Restricted applicability of Onsager's reciprocity relations to models of interface motion

Theodore Kaplan
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

M. J. Aziz
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

L. J. Gray
Engineering Physics and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Onsager's reciprocity relations have been applied to the motion of a planar interface in a phase transformation in a two-component system, in order to provide a test of kinetic models of alloy solidification. Although applicable to such models in general, Onsager's relations yield no information for a subclass of models in which the thermodynamic driving forces are linearly dependent to first order, as is the case for several models of alloy solidification including the continuous growth model (CGM) of Aziz and Kaplan. As a consequence, experimental tests will likely be required to distinguish between these models. If the CGM is generalized to include diffusion in the growing phase, Onsager's relations are applicable under some circumstances.

I. INTRODUCTION

Rapid solidification experiments in binary alloys[1-3] have demonstrated that there is a breakdown of local equilibrium at the crystal-melt interface and a kinetic coupling between the motions of the two atomic species across the interface during rapid interface motion. A number of models for interface motion have been developed to account for this behavior,[4-14] as well as for similar behavior in other growth processes.[15-17] A common goal of this work is the prediction of the interface velocity and the composition of the growing phase in terms of the temperature and composition of the parent phase at the interface. Due to the experimental difficulties involved in measuring the relevant quantities at a rapidly moving interface, only partial tests of some of these models have been possible[18-21] to date.

Onsager's theorem for irreversible processes,[22] deduced from time-reversal symmetry of the microscopic fluctuations that comprise steady-state behavior, identifies certain symmetries that hold for the coefficients of the linear flow equations near equilibrium. These symmetries are referred to as Onsager's reciprocity relations. For theories of phase transformations in alloys, Onsager's theorem can provide an important test of their validity near equilibrium and potentially reduce the number of theories that need to be tested experimentally. In an earlier paper,[23] Onsager's relations were applied to a phase transformation at a moving planar interface in a two-component system. The appropriate pairs of thermodynamic forces and conjugate fluxes were determined and then used to test two proposed models for binary alloy solidification, the continuous growth model (CGM) "with solute drag" and "without solute drag" of Aziz and Kaplan.[6] In this paper, it is shown that these two models and several others are members of a class of models for which Onsager's relations do *not* apply, due to a dependency in the thermodynamic driving forces near equilibrium.

In Sec. II, Onsager's relations for the case of dependent fluxes and/or forces is examined. The dependencies in the two versions of the CGM is demonstrated in Sec. III, and the inapplicability of Onsager's relations is discussed. Section IV considers a new model proposed by Ågren,[12-14] and it is shown that the same conclusions apply. In Sec. V the CGM is generalized to include diffusion in the growing phase, and it is shown that Onsager's relations are applicable under come circumstances. in Sec. VI there is a discussion of the results and in Sec. VII the work is summarized.

II. DEPENDENT FORCES AND FLUXES

Onsager's theorem deals with systems near equilibrium, where to first order the irreversible flows J are linear functions of the thermodynamic forces F. Consider a system where

$$J_i^\alpha = \sum_{j\beta} L_{ij}^{\alpha\beta} F_j^\beta, \tag{1}$$

$\alpha(\beta)$ denoting the Cartesian component of a type of current density $i(j)$. For the proper choice of *independent* fluxes J and forces F, Onsager's theorem states that the coefficients of L are symmetric,

$$L_{ij}^{\alpha\beta} = L_{ji}^{\beta\alpha}. \tag{2}$$

It has been assumed that the magnetic field is zero and that the properties of interest have even parity; this is appropriate for the solidification problem investigated.[24]

