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Evolution Equations for Phase Separation and Ordering in Binary Alloys

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We explore two phenomenological approaches leading to systems of coupled Cahn–Hilliard and Cahn–Allen equations for describing the dynamics of systems which can undergo first-order phase separation and order–disorder transitions simultaneously, starting from the same discrete lattice free energy function. In the first approach, a quasicontinuum limit is taken for this discrete energy and the evolution of the system is then assumed to be given by gradient flow. In the second approach, a discrete set of gradient flow evolution equations is derived for the lattice dynamics and a quasicontinuum limit is then taken. We demonstrate in the context of BCC Fe–Al binary alloys that it is important that variables be chosen that accommodate the variations in the average concentration as well as the underlying ordered structure of the possible coexistent phases. Only then will the two approaches lead to roughly the same continuum descriptions. We conjecture that in general the number of variables necessary to describe the dynamics of such systems is equal to $N_1 + N_2 - 1$, where N_1 is given by the dimension of the span of the bases of the irreducible representations needed to describe the symmetry groups of the possible equilibrium phases and N_2 is the number of chemical components. N_1 of these variables are nonconserved, and the remaining are conserved and represent the average concentrations. For the Fe–Al alloys this implies a description of one conserved order parameter and one nonconserved order parameter. The resultant description is given by a Cahn–Hilliard equation coupled to a Cahn–Allen equation via the lower-order nonlinear terms. The rough equivalence of the two phenomenological methods adds credibility to the validity of the resulting evolution equations. A similar description should also be valid for alloy systems in which the structure of the competing phases is more complicated.

KEY WORDS: Phase separation and ordering, Allen–Cahn and Cahn–Hilliard equations.

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1. INTRODUCTION

Our goal is to develop a description for the evolution of coexistent phases in alloy systems that exhibit simultaneous phase separation and one or more order–disorder transitions, leading to a variety of symmetries at a local level. At least two length scales are necessary to describe the composition variations, one on an atomic scale in the ordered domains, and the other on the scale of distances between phase and domain boundaries. Thus, it is apparent that it is not reasonable to expect to find a continuum description based on the mean concentration as the sole dominant variable. We discuss in depth the various problems which arise in the development of these equations, with the long-term aim of facilitating the development of similar systems of equations that should be appropriate for more complicated contexts.

We treat in detail the case of Fe–Al binary alloys near the tricritical point where two phases differing in average composition can coexist in equilibrium, one ordered (occurring as domains of two variants) and one disordered. This may be modeled by assuming that atoms in Fe–Al alloys occupy points of a BCC lattice in which the neighbor interactions are "antiferromagnetic" and next-nearest-neighbor interactions are "ferromagnetic," or more simply that nearest neighbors prefer to be different species, leading to ordering, and next nearest neighbors prefer to be the same. Two phases arise in nonstoichiometric alloys because this next-neighbor condition causes the minority atoms to cluster into second-neighbor positions that form a primitive cubic sublattice, leading to ordered regions in which the concentration of minority atoms is raised, reaching 50% stoichiometry in the 0 K limit. The ordering splits the BCC lattice into two sublattices with different occupation probabilities; this prototype for this structure is CsCl, and the Strukturbericht designation is B2. The excess of the major component is expelled from these ordered regions and forms a relatively pure phase, in which at low, but nonzero, temperatures there are some stragglers of the minor component in disordered positions.

One option is to work with a discrete description for the dynamics of these systems. Such an approach has been explored by Richards(1) and more recently by Cahn *et al.*(2) Indeed, the classical statistical mechanics approach to the equilibrium properties of such systems has a discrete free energy as its starting point. The advantages of a continuum description for the dynamics of such systems becomes apparent when one stops to consider the various features of alloy dynamics which one desires to capture. Consider for a moment some of the details of the evolution of an Fe–Al alloy in the two-phase region of the phase diagram near the tricritical point. The system as a whole could either be a single grain or a composite of many grains meeting at grain boundaries, across which the translational symmetry of the lattice is lost. Each crystalline grain is a represented by a finite segment of a BCC lattice. We shall focus on the dynamics within a single grain. This single grain will comprise the system. As equilibrium is approached, the system should consist of three types of roughly homogeneous domains—domains of the disordered phase and of the two variants of the ordered phase. The boundaries between the ordered and disordered phases are known as interphase boundaries, and the boundaries between different domains of the ordered phases are known as antiphase boundaries. As the system evolves toward equilibrium, the various phases rearrange themselves and the interfaces slowly evolve. The dynamics of this motion is of interest since it determines the evolution of microstructure and the properties of the material. The theory can be tested when this motion occurs on laboratory time scales as it does in Fe–Al alloys near the tricritical temperature, but is particularly useful in modeling the many systems in which this motion is either too fast or too slow to be followed on a laboratory time scale. Questions one would like to answer are:

(i) How does an initially disordered system evolve to a state that can be described by phases and domains? How do the surfaces of the grains affect this process?

(ii) How do the dynamics of motion of the two kinds of interfaces reflect the presence or absence of a need for long-range mass transport resulting from jumps in composition?

(iii) Under what conditions are the antiphase boundaries "wetted" by a thin layer of the disordered phase(3,4)? What happens to the such layers when an interface moves? Is it possible to give an accurate dynamic description of an instability observed by Krzanowski—the coagulation of droplets of the disordered phase along antiphase boundaries sometimes under partial wetting conditions and sometimes under conditions where the disordered phase is not stable in bulk(5–8)?

These questions are naturally approached within the context of a continuum approach in which the interface between phases can be considered to be a well-defined surface or a thin region of smooth, high gradients. To approach these questions via a system of discrete evolution equations, one is limited primarily to the use of numerical experimentation which does not readily lend itself to global predictions.

Since, as we have seen above, the concentration is not an appropriate variable with which to continuize, the question arises as to which are the appropriate variables. In tackling this question we first present certain variables for the Fe–Al system with which to continuize and then discuss their possible generalization. Continuum approaches have been employed in the past (see, for example, the work of Eguchi *et al.*(3,4) and Krzanowski and Allen(5–8)); however, the connection between the continuum approach and the discrete approach has not been studied in detail, and it is not clear to what degree it should be possible to pass from one description to the other and obtain equivalent results. Eguchi starts from a free energy which is written in terms of a nonconserved order parameter and a conserved parameter which represents average concentration. He then writes down gradient flow equations which he proceeds to study via numerical methods. Krzanowski's starting point is similar, and while he does attempt to study questions (i)–(iii), his approach does not employ modern asymptotic methods. In a companion paper(9) we explore the predictions of such methods for the motion of the relevant interfaces. In the present paper we limit ourselves to a discussion of the relevant continuum equations and their derivation.

The organization of this paper is as follows. In the next section we outline which features of the discrete model we wish to preserve in choosing an appropriate continuum limit. In particular, we need a well-posed model with similar minima which mimics the dynamics of the discrete model. In Section 3 we outline the dominant features of interest of Fe–Al alloys on BCC lattices in which the free energy in assumed to depend both on nearest neighbors and next nearest neighbors. In Section 4 we describe what happens when one tries to continuize using the mean concentration as the sole variable. In particular, we see that even if the resultant equations are well-posed, the possibility of order–disorder transitions has been eliminated. In Section 5 possible choices of variables are discussed which should be capable of capturing the order–disorder transition as well as phase separation. In Sections 6 and 7 we discuss the application of these variables to (quasi-) continuization of the free energy and the discrete evolution equations. Finally, in Section 8 general considerations are discussed for choosing variables when a number of phases and components occur in the system.

2. FORMULATION OF THE PROBLEM

We wish to outline the difficulties which may arise in passing from a discrete description of lattice dynamics to a continuum description of phase dynamics when microstructure is involved. We will not treat the problem in full generality; rather, we confine our discussions to those systems whose evolution is governed by a conserved gradient flow from a discrete mean-field free energy per unit site, defined in terms of the concentrations (or probabilities) of the various components at the lattice vertices or points; i.e.,

$$\mathscr{F} = \frac{1}{\tilde{N}} \sum_{\mathbf{n} \in \Lambda} \sum_{\mathbf{a} \in \mathbf{A}} \sum_{\mathbf{b} \in \mathbf{B}} \phi(c(\mathbf{n}), c(\mathbf{n}+\mathbf{a}), c(\mathbf{n}+\mathbf{b})) \tag{2.1}$$

where $\mathbf{A}$ is the set of vector distances to nearest neighbors, $\mathbf{B}$ is the set of vector distances to next nearest neighbors, Λ is a finite segment of a lattice, and $\tilde{N} = |\Lambda|$. The interactions between neighbors are essential for the production of microstructure.

As mentioned earlier, we shall assume that the evolution of the discrete system is governed by conserved gradient flow; i.e.,

$$\frac{\partial c(\mathbf{n})}{\partial t} = Q\tilde{N} \sum_{\mathbf{a} \in \mathbf{A}} \left\{ \frac{\delta \mathscr{F}}{\delta c(\mathbf{n}+\mathbf{a})} - \frac{\delta \mathscr{F}}{\delta c(\mathbf{n})} \right\}, \qquad \mathbf{n} \in \Lambda \tag{2.2}$$

Two possible paths present themselves for formulating a continuum description for the evolution of the system; one is to take a continuum limit in the free energy $\mathscr{F}$ and then describing the dynamics of the system in terms of some type of gradient flow, and another is to directly continuize (quasicontinuize) the discrete gradient flow prescribed in Eq. (2.2).

When there is no ordering, the concentration may be expected to be an appropriate variable for describing the continuized system. However, in systems such as Fe–Al near the critical point nearest neighbors in the domains of the ordered phase are of different species. Clearly then in these systems the concentration cannot be expected to be an appropriate variable in which to continuize, because on the scale of the lattice spacing h it will be rapidly varying.

The task is to choose a set of continuum variables and to derive equations for these variables from (2.1) and (2.2) by either of the two paths. The decision of which set of variables to choose has to be made on the basis of a comparison of the dynamics and possible equilibria of the resultant equations with those obtained from (2.1) and (2.2). Some of the criteria are based on properties of the discrete system which we would wish to be preserved in continuum models:

(i) The resultant equations must be well-posed.

This is not a sufficient condition. We will see that it is possible to obtain a description which is well-posed but which fails to capture the full richness of the system.

(ii) The equations must exhibit sets of minima that are in some sense equivalent to those of the discrete equations.

(iii) In some sense the dynamics of the two systems must also be similar.

While it is difficult to obtain a global comparison between the two systems, it may be possible to compare early- and late-time behavior for the two systems. Though such a comparison will not be undertaken here, in a forthcoming paper the long-time asymptotics will be described and it will be possible to at least compare the predicted long-time asymptotic dynamics with the final stages of dynamic evolution which are seen experimentally. These questions are discussed in the subsequent sections. Rather than to treat these questions in full generality, these problems are first discussed in the context of a simplest nontrivial model, an idealization of the Fe–Al system. The properties and phase diagram for this model will be outlined in the next section.

3. AN EXAMPLE OF A DISCRETE FREE ENERGY

Consider a rectangular segment of a three-dimensional BCC lattice which contains many points or lattice sites and assume each site to be occupied either by an Fe atom or by an Al atom (the possibility of vacancies is assumed here to be negligible). We take each site to be occupied by an Fe atom with probability c_A or by an Al atom with probability $c = c_B = 1 - c_A$. Thus c assumes here the role of a concentration. We now write the free energy of our discrete periodic lattice system in terms of these probabilities.

