Lecture 15: Phase Field Modelling

Introduction

Imagine the growth of a precipitate which is isolated from the matrix by an interface. There are three distinct quantities to consider: the precipitate, matrix and interface. The interface can be described as an evolving surface whose motion is controlled according to the boundary conditions consistent with the mechanism of transformation. The interface in this mathematical description is simply a two–dimensional surface with no width or structure; it is said to be a *sharp interface.*

In the phase–field method, the state of the entire microstructure is represented continuously by a single variable known as the *order parameter* ϕ. For example, $\phi = 1$, $\phi = 0$ and $0 < \phi < 1$ represent the precipitate, matrix and interface respectively. The latter is therefore located by the region over which ϕ changes from its precipitate–value to its matrix–value (Fig. 1). The range over which it changes is the *width* of the interface. The set of values of the order parameter over the whole microstructure is the *phase field.*

The evolution of the microstructure with time is assumed to be proportional to the variation of the free energy functional with respect to the order parameter:

$$\frac{\partial \phi}{\partial t} = M \frac{\partial g}{\partial \phi}$$

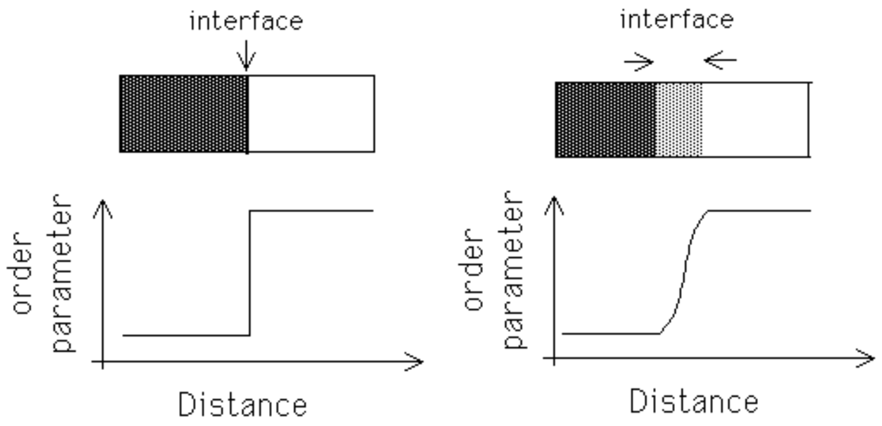

Fig. 1: (a) Sharp interface. (b) Diffuse interface.

where M is a mobility. The term g describes how the free energy varies as a function of the order parameter; at constant T and P, this takes the typical form (Appendix 1)†:

$$g = \int_V \Big[g_0\{\phi, T\} + \epsilon(\nabla\phi)^2 \Big] dV \tag{1}$$

where V and T represent the volume and temperature respectively. The second term in this equation depends only on the gradient of ϕ and hence is non–zero only in the interfacial region; it is a description therefore of the interfacial energy. The first term is the sum of the free energies of the precipitate and matrix, and may also contain a term describing the activation barrier across the interface. For the case of solidification,

$$g_0 = hg^S + (1-h)g^L + Qf$$

where g^S and g^L refer to the free energies of the solid and liquid phases

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† If the temperature varies then the functional is expressed in terms of entropy rather than free energy.

respectively, Q is the height of the activation barrier at the interface,

$$h = \phi^2(3 - 2\phi) \qquad \text{and} \qquad f = \phi^2(1 - \phi)^2$$

Notice that the term $hg^S + Qf$ vanishes when $\phi = 0$ (*i.e.* only liquid is present), and similarly, $(1 - h)g^L + Qf$ vanishes when $\phi = 1$ (*i.e.* only solid present). As expected, it is only when both solid and liquid are present that Qf becomes non–zero. The time–dependence of the phase field then becomes:

$$\frac{\partial \phi}{\partial t} = M[\epsilon \nabla^2 \phi + h'\{g^L - g^S\} - Qf']$$

The parameters Q, ϵ and M have to be derived assuming some mechanism of transformation.

Two examples of phase–field modelling are as follows: the first is where the order parameter is conserved. With the evolution of composition fluctuations into precipitates, it is the average chemical composition which is conserved. On the other hand, the order parameter is not conserved during grain growth since the amount of grain surface per unit volume decreases with grain coarsening.

Cahn–Hilliard Treatment of Spinodal Decomposition

In this example, the order parameter is the chemical composition. In solutions that tend to exhibit clustering (positive ΔH_M), it is possible for a homogeneous phase to become unstable to infinitesimal perturbations of chemical composition. The free energy of a solid solution which is chemically heterogeneous can be factorised into three components.

First, there is the free energy of a small region of the solution in isolation, given by the usual plot of the free energy of a homogeneous solution as a function of chemical composition.

The second term comes about because the small region is surrounded by others which have different chemical compositions. Fig. 2 shows that the average environment that a region **a** feels is different (*i.e.* point **b**) from its own chemical composition because of the curvature in the concentration gradient. This gradient term is an additional free energy in a heterogeneous system, and is regarded as an interfacial energy describing a "soft interface" of the type illustrated in Fig. 1b. In this example, the soft–interface is due to chemical composition variations, but it could equally well represent a structural change.

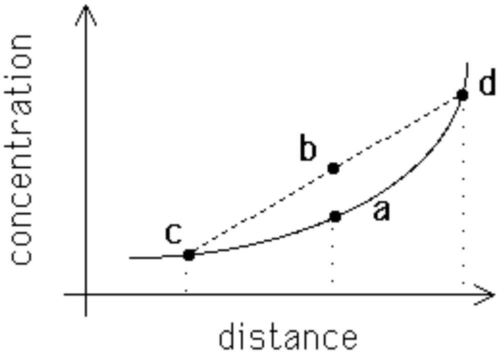

Fig. 2: Gradient of chemical composition. Point a represents a small region of the solution, point b the average composition of the environment around point a, *i.e.* the average of points c and d.

