measurement of the microstructure [56].

REFERENCES

1. W. W. Mullins, *J. appl. Phys.* **59**, 1341 (1986).
2. S. M. Allen and J. W. Cahn, *Acta metall.* **27**, 1085 (1979).
3. Reviews of the field are given in: J. D. Gunton, M. San Miguel and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, Vol. 8 (edited by C. Domb and J. L. Lebowitz) Academic Press, New York (1983); K. Binder in *Condensed Matter Research Using Neutrons* (edited by S. W. Lovesey and R. Scherm) Plenum Press, New York (1984); reviews of recent progress are given in H. Furukawa, *Adv. Phys.* **34**, 703 (1985); K. Binder, *Statphys 16, Physica* **140A**, 35 (1986); J. D. Gunton, in Proc. *NATO ASI on "Time Dependent Effects in Disordered Materials"*, Geilo, Norway ,1987 (edited by R. Pynn) Plenum Press, New York. To be published.
4. I. M. Lifshitz and V. V. Slyozov, *J. Phys. Chem. Solids* **19**, 35 (1961).
5. C. Wagner, *Z. Electrochem.* **65**, 581 (1957).
6. K. Binder, *Phys. Rev.* **B15**, 4425 (1977).
7. K. Kawasaki, C. Yalabik and J. D. Gunton, *Phys. Rev.* **A17**, 455 (1978).
8. C. Billotet and K. Binder, *Z. Phys.* **B32**, 195 (1979).
9. T. Ohta, D. Jasnow and K. Kawasaki, *Phys. Rev. Lett.* **49**, 1223 (1982).
10. K. Kawasaki and T. Ohta, *Prog. theoret. Phys.* **67**, 147 (1982); **68**, 129 (1982).
11. K. Kawasaki and T. Ohta, *Physica* **118A**, 175 (1983).
12. T. Ohta, *Ann. Phys.* **158**, 31 (1984).
13. M. K. Phani, J. L. Lebowitz, M. H. Kalos and O. Penrose, *Phys. Rev. Lett.* **45**, 366 (1980); P. S. Sahni, G. Dee, J. D. Gunton, M. K. Phani, J. L. Lebowitz and M. H. Kalos, *Phys. Rev.* **B24**, 410 (1981); J. L. Lebowitz, J, Marro and M. H. Kalos, *Acta metall.* **30**, 297 (1982); K. Kaski, M. C. Yalabik, J. D. Gunton and P. S. Sahni, *Phys. Rev.* **B28**, 5263 (1983); A Sadiq and K. Binder, *J. Stat. Phys.* **35**, 517 (1984); E. T. Gawlinski, M. Grant, J. D. Gunton and K. Kaski, *Phys. Rev.* **B31**, 281 (1985).
14. P. S. Sahni, G. S. Grest, M. P. Anderson and D. Srolovitz, *Phys. Rev. Lett.* **50**, 263 (1983).
15. P. S. Sahni, D. J. Srolovitz, G. S. Grest, M. P. Anderson and S. A. Safran, *Phys. Rev.* **B28**, 2705 (1983).
16. K. Kaski, J. Nieminen and J. D. Gunton, *Phys. Rev.* **B31**, 2998 (1985).
17. J. Viñals and J. D. Gunton, *Phys. Rev.* **B33**, 7795 (1986).
18. S. Kumar, J. D. Gunton and K. Kaski, *Phys. Rev.* **B35**, 8517 (1987).
19. G. S. Grest, M. P. Anderson and D. J. Srolovitz, in *Proc. NATO ASI on "Time Dependent Effects in Disordered Materials"* Geilo, Norway, 1987 (edited by R. Pynn). Plenum Press, New York, to be published; *Phys. Rev.* **B38**, 4752 (1988).
20. G. F. Mazenko, O. T. Valls and F. C. Zhang, *Phys. Rev.* **B31**, 4453 (1985); **B32**, 5807 (1985).
21. G. F. Mazenko and O. T. Valls, *Phys. Rev.* **B33**, 1823 (1986).
22. D. Huse, *Phys. Rev.* **B34**, 7845 (1986).
23. J. G. Amar, F. E. Sullivan and R. D. Mountain, *Phys. Rev.* **B37**, 196 (1988).
24. K. Kaski and J. D. Gunton, Temple University preprint, 1987; J. D. Gunton, E. T. Gawlinski and K. Kaski, in *Dynamics of Ordering Processes at a Phase Transition* (edited by S. Komura). Plenum Press, New York. To be published.
25. C. Roland and M. Grant, *Phys. Rev. Lett.* **60**, 2657 (1988).
26. C. W. J. Beenakker, *Phys. Rev.* **A37**, 1697 (1988); Phillips Research Laboratories preprints (1987).
27. E. T. Gawlinski, J. Viñals and J. D. Gunton, Temple University preprint (1987).
28. T. M. Rogers, K. R. Elder and R. C. Desai, *Phys. Rev.* **B37**, 9636 (1988).
29. Y. Oono and S. Puri, *Phys. Rev. Lett.* **58**, 836 (1987); *Phys. Rev.* **A38**, 1542 (1988).
30. A. Chakravarti and J. D. Gunton, *Phys. Rev.* **B37**, 3798 (1988).
31. H. C. Fogedby and O. G. Mouritsen, *Phys. Rev.* **B37**, 5962 (1988).
32. J. Viñals and J. D. Gunton, *Surf. Sci.* **157**, 473 (1985).
33. M. T. Collins and H. C. Teh, *Phys. Rev. Lett.* **30**, 781 (1973); F. N. Rhines, K. R. Craig and R. T. DeHoff, *Metall. Trans.* **5**, 413 (1974); P. A. Beck, J. C. Kremer, L. J. Demer and M. L. Holzworth, *Trans. metall. Soc. A.I.M.E.* **175**, 372 (1948); H. Hu, *Can. Metall. Q.* **13**, 275 (1974); T. Hashimoto, T. Miyoshi, and M. Ohtsuka, *Phys. Rev.* **B13**, 1119 (1976); M. Hennion, D. Ronzaud and P. Guyot, *Acta metall.* **30**, 599 (1982); G.-C. Wang, T.-M. Lu, *Phys. Rev. Lett.* **50**, 2014 (1983).
34. B. D. Gaulin, S. Spooner and Y. Morii, *Phys. Rev. Lett.* **59**, 668 (1987).
35. M. C. Tringides, P. K. Wu and M. G. Lagally, *Phys. Rev. Lett.* **59**, 315 (1987).
36. J. Viñals and M. Grant, *Phys. Rev.* **B36**, 7036 (1987).
37. G. F. Mazenko and O. T. Valls, *Phys. Rev. Lett.* **59**, 680 (1987).
38. M. Grant and J. D. Gunton, *Phys. Rev.* **B28**, 5496 (1983).
39. K. Kawasaki, *Ann. Phys.* **154**, 319 (1984).