Recall that the free energy given by Eq. (2.1) is an average over lattice points of functions ϕ of the composition at a lattice point and its neighbors. Since we wish to examine the mathematical problems introduced by continuizing, any model will do if it has this neighborhood property and produces equilibria containing both ordered and disordered phases.

The free energy per unit site is composed of two parts

$$\mathscr{F} = E - TS$$

where E and S are the energy and entropy per unit site, respectively, and T is a normalized temperature ($T = k_B T$). At low temperatures far below the critical points, the contribution from S is relatively unimportant, since it is multiplied by T. If E is assumed to contain contributions from nearest- and next-nearest-neighbor pairwise interactions, it will by itself convey the desired neighborhood dependence on $\mathscr{F}$. Therefore it is not necessary for S to be a sum of such functions and the simplest entropy expression, an ideal mixing form on each lattice point, can be used.

Let us recall that a BCC lattice may be viewed as two interpenetrating primitive cubic lattices, which we shall call sublattices. One of the sublattice segments is taken to be the points $\mathbf{n} = (n_1, n_2, n_3) \in \Lambda_1$, where the n_i, $i = 1, 2, 3$, vary over a given interval of integers, and the second sublattice segment is taken to be the points $\mathbf{n} + \frac{1}{2} = (n_1 + \frac{1}{2}, n_2 + \frac{1}{2}, n_3 + \frac{1}{2}) \in \Lambda_2$, where $\mathbf{n} \in \Lambda_1$. The total number of points of each sublattice segment is given by N. Furthermore, we define $\Lambda = \Lambda_1 \cup \Lambda_2$ and note that $2N = |\Lambda|$. In terms of this notation the ideal mixing form for the entropy per unit site is

$$\frac{1}{2N} \sum_{\mathbf{n} \in \Lambda} S(c(\mathbf{n})) = -\frac{1}{2N} \sum_{\mathbf{n} \in \Lambda} \{c(\mathbf{n}) \ln c(\mathbf{n}) + [1 - c(\mathbf{n})] \ln[1 - c(\mathbf{n})]\}$$

Noting that a sum over nearest neighbors is given by a sum over $\mathbf{a} \in \mathbf{A}$, where

$$\mathbf{A} = \{(i_1, i_2, i_3) \mid i_k = \pm\tfrac{1}{2}, k = 1, 2, 3\}$$

and a sum over next nearest neighbors is given by a sum over $\mathbf{b} \in \mathbf{B}$, where

$$\mathbf{B} = \{(j_1, j_2, j_3) \mid j_k = \pm 1, k = 1, 2, 3, j_l = 0 \text{ if } l \neq k\}$$

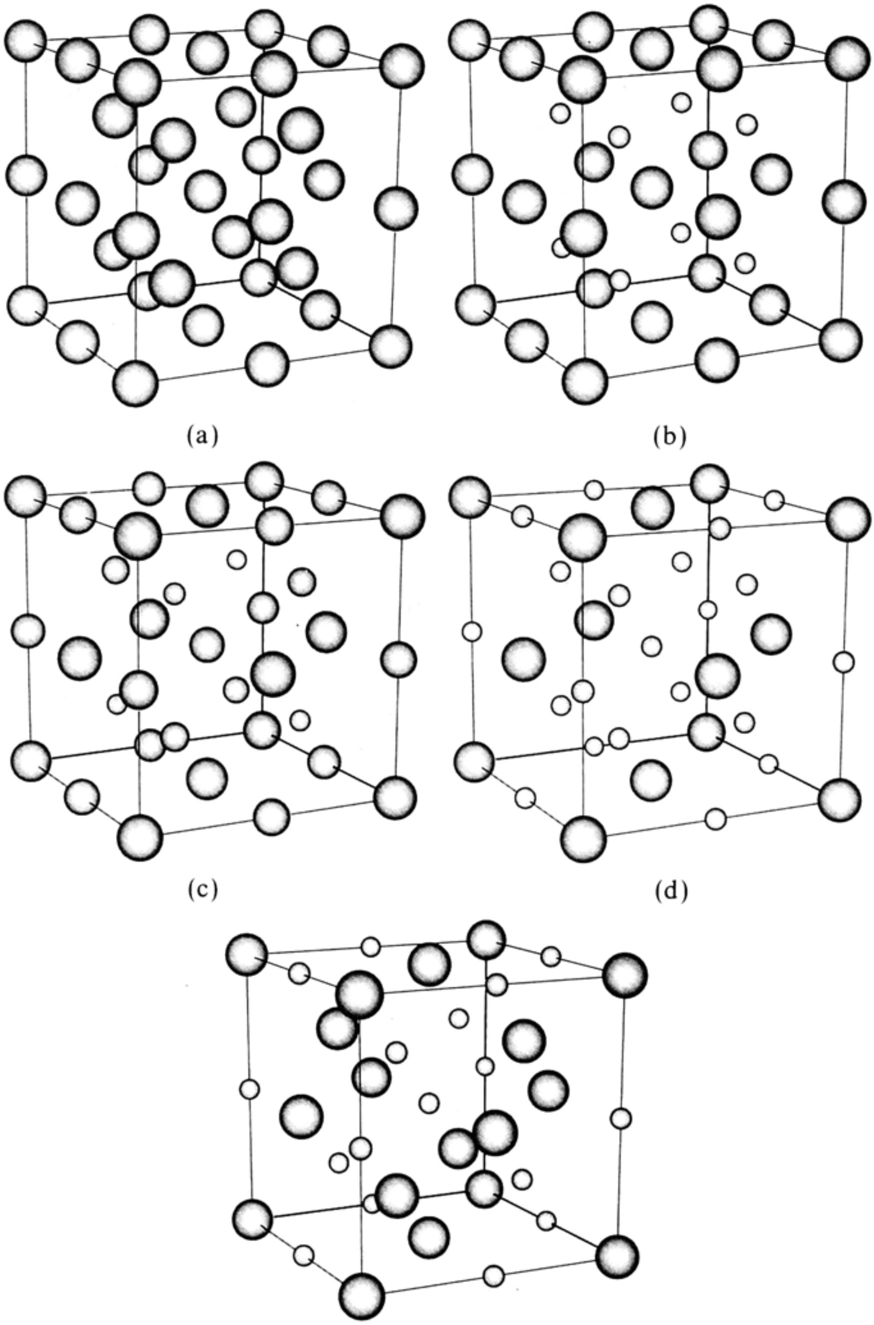
if the energetic contribution from each nearest-neighbor bond is taken to be λ_1 and that from each next nearest neighbor bond is λ_2, then we may write two equivalent expressions for the free energy per unit site, whose variations are identical when the average concentration is held constant,

$$\mathscr{F} = \frac{1}{2N} \sum_{\mathbf{n} \in \Lambda} \left\{\frac{1}{2} \lambda_1 \sum_{\mathbf{a} \in \mathbf{A}} c(\mathbf{n}) c(\mathbf{n} + \mathbf{a}) + \frac{1}{2} \lambda_2 \sum_{\mathbf{b} \in \mathbf{B}} c(\mathbf{n}) c(\mathbf{n} + \mathbf{b}) - TS(c(\mathbf{n}))\right\} \tag{3.1a}$$

or

$$\begin{aligned}\mathscr{F} = \frac{1}{2N} \sum_{\mathbf{n} \in \Lambda} \Bigg\{ &-\frac{1}{2} \lambda_1 \sum_{\mathbf{a} \in \mathbf{A}} c(\mathbf{n})[1 - c(\mathbf{n} + \mathbf{a})] \\ &-\frac{1}{2} \lambda_2 \sum_{\mathbf{b} \in \mathbf{B}} c(\mathbf{n})[1 - c(\mathbf{n} + \mathbf{b})] - TS(c(\mathbf{n}))\Bigg\}\end{aligned} \tag{3.1b}$$

In order to evaluate the terms in (3.1) for a lattice segment, it is necessary to extend the definition of $c(\mathbf{n})$ beyond Λ. We do this by defining $c(\mathbf{n})$ on an extended lattice segment $\hat{\Lambda}$ in which the values of $c(\mathbf{n})$ outside of Λ are defined by reflecting the values assumed on the lattice through the final bounding planes. The final bounding planes are taken here to pass through the occupied faces of the finite lattice segment, which may



(a)

(b)

(c)

(d)

(e)

correspond either to integer or half-integer points. This extension will correspond both to Neumann boundary conditions,

$$\mathbf{m} \cdot \nabla c(\mathbf{n}) = 0$$

(where $\mathbf{m}$ is the unit normal to the exterior face of the finite lattice segment) and to Neumann–Neumann (or double Neumann) type boundary conditions,

$$\mathbf{m} \cdot \nabla c(\mathbf{n}) = \mathbf{m} \cdot \nabla \Delta c(\mathbf{n}) = 0$$

depending on the extent of the extension. Using these boundary conditions, it is now possible to rewrite (3.1) in terms of squares of differences,

$$\begin{aligned}\mathscr{F} = \frac{1}{2\tilde{N}} \sum_{\mathbf{n} \in A} \Bigg\{ &(4\lambda_1 + 3\lambda_2)\, c^2(\mathbf{n}) - TS(c(\mathbf{n})) \\ &- \frac{1}{4}\lambda_1 \sum_{\mathbf{a} \in A} [c(\mathbf{n}) - c(\mathbf{n}+\mathbf{a})]^2 - \frac{1}{4}\lambda_2 \sum_{\mathbf{b} \in B} [c(\mathbf{n}) - c(\mathbf{n}+\mathbf{b})]^2 \Bigg\}\end{aligned} \tag{3.2}$$

The equilibria (minimizers) of this free energy have been studied in detail, and can be summarized as phase diagrams.(10) At high temperature there is a single disordered phase; at lower temperatures there may be one or more phases, some of which may be ordered. We recall that a phase is said to be disordered if the concentration is evenly and randomly distributed over an entire lattice segment. Likewise, a phase is said to be ordered if the concentration distribution distinguishes between two or more sublattice segments. As shown in Fig. 1, the BCC lattice can be divided into two primitive cubic lattices which can each be further divided into two face-centered cubic (FCC) sublattices. These subdivisions allow for a set of possible ordered phases. Each phase has a uniform average concentration, and when there are two phases, the average concentrations of the individual phases will be different from each other and from the global average concentration. In particular, in the zero-temperature limit the con-

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Fig. 1. A description of crystal structures. (a) A BCC lattice segment for a cube with edge length equal to two unit cell constants. (b) The BCC can be subdivided into two primitive cubic sublattices. When the "corner" and "body center" sublattices are occupied by different species, the ordered B2 structure results. (c) Both primitive cubic sublattices can be further subdivided into two FCC sublattices. The four sublattices are shown occupied by four different-sized spheres. (d) When three of the FCC sublattices are occupied by the same species and a different species occupies the fourth, the result is the DO_3 structure. (e) When one species occupies one corner and one body-center FCC sublattice and another species occupies the remaining two sublattices, the B32 structure results.

centration of the disordered phases may under some conditions approach 0 or 1, and that of the stoichiometric ordered phases will approach some rational fraction. If we denote by $\bar{c}$ the average concentration of the alloy, then the low-temperature limit will fall into five parameter regions as shown in Fig. 2.