The third term arises because a variation in chemical composition also causes lattice strains in the solid–state. We shall assume here that the material considered is a fluid so that we can neglect these *coherency* *strains.*

The free energy per atom of an inhomogeneous solution is given by (Appendix 1):

$$g_{ih} = \int_V \left[g\{c_0\} + v^3 \kappa (\nabla c)^2 \right] dV \tag{2}$$

where $g\{c_0\}$ is the free energy per atom in a homogeneous solution of concentration c_0, v is the volume per atom and κ is called the *gradient energy coefficient.* g_{ih} is often referred to as a free energy *functional* since it is a function of a function. See Appendix 1 for a detailed derivation.

Equilibrium in a heterogeneous system is then obtained by minimising the functional subject to the requirement that the average concentration is maintained constant:

$$\int (c - c_0) dV = 0$$

where c_0 is the average concentration. Spinodal decomposition can therefore be simulated on a computer using the functional defined in equation 2. The system would initially be set to be homogeneous but with some compositional noise. It would then be perturbed, allowing those perturbations which reduce free energy to survive. In this way, the whole decomposition process can be modelled without explicitly introducing an interface. The interface is instead represented by the gradient energy coefficient. For a simulation, see

$$www.msm.cam.ac.uk/phase-trans/mphil/spinodal.movie.html$$

A theory such as this is not restricted to the development of composition waves, ultimately into precipitates. The order parameter can be chosen to represent strain and hence can be used to model phase changes and the associated microstructure evolution.

In the phase field modelling of solidification, there is no distinction made between the solid, liquid and the interface. All regions are described in terms of the order parameter. This allows the whole domain to be treated simultaneously. In particular, the interface is not tracked but is given implicitly by the chosen value of the order parameter as a function of time and space. The classical formulation of the free boundary problem is replaced by equations for the temperature and phase field.

Appendix 1

Recall (MP4–6) that a Taylor expansion for a single variable about $X = 0$ is given by

$$J\{X\} = J\{0\} + J'\{0\}\frac{X}{1!} + J''\{0\}\frac{X^2}{2!} \ldots$$

A Taylor expansion like this can be generalised to more than one variable. Cahn assumed that the free energy due to heterogeneities in a solution can be expressed by a multivariable Taylor expansion:

$$\begin{aligned} g\{y, z, \ldots\} =& g\{c_0\} + y\frac{\partial g}{\partial y} + z\frac{\partial g}{\partial z} + \ldots \\ & + \frac{1}{2}\left[y^2\frac{\partial^2 g}{\partial y^2} + z^2\frac{\partial^2 g}{\partial z^2} + 2yz\frac{\partial^2 g}{\partial y \partial z} + \ldots\right] + \ldots \end{aligned}$$

in which the variables, $y, z, \ldots$ in our context are the spatial composition derivatives (dc/dx, d^2c/dx^2, etc). For the free energy of a small volume element containing a one–dimensional composition variation (and neglecting third and high–order terms), this gives

$$g = g\{c_0\} + \kappa_1 \frac{dc}{dx} + \kappa_2 \frac{d^2c}{dx^2} + \kappa_3 \left(\frac{dc}{dx}\right)^2 \tag{3}$$

where c_0 is the average composition.

$$\text{where} \qquad \begin{aligned} \kappa_1 &= \frac{\partial g}{\partial(dc/dx)} \\ \kappa_2 &= \frac{\partial g}{\partial(d^2c/dx^2)} \\ \kappa_3 &= \frac{1}{2}\frac{\partial^2 g}{\partial(dc/dx)^2} \end{aligned}$$

In this, κ_1 is zero for a centrosymmetric crystal since the free energy must be invariant to a change in the sign of the coordinate x.

The total free energy is obtained by integrating over the volume:

$$g_T = \int_V \left[g\{c_0\} + \kappa_2 \frac{d^2c}{dx^2} + \kappa_3 \left(\frac{dc}{dx}\right)^2 \right] \tag{4}$$

On integrating the third term in this equation by parts†:

$$\int \kappa_2 \frac{d^2c}{dx^2} = \kappa_2 \frac{dc}{dx} - \int \frac{d\kappa_2}{dc} \left(\frac{dc}{dx}\right)^2 dx \tag{5}$$

As before, the first term on the right is zero, so that an equation of the form below is obtained for the free energy of a heterogeneous system:

$$g = \int_V \left[g_0\{\phi, T\} + \epsilon(\nabla\phi)^2 \right] dV \tag{6}$$

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$$\int uv' \; dx = uv - \int u'v \; dx$$

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REVIEW

Phase field method

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In an ideal scenario, a phase field model is able to compute quantitative aspects of the evolution of microstructure without explicit intervention. The method is particularly appealing because it provides a visual impression of the development of structure, one which often matches observations. The essence of the technique is that phases and the interfaces between the phases are all incorporated into a grand functional for the free energy of a heterogeneous system, using an order parameter which can be translated into what is perceived as a phase or an interface in ordinary jargon. There are, however, assumptions which are inconsistent with practical experience and it is important to realise the limitations of the method. The purpose of this review is to introduce the essence of the method, and to describe, in the context of materials science, the advantages and pitfalls associated with the technique.

Keywords: Phase field models, Structural evolution, Multiphase, Multicomponent, Gradient energy

Introduction

The phase field method has proved to be extremely powerful in the visualisation of the development of microstructure without having to track the evolution of individual interfaces, as is the case with sharp interface models. The method, within the framework of irreversible thermodynamics, also allows many physical phenomena to be treated simultaneously. Phase field equations are quite elegant in their form and clear for all to appreciate, but the details, approximations and limitations which lead to the mathematical form are perhaps not as transparent to those whose primary interest is in the application of the method. The materials literature in particular thrives in comparisons between the phase field and classical sharp interface models which are not always justified. The primary purpose of this review is to present the method in a form as simple as possible, but without avoiding a few of the derivations which are fundamental to the appreciation of the method. Example applications are not particularly cited because there are other excellent reviews and articles which contain this information together with detailed theory, for example, Refs. 1–7.

Imagine the growth of a precipitate which is isolated from the matrix by an interface. There are three distinct entities to consider: the precipitate, matrix and interface. The interface can be described as an evolving surface whose motion is controlled according to the boundary conditions consistent with the mechanism of transformation. The interface in this mathematical description is simply a two-dimensional surface; it is said to be a sharp interface which is associated with an interfacial energy σ per unit area.