Onsager's relations are applied to the interface region of an alloy composed of A and B atoms at temperature T.
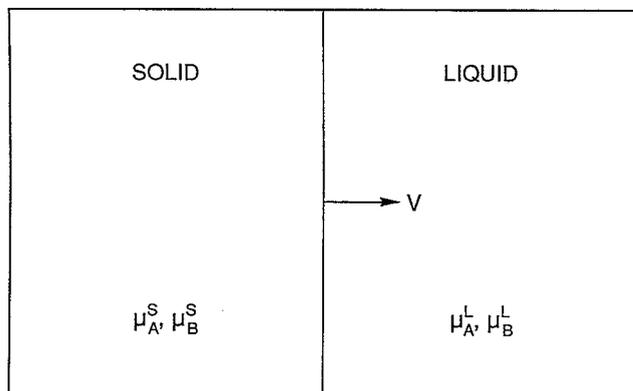
FIG. 1. A planar solid-liquid interface moving with steady-state velocity v into the liquid. The indicated chemical potentials are evaluated immediately adjacent to the interface.

The liquid and solid phases are separated by a planar interface moving into the liquid at steady state velocity v (see Fig. 1). It is assumed for simplicity that

$$n_A^S + n_B^S = n_A^L + n_B^L = n, \tag{3}$$

where $n_A^S(n_B^S)$ and $n_A^L(n_B^L)$ are the number density of $A(B)$ atoms in the solid and liquid immediately adjacent to the interface, respectively. For notational simplicity, we introduce the concentration, $x_\alpha = n_B^\alpha/n$, $\alpha = S, L$.

It is shown in Ref. 23 (hereafter referred to as paper I), that a proper choice of fluxes and forces that satisfy the hypothesis of Onsager's theorem is

$$J_1 = n_A^S v = n(1 - x_S) v, \tag{4a}$$

$$J_2 = n_B^S v = n x_S v, \tag{4b}$$

$$F_1 = (\mu_A^L - \mu_A^S)/T = -\Delta\mu_A/T, \tag{4c}$$

$$F_2 = (\mu_B^L - \mu_B^S)/T = -\Delta\mu_B/T, \tag{4d}$$

where $\mu_A^S(\mu_B^S)$ and $\mu_A^L(\mu_B^L)$ are the chemical potentials of the $A(B)$ atoms in the solid and liquid, respectively. This choice of fluxes and forces is not unique. Two other choices as well as a general transformation are given in paper I. We reemphasize our conclusions in paper I that in order to make a proper choice, one cannot examine only the expression for the entropy production rate but rather one must start with the expression for the entropy and take the partial derivatives according to Onsager's prescription.

For the analysis of the solidification models, the assumption in Onsager's theorem of independent forces and fluxes will turn out to be an important issue. This assumption can in fact be relaxed somewhat. First of all, DeGroot and Mazur proved that if there is a linear homogeneous dependency, $\Sigma_{i=1}^m \alpha_i J_i = 0$, amongst the fluxes but the forces remain independent, Eq. (2) remains valid.[25] (Note that in this case the L matrix must be singular.) If, however, both the fluxes and the forces are dependent, then the phenomenological coefficients, L, are not uniquely defined and Onsager's relations are not necessarily fulfilled (among the unlimited number of choices for L, there will be a

symmetric system).[25] Therefore, for dependent fluxes and forces, Onsager's theorem does not say anything about the form of the L matrix and it cannot be used to test a particular model. Finally, it should also be noted that just having dependent forces together with Eq. (1), is sufficient to rule out a unique set of coefficients L. It is clear that adding any constant times the force dependency equation, $\Sigma_{i=1}^m \beta_i F_i = 0$, to the right-hand side of Eq. (1) results in a different L matrix.

For the two-component solidification models under consideration, note that

$$x_S J_1 = (1 - x_S) J_2, \tag{5}$$

and thus at equilibrium

$$J_1/J_2 \to (1 - x_{S0})/x_{S0}, \tag{6}$$

where x_{S0} is the equilibrium mole fraction of B atoms in the solid. The existence of this limit as $\|F\| \to 0$ $[F = (F_1, F_2)]$ indicates that, to first order in the forces, there is a homogeneous relationship between the fluxes. This is sufficient to establish the dependence of the fluxes, as Onsager's theorem only deals with first-order quantities. As indicated earlier, this dependence does not rule out the use of Onsager's theorem. However, it will turn out that, in three of the models discussed below, the forces are dependent in the same sense as the fluxes, that is to first order. Onsager's theorem therefore will not provide any information about these models.