1. $\lambda_1 < 0, 3\lambda_2 < -2\lambda_1$: For $0 < \bar{c} < 1$, there is phase separation into two pure (called "terminal") phases, $c = 0$ and $c = 1$.

2. $\lambda_1 > 0, \lambda_2 < 0$: For $0 < \bar{c} < 50\%$ $(50\% < \bar{c} < 1)$ there is separation into a pure phase $c = 0$ $(c = 1)$ and into one or both of the domains of the ordered CsCl structure (Fig. 1b); Strukturbericht designation B2, space group Pm3m, with average concentration $c = 1/2$. Two thermodynamically equivalent domains arise because the species can occupy either of the two primitive cubic sublattices of the original BCC lattice.

3. $0 < 3\lambda_2 < 2\lambda_1$: In this region each of the two primitive cubic sublattices subdivides further into two face-centered cubic (FCC) sublattices with a unit cell constant that is twice that of the BCC unit cell. No two-phase coexistence occurs. Higher-order phase changes occur with increasing $\bar{c}$ from disordered BCC to preferential occupation of one of the four FCC sublattices with variable composition until the stoichiometric composition at 25% is reached. (This structure, shown in Fig. 1d, is known as DO_3,

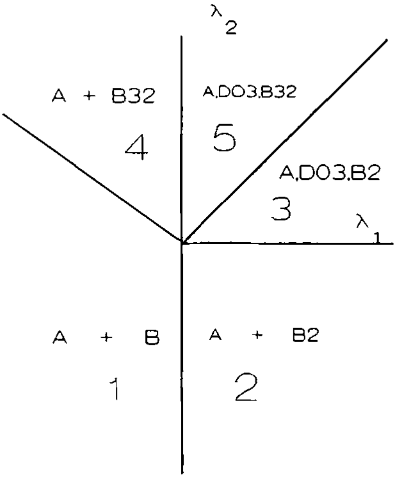

Fig. 2. The ground-state configurations of a binary nonstoichiometric alloy on a BCC lattice with first (λ_1) and second (λ_2) neighbor interactions fall into five parameter regions. Ordered structures are seen in regions 2, 3, 4, and 5. Separation into two phases occurs in regions 1, 2, and 4.

space group Fm3m with a doubled cubic cell constant.) Further increases in $\bar{c}$ lead to the gradual occupation of the second of the pair of FCC sublattices from the same primitive cubic sublattice and to a CsCl structure at 50%.

4. $0 < -2\lambda_1 < 3\lambda_2$: For $0 < \bar{c} < 50\%$ there is separation into a pure phase, $c = 0$, and into one or more of four of the domains of an ordered stoichiometric structure in which one FCC sublattice from each of the different primitive cubic sublattices (one FCC sublattice from the BCC sublattice of corners and one from the BCC sublattice of body centers) is occupied by a given species. The prototype structure is NaTl, shown in Fig. 1e (Strukturbericht designation B32; space group Fd3m with a doubled cubic cell constant).

5. $0 < 2\lambda_1 < 3\lambda_2$: No two-phase coexistence occurs. Higher-order phase changes occur with increasing $\bar{c}$ from disordered to DO_3 at 25% to NaTl at 50%, both with variable stoichiometry.

In fact, it is known that these mixtures of structures persist at higher temperatures and no additional types of structures appear. Furthermore, the values of the parameters that bound the stability regions of the various ordered structures are known to be insensitive to temperature.

In terms of length scales for describing the composition, we then expect three types of behavior. In parameter region 1, there is a length scale long compared to the cell length. In regions 3 and 5, the length scale is that of the unit cell for the composition, and varies rapidly from site to site. In regions 2 and 4, however, both length scales enter, and in region 4 further complications are introduced by the NaTl structure. Therefore in the following sections we concentrate on the second parameter region, as both phase separation and ordering can be expected to occur simultaneously there. Hence, this is a suitable parameter range for testing our ability to find continuum (quasicontinuum(11,12)) limits in systems in which various types of microstructure appear.

4. CONTINUIZING IN TERMS OF THE VARIABLE $c(x)$

Let us now consider the continuum (or quasicontinuum) limit of the free energy in terms of the variable $c(x)$. Let h be the length of the side of a cell in a BCC lattice, and expand the terms that are the squares of differences in a Taylor series:

$$\sum_{\mathbf{b} \in B} [c(\mathbf{n}+\mathbf{b}) - c(\mathbf{n})]^2 = 2h^2 \, |\nabla c(\mathbf{n})|^2 + O(h^3)$$

$$\sum_{\mathbf{a} \in A} [c(\mathbf{n}+\mathbf{a}) - c(\mathbf{n})]^2 = 2h^2 \, |\nabla c(\mathbf{n})|^2 + O(h^3)$$

[where $O(h^n)$ stands for terms of order h^n]. Note that by the error estimate for the trapezoid rule

$$\frac{1}{2N}\sum_{\mathbf{n}\in\Lambda} g(\mathbf{n})=\frac{1}{|L|}\int_{\text{lattice}} g(x)\,dx+O(h^2)$$

where $2N=|\Lambda|$. We obtain

$$\mathscr{F}=\frac{1}{|L|}\int_{\text{lattice}}\left\{[(4\lambda_1+3\lambda_2)\,c^2(x)-TS(c(x))+O(h^2)]\right.$$
$$\left.+\left[-\frac{1}{2}\lambda_1 h^2\,|\nabla c|^2-\frac{1}{2}\lambda_2 h^2\,|\nabla c|^2+O(h^3)\right]\right\}dx \tag{4.1}$$

Clearly it would be desirable to keep all terms to the same order. Here that would imply that all terms should either be kept to $O(1)$ or $O(h^2)$. If $O(1)$ terms are kept, the resultant equation would not be well-posed within the spinodal, region which would occur at sufficiently low temperatures whenever $4\lambda_1+3\lambda_2<0$. If we keep all terms to $O(h^2)$ accuracy, we would be faced with the difficulty that not all terms are known to $O(h^2)$ accuracy. Hence we employ the philosophy of incorporating all terms to leading order with the thought that in this manner all terms will be in some sense represented. It will always be possible later to delete small terms which do not play a critical regularizing role.

If we assume that the dynamics follows a "conserved gradient flow," i.e.,

$$\frac{\partial c}{\partial t}=M|L|\Delta\frac{\delta\mathscr{F}}{\delta c}$$

(where Δ represents the Laplacian operator), then we obtain the equation (keeping all terms to lowest order)

$$\frac{\partial c}{\partial t}=M\Delta\{2(4\lambda_1+3\lambda_2)\,c-TS'(c)+(\lambda_1+\lambda_2)\,h^2\,\Delta c\} \tag{4.2}$$

Equation (4.2) will be well-posed only if $(\lambda_1+\lambda_2)<0$. If $4\lambda_1+3\lambda_2$ is sufficiently negative, then $2(4\lambda_1+3\lambda_2)\,c(x)-TS'(c(x))$ will be nonmonotone when the temperature is sufficiently low, and a separation of phases will be predicted. Alternating regions of "order" and "disorder" will not be seen. This is inherent in the assumptions of the approach, since if $c(\mathbf{n})$ has been assumed to be a continuum variable, it cannot be rapidly varying and neither can ordering appear.

The result are summarized in Figs. 3a and b. Note that the criterion of well-posedness suggested in Section 2 is not sufficient for guaranteeing

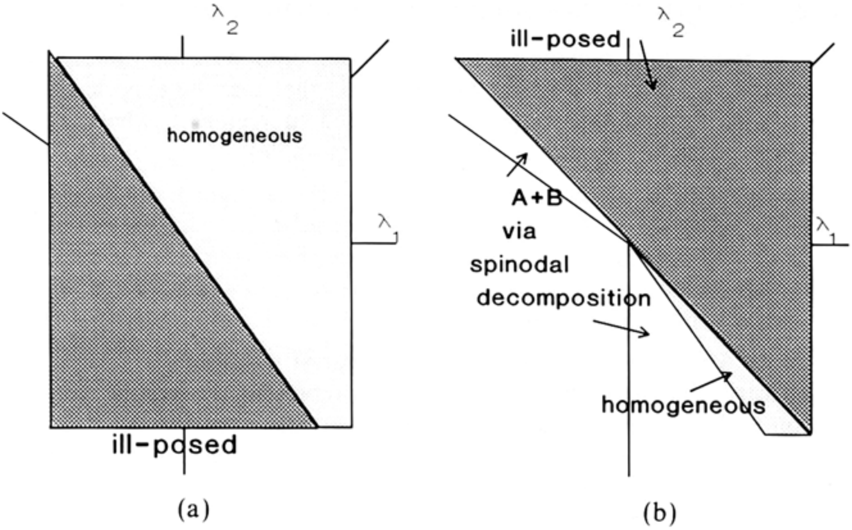

Fig. 3. The low-temperature behavior of Eq. (4.2). (a) The higher-order term is neglected, and (4.2) reduces to a nonlinear diffusion equation that is either ill-posed or yields equilibrium solutions that are constant. (b) the higher-order term is included. For some range of the parameters, the higher order term regularizes the equation, but renders the equation ill-posed elsewhere. In the figure the region labelled ill-posed is ill-posed with regard to the regularized equation. The region labelled "homogeneous" is the region with constant equilibrium. The region labelled $A+B$ is the region which yields spinodal decomposition for the regularised equations and is ill-posed for the unregularized equations. The equilibria can not account for ordering.

good modeling. If only terms of $O(1)$ are kept, the results are as shown in Fig. 3a; on the basis of the free energy, a homogeneous single phase occurs overpart of the parameter domain with a heat of mixing, $4\lambda_1 + 3\lambda_2$, that is negative, and two terminal phases occur over the remainder of the domain. However, in this latter region, the evolution equation would be ill-posed in that domain without the inclusion of the $O(h^2)$ terms. When terms of $O(h^2)$ are included, the results are as shown in Fig. 3b. Note that much of the region that previously was labeled "homogeneous" is now ill-posed, and that most of the spinodal region has been regularized by the appearance of the fourth-order term. The spinodal region has expanded to cover parts of regions 2 and 4, and at low temperature gives the two terminal phases, but in which the second phase in the discrete formulation is expected to be ordered and at 50%. Only in region 1 can Eq. (4.2) properly describe the dynamics. Elsewhere Eq. (4.2) does not even properly describe the evolution of the local mean concentration.

5. APPROPRIATE VARIABLES FOR A MODEL SYSTEM

We would like to choose some linear combination of the values of the concentrations evaluated at the lattice points that may be expected to be slowly varying and thus may be continuized in region 2, where $\lambda_1 > 0$, $\lambda_2 < 0$. A possibility would be to define the variables

$$\left.\begin{aligned} u_i(\mathbf{n}) &= \tfrac{1}{16} \sum_{\mathbf{a} \in \mathbf{A}} [c(\mathbf{n}+\mathbf{a}) + c(\mathbf{n})] \\ v_i(\mathbf{n}) &= \tfrac{1}{16} \sum_{\mathbf{a} \in \mathbf{A}} [c(\mathbf{n}+\mathbf{a}) - c(\mathbf{n})], \end{aligned}\right\} \quad \mathbf{n} \in \Lambda_i, \quad i = 1, 2 \qquad (5.1)$$

where $\mathbf{a} \in \mathbf{A}$ varies over the indices of the nearest neighbors.