In the phase field method, the state of the entire microstructure is represented continuously by a single variable known as the order parameter ϕ. For example, $\phi=1$, $\phi=0$ and $0<\phi<1$ represent the precipitate, matrix and interface respectively. The latter is therefore located by the region over which ϕ changes from its precipitate value to its matrix value (Fig. 1). The range over which it changes is the width of the interface. The set of values of the order parameter over the whole volume is the phase field. The total free energy G of the volume is then described in terms of the order parameter and its gradients, and the rate at which the structure evolves with time is set in the context of irreversible thermodynamics, and depends on how G varies with ϕ. It is the gradients in thermodynamic variables that drive the evolution of structure.

Consider a more complex example, the growth of a grain within a binary liquid (Fig. 2). In the absence of fluid flow, in the sharp interface method, this requires the solution of seven equations involving heat and solute diffusion in the solid, the corresponding processes in the liquid, energy conservation at the interface and the Gibbs–Thomson capillarity equation to allow for the effect of interface curvature on local equilibrium. The number of equations to be solved increases with the number of domains separated by interfaces and the location of each interface must be tracked during transformation. This may make the computational task prohibitive. The phase field method clearly has an advantage in this respect, with a single functional to describe the evolution of the phase field, coupled with equations for mass and heat conduction, i.e. three equations in total, irrespective of the number of particles in the system. The interface illustrated in Fig. 2*b* simply becomes a region over which the order parameter varies between the values specified for the phases on either side. The locations of the interfaces no longer need to be tracked but can be inferred from the field parameters during the calculation.

Notice that the interface in Fig. 2*b* is drawn as a region with finite width, because it is defined by a smooth variation

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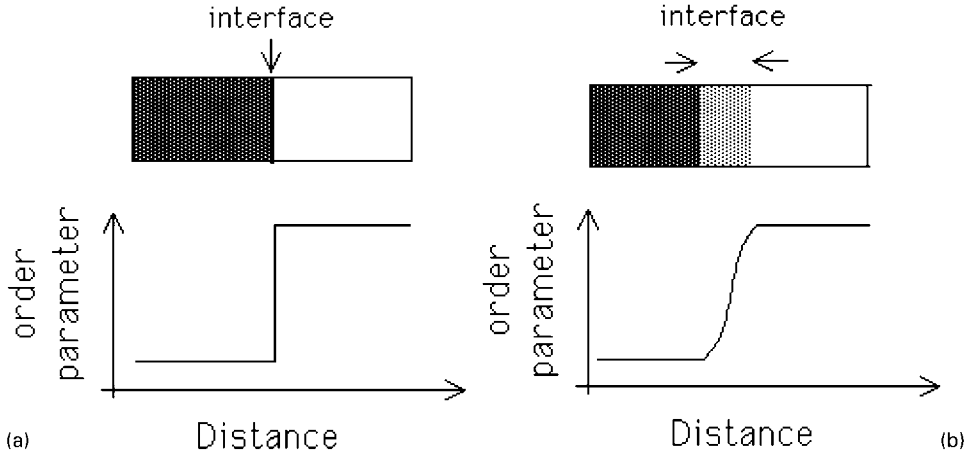


1 ***a*** **sharp interface and** ***b*** **diffuse interface**

in ϕ between $\phi=0$ (solid) and $\phi=1$ (liquid). The order parameter does not change discontinuously during the traverse from the solid to the liquid. The position of the interface is fixed by the surface where $\phi=0{\cdot}5$. The mathematical need for this continuous change in ϕ to define the interface requires that it has a width (2λ), and therein lies one of the problems of phase field models. Boundaries between phases in real materials tend, with few exceptions, to be at most a few atoms in width, as defined for example by the extent of the strain field of interfacial dislocations. Phase–field models can cope with narrow boundaries, but the computational time t scales with interface thickness as $t/t_0 \propto (\lambda/\lambda_0)^{-D}$ where D represents the dimension of the simulation. Defining a broader interface reduces the computational resources required, but there is a chance that detail is lost, for example at the point marked 'P' in Fig. 2.

There are ways of using adaptive grids in which the grid spacing is finer in the vicinity of the interface, assuming that ϕ varies significantly only in the region near the interface.[8] This approach is useful if most of the field is uniform, or when interfaces occupy only a small portion of the volume, for example when considering a single thermal dendrite growing in a matrix. It is less useful when there are many particles involved since the extent of uniformity then decreases.

Order parameter

The order parameters in phase field models may or may not have macroscopic physical interpretations. For two-phase materials, ϕ is typically set to 0 and 1 for the individual phases, and the interface is the domain where $0<\phi<1$. For the general case of N phases present in a matrix, there will be a corresponding number of phase field order parameters ϕ_i with $i=1$ to N. $\phi_i=1$ then represents the domain where phase i exists, $\phi_i=0$ where it is absent and $0<\phi_i<1$ its bounding interfaces. Suppose that the matrix is represented by ϕ_0 then it is necessary that at any location

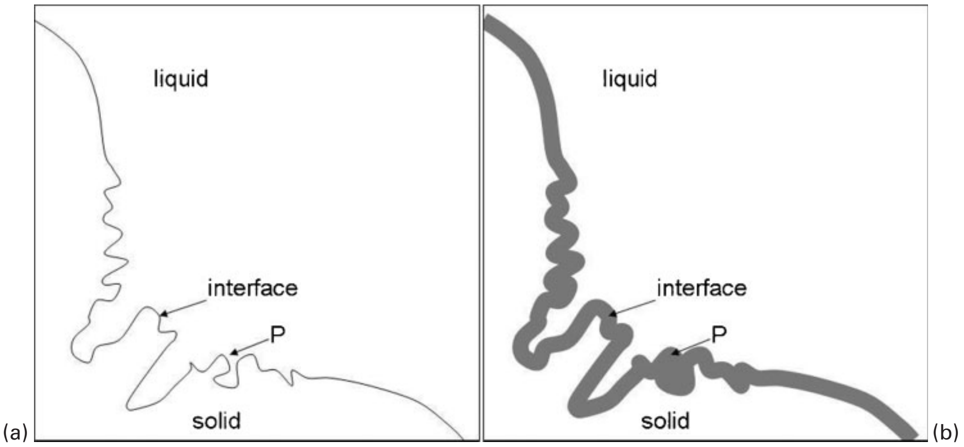
$$\sum_{i=0}^{N} \phi_i = 1 \tag{1}$$

It follows that the interface between phases 1 and 2, where $0<\phi_1<1$ and $0<\phi_2<1$ is given by $\phi_1+\phi_2=1$; similarly, for a triple junction between three phases where $0<\phi_i<1$ for $i=1,2,3$, the junction is the domain where $\phi_1+\phi_2+\phi_3=1$.