It is worth noting that dependent forces, while not typical, are not ruled out by thermodynamics. For example, the thermodynamic forces for diffusion in a two-component liquid are dependent, a consequence of the Gibbs–Duhem relationship.

III. ANALYSIS OF CONTINUOUS GROWTH MODELS

Two models were considered in paper I, the continuous growth models "with solute drag" and "without solute drag."[6] The essential assumption of these models is that the interface velocity is related to the chemical potential differences across the interface.

A. Driving forces

The conclusions that can be drawn by considering only the flux equations (4a) and (4b) and equations in the models relating solidification velocity to a driving force, will first be discussed.

1. Continuous growth model without solute drag

For the model "without solute drag," near equilibrium, the velocity-driving force equation reduces to the form

$$v = v_R[(1 - x_S) F_1 + x_S F_2], \tag{7}$$

where $v_R = v_0/R$ and R and v_0 are constants defined in paper I [see Eqs. (4.3) and (4.5) of paper I]. Near equilibrium the concentrations can be expanded,
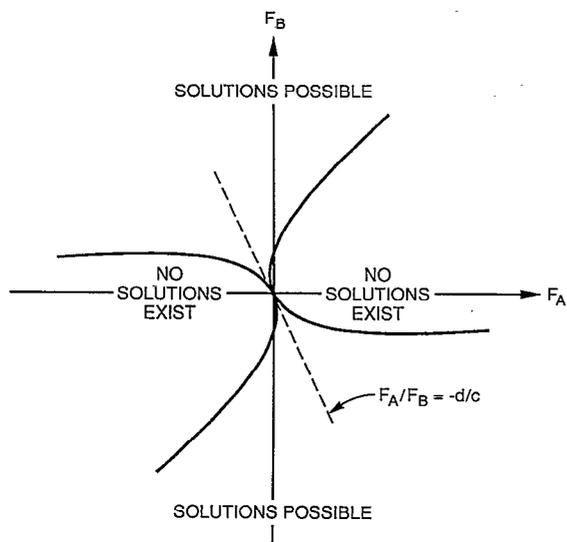
FIG. 2. Sketch of the solution space for the continuous growth model. Note that Eq. (11) restricts the solution to be very near the straight line $F_1/F_2 = -d/c$ near equilibrium.

$$x_L = x_{L0} + \Delta x_L,$$

$$x_S = x_{S0} + \Delta x_S, \tag{8}$$

where x_{L0} and x_{S0} are the equilibrium concentrations. Combining Eqs. (4), (7), and (8), and keeping terms to second order in F_1, F_2, and Δx_S yields

$$J_1 = n v_R \{ [(1-x_{S0})^2 F_1 + (1-x_{S0}) x_{S0} F_2]$$

$$+ \Delta x_S [2(x_{S0}-1) F_1 + (1-2x_{S0}) F_2] \}, \tag{9a}$$

$$J_2 = n v_R \{ [(1-x_{S0}) x_{S0} F_1 + x_{S0}^2 F_2]$$

$$+ \Delta x_S [(1-2x_{S0}) F_1 + 2x_{S0} F_2] \}. \tag{9b}$$

Consider the terms involving Δx_S in Eq. (9). One way to get a contribution to the J's that is linear in F's is for Δx_S to have the form

$$\Delta x_S = \frac{c F_1 + d F_2}{e F_1 + f F_2} + \mathcal{O}(\|F\|), \tag{10}$$

where c, d, e, and f are constants. By definition $\Delta x_S \to 0$ as $F_1, F_2 \to 0$. Therefore the first term on the right-hand side of the equation is not well defined at equilibrium ($F_1, F_2 \to 0$) unless