Clearly the variables $u_1(\mathbf{n}_1)$ and $u_2(\mathbf{n}_2)$ represent the average concentration and may be expected to be slowly varying when $\mathbf{n}_i \in \Lambda_i$. It is also readily seen that these variables defined on the extended lattice $\hat{\Lambda}$ can be expected to be conserved; i.e., ignoring boundary effects,

$$\sum_{\mathbf{n} \in \Lambda_1} u_1(\mathbf{n}) + \sum_{\mathbf{n} \in \Lambda_2} u_2(\mathbf{n}) = \sum_{\mathbf{n} \in \Lambda} c(\mathbf{n}) \qquad (5.2)$$

Similarly, the variables $v_1(\mathbf{n}_1)$ and $v_2(\mathbf{n}_2)$ are seen to give a measure of the local ordering and may be considered to act as order parameters. Since the concentrations on the different lattices are being summed together with opposite signs, these variables, too, may be expected to be slowly varying for $\mathbf{n}_i \in \Lambda_i$. We note here that there is no reason to expect this second set of variables to act as conserved quantities.

This choice of variables, however, is not unique, as is readily seen by defining the "further symmetrized" variables

$$\left.\begin{aligned} a(\mathbf{n}) &= \tfrac{1}{16} \sum_{\mathbf{a} \in \mathbf{A}} [u_1(\mathbf{n}) + u_2(\mathbf{n}+\mathbf{a})] \\ b(\mathbf{n}) &= \tfrac{1}{16} \sum_{\mathbf{a} \in \mathbf{A}} [v_1(\mathbf{n}) - v_2(\mathbf{n}+\mathbf{a})], \end{aligned}\right\} \quad \mathbf{n} \in \Lambda_1$$

Similar variables may also be defined on the "second" lattice. Again, $a(\mathbf{n})$ may be taken to describe an average concentration and satisfies up to boundary effects

$$\sum_{\mathbf{n} \in \Lambda_1} a(\mathbf{n}) = \tfrac{1}{2} \sum_{\mathbf{n} \in \Lambda} c(\mathbf{n}) \qquad (5.4)$$

and $b(\mathbf{n})$ acts again as an order parameter and is not a conserved variable. The primary difference in these two sets of variables is the number of lattice points taken into consideration in defining the "averaged" variables. We will discuss the distinctions between these two sets of variables further in Section 7.

We remark that while these variables have been defined with region 2 of the phase diagram in mind, these variables should also be appropriate in region 1, where simpler structure is seen, since in the absence of ordering the order parameter should assume the value zero approximately, and the average concentration should give a good description of the disordered phases. In regions 3–5, where additional structures are seen, the variables defined above cannot be expected to suffice.

Next we outline the evolution behavior which results when the newly defined variables are employed. We call attention to some of the properties of these variables which we have defined. In particular, it is easy to check that for $i = 1, 2$

$$c(\mathbf{n}) = u_i(\mathbf{n}) - v_i(\mathbf{n}), \qquad \mathbf{n} \in \Lambda_i \tag{5.5}$$

$$\tfrac{1}{8} \sum_{\mathbf{a} \in \mathbf{A}} c(\mathbf{n}+\mathbf{a}) = u_i(\mathbf{n}) + v_i(\mathbf{n}), \qquad \mathbf{n} \in \Lambda_i \tag{5.6}$$

Hence, if our variables have been chosen so that they will be slowly varying, we find from the above relations that

$$\begin{aligned} u_i(\mathbf{n}) + v_i(\mathbf{n}) &= \tfrac{1}{8} \sum_{\mathbf{a} \in \mathbf{A}} \{u_j(\mathbf{n}+\mathbf{a}) - v_j(\mathbf{n}+\mathbf{a})\} \\ &= u_j(\mathbf{n}) - v_j(\mathbf{n}), \qquad \mathbf{n} \in \Lambda_i, \quad i \neq j, \quad i, j \in \{1, 2\} \end{aligned} \tag{5.7}$$

where $u_j(\mathbf{n})$, $v_j(\mathbf{n})$, $\mathbf{n} \in \Lambda_i$, refer now to the interpolated values,

$$u_j(\mathbf{n}) = \tfrac{1}{8} \sum_{\mathbf{a} \in \mathbf{A}} u_j(\mathbf{n}+\mathbf{a}), \qquad v_j(\mathbf{n}) = \tfrac{1}{8} \sum_{\mathbf{a} \in \mathbf{A}} v_j(\mathbf{n}+\mathbf{a}), \qquad \mathbf{n} \in \Lambda_i$$

Recall that

$$\begin{aligned} \mathscr{F} = \frac{1}{2N} \sum_{\mathbf{n} \in \Lambda} \Big\{ &(4\lambda_1 + 3\lambda_2)\, c^2(\mathbf{n}) - TS(c(\mathbf{n})) \\ &- \tfrac{1}{4}\lambda_1 \sum_{\mathbf{a} \in \Lambda} [c(\mathbf{n}) - c(\mathbf{n}+\mathbf{a})]^2 - \tfrac{1}{4}\lambda_2 \sum_{\mathbf{b} \in \mathbf{B}} [c(\mathbf{n}) - c(\mathbf{n}+\mathbf{b})]^2 \Big\} \end{aligned} \tag{5.8}$$

We wish now to express (5.8) in terms of the functions u_i and v_i. Note that

$$\begin{aligned} &\sum_{\mathbf{n} \in \Lambda_i} \{(4\lambda_1 + 3\lambda_2)\, c^2(\mathbf{n}) - TS(c(\mathbf{n}))\} \\ &\quad = \sum_{\mathbf{n} \in \Lambda_i} \{(4\lambda_1 + 3\lambda_2)[u_i(\mathbf{n}) - v_i(\mathbf{n})]^2 - TS(u_i(\mathbf{n}) - v_i(\mathbf{n}))\} \end{aligned}$$

From (5.5)–(5.7)

$$\begin{aligned}\sum_{\mathbf{a}\subset\mathbf{A}}[c(\mathbf{n})-c(\mathbf{n}+\mathbf{a})]^2&=\sum_{\mathbf{a}\in\mathbf{A}}\{[u_i(\mathbf{n})-v_i(\mathbf{n})]-[u_j(\mathbf{n}+\mathbf{a})-v_j(\mathbf{n}+\mathbf{a})]\}^2\\&=\sum_{\mathbf{a}\in\mathbf{A}}[u_i(\mathbf{n})-v_i(\mathbf{n})-u_i(\mathbf{n}+\mathbf{a})-v_i(\mathbf{n}+\mathbf{a})]^2\\&=32v_i^2(\mathbf{n})+\mathcal{O}(h^2)\end{aligned}$$

for $\mathbf{n}\in\Lambda_i$, $i\neq j$, $i, j\in\{1, 2\}$. Similarly,

$$\begin{aligned}\sum_{\mathbf{a}\in\mathbf{A}}[c(\mathbf{n})-c(\mathbf{n}+\mathbf{a})]^2&=\sum_{\mathbf{a}\in\mathbf{A}}\{[u_i(\mathbf{n})-v_i(\mathbf{n})]-[u_j(\mathbf{n}+\mathbf{a})-v_j(\mathbf{n}+\mathbf{a})]\}^2\\&=\sum_{\mathbf{a}\in\mathbf{A}}[u_j(\mathbf{n})+v_j(\mathbf{n})-u_j(\mathbf{n}+\mathbf{a})+v_j(\mathbf{n}+\mathbf{a})]^2\\&=32v_j^2(\mathbf{n})+\mathcal{O}(h^2)\end{aligned}$$

for $\mathbf{n}\in\Lambda_i$, $i\neq j$, $i, j\in\{1, 2\}$. Likewise

$$\begin{aligned}&\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n})-c(\mathbf{n}+\mathbf{b})]^2\\&\quad=\sum_{\mathbf{b}\in\mathbf{B}}\{[u_i(\mathbf{n})-v_i(\mathbf{n})]-[u_i(\mathbf{n}+\mathbf{b})-v_i(\mathbf{n}+\mathbf{b})]\}^2, \qquad \mathbf{n}\in\Lambda_i\\&\quad=2h^2\,|\nabla(u_i-v_i)(\mathbf{n})|^2+\mathcal{O}(h^3)\end{aligned}$$

Noting by the trapezoid rule that

$$\frac{1}{N}\sum_{\mathbf{n}\in\Lambda_i}g(\mathbf{n})=\frac{1}{|L|}\int_{\text{lattice}}g(x)\,dx+\mathcal{O}(h^2), \qquad i=1, 2$$

we may combine the previous estimates to obtain

$$\begin{aligned}\mathscr{F}=\sum_{i=1,2}&\left\{\frac{1}{|L|}\int_{\text{lattice}}[(4\lambda_1+3\lambda_2)(u_i-v_i)^2-TS(u_i-v_i)-\lambda_1 8v_i^2+\mathcal{O}(h^2)]\right.\\&\left.+\left[-\frac{1}{2}\lambda_2h^2(|\nabla(u_i-v_i)|^2)+\mathcal{O}(h^3)\right]dx\right\}\end{aligned}$$

Next, using (5.7), we obtain

$$\begin{aligned}\mathscr{F}=\frac{1}{|L|}\int_{\text{lattice}}&\{[2(4\lambda_1+3\lambda_2)(u_i^2+v_i^2)\\&-TS(u_i-v_i)-TS(u_i+v_i)-\lambda_1 16v_i^2+\mathcal{O}(h^2)]\\&-[\lambda_2h^2(|\nabla u_i|^2+|\nabla v_i|^2)+\mathcal{O}(h^3)]\}\,dx, \qquad i=1, 2\end{aligned}$$

Representing each term by its lowest-order approximation nonvanishing contribution, we obtain the approximation

$$\hat{\mathscr{F}} = \frac{1}{|L|} \int_{\text{lattice}} [2(4\lambda_1 + 3\lambda_2)(u^2 + v^2) - TS(u - v) - TS(u + v) \\ - 16\lambda_1 v^2 - \lambda_2 h^2(|\nabla u|^2 + |\nabla v|^2)]\, dx \tag{5.9}$$

where $u \approx u_i$, $v \approx v_i$, $i = 1$ or 2. Note that the free energy is not bounded from below if $\lambda_2 > 0$.