The order parameter can also be expressed as a vector function, for example in representing the variation of interfacial energy as a function of interface orientation[9–11] and this kind of theory has been used in the phase field modelling of crystal shapes, for example, Refs. 12 and 13.

Thermodynamics

The thermodynamic function of state selected for the phase field simulation depends on the definition of the problem. Entropy is appropriate for an isolated system



a **sharp interface model;** ***b*** **phase field model**
2 Solidification

which is not isothermal, the Gibbs free energy is appropriate for an isothermal system at constant pressure, and the Helmholtz free energy when temperature and volume are kept constant. The remainder of the discussion is in terms of the Gibbs free energy, which is knowable for a homogeneous phase, but is required for a heterogeneous system in which the order parameter is not uniform. Cahn and Hilliard developed the necessary theory by considering a multivariate Taylor expansion.[14–17] Writing $g_0\{\phi, c, T\}$ as the free energy per unit volume of a homogeneous phase of composition c at temperature T, and the corresponding term for a heterogeneous system as g, the Taylor expansion gives

$$\begin{aligned}g={}&g_0+\frac{\partial g_0}{\partial \nabla\phi}\nabla\phi+\frac{1}{2}\frac{\partial^2 g_0}{\partial(\nabla\phi)^2}\partial(\nabla\phi)^2+\ldots+\frac{\partial g_0}{\partial \nabla^2\phi}\partial\nabla^2\phi\\&+\frac{1}{2}\frac{\partial^2 g_0}{\partial(\nabla^2\phi)^2}(\nabla^2\phi)^2+\ldots+\frac{\partial g_0}{\partial\nabla c}\nabla c+\frac{1}{2}\frac{\partial^2 g_0}{\partial(\nabla c)^2}\partial(\nabla c)^2+\ldots\\&+\frac{\partial g_0}{\partial\nabla^2 c}\partial\nabla^2 c+\frac{1}{2}\frac{\partial^2 g_0}{\partial(\nabla^2 c)^2}(\nabla^2 c)^2+\ldots+\frac{\partial g_0}{\partial\nabla T}\nabla T\\&+\frac{1}{2}\frac{\partial^2 g_0}{\partial(\nabla T)^2}\partial(\nabla T)^2+\ldots+\frac{\partial g_0}{\partial\nabla^2 T}\partial\nabla^2 T+\frac{1}{2}\frac{\partial^2 g_0}{\partial(\nabla^2 T)^2}(\nabla^2 T)^2\\&+\ldots+\frac{1}{2}\left(\frac{\partial^2 g_0}{\partial\nabla\phi\partial\nabla c}\nabla\phi\nabla c+\frac{\partial^2 g_0}{\partial\nabla\phi\partial\nabla T}\nabla\phi\nabla T\right.\\&\left.+\frac{\partial^2 g_0}{\partial\nabla c\partial\nabla T}\nabla c\nabla T+\ldots\right)+\ldots\end{aligned}\tag{2}$$

The coefficients of odd orders of differentiation must be set to zero since the free energy must be invariant to a change in the sign of the coordinate. Integration by parts can be used to achieve further simplification since

$$\int_V\frac{\partial g_0}{\partial\nabla^2\phi}\mathrm{d}r=\frac{\partial g_0}{\partial\nabla^2\phi}\hat{\mathbf{n}}\cdot\nabla\phi-\int_V\frac{\partial}{\partial\phi}\left(\frac{\partial g_0}{\partial\nabla^2\phi}\right)(\nabla\phi)^2\mathrm{d}r\tag{3}$$

where $\hat{\mathbf{n}}$ is a unit vector along the coordinate. The first (odd) term on the right again reduces to zero, whereas the second term is combined with an existing $(\nabla\phi)^2$ term in equation (2). Similar procedures apply to the terms containing $\nabla^2 c$ and $\nabla^2 T$. Since the diffusion length of solute and particularly of heat are generally large, their spatial gradients are likely to be small so that $\nabla T \leqslant \nabla c \leqslant \nabla\phi$ (There are of course circumstances where concentration gradients are the key phenomena studied, such as in spinodal decomposition, in which case the solute gradient term clearly must be retained). Taking this into account and limiting the Taylor expansion to first and second order terms, it follows that the free energy for a heterogeneous system is given by integrating over the volume V

$$G=\int_V\left[g_0\{\phi,c,T\}+\frac{\varepsilon^2}{2}(\nabla\phi)^2\right]\mathrm{d}V\tag{4}$$

where g_0 is the free energy per unit volume, $\varepsilon^2=\partial^2 g_0/\partial(\nabla\phi)^2-2\partial(\partial g_0/\partial\nabla^2\phi)/\partial\phi$ is the gradient energy coefficient. In actual computations ε is determined in such a way as to give an accurate description of interface properties such as the energy per unit area and anisotropy of interfacial energy, as described later.