$$c F_1 + d F_2 = 0. \tag{11}$$

This condition constrains the solution near equilibrium to exist in a limited region of $\{F_1, F_2\}$ space. This space is roughly characterized as points $\{F_1, F_2\}$ whose distance from the line $c F_1 + d F_2 = 0$ is of order $F_1^2 + F_2^2$. A schematic of the solution space is depicted in Fig. 2. Although the linear homogeneous relationship $c F_1 + d F_2 = 0$ holds only *at* equilibrium, it nevertheless holds *to first order* in the neighborhood of the equilibrium point. As Onsager's theorem applies only to the first order expansion of the fluxes in terms of forces, the forces must therefore be considered to be dependent. According to the theorems, the L

matrix is not unique and Onsager's theorem does not tell us anything about the validity of this type of model.

A second possibility is that

$$\Delta x_S \sim \mathcal{O}(\|F\|). \tag{12}$$

Then the terms proportional to Δx_S in Eq. (9) are second order and can be neglected. In this case,

$$J_1 = n v_R [(1-x_{S0})^2 F_1 + (1-x_{S0}) x_{S0} F_2],$$

$$J_2 = n v_R [(1-x_{S0}) x_{S0} F_1 + x_{S0}^2 F_2], \tag{13}$$

$$L_{12} = L_{21} = n v_R (1-x_{S0}) x_{S0},$$

and Onsager's theorem is satisfied. As indicated in Sec. II, the L matrix must be singular.

2. Continuous growth model with solute drag

A similar analysis can be carried out for the continuous growth model "with solute drag." In this model

$$v = v_R [(1-x_L) F_1 + x_L F_2]. \tag{14}$$

Again a solution can be constructed of the form of Eq. (10) for Δx_S and Δx_L. This leads to a constraint of the form given in Eq. (11). As before, the forces and fluxes are dependent and Onsager's theorem does not apply. If, however, Δx_S and Δx_L are linear in the forces, all terms in Eq. (9) with Δx_S are second order and can be neglected. This yields

$$J_1 = n v_R [(1-x_{S0})(1-x_{L0}) F_1 + (1-x_{S0}) x_{L0} F_2],$$

$$J_2 = n v_R [x_{S0}(1-x_{L0}) F_1 + x_{S0} x_{L0} F_2], \tag{15}$$

$$L_{12} = n v_R (1-x_{S0}) x_{L0},$$

$$L_{21} = n v_R x_{S0}(1-x_{L0}),$$

$$L_{12} \neq L_{21},$$

and Onsager's theorem is not satisfied. Once again the fluxes are dependent and the L matrix is singular.

B. Complete models

While it is interesting to look at the possibilities dictated by considering only the flux equations (4a) and (4b) and the velocity-driving force equations (7) or (14), the actual solution to the complete model for the concentrations in terms of the forces does not depend on the flux equations at all. The complete model is given by Eqs. (7) or (14) combined with the kinetic equations for the partition coefficient [Eqs. (4.1) and (4.2) in paper I] and the constitutive relations for the material [Eqs. (4.6) and (4.7) in paper I]. The solution for both versions of the continuous growth model is given in paper I, the model "with solute drag" in Eqs. (4.10) and (4.11) and the model "without solute drag" in Eqs. (4.20) and (4.21). It was found that the first possibility described in Sec. III A 1 and III A 2 arises for both theories; i.e., an equation of the form of Eq. (10) rather than Eq. (12) is found and thus $c F_1 + d F_2 \sim \mathcal{O}(\|F\|^2)$. Due to this homogeneous depen-

dence of the forces, a unique L matrix does not exist and Onsager's theorem does not apply to either of the models.

It is not clear whether the dependency in the forces is due to the simplifying assumptions used in constructing the models, or whether it is an implicit physical constraint associated with the maintenance of the interface region in steady-state solidification (e.g., the infinite planar interface with no solid-phase diffusion). Regardless, this result indicates that Onsager's theorem cannot tell us anything about the validity of these models, and some other methods (e.g., experiment) must be considered.