In order to derive gradient flow equations, we determine which of our variables are conserved. It is easily checked that the way we have defined $c(\mathbf{n})$ on the extended lattice implies that within boundary effects

$$\tfrac{1}{8} \sum_{\mathbf{n} \in \Lambda_i} \sum_{\mathbf{a} \in \mathbf{A}} c(\mathbf{n} + \mathbf{a}) = \sum_{\mathbf{n} \in \Lambda_j} c(\mathbf{n}), \qquad i \neq j, \quad i, j = \{1, 2\}$$

and hence for $i, j \in \{1, 2\}$.

$$\sum_{\mathbf{n} \in \Lambda_i} u_i(\mathbf{n}) = \sum_{\mathbf{n} \in \Lambda_i} \left\{ \tfrac{1}{16} \sum_{\mathbf{a} \in \mathbf{A}} [c(\mathbf{n} + \mathbf{a}) + c(\mathbf{n})] \right\} = \tfrac{1}{2} \sum_{\mathbf{n} \in \Lambda} c(\mathbf{n}) \tag{5.10}$$

$$\sum_{\mathbf{n} \in \Lambda_i} v_i(\mathbf{n}) = \sum_{\mathbf{n} \in \Lambda_i} \left\{ \tfrac{1}{16} \sum_{\mathbf{a} \in \mathbf{A}} [c(\mathbf{n} + \mathbf{a}) - c(\mathbf{n})] \right\} = \tfrac{1}{2} \sum_{\mathbf{n} \in \Lambda_j} c(\mathbf{n}) - \tfrac{1}{2} \sum_{\mathbf{n} \in \Lambda_i} c(\mathbf{n}) \quad j \neq i \tag{5.11}$$

Clearly $\sum_{\mathbf{n} \in \Lambda} c(\mathbf{n})$ represents the total concentration of Fe on the finite lattice Λ, and thus $\sum_{\mathbf{n} \in \Lambda_i} u_i(\mathbf{n})$ is a conserved quantity. On the other hand, from (5.11) there is no reason to expect $v_i(\mathbf{n})$ to be a conserved quantity. Therefore it is consistent to assume that $u(x, t)$ is governed by a conserved gradient flow and that $v(x, t)$ is governed by a nonconserved flow. Hence we write

$$M_1 \to M_1|L| \frac{\partial u}{\partial t} = \nabla \cdot \left[M_1 \nabla \frac{\delta \hat{\mathscr{F}}}{\delta u} \right] \quad \text{and} \quad \frac{\partial v}{\partial t} = M_2 \to M_2|L| - M_2 \frac{\delta \hat{\mathscr{F}}}{\delta v} \tag{5.12}$$

While one might hope to also include cross-terms in the gradient flow, we refrain from using this more general formulation here since it will not in general imply a monotonically decreasing free energy. Employing the definition of $\hat{\mathscr{F}}$, we can write Eqs. (5.12) explicitly as

$$\frac{\partial u}{\partial t} = M_1 \Delta \{4(4\lambda_1 + 3\lambda_2)\, u - TS'(u - v) - TS'(u + v) + 2\lambda_2 h^2 \Delta u\} \tag{5.13a}$$

$$\frac{\partial v}{\partial t} = M_2 \{4(4\lambda_1 - 3\lambda_2)\, v - TS'(u - v) + TS'(u + v) - 2\lambda_2 h^2 \Delta v\} \tag{5.13b}$$

From the way in which the lattice has been extended, it is clear that the boundary conditions

$$\mathbf{m}\cdot\nabla u=\mathbf{m}\cdot\nabla\Delta u=0 \qquad \text{and} \qquad \mathbf{m}\cdot\nabla v=0, \qquad x\in\partial\Omega \tag{5.14}$$

should be imposed. Note here that this method does not yield guidelines for the relative size of the coefficients M_1 and M_2. We will return to discuss this point further in the next section.

Figure 4 gives the parameter spaces for the low-temperature behavior of an initially disordered nearly homogeneous specimen, modeled by equations (5.13) with initial conditions close to $u=\text{const}$ and $v=0$. Note that the equations are ill-posed for $\lambda_2>0$. As depicted in Fig. 4, when $\lambda_2\leqslant 0$ ordering commences if $4\lambda_1-3\lambda_2>0$, and modulations in u, that is, spinodal decomposition, for the disordered case, $v=0$, commence if $4\lambda_1+3\lambda_2<0$. The final states of the well-posed region are portrayed in Fig. 4. In particular, we see that if $\lambda_1<0$ and $\lambda_2<0$, then the final state corresponds to two terminal states with no ordering, and if $\lambda_1>0$ and $\lambda_2<0$, then the final state corresponds to separation into a pure phase $c=0$ or $c=1$ and one or both domains of an ordered CsCl. Thus we see that the final states are considerably at variance with the nature of the

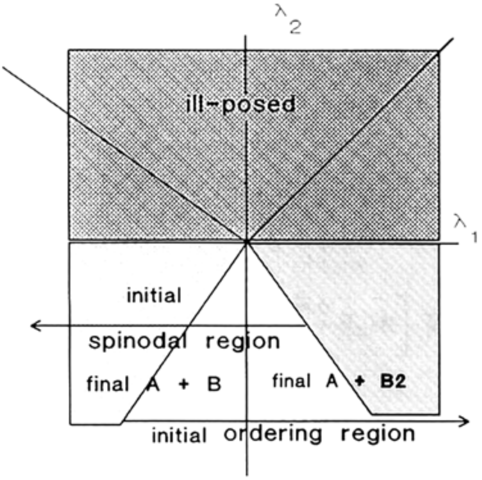

Fig. 4. The low-temperature behavior of Eqs. (5.13) for an initial state which is nearly homogeneous and disordered. Note that the equations are ill-posed for $\lambda_2>0$. The initial instabilities are described by two dividing lines, one for ordering instabilities and one for compositional instabilities; they divide the parameter region in which the equations are well-posed into three regions. In the middle region there are both compositional and ordering instabilities. The final equilibrium states of (5.13) are portrayed by one dividing line. In the region $\lambda_1<0$, $\lambda_2<0$, there is separation into two terminal phases. In the region described by $\lambda_1>0$, $\lambda_2<0$, the final equilibrium state corresponds to a mixture of ordered and thermal phases.

initial instabilities, and many interesting dynamic questions need to be addressed here. Note, though, that in terms of the final states, in the regions in which the equations are well-posed, the predictions for the well-posed region described in Fig. 2 have been reproduced.

In summary, the half-space $\lambda_2 < 0$ in which the equations are well-posed may be subdivided into four regions:

(i) The separation into two terminal phases by spinodal decomposition without ordering occupies the portion of region 1 of Fig. 2 where the coefficients of the u and v terms in Eqs. (5.13) are both negative, that is, when $4\lambda_1 < 3\lambda_2 < 0$.

(ii) Initially in the region defined by $3\lambda_2 < 4\lambda_1 < 0$, both spinodal decomposition and order–disorder type instabilities occur; however, as the final equilibrium is approached, only separation into two terminal phases is seen.

(iii) Ordering without initial phase separation occupies the portion of region 2 of Fig. 2 where the coefficients of the u and v terms in Eqs. (5.13) are both positive, that is, when $-4\lambda_1 < 3\lambda_2 < 0$. Since the final equilibrium corresponds to a mixture of ordered and terminal phases, there is a delayed spinodal decomposition that begins only after some ordering has occurred. This has been termed a conditional spinodal and has been observed in Fe–Al alloys.(13)

(iv) Ordering and simultaneous phase separation onset initially and dominate the final states in the remainder of region 2; i.e. $3\lambda_2 < -4\lambda_1 < 0$.

6. THE QUASICONTINUUM LIMIT OF THE DISCRETE EVOLUTION EQUATIONS

In this section we derive continuum equations to model the evolution of the Fe–Al system by writing down discrete evolution equations on the lattice and taking a quasicontinuum limit. We follow Richards,(1) where discrete evolution equations were written down for Fe–Al in one dimension, and develop an appropriate three-dimensional analog. Then, following the philosophy of Section 3, we introduce the variables u_i and v_i as defined in (5.1). In order to obtain a connection with the equations obtained at the end of Section 5, we further symmetrize the resultant equations by introducing variables a and b obtained by averaging over the variables u_i and v_i.

Following Richards, we assume that the evolution of the probabilities $c(\mathbf{n})$ is governed by a conserved gradient flow. In three dimensions, this implies that

$$\frac{d}{dt} c(\mathbf{n}) = Q \sum_{\mathbf{a} \in \mathbf{A}} \left\{ \frac{\delta \mathscr{F}}{\delta c(\mathbf{n}+\mathbf{a})} - \frac{\delta \mathscr{F}}{\delta c(\mathbf{n})} \right\}, \qquad \mathbf{n} \in \Lambda \qquad (6.1)$$

where $\delta\mathcal{F}/\delta c$ is the first variation of the free energy in its discrete form and Q is a mobility coefficient. Recalling (3.2), we may write the free energy $\mathcal{F}$ as

$$\mathcal{F}=\frac{1}{2N}\sum_{\mathbf{n}\in\Lambda}\left\{\frac{\alpha}{2}c^2(\mathbf{n})+G(c(\mathbf{n}))-\frac{1}{4}\lambda_1\sum_{\mathbf{a}\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a})-c(\mathbf{n})]^2\right.$$
$$\left.-\frac{1}{4}\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{b})-c(\mathbf{n})]^2\right\}$$

where $\alpha=2(4\lambda_1+3\lambda_2)$ and $G(y)=-TS(y)$. In this section it will be convenient to work with the following variant of the definition of the free energy:

$$\tilde{\mathcal{F}}=\frac{1}{2N}\sum_{\mathbf{n}\in\hat{\Lambda}}\left\{\frac{\alpha}{2}c^2(\mathbf{n})+G(c(\mathbf{n}))-\frac{1}{4}\lambda_1\sum_{\mathbf{a}\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a})-c(\mathbf{n})]^2\right.$$
$$\left.-\frac{1}{4}\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{b})-c(\mathbf{n})]^2\right\}\tag{6.2}$$

where $\hat{\Lambda}$ denotes the points of the extended lattice. We note that $\mathcal{F}$ and $\tilde{\mathcal{F}}$ vary by the contributions from the boundary effects. From (6.2), it follows that for $\mathbf{n}\in\Lambda$

$$\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n})}=\left\{\alpha c(\mathbf{n})+g(c(\mathbf{n}))+\lambda_1\sum_{\mathbf{a}\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a})-c(\mathbf{n})]\right.$$
$$\left.+\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{b})-c(\mathbf{n})]\right\}\tag{6.3}$$

where $g=G'$.