It is useful to comment further on $g_0\{\phi, c, T\}$ in heterogeneous materials. Consider a phase β ($\phi=1$) growing in α ($\phi=0$) and with $0<\phi<1$ defining the α–β interface. g_0 is likely to be known for the homogeneous phases α and β but not for the interface region given a continuous variation in concentration over this region, into which the free energy density must somehow be extrapolated. Any general expression for g_0 covering the entire domain of order parameter ($0\leqslant\phi\leqslant 1$) must at the same time reduce to the appropriate term when only one phase is present. There are versatile expressions suggested in the literature for g_0, usually assuming a double well potential shape[18] with the two minima corresponding to the α and β phases

$$\begin{aligned}g_0\{\phi,c,T\}={}&h\{\phi\}g_0^{\alpha}\{c^{\alpha},T\}+(1-h\{\phi\})g_0^{\beta}\{c^{\beta},T\}\\&+\frac{1}{4\omega}\phi^2(1-\phi)^2\end{aligned}\tag{5}$$

where $h=\phi^3(6\phi^2-15\phi+10)$,[19] and g_0^{α} and g_0^{β} are the free energy densities of the respective phases; c^{α} and c^{β} are similarly the solute contents of these phases. ω is a coefficient which can be adjusted to fit the desired interfacial energy but has to be positive to be consistent with a double well potential as opposed to one with two peaks. The third term on the right in equation (5) is a symmetrical double well. $h\{\phi\}$ is a monotonic function such that $h\{0\}=0$ and $h\{1\}=1$ so that the free energies of bulk α and β phases are reproduced. The first two terms on the right hand side of equation (5) generate the possible asymmetry. Because g_0 may contain assumptions inconsistent with real data, ε has to be modified accordingly to reproduce the correct interface properties.

Equation (5) is sufficient for computing transitions which do not involve a change in composition. For the case where solute is partitioned during transformation, it becomes difficult to specify the nature of the interfacial region where the order parameter is neither 1 nor 0. The solute content c_{I} within the interface will vary monotonically between the limits of the concentrations in the phases ($\phi=0,1$, c^{α} and c^{β} respectively) in contact with the interfacial region. Suppose that the interface is considered to be a (heterogeneous) phase in its own right, and assumed to be composed of a mixture of α and β, of solute concentrations c_{I}^{α} and c_{I}^{β}, then the compositions of these phases within the interface will vary with position if

$$c_{\mathrm{I}}=h\{\phi\}c_{\mathrm{I}}^{\alpha}\{\phi\}+(1-h\{\phi\})c_{\mathrm{I}}^{\beta}\{\phi\}\tag{6}$$

The question then arises as to what determines c_{I}^{α} and c_{I}^{β} because these quantities are necessary not simply to set the variation in c_{I} with position within the interface, but also to calculate the corresponding variation in free energy. For a given interface thickness, this leads to the definition of the excess energy of the interfacial region, which can then be compared directly with independent measurements of interfacial energy per unit area. The experimental data set the upper limit to the interface thickness in a phase field simulation.

A simple assumption in the past has been to take $c_{\mathrm{I}}^{\alpha}=c_{\mathrm{I}}^{\beta}=c_{\mathrm{I}}$ particularly where the phases concerned are solutions, i.e. their free energy does not vary sharply with solute content, even though this would lead to unequal chemical potentials. Phase field simulations of solidification involving such phases in the Cu–Ni system have used large interface thicknesses of about $2\lambda=18$ nm without compromising details of the dendrite patterns.[19] Difficulties arise when dealing with compounds which tend to have narrow composition ranges (free energy increases with deviation from stoichiometry). An example is that in a simulation of Al–2 wt-%Si solidification, the thickness of interface between primary aluminium rich dendrites and liquid had a maximum of about $2\lambda=6{\cdot}5$ nm but had to be restricted to $<0{\cdot}2$ nm for that between silicon particles and the liquid.[20] This is to ensure that a realistic interfacial energy is obtained, but the small width dramatically increases the computational effort.

Others[20–22] have assumed that the phase compositions inside the interface are governed by the equation

$$\frac{\partial g^{\alpha}}{\partial c^{\alpha}}=\frac{\partial g^{\beta}}{\partial c^{\beta}} \tag{7}$$

and have mistakenly identified these derivatives with chemical potential $\partial G/\partial n$, where G is the total chemical free energy of the phase concerned and n the number of moles of the solute concerned. It is of course gradients in the chemical potential which govern diffusion so it may be misleading to call the derivatives in equation (7) the phase diffusion potential.[23] Note also that equation (7) does not reduce to an equilibrium condition when the chemical potential is uniform in the parent and product phases. When equation (7) is applied in phase field modelling, it has been suggested[23] that because the gradients in $\partial g/\partial c$ do not reduce to zero even at equilibrium, it is necessary to compensate for this by some additional component to the free energy density g, which might be interpreted in terms of the structure of the interface. However, this is arbitrary and as has been pointed out previously,[23] difficulties arise when the interface width in the simulation is greater than the physical width.

Thermodynamics of irreversible processes

The determination of the rate of change requires ultimately a relationship between time, the free energy density and the order parameter. The approach in sharp interface models is usually atomistic, with activation energies for the rate controlling process and some consideration of the structure of the interface in partitioning the driving force between the variety of possible dissipative processes. The phase field method has no such detail, but rather relies on a fundamental approximation of the thermodynamics of irreversible processes,[24–27] that the flux describing the rate is proportional to the force responsible for the change. For irreversible processes the equations of classical thermodynamics become inequalities. For example, at the equilibrium melting temperature, the free energies of the pure liquid and solid are identical ($G_{\mathrm{liquid}}=G_{\mathrm{solid}}$) but not so below that temperature ($G_{\mathrm{liquid}}>G_{\mathrm{solid}}$).

The thermodynamics of irreversible processes deals with systems which are not at equilibrium but are nevertheless stationary. It deals, therefore, with steady state processes where free energy is being dissipated making the process irreversible in the language of thermodynamics since after the application of an infinitesimal force, the system then does not revert to its original state on removal of that force.

The rate at which energy is dissipated in an irreversible process is the product of the temperature and the rate of entropy production ($T\dot{S}$) with

$$T\dot{S}=JX \text{ or for multiple processes, } T\dot{S}=\sum_{\mathrm{i}} J_{\mathrm{i}}X_{\mathrm{i}} \tag{8}$$

where J is a generalised flux of some kind, and X a generalised force (Table 1).