For any of these models the L matrix can be calculated by examining the expansion for Δx_S and Δx_L as was done in paper I or by evaluating the derivatives of the fluxes,

$$L_{ij}=\lim_{\|F\|\to 0}\left(\frac{\partial J_i}{\partial F_j}\bigg|_{cF_1+dF_2=0}\right).$$

These methods yield two different solutions for the L matrix, members of an infinite set of solutions that are simply related to one another: the difference between any two solutions in this set is a constant times Eq. (11) [Eq. 4.16] for the model with solute drag and Eq. (4.25) for the model without solute drag in paper I]. We see that several differing but perfectly valid derivations yield apparently different L matrices. However, they all give the same physical behavior due to the dependency in the F's, Eq. (11).

IV. ÅGREN'S MODEL

Ågren[12-14] has developed a model that is very similar to the continuous growth model. In linearized form the equations that define his model are

$$J_D=-(L'T/V_m)(F_1-F_2),\tag{16a}$$

$$J_D=\frac{v}{V_m}(x'-x_S),\tag{16b}$$

$$v=-MT[x'F_2+(1-x')F_1],\tag{16c}$$

$$x'=(x_L+x_S)/2,\tag{16d}$$

where V_m is the molar volume and L' and M are constants.[14] These equations do not completely define the problem; a set of thermodynamic relations describing the material are needed as well. Combining Eq. (16) with the material constitutive relations given in Eqs. (4.6) and (4.7) of paper I, completes the statement of the model. The solution for the concentrations is once again of the form given in (10), and the forces are dependent. This is not surprising, as Ågren has pointed out that his model reduces to the continuous growth model with and without solute drag if Eq. (16d) is replaced by $x'=x_L$ and x_S, respectively.[14]

Ågren's choice for the fluxes is

$$J_D=\frac{v}{V_m}(x'-x_S),\tag{17a}$$
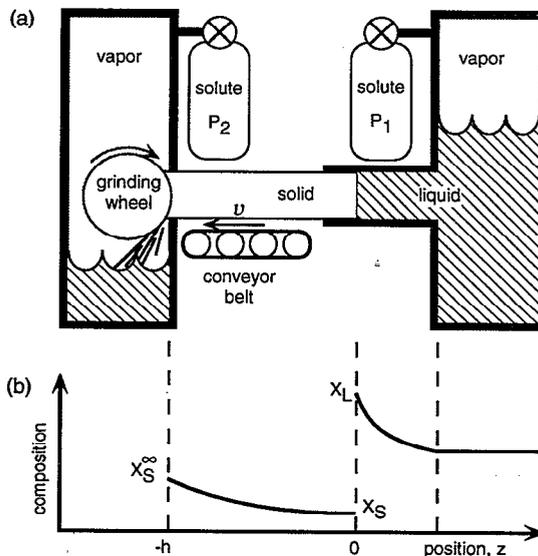
$$J_C=\frac{v}{V_m}.\tag{17b}$$

FIG. 3. Steady-state solidification with steady-state diffusion in growing solid. (a) Crystal is pulled at constant velocity v to left. Grinding wheel results in solute source/sink at a fixed distance from the growth front. Solute diffusion is controlled independent of solidification rate by varying solute partial pressure in the reservoirs. (b) A plot of what the concentration of solute (B) atoms might look like as a function of position perpendicular to the interface, z.

Taking the ratio of J_D and J_C near equilibrium and using Eq. (16d) yields

$$\frac{J_D}{J_C}\to\frac{x_{L0}-x_{S0}}{2}.\tag{18}$$

Both the fluxes and forces are homogeneously dependent and once again the L matrix is not uniquely defined. Thus, although Ågren was able to cast his coefficient matrix in a symmetric form, he just as easily could have written it in an asymmetric form. Again we reach the conclusion that Onsager's theorem does not require either of these forms.