In terms of the variables u_i and v_i, we obtain from (5.1) and (6.1) that for $\mathbf{n}\in\Lambda_i$

$$\frac{d}{dt}u_i(\mathbf{n})=\frac{1}{16}\sum_{\mathbf{a}\in\mathbf{A}}\frac{d}{dt}[c(\mathbf{n}+\mathbf{a})+c(\mathbf{n})]$$
$$=\frac{QN}{8}\sum_{\mathbf{a}_1\in\mathbf{A}}\left\{\sum_{\mathbf{a}_2\in\mathbf{A}}\left[\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)}-\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n}+\mathbf{a}_1)}\right]\right.$$
$$\left.+\sum_{\mathbf{a}_2\in\mathbf{A}}\left[\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n}+\mathbf{a}_2)}-\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n})}\right]\right\}$$
$$=\frac{QN}{8}\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left[\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)}-\frac{\delta\tilde{\mathcal{F}}}{\delta c(\mathbf{n})}\right]\tag{6.4}$$

and

$$\begin{aligned}
\frac{d}{dt}v_i(\mathbf{n}) &= \frac{1}{16}\sum_{\mathbf{a}\in\mathbf{A}}\frac{d}{dt}[c(\mathbf{n}+\mathbf{a})-c(\mathbf{n})]\\
&= \frac{QN}{8}\sum_{\mathbf{a}_1\in\mathbf{A}}\left\{\sum_{\mathbf{a}_2\in\mathbf{A}}\left[\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)}-\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n}+\mathbf{a}_2)}\right]\right.\\
&\quad\left.-\sum_{\mathbf{a}_2\in\mathbf{A}}\left[\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n}+\mathbf{a}_2)}-\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n})}\right]\right\}\\
&= \frac{QN}{8}\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left[\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)}-2\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n}+\mathbf{a}_1)}+\frac{\delta\tilde{\mathscr{F}}}{\delta c(\mathbf{n})}\right] \qquad (6.5)
\end{aligned}$$

Substituting (6.3) into (6.4) and (6.5), respectively, we obtain that for $\mathbf{n}\in\Lambda_i$

$$\begin{aligned}
\frac{d}{dt}u_i(\mathbf{n}) = M\Bigg\{&\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}[\alpha c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)-\alpha c(\mathbf{n})]\\
&+\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}[g(c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2))-g(c(\mathbf{n}))]\\
&+\lambda_1\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left\{\sum_{\mathbf{a}_3\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)-c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)]\right.\\
&\left.-\sum_{\mathbf{a}_3\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a}_3)-c(\mathbf{n})]\right\}\\
&+\lambda_2\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left\{\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})-c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)]\right.\\
&\left.-\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{b})-c(\mathbf{n})]\right\}\Bigg\}
\end{aligned}$$

and

$$\begin{aligned}
\frac{d}{dt}v_i(\mathbf{n}) = M\Bigg\{&\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}[\alpha c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)-2\alpha c(\mathbf{n}+\mathbf{a}_1)+\alpha c(\mathbf{n})]\\
&+\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}[g(c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2))-2g(c(\mathbf{n}+\mathbf{a}_1))+g(c(\mathbf{n}))]\\
&+\lambda_1\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left\{\sum_{\mathbf{a}_3\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)-c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)]\right.\\
&\left.-2\sum_{\mathbf{a}_3\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_3)-c(\mathbf{n}+\mathbf{a}_1)]+\sum_{\mathbf{a}_3\in\mathbf{A}}[c(\mathbf{n}+\mathbf{a}_3)-c(\mathbf{n})]\right\}
\end{aligned}$$

$$+\lambda_2 \sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left\{\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})-c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)]\right.$$

$$\left.-2\sum_{\mathbf{b}\in\mathbf{B}}\left[c(\mathbf{n}+\mathbf{a}_1+\mathbf{b})-c(\mathbf{n}+\mathbf{a}_1))\}+\sum_{\mathbf{b}\in\mathbf{B}}\{c(\mathbf{n}+\mathbf{b})-c(\mathbf{n})\right]\right\}\Bigg\}$$

where $M=Q/32$.

Because the variables u_i and v_i have been constructed to be slowly varying for $\mathbf{n}_i\in\Lambda_i$, we can proceed by Taylor expanding. Furthermore, since by (5.5)

$$c(\mathbf{n})=u_i(\mathbf{n})-v_i(\mathbf{n}),\qquad \mathbf{n}\in\Lambda_i$$

it follows that $c(\mathbf{n}_1)$ and $c(\mathbf{n}_2)$ may also be assumed to be smoothly varying functions as long as the argument is constrained to vary only over $\mathbf{n}_i\in\Lambda_i$.

Noting that for $\mathbf{b}\in\mathbf{B}$, $\mathbf{a}_1,\mathbf{a}_2\in\mathbf{A}$, and $\mathbf{n}\in\Lambda_i$

$$\mathbf{n}+\tfrac{1}{2}+\mathbf{a}_1+\mathbf{a}_2\in\Lambda_j,\quad \mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b}\in\Lambda_i,\quad \mathbf{n}+\mathbf{b}\in\Lambda_i,\quad j\neq i$$

and that

$$|\mathbf{A}|=8\qquad\text{and}\qquad|\mathbf{B}|=6$$

and recalling the definition of v_i, we may write

$$\frac{d}{dt}u_i(\mathbf{n})=M\left\{\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left\{\alpha c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)+g(c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2))\right.\right.$$

$$+16\lambda_1 v_i(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)+\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}[\mathrm{c}(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})$$

$$\left.-c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)]\right\}-64\left\{\alpha c(\mathbf{n})+g(c(\mathbf{n}))+16\lambda_1 v_i(\mathbf{n})\right.$$

$$\left.\left.+\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{b})-c(\mathbf{n})]\right\}\right\}$$

or

$$\frac{d}{dt}u_i(\mathbf{n})=M\left\{\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\left[(\alpha-6\lambda_2)\,c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)\right.\right.$$

$$+g(c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2))+16\lambda_1 v(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)$$

$$\left.+\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})\right]-64\left[(\alpha-6\lambda_2)\,c(\mathbf{n})+g(c(\mathbf{n}))\right.$$

$$\left.\left.+16\lambda_1 v_i(\mathbf{n})+\lambda_2\sum_{\mathbf{b}\in\mathbf{B}}c(\mathbf{n}+\mathbf{b})\right]\right\}\tag{6.6}$$

Similarly,

$$\begin{aligned}\frac{d}{dt} v_i(\mathbf{n}) = M\Bigg\{ &\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}} \Bigg[(\alpha-16\lambda_1-6\lambda_2)\,c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)\\ &+ g(c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)) + 16\lambda_1 v_i(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)\\ &+\lambda_2\sum_{\mathbf{b}\in\mathbf{B}} c(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})\Bigg]\\ &-64\lambda_2 \sum_{\mathbf{b}\in\mathbf{B}}[c(\mathbf{n}+\mathbf{b})+4v_i(\mathbf{n}+\mathbf{b})] - 16\sum_{\mathbf{a}_1\in\mathbf{A}} g(c(\mathbf{n}+\mathbf{a}_1))\\ &+64[-(\alpha-16\lambda_1-6\lambda_2)\,c(\mathbf{n})+g(c(\mathbf{n}))\\ &-4(\alpha-12\lambda_1-6\lambda_2)\,v_i(\mathbf{n})]\Bigg\}\end{aligned} \qquad (6.7)$$

Equations (6.6) and (6.7) suggest that we Taylor expand expressions of the form

(i) $\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}} f(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)$

(ii) $\sum_{\mathbf{b}\in\mathbf{B}} f(\mathbf{n}+\mathbf{b})$

(iii) $\sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\sum_{\mathbf{b}\in\mathbf{B}} f(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})$

where the function f varies smoothly over $\mathbf{n}_1\in\Lambda_1$ or $\mathbf{n}_2\in\Lambda_2$. Additionally we must treat the term

(iv) $\sum_{\mathbf{a}\in\mathbf{A}} g(c(\mathbf{n}+\mathbf{a}))$

where $\mathbf{n}\in\Lambda_i$.

We introduce the notation $\mathscr{L}_4^1$, where

$$\mathscr{L}_4^1 \doteq \Delta^2 = \sum_{i,j=1}^{3} A_{ij}^1 \frac{\partial^4}{\partial^2 x_i\,\partial^2 x_j}, \qquad A_{ij}^1 = 1 \quad \forall i, j, \quad i, j = \{1, 2, 3\}$$

and $\mathscr{L}_4^2$, where

$$\mathscr{L}_4^2 \doteq \sum_{i,j=1}^{3} A_{ij}^2 \frac{\partial^4}{\partial^2 x_i\,\partial^2 x_j}, \qquad A_{ij}^2 = \delta_{ij}$$

A Taylor expansion then gives

$$\text{(i)}\qquad \sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}} f(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2)$$
$$= 64f(\mathbf{n}) + 16h^2\Delta f(\mathbf{n}) + h^4\mathscr{L}_4^3 f(\mathbf{n}) + \mathcal{O}(h^6), \qquad \mathbf{n}\in\Lambda_i$$

where $\mathscr{L}_4^3 \doteq \{2\mathscr{L}_4^1 - \frac{2}{3}\mathscr{L}_4^2\}$. Similarly,

$$\text{(ii)}\qquad \sum_{\mathbf{b}\in\mathbf{B}} f(\mathbf{n}+\mathbf{b})$$
$$= 6f(\mathbf{n}) + h^2\Delta f(\mathbf{n}) + \frac{1}{12}h^4\mathscr{L}_4^2 f(\mathbf{n}) + \mathcal{O}(h^6), \qquad \mathbf{n}\in\Lambda_i$$

Combining the above results, we obtain

$$\text{(iii)}\qquad \sum_{\mathbf{a}_1\in\mathbf{A}}\sum_{\mathbf{a}_2\in\mathbf{A}}\sum_{\mathbf{b}\in\mathbf{B}} f(\mathbf{n}+\mathbf{a}_1+\mathbf{a}_2+\mathbf{b})$$
$$= 384f(\mathbf{n}) + 160h^2\Delta f(\mathbf{n}) + h^4\mathscr{L}_4^4 f(\mathbf{n}) + \mathcal{O}(h^6), \qquad \mathbf{n}\in\Lambda_i$$

where $\mathscr{L}_4^4 \doteq \{28\mathscr{L}_4^1 + \frac{4}{3}\mathscr{L}_4^2\}$. Lastly, by (5.7) for $\mathbf{n}\in\Lambda_i$

$$\text{(iv)}\qquad \sum_{\mathbf{a}\in\mathbf{A}} g(c(\mathbf{n}+\mathbf{a})) = \sum_{\mathbf{a}\in\mathbf{A}} g(u_j(\mathbf{n}+\mathbf{a}) - v_j(\mathbf{n}+\mathbf{a}))$$
$$= \{8 + h^2\Delta + \mathcal{O}(h^4)\}\; g(u_j(\mathbf{n}) - v_j(\mathbf{n})),$$
$$i\neq j, \quad i, j\in\{1, 2\}$$

We comment that the expression in (iv) is somewhat dubious since $g(c)$ contains logarithmic terms and hence the derivatives of g cannot be guaranteed in advance to remain bounded.