Given equation (8), it is often found experimentally that the flux is proportional to the force ($J\propto X$); familiar examples include Ohm's law for electrical current flow and Fourier's law for heat diffusion. When there are multiple forces and fluxes, each flow J_{i} is related linearly not only to its conjugate force X_{i}, but also is related linearly to all other forces present ($J_{\mathrm{i}}=M_{\mathrm{ij}}X_{\mathrm{j}}$)$i$, j=1,2,3…; thus, the gradient in the chemical potential of one solute will affect the flux of another. It is emphasised here that the linear dependence described is not fundamentally justified other than by the fact that it works. The dependence can be recovered by a Taylor expansion of $J\{X\}$ about equilibrium where $X=0$

$$J\{X\}=J\{0\}+J'\{0\}\frac{X}{1!}+J''\{0\}\frac{X^2}{2!}\ldots$$

$J\{0\}=0$ since there is no flux at equilibrium. The proportionality of J to X is obtained when all terms beyond the second are neglected. The important point is that the approximation is only valid when the forces are small. There is no phase field model that the authors are aware of which considers higher order terms in the relation between J and X.

Implementation in rate equations

Non-conserved order parameter

The dissipation of free energy as a function of time in an irreversible process must satisfy the inequality

$$\frac{\delta G}{\delta t}\leqslant 0 \tag{9}$$

as the system approaches equilibrium. When there are multiple processes occurring simultaneously, it is only the overall condition which needs to be satisfied rather than for each individual process; an expansion of equation (9) gives

$$\left(\frac{\delta G}{\delta\phi}\right)_{\mathrm{c,T}}\left(\frac{\partial\phi}{\partial t}\right)_{\mathrm{c,T}}+\left(\frac{\delta G}{\delta c}\right)_{\phi,\mathrm{T}}\left(\frac{\partial c}{\partial t}\right)_{\phi,\mathrm{T}}$$
$$+\left(\frac{\delta G}{\delta T}\right)_{\phi,\mathrm{c}}\left(\frac{\partial T}{\partial t}\right)_{\phi,\mathrm{c}}\leqslant 0 \tag{10}$$

but to ensure that the free energy of the system decreases monotonically with time, it is sufficient that

Table 1 Examples of forces and their conjugate fluxes*

Force	Flux
e.m.f. $\equiv\frac{\partial\psi}{\partial z}$	Electrical Current
$-\frac{1}{T}\frac{\partial T}{\partial z}$	Heat flux
$-\frac{\partial\mu_{\mathrm{i}}}{\partial z}$	Diffusion flux
Stress	Strain rate

*z is distance, ψ is the electrical potential in volts, and μ is a chemical potential. 'e.m.f.' stands for electromotive force.

$$\left(\frac{\delta G}{\delta \phi}\right)_{\mathrm{c,T}}\left(\frac{\partial \phi}{\partial t}\right)_{\mathrm{c,T}} \leqslant 0 \tag{11}$$

If it is now assumed from the approximations in the theory of irreversible thermodynamics that the 'flux' is proportional to the 'force' then

$$\underbrace{\left(\frac{\partial \phi}{\partial t}\right)_{\mathrm{c,T}}}_{\text{flux}} = -M_{\phi}\underbrace{\left(\frac{\delta G}{\delta \phi}\right)_{\mathrm{c,T}}}_{\text{force}} \tag{12}$$

This gives

$$-M_{\phi}\left[\left(\frac{\delta G}{\delta \phi}\right)_{\mathrm{c,T}}\right]^2 \leqslant 0, \text{ i.e., } M_{\phi} \geqslant 0 \tag{13}$$

so that the mobility M must be positive or zero. It can be shown that[28]

$$\frac{\delta G}{\delta \phi} = \frac{\partial g}{\partial \phi} - \varepsilon_{\phi}^2 \nabla^2 \phi$$

$$\text{so that } \frac{\partial \phi}{\partial t} = M_{\phi}\left(\varepsilon_{\phi}^2 \nabla^2 \phi - \frac{\partial g\{\phi\}}{\partial \phi}\right) \tag{14}$$

The equation on the right is a generic form for the evolution of a non-conserved order parameter in a manner which leads to the reduction of free energy.

Conserved order parameter

Some order parameters are conserved during evolution whereas others need not be. For example, when ϕ describes solidification the integrated value of ϕ over the whole phase field will not be the same once solidification is completed. In such a case, equation (12) is sufficient to initiate a phase field calculation. On the other hand, solute must be conserved during a diffusion process. The authors illustrate this with the classical example of solute diffusion, where the equivalent of equation (4) is[29]

$$G = \int_{\mathrm{V}} \left[g\{c\} + \frac{1}{2}\varepsilon_{\mathrm{c}}^2 (\nabla c)^2\right] \mathrm{d}V \tag{15}$$

but because concentration is a conserved quantity, it is necessary to also satisfy

$$\frac{\partial c}{\partial t} = \nabla \cdot J_{\mathrm{c}} \tag{16}$$

where J_{c} is the solute flux. From the appropriate term for solute in equation (10), substituting for $\partial c/\partial t$, the authors see that

$$\left(\frac{\delta G}{\delta c}\right)_{\phi,\mathrm{T}}\left(\frac{\partial c}{\partial t}\right)_{\phi,\mathrm{T}} \leqslant 0 \text{ is equivalent to} \left(\frac{\delta G}{\delta c}\right)_{\phi,\mathrm{T}} \times (\nabla \cdot J_{\mathrm{c}}) \leqslant 0$$

and given the identity $B\nabla \cdot A \equiv \nabla \cdot (AB) - A \cdot \nabla B$

it follows that

$$\underbrace{-\nabla \cdot \left[J_{\mathrm{c}}\left(\frac{\delta G}{\delta c}\right)_{\phi,\mathrm{T}}\right]}_{=0} + J_{\mathrm{c}} \cdot \nabla \left(\frac{\delta G}{\delta c}\right)_{\phi,\mathrm{T}} \leqslant 0 \tag{17}$$

The term on the left is identified to be zero because there can be no flux through the bounding surface of a closed system (G is an integral over volume, which by the Gauss theorem, can be expressed as an integral over its bounding surface). A combination of equations (17) and (16) gives

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(M_{\mathrm{c}} \nabla \frac{\delta G}{\delta c}\right)_{\phi,\mathrm{T}} \tag{18}$$

where M_{c} is the diffusional mobility and $\delta G/\delta c$ is the variational derivative of G with respect to c. The same assumption applies here as emphasised in the derivation of equation (12) that the force and flux are assumed to be linearly dependent.