40. K. Kawasaki, *Phys. Rev.* **A31**, 3880 (1985).
41. W. W. Mullins, *J. appl. Phys.* **27**, 900 (1956).
42. J. E. Burke, *Trans. metall. Soc. A.I.M.E.* **180**, 73 (1949).
43. C. S. Smith, in *Metal Interfaces*, p. 654. Am. Soc. Metals, Cleveland, Ohio (1952).
44. P. Feltham, *Acta metall.* **5**, 97 (1957).
45. M. Hillert, *Acta metall.* **13**, 227 (1965).
46. J. W. Cahn and D. W. Hoffmann, *Acta metall.* **22**, 1205 (1974).
47. O. Hunderi, N. Ryum and H. Westingen, *Acta metall.* **27**, 161 (1979).
48. H. J. Frost, C. V. Thompson, C. L. Howe and J. Whang, *Scripta metall.* **22**, 65 (1988).
49. F. Haessner and S. Hofmann, in *Recrystallization of Metallic Materials* (edited by F. Haessner), p. 63. Springer, Berlin (1978).
50. S. K. Kurtz and F. M. A. Carpay, *J. appl. Phys.* **51**, 5745 (1980).
51. C. J. Simpson, K. T. Aust and W. C. Winegard, *Metall. Trans.* **2**, 993 (1971).
52. P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977).
53. P. W. Voorhees and M. E. Glicksman, *Acta metall.* **32**, 2013 (1984).
54. P. W. Voorhees, G. B. McFadden and R. F. Boisvert, *Acta metall.* **36**, 207 (1988).
55. M. G. Lagally, T.-M. Lu and G.-C. Wang, in *Ordering in Two Dimensions* (edited by S. Sinha). Elsevier, Amsterdam (1980).
56. C. S. Smith and L. Guttman, *Trans. A.I.M.E.* **197**, 81 (1953).