First we treat the equations for u_i. Substituting (i)–(iv) into (6.6), we obtain

$$\frac{\partial u_i}{\partial t} = M\{[16h^2\Delta + h^4\mathscr{L}_4^3 + \mathcal{O}(h^6)][\alpha c(\mathbf{n}) + g(c(\mathbf{n})) + 16\lambda_1 v_i(\mathbf{n})]$$
$$+ [16\lambda_2 h^4\Delta^2 c(\mathbf{n}) + \mathcal{O}(h^6)]\}, \qquad \mathbf{n}\in\Lambda_i \tag{6.8}$$

Similarly we obtain

$$\frac{\partial v_i}{\partial t} = M(\{16(\alpha - 16\lambda_1)\,h^2\Delta c(\mathbf{n}) + \mathcal{O}(h^4)\}$$
$$256[(\alpha - 16\lambda_1)\,v_i(\mathbf{n}) + (-\lambda_1 + \lambda_2)\,h^2\Delta v_i(\mathbf{n}) + \mathcal{O}(h^4)]$$
$$+ 16h^2\{[8 + h^2\Delta + \mathcal{O}(h^4)][g(u_i(\mathbf{n}) - v_i(\mathbf{n})) - g(u_j(\mathbf{n}) - v_j(\mathbf{n}))]\}) \tag{6.9}$$

To obtain a suitably symmetric form of equation analogous to the results which were obtained in the previous section, it is necessary to introduce further symmetrized variables. Therefore, we define

$$\begin{aligned} a(\mathbf{n}) &\doteq \tfrac{1}{16} \sum_{\mathbf{a}\in\mathbf{A}} [u_1(\mathbf{n}) + u_2(\mathbf{n}+\mathbf{a})] \\ b(\mathbf{n}) &\doteq \tfrac{1}{16} \sum_{\mathbf{a}\in\mathbf{A}} [v_1(\mathbf{n}) - v_2(\mathbf{n}+\mathbf{a})], \qquad \mathbf{n}\in\Lambda_1 \end{aligned} \tag{6.10}$$

In order to exploit these variables, we note that from (5.7) it follows that for $\mathbf{n}\in\Lambda$

$$\begin{aligned} u_1(\mathbf{n}) &= u_2(\mathbf{n}) \\ v_1(\mathbf{n}) &= -v_2(\mathbf{n}) \end{aligned} \tag{6.11}$$

From (6.10) and (6.11) it then follows that for $\mathbf{n}\in\Lambda$

$$\begin{aligned} a(\mathbf{n}) &= u_1(\mathbf{n}) + \mathcal{O}(h^2) = u_2(\mathbf{n}) + \mathcal{O}(h^2) \\ b(\mathbf{n}) &= v_1(\mathbf{n}) + \mathcal{O}(h^2) = -v_2(\mathbf{n}) + \mathcal{O}(h^2) \end{aligned} \tag{6.12}$$

We now put these estimates to use. From (6.8) and the definitions of $u_i(\mathbf{n})$ and $a(\mathbf{n})$, we obtain that

$$\begin{aligned} \frac{\partial a}{\partial t} = M\Bigg(& [16h^2\Delta + h^4\mathscr{L}_4^3 + \mathcal{O}(h^6)]\Bigg\{\alpha u_1(\mathbf{n}) + \tfrac{1}{16}\sum_{\mathbf{a}\in\mathbf{A}} [g(c(\mathbf{n})) + g(c(\mathbf{n}+\mathbf{a}))] \\ & + 16\lambda_1 \sum_{\mathbf{a}\in\mathbf{A}} [v_1(\mathbf{n}) + v_2(\mathbf{n}+\mathbf{a})]\Bigg\} + [16\lambda_2 h^4\Delta^2 u_1(\mathbf{n}) + \mathcal{O}(h^6)]\Bigg) \end{aligned} \tag{6.13}$$

Note that by (5.5), (iv), and (6.12),

$$\begin{aligned} & \tfrac{1}{16}\sum_{\mathbf{a}\in\mathbf{A}} [g(c(\mathbf{n})) + g(c(\mathbf{n}+\mathbf{a}))] \\ &\quad = \tfrac{1}{16}\sum_{\mathbf{a}\in\mathbf{A}} [g(u_1(\mathbf{n}) - v_1(\mathbf{n})) + g(u_2(\mathbf{n}+\mathbf{a})) - v_2(\mathbf{n}+\mathbf{a}))] \\ &\quad = \tfrac{1}{2}[g(u_1(\mathbf{n})) - v_1(\mathbf{n})) + g(u_2(\mathbf{n}) - v_2(\mathbf{n})) + \mathcal{O}(h^2)] \\ &\quad = \tfrac{1}{2}[g(a(\mathbf{n})) - b(\mathbf{n})) + g(a(\mathbf{n}) + b(\mathbf{n})) + \mathcal{O}(h^2)] \end{aligned}$$

We note further that by (6.11)

$$\tfrac{1}{16}\sum_{\mathbf{a}\in\mathbf{A}} [v_1(\mathbf{n}) + v_2(\mathbf{n}+\mathbf{a})] = \tfrac{1}{2}[v_1(\mathbf{n}) + v_2(\mathbf{n})] + \mathcal{O}(h^2) = \mathcal{O}(h^2)$$

By (6.12) and the above estimates, (6.13) becomes

$$\begin{aligned}\frac{\partial a(\mathbf{n})}{\partial t} = M\{&(16h^2\Delta + h^4\mathcal{L}_4^3)[\alpha a(\mathbf{n}) + \tfrac{1}{2}[g(a(\mathbf{n}) - b(\mathbf{n}))] \\ &+ g(a(\mathbf{n}) + b(\mathbf{n})) + \mathcal{O}(h^2)] + [16\lambda_2 h^4 \Delta^2 a(\mathbf{n}) + \mathcal{O}(h^6)]\}\end{aligned}$$

Similarly from (6.9), and the definitions of $v_i(\mathbf{n})$ and $b(\mathbf{n})$,

$$\begin{aligned}\frac{\partial b(\mathbf{n})}{\partial t} = M\Bigg(&[-16(\alpha - 16\lambda_1)\, h^2\Delta v_1(\mathbf{n}) + \mathcal{O}(h^4)] \\ &- 256[(\alpha - 16\lambda_1)\, b(\mathbf{n}) + (-\lambda_1 + \lambda_2)\, h^2\Delta b(\mathbf{n}) + \mathcal{O}(h^4)] \\ &+ [8 + h^2\Delta + \mathcal{O}(h^4)]\Bigg\{\sum_{\mathbf{a}\in\mathbf{A}} [g(u_1(\mathbf{n}) - v_1(\mathbf{n})) \\ &+ g(u_1(\mathbf{n}+\mathbf{a}) - v_1(\mathbf{n}+\mathbf{a}))] \\ &- \sum_{\mathbf{a}\in\mathbf{A}} [g(u_2(\mathbf{n}) - v_2(\mathbf{n})) + g(u_2(\mathbf{n}+\mathbf{a}) - v_2(\mathbf{n}+\mathbf{a}))]\Bigg)\end{aligned} \tag{6.14}$$

From (6.12), we obtain that

$$\begin{aligned}&\sum_{\mathbf{a}\in\mathbf{A}} [g(u_1(\mathbf{n}) - v_1(\mathbf{n})) + g(u_1(\mathbf{n}+\mathbf{a}) - v_1(\mathbf{n}+\mathbf{a}))] \\ &\qquad - \sum_{\mathbf{a}\in\mathbf{A}} [g(u_2(\mathbf{n}) - v_2(\mathbf{n})) + g(u_2(\mathbf{n}+\mathbf{a}) - v_2(\mathbf{n}+\mathbf{a}))] \\ &\quad = 16g(a(\mathbf{n}) - b(\mathbf{n})) - 16g(a(\mathbf{n}) + b(\mathbf{n})) + \mathcal{O}(h^2)\end{aligned}$$

In considering (6.12)–(6.13), since there are already terms of $\mathcal{O}(h^4)$ which we cannot control, we employ the method of maintaining each term to lowest nontrivial order. In this fashion, we obtain from (6.12) and (6.13) the (phenomenological) equations

$$\begin{aligned}\frac{\partial a(\mathbf{n})}{\partial t} = 16Mh^2\Delta\{&\alpha a(\mathbf{n}) + \tfrac{1}{2}[g(a(\mathbf{n}) + b(\mathbf{n})) + g(a(\mathbf{n}) \\ &- b(\mathbf{n}))] + \lambda_2 h^2 \Delta a(\mathbf{n})\}\end{aligned} \tag{6.15}$$

and

$$\begin{aligned}\frac{\partial b(\mathbf{n})}{\partial t} = 256M\{&-(\alpha - 16\lambda_1)\, b(\mathbf{n}) \\ &+ \tfrac{1}{2}[-g(a(\mathbf{n}) + b(\mathbf{n})) + g(a(\mathbf{n}) - b(\mathbf{n}))] - \lambda_2 h^2 \Delta b(\mathbf{n})\}\end{aligned} \tag{6.16}$$

Noting that all quantities are assumed to be slowly varying and are evaluated at the same point, and recalling the definitions of α, g, and M, one can write (6.15)–(6.16) as

$$\frac{\partial a}{\partial t}=\frac{Q}{4}h^2\Delta\{4(4\lambda_1+3\lambda_2)\,a-T[S'(a+b)+S'(a-b)]+2\lambda_2 h^2\Delta a\} \tag{6.17a}$$

and

$$\frac{\partial b}{\partial t}=4Q\{4(4\lambda_1-3\lambda_2)\,b+T[S'(a+b)-S'(a-b)]-2\lambda_2 h^2\Delta b\} \tag{6.17b}$$

which are identical to Eqs. (5.13) in Section 5, except that the coefficients M_1 and M_2 are determined now in terms of the original coefficient Q. Again, noting the construction of the extended lattice, it is clear that double Neumann boundary conditions

$$\mathbf{m}\cdot\nabla a=0, \qquad \mathbf{m}\cdot\nabla b=0, \qquad \mathbf{m}\cdot\nabla\Delta b=0 \tag{6.18}$$

again apply.

7. SKETCH OF THE GENERAL CASE: VARIABLES AND DYNAMICS

Let us consider what is to be done in the general case. Here by the general case we refer to gradient systems governed by a free energy. It may be that the approach outlined in this section may also be useful in certain more general settings.

Let $\mathscr{F}$ denote the discrete free energy which governs the system and let us assume that our system is not too far from equilibrium. Consider now the set of homogeneous minima of $\mathscr{F}$ on an infinite lattice. If $\mathscr{F}$ is an arbitrary free energy, it will be necessary to search for these minima. If, however, we are working with some well-known system such as in the case of Fe–Al discussed in Section 3, then the set of such equilibrium states is already well known.

We denote these states by $\phi_1, \phi_2,..., \phi_l$. Each of these states is determined by prescribing the values of the concentration at the lattice vertices. In the case of multicomponent systems, it may be necessary to specify a vector of concentrations at each lattice site. With each state ϕ_i we associate a function Φ_i which prescribes this state on the infinite lattice. This may be done in one of two ways: (i) A function (or a vector function) may be prescribed which is discretely defined only at the lattice points, or which is globally defined via an array of delta functions. (ii) A suitably interpolated version of (i) may be prescribed, so that the resultant functions will be defined smoothly over the entire lattice.

We will opt here primarily for the first method; however, the second method will also be discussed below. Let us consider what these two descriptions might be for our model system, Fe–Al near the tricritical point. In such a system, two ordered variants and one disordered phase are to be expected in a region which was denoted as region 2 in Section 3. The corresponding Φ_i may be defined by

$$\begin{pmatrix}\Phi_0\\ \Phi_1\\ \Phi_2\end{pmatrix}=\begin{cases}+1 & \text{at all points of lattices } \Lambda_1 \text{ and } \Lambda_2\\ +1 & \text{on lattice } \Lambda_1 \quad \text{and} \quad -1 \text{ on lattice } \Lambda_2\\ -1 & \text{on lattice } \Lambda_1 \quad \text{and} \quad +1 \text{ on lattice } \Lambda_2\end{cases} \tag{7.1}$$

In terms of an interpolated representation we could write

$$\begin{pmatrix}\tilde{\Phi}_0\\ \tilde{\Phi}_1\\ \tilde{\Phi}_2\end{pmatrix}=\begin{cases}1\\ \cos(\pi x/h)\cos(\pi y/h)\cos(\pi z/h)\\ -\tilde{\Phi}_1\end{cases} \tag{7.2}$$

where h is the lattice spacing. Obviously, the definition of Φ_i is not unique, and there are many alternative choices, but we have chosen this description in terms of Fourier modes since this corresponds to the description given commonly in statistical physics.(14) Note that the functions Φ_i and $\tilde{\Phi}_i$ are rapidly varying if h is small.