If the gradient energy can be neglected then in a binary alloy the term $\delta G/\delta c$ corresponds to the difference in the chemical potentials of the two components.[30]

The general theory that describes governing equations for various types of order parameters has been reviewed in detail by Hohenberg and Halperin.[31]

Parameter specification

In order to apply the phase field equations, it is necessary to know the mobility M, gradient energy coefficient ε and the interfacial fitting parameter ω in order to utilise the phase field method.

The interfacial energy per unit area σ is derived from the excess free energy density associated with the interfacial region.[32] The following derivation due to Wheeler[11] is for the case where ϕ is not conserved. Since the authors focus on the interfacial region only, equation (5) reduces to $g_0\{\phi\} = \frac{1}{4\omega}\phi^2(1-\phi)^2$. At equilibrium since $\partial\phi/\partial t = 0$, the one-dimensional form of equation (14) becomes

$$\varepsilon^2 \frac{\mathrm{d}^2 \phi}{\mathrm{d}x^2} - \frac{\partial g\{\phi\}}{\partial \phi} = 0$$

$$\text{which on integration gives } \frac{\varepsilon^2}{2}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2 - g\{\phi\} = 0 \tag{19}$$

ϕ with its origin redefined at the centre of the interface is designated ϕ_0; an exact solution to equation (19)[11] showing the smooth variation in the order parameter between its bulk values is

$$\phi_0 = \frac{1}{2}\left\{1 + \tanh\left[\frac{x}{2(2\omega)^{1/2}\varepsilon}\right]\right\}$$

$$\text{so that the interface thickness } 2\lambda = 4(2\omega)^{1/2}\varepsilon \tag{20}$$

The authors note that with the assumptions outlined, the thickness of the interface is proportional to the gradient energy coefficient. The energy of the interface per unit area is then given by integrating equation (19)

$$\sigma = \int_{-\infty}^{+\infty} \varepsilon^2 \left(\frac{\mathrm{d}\phi_0}{\mathrm{d}x}\right)^2 \mathrm{d}x = \frac{(2)^{1/2}\varepsilon}{12(\omega)^{1/2}} \tag{21}$$

The width of the interface 2λ is treated as a parameter which is adjusted to minimise computational expense or using some other criterion such as the resolution of detail in the interface. Values of the interfacial energy per unit area σ may be available from experimental measurements. Given these two quantities, the expressions for interfacial energy and interfacial width can be solved simultaneously to yield ε and ω. Both of the terms in equation (19) contribute to the interface energy, i.e. through the existence of gradients in the order parameter and because the free energy density there is defined to be different from that of the bulk phases.

The mobility M is determined experimentally, for example in a single component system, by relating the interface velocity v to driving force ΔG using chemical rate theory in which $v = M \times \Delta G$.[27] In simulating spinodal decomposition, diffusion data and thermodynamics can be used to obtain mobilities. When the models are used simply for illustrating the general principles of morphological evolution, the mobility is often fixed by trial and error. Too large a mobility leads to numerical instabilities and the computing time becomes intolerable if the mobility is set to be too small.

Numerical procedures and interpretations

The governing equations of phase fields are usually solved using the finite difference or finite element techniques. The following discussion will for simplicity focus on the explicit finite difference method at two-dimensional square regular lattices. The lattice spacing Δx is then uniform and set so that the interface is described by at least four cells in order to capture moderate detail in the interface. As in all numerical methods, coarse spacings may not have sufficient resolution to deal with the problem posed, and may lead to numerical instabilities. The discrete time step is accordingly set such that $\Delta t < \frac{1}{2}(\Delta x)^2 / D$ where D is the largest of all included solute and heat diffusivities.

An interesting aspect of using a value of Δx which is large relative to the detail in the microstructure is that noise, to a level of ~1%, is introduced into the system. It is found, in the absence of such noise, that dendrites in pure systems tend to grow without side-branching;[1,33] expressed differently, a fine Δx leads to needle-like dendrites without side branches. This confirms other theory which suggests that small perturbations corresponding to thermal noise are responsible for the side-branching dendrites.[8,34,35]

The finite element lattice has to be initialised with values of ϕ, c and T but sharp changes in ϕ should be avoided to prevent calculation instabilities. The initial configuration should also account for boundary conditions and this may necessitate the introduction of a ghost layer of lattices compatible with the boundary conditions. There is no simple method of introducing heterophase fluctuations of the kind associated with classical nucleation theory. But the latter can be used to calculate the appropriate number of nuclei and implement them on to the lattice.

It is normal, for the sake of computational stability, to use dimensionless variables in the governing equations so that the occurrence of very small or very large numbers is avoided $\Delta\tilde{x} = \Delta x / L_c$, $\Delta\tilde{t} \propto \Delta\tilde{x}^2 / D_c$, $\tilde{M}_\phi = L_c^2 R T_c / D_c V_m$, $\tilde{\varepsilon} = \varepsilon (V_m / R T_c)^{1/2} / L_c$, $\tilde{\omega} = \omega R T_c / V_m$ and $\tilde{g}^\alpha - \tilde{g}^\beta = (g^\alpha - g^\beta) V_m / R T_c$, where L_c is a characteristic length, T_c a characteristic temperature (for example a transition temperature) and V_m is the molar volume. After expressing the variables in this way, they range roughly between 0 and 1. The variables are unnormalised when interpreting the outputs of the model. It may be necessary in some cases to introduce fluctuations, which can be conducted by disturbing the driving force rather than the variables such as solute concentration or temperature in order to avoid the violation of conservation conditions by the fluctuations.

Comparison with overall transformation kinetics models

Attempts have been made to compare and contrast the overall transformation kinetics theory invented by Kolmogorov in its most general form[36] and also developed by Avrami,[37–39] Johnson and Mehl[40] (this theory is henceforth referred to using the acronym KJMA). The essence of the method is that given the nucleation and growth rates of particles forming from a parent phase in a volume, the total extended volume V_e^α of α particles can be calculated first without accounting for impingement, and then a correct volume V^α is obtained by multiplying the extended fraction by the probability of finding untransformed material (i.e. the fraction $(1 - V^\alpha / V)$ of the parent phase that remains) where V is the total volume, so that

$$\mathrm{d}V^\alpha = \left(1 - \frac{V^\alpha}{V}\right) \mathrm{d}V_e^\alpha$$

which on integration gives $\frac{V^\alpha}{V} = 1 - \exp\left(-\frac{V_e^\alpha}{V}\right)$ (22)

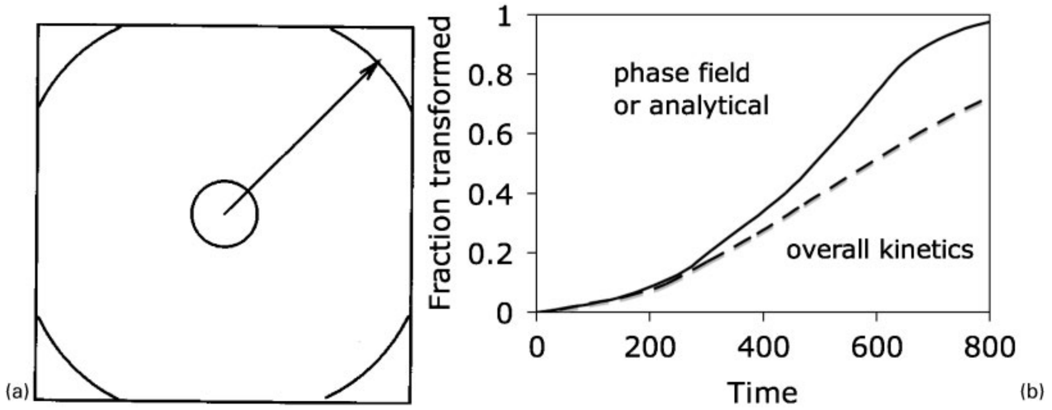
This conversion between extended and real space permits hard impingement to be taken into account, and requires an assumption that the volume of an arbitrary transformed crystal is much smaller than that of the total volume. In addition, it is assumed that nuclei will develop at random sites because the conversion relies on probabilities. Nevertheless, grain boundary nucleation can be treated as in Ref. 41 and this method has in practice been applied with useful results.[42] There is a huge variety of equations that result depending on the specific mechanisms of transformation; these have been reviewed by Christian.[43]

For two-dimensional growth at a rate G of initially spherical particles beginning with a constant number of sites N_0 which can develop from time $t = 0$ into particles, equation (22) becomes

$$\frac{V^\alpha}{V} = 1 - \exp\left(-\frac{N_0 G^2}{4\pi} t^2\right) \tag{23}$$

Jou and Lusk[44] attempted to compare this equation with a phase field which was designed to emulate spherical particles growing in the manner described by equation (23). The comparison is approximate because they were not able to suppress capillarity effects in the phase field model, which resulted in slower growth at small particle size, so that the phase field model underestimated relative to equation (23). Capillarity can of course be included in equations based on overall transformation kinetics,[45–49] but this was not taken into account in making the comparison.

Jun and Lusk also examined an extreme scenario in which a single particle is placed at the centre of a square parent phase, and modelled transformation using the phase field method and a geometrical exact-solution. The results, shown in Fig. 3, seem to suggest that the KJMA method fails since it predicts a slower evolution of phase fraction when compared with the exact analytical solution and the phase field technique. The



a particle located at centre of square, growing radially and impinging with boundary of square; *b* comparison of overall kinetics calculated using equation (23), phase field model and exact analytical solution (latter two are plotted as single curve since they gave similar results)

3 Single particle growth: data from Ref. 44

KJMA method relies on randomness – had the particle been placed anywhere other than the centre, impingement would have occurred earlier. Furthermore, as stated earlier, the theory requires the growing particle to be much smaller than the volume of the material as a whole.[36,50] While it is true that impingement effects are likely to underestimate the fraction of transformation when there are very few particles present and which grow to consume large fractions of the matrix, this is not a realistic scenario for applications where real microstructural evolution is calculated.

The most obvious difference between the mechanistic KJMA method and the phase field method, in which it is difficult to incorporate atomistic information, is that the latter allows the structure to be pictured as it evolves. This is not possible for the KJMA method given its reliance on probabilities and the conversion between extended and real space. In suitably chosen problems, the phase field method can better account for phenomena in which there is an overlap between the diffusion or temperature fields of particles which grow from different locations; indeed, it is routine to define such fields accurately throughout the modelling space. In the case of KJMA, one uses either the mean field approximation in which it is assumed for the calculation of boundary conditions that, for example, the diffusing solute is uniformly distributed throughout the parent phase during transformation, or some approximate analytical solution (or an approximate treatment of the real geometry of the problem) is used to treat overlapping fields.[42,51–58]

Summary

The basic concepts of phase field models and fundamental mathematical procedures for derivation of phase field theoretical frame are reviewed. The method for specifying phase field parameters according to known quantities and ways to achieve these are illustrated. Numerical simulation procedures are described in detail. It is shown finally the straightforward applicability of phase field models to multiphase and multicomponent materials.

The authors highlight here the features of phase field techniques which make them useful but at the same time emphasise the difficulties so that claims associated with the method can be moderated. The compilation is based on the references listed in the present paper.

Advantages

1. Particularly suited for the visualisation of microstructural development.
2. Straightforward numerical solution of a few equations.
3. The number of equations to be solved is far less than the number of particles in system.
4. Flexible method with phenomena such as morphology changes, particle coalescence or splitting and overlap of diffusion fields naturally handled. Possible to include routinely, a variety of physical effects such as the composition dependence of mobility, strain gradients, soft impingement, hard impingement, anisotropy etc.

Disadvantages

1. Very few quantitative comparisons with reality; most applications limited to the observation of shape.
2. Large domains computationally challenging.
3. Interface width is an adjustable parameter which may be set to physically unrealistic values. Indeed, in most simulations the thickness is set to values beyond those known for the system modelled. This may result in a loss of detail and unphysical interactions between different interfaces.
4. The point at which the assumptions of irreversible thermodynamics would fail is not clear.
5. The extent to which the Taylor expansions that lead to the popular form of the phase field equation remain valid is not clear.
6. The definition of the free energy density variation in the boundary is somewhat arbitrary and assumes the existence of systematic gradients within the interface. In many cases there is no physical justification for the assumed forms. A variety of adjustable parameters can therefore be used to fit an interface velocity to experimental data or other models.

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