In the general case, some analog of the functions given in (7.1) and (7.2) which may correspond to vector functions in multicomponent systems will be prescribed. In all events, the resultant functions will be rapidly varying except for the representation of the disordered phase, which in the sequel we denote by Φ_0 and by $\tilde{\Phi}_0$. In the above example, Φ_1 and Φ_2 (or $\tilde{\Phi}_1$ and $\tilde{\Phi}_2$) are linearly dependent and are variants of the same phase. We eliminate this redundancy by defining Ψ (or $\tilde{\Psi}$) to be the largest linearly independent subset of these functions. We note that in general it is also possible to choose the set Ψ ($\tilde{\Psi}$) by group-theoretic means by considering the symmetry properties of the various phases. The possible equilibria should typically contain a number of phases and their variants. In order to describe a phase and its variants, it is necessary to include in Ψ a number of functions equal to the dimension of the span of the bases of one or more irreducible representations corresponding to the space group of that phase(18) (an upper limit is given by the order of the regular representation of that group). If the possible equilibria contain a number of different types of phases, then since by our remarks above each and its variants may be described by

$$\mathrm{span}\{\Phi_0, \Phi_{i1}, \ldots, \Phi_{ij_i}\}$$

where $j_i + 1$ is the number of functions needed for the ith phase, clearly the minimal number of functions necessary to describe the different possible phases is given by

$$m + 1 = \dim\left\{\bigcup_{i=1}^{k} \{\Phi_0, \Phi_{i1}, \ldots, \Phi_{ij_i}\}\right\}$$

where k is the number of distinct types of phases. Equivalently $m + 1$ is equal to the number of linearly independent functions in the union of the bases of one or more irreducible representations of each of the individual phases.

Let us suppose that Ψ contains m functions Φ_i in addition to Φ_0 which may be considered to be functions of x/h. We introduce the following ansatz which we wish to employ to describe the concentration:

$$c(x, t) = \eta_0(x, t)\, \Phi_0 + \sum_{i=1}^{m} \eta_i(x, t)\, \Phi_i(x/h) \tag{7.3}$$

Note that if there are more than two components in the system, then $c(x, t)$, $\eta_0(x, t)$, and $\Phi_i(x/h)$ must be vector functions. However, the $\eta_i(x, t)$, $i \in \{1, \ldots, m\}$, should be scalar functions. Thus the concentration will be assumed to be a slowly varying linear combination of all the phases. The rationale for this ansatz is the principle of effective separation of scales. Near equilibrium the system may be expected to be dominated in most regions by one phase only, and all the η_i, $i \in \{1, \ldots, m\}$, except one may be expected to be nearly vanishing. In interfacial regions, the description will be less simple and a combination of the various phases will be necessary in order to give an adequate description of the phase dynamics. Ultimately the relative sizes of the various η_i must be determined by the underlying dynamics.

Earlier descriptions of order–disorder phase transitions have also been given in terms of a linear combination of phases (e.g., refs. 14 and 15) and for order–disorder transitions on BCC lattices such a description would be

$$\rho = \rho_0 + \eta \cos(\pi x/h) \cos(\pi y/h) \cos(\pi z/h) \tag{7.4}$$

where η is the order parameter. Essentially our ansatz is a slowly varying variant of (7.4) and includes the average concentration as an additional slowly varying variable. We shall speak of slowly varying variables even though they indeed vary on an $\mathcal{O}(1)$ scale, since they are slowly varying relative to the scale of the phase ordering.

We must now discuss how the $\eta_i(x, t)$ are to be determined as the continuum limit of some linear combination of the values of the concentration at the lattice vertices. In the following discussion, we assume for simplicity that the system contains no more than two components, in which case we may set $\Phi_0 = 1$. Now, since the functions Φ_i, $i = 1,..., m$, represent ordered phases on a fixed lattice, it is possible to associate with each phase a unit cell of a superlattice; i.e., the periodic unit cell of the phase. Since there are a finite number of phases, we may determine the smallest possible "unit" cell which accommodates the set of all phases Ψ. This may be accomplished as long as we do not allow for distortions of the underlying lattice.

By the assumptions stated above, the functions $\eta_i(x, t)$ are slowly varying; hence, since the dimensions of the lattice unit cell are $O(h)$, we may assume the $\eta_i(x, t)$ to be roughly constant over the unit cell. On the other hand, the function $c(x, t)$ may be expected to be rapidly varying. Assume now that $\mathbf{n} = \mathbf{n}(x)$ represents the vertex of the lattice located closest to x; then, employing the above assumptions, we deduce that (7.3) may be approximated by

$$c(x, t) = \eta_0(\mathbf{n}, t) + \sum_i \eta_i(\mathbf{n}, t)\, \Phi_i(x/h) \tag{7.5}$$

Let us now define an inner product by

$$\langle c, \Phi_i \rangle = \sum_{\mathbf{n} \in \Omega} c(\mathbf{n}, t)\, \Phi_i(\mathbf{n}/h) \tag{7.6}$$

where Ω represents the unit cell with the point x approximately at its center. Once $c(x)$ is known, $m+1$ linear equations may be obtained for the η_i, $i = 0,..., m$, by taking the appropriate inner products. While we will not elaborate on this process in detail here, it is easy to check that for the case of phase separation and ordering of binary alloys on a BCC lattice, this prescription reduces to the definitions of $u_i(\mathbf{n})$ and $v_i(\mathbf{n})$ given in (5.1) if the unit cell Ω is taken to include a vertex of the lattice and its nearest neighbors. Note also that

$$\langle c, 1 \rangle = \eta_0(\mathbf{n}, t) + \sum_i \eta_i(\mathbf{n}, t) \langle \Phi_i, 1 \rangle \tag{7.7}$$

Thus if the Φ_i have been constructed so as to be orthogonal to 1, then $\eta_0(\mathbf{n}, t)$ will represent the average concentration(s) and will be a conserved variable(s). Otherwise the linear combination of variables which appear on the right-hand side of (7.7) will represent the average concentration(s).

We now wish to return and understand the difference between the variables $u_i(\mathbf{n})$ and $v_i(\mathbf{n})$ and the variables $a(\mathbf{n})$ and $b(\mathbf{n})$. Suppose we were to return to (7.6) and redefine the inner product by integrating over some multiple of the unit cell which we denote by Ω'. Then again a set of $m+1$ equations would result, which would not necessarily coincide with the definitions for the η_i as occurred previously. The advantage of using a multiple of the unit cell is that the structure of the equilibria is more accurately represented. The disadvantage in using the larger cell is that the interfaces, which may in fact be physically quite sharp, become "blurred" over a larger region. We will not venture here into the problematics of taking a true hydrodynamic limit.(16) While we could have used definitions of variables $a(\mathbf{n})$ and $b(\mathbf{n})$ based on multiples of the unit cell, these variables have indeed been defined here by taking linear combinations of the variables $u_i(\mathbf{n})$ and $v_i(\mathbf{n})$ and their translates, which has roughly the same overall effect.

Although we will not elaborate here on the possibility of using other choices of Φ_i, clearly if the Φ_i are given in terms of Fourier modes, then the above procedure reduces to inverting a finite Fourier transform. As different variants are used for the functions Φ_i, the precise definition of the functions η_i changes accordingly.

Once the variables have been decided upon, then by going through either of the formalisms outlined in Section 5 and 6, a set of $m+1$ equations will be obtained. Clearly it is to be expected that there will be one conserved equation and m nonconserved equations. If the Φ_i are chosen appropriately, then this method should be capable of capturing anisotropy effects, if they occur in the system.

Lastly we remark that if systems with k components are treated, where $k>2$, then a similar approach should be valid. In this case, however, $k-1$ conserved equations will result, in addition to the nonconserved equations which arise from consideration of the phase variables.

8. CONCLUSION

We began with a system of discrete equations for describing the dynamics on a BCC lattice of phase separation into two phases, where the phases may be ordered. The low-temperature behavior splits into five parameter regimes. We have focused on parameter region 2, which should describe aspects of alloys, for which at low temperatures a terminal BCC solid solution coexists in equilibrium with a structure designated as B2, structure type CsCl or CuZn. We have taken continuum limits of these equations. Much hinges on what variables are chosen for the continuizing. The derivation is not rigorous in that a quasicontinuum limit has been taken and only the leading representative terms are maintained. Many open questions remain to be addressed. However, the structure of our equations is more transparent than in refs. 3 and 4. Even though the discrete system of equations describes a single diffusional process, the continuization results in a system of partial differential equations, a bistable reaction-diffusion equation for the order parameter coupled to a Cahn–Hilliard equation for the composition. Because there is only one underlying process, the kinetic coefficients in these two equations are linked.

To guarantee well-posedness, it suffices to require that the diffusion coefficient in reaction-diffusion equations and the coefficient of the fourth-order term in the Cahn–Hilliard equation be positive. We have shown that well-posedness, while clearly necessary, is not sufficient for accurate continuizing. Section 4 shows as expected, that continuizing with respect to a mean composition cannot describe ordering. Depending on the parameters, the evolution equations are either ill-posed or lead to a single homogeneous phase or separation into two terminal phases. But there the homogeneous phase is almost never a low-temperature solution of the discrete equations from which the partial differential equation was derived. Furthermore, the parameter range leading to phase separation into two terminal phases was much expanded in the partial differential equation from its domain, region 1, in the discrete equations. The processes described by the partial differential equation are constrained to avoid ordering, and will describe a phase separation without ordering when that will lower the free energy. The well-posed evolution equation in terms of mean concentration are clearly inadequate.

The simplest sets of variables that could describe both ordering into a B2 structure and phase separation were local means of composition and combinations with the structure of second differences which behave like order parameters. Continuizing leads naturally to a pair of quite different equations; a second-order reaction-diffusion or Ginzburg–Landau equation for an order parameter that is not conserved, and a fourth-order Cahn–Hilliard equation for a conserved composition. Because of the choice of the order parameter, this set of equations was not expected to be accurate in parameter regions 3, 4, and 5. Indeed they are ill-posed in those regions and in part of region 1. However, if we limit our considerations to those parameter regions in which the resultant equations are well-posed, then we see that at low temperatures, phase separation into two terminal phases is predicted in the subset of region 1 in which the equations are well-posed, and phase separation into a terminal phase and B2 is predicted in region 2 where our equations are well-posed.

We have demonstrated with these variables that the order of continuizing can be interchanged to give roughly the same results. Thus the discrepancy between the discrete and continuum equations derived from them lies elsewhere, in the fact that only the leading representative terms are maintained in these quasicontinuum limits. In Section 7, we have sketched how this approach may be extended from multicomponent multiphase systems. In forthcoming papers[9,17] further analytic as well as physical features of the equations derived here will be discussed.

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