V. INCLUSION OF DIFFUSION IN THE GROWING PHASE

It has been suggested that the dependency of the forces is an artifact of setting up the problem with no solid diffusion, and that incorporating even a small amount of solid diffusion would eliminate the force constraints.[11] In this section, the consequence of having nonzero diffusion in the growing phase is considered.

The steady state solidification model can be changed by adding diffusion in the solid so that Onsager's theorem can be applied to a generalized version of the continuous growth model. In order to have the diffusion affect the steady-state process, an additional boundary is included in the solid, also moving at velocity v at a distance h from the interface. (We show in Fig. 3 that such a steady state is physically possible.) At this new planar boundary, the concentration of B atoms is fixed at x_S^∞ (see Fig. 3). For this model, near equilibrium,

$$J_1 = n(1-x_S)v - nD\frac{\partial x_S}{\partial z}\Big|_{\text{interface}},$$

$$J_2 = nx_S v + nD\frac{\partial x_S}{\partial z}\Big|_{\text{interface}}, \tag{19}$$

where D is the diffusion coefficient in the solid and the gradient is evaluated on the solid side of the interface. J_1 and J_2 are the time derivatives of the total number of A and B atoms, respectively, on the solid side of the interface per unit area.

We wish to construct equations for the solidification process that reduce to the continuous growth model in the limit $D\to 0$ and $h\to\infty$. At the solid-liquid interface, the composition of material incorporated into the solid, x_r, is defined as

$$x_r = J_2/(J_1+J_2) = J_2/vn. \tag{20}$$

If we construct the velocity-driving force equation to be of the form

$$v = v_R[(1-x_r)F_1 + x_r F_2] \tag{21}$$

then in the limit $D/h\to 0$, we find $J_2\to x_S v$, $x_r\to x_S$ and Eqs. (19) and (21) reduce to the no solute drag version of the continuous growth model. The equations needed to complete the model are the same as before. They are the kinetic equations, (4.1) and (4.2), and the constitutive relations, Eqs. (4.6) and (4.7), all from paper I.

Expanding the concentrations about equilibrium as was done in Eq. (8), combining with Eqs. (4.1), (4.2), (4.6), and (4.7) of paper I, and keeping terms to second order yields

$$\Delta x_S[a_S v + b_S(F_2-F_1)]$$

$$= a_0 v + b_0(F_2-F_1) + \left(\frac{F_1}{T_A c_L} - \frac{F_2}{T_B c_L}\right)$$

$$\times [v + b_L(F_2-F_1)] + \cdots,$$

$$a_0 = (x_{S0} - x_{L0}),$$

$$b_0 = v_D(x_{L0}-1)x_{S0},$$

$$a_S = (c_S/c_L - 1), \tag{22}$$

$$b_S = v_D[(1-x_{L0}) - x_{S0}c_S/c_L],$$

$$b_L = -v_D x_{S0},$$

where the various constants v_D, c_S, c_L, T_A, T_B are defined in paper I. To lowest order (recall v is linear in F_1 and F_2)

$$\Delta x_S = \frac{a_0 v + b_0(F_2-F_1)}{a_S v + b_S(F_2-F_1)} + \mathcal{O}(\|F\|). \tag{23}$$

This fraction must be treated in the same manner as was done in Eq. (10). In order for $\Delta x_S\to 0$ as $F_1, F_2\to 0$, it is required that to first order

$$a_0 v + b_0(F_2-F_1) = 0. \tag{24}$$

Substituting the expression (21) for v in Eq. (24) yields

$$x_r = -\frac{b_0}{a_0 v_R} - \frac{F_1}{F_2-F_1}. \tag{25}$$

From Eq. (25) we see that F_1 and F_2 are now independent and x_r is undefined at equilibrium. Its value depends on the direction of approach. The solution is undefined on the line $F_1 = F_2$ as well. Combining Eq. (25) with Eqs. (19) and (20), we can solve for the L matrix.

$$J_1 = nv_R[g^2 F_1 + (g-g^2)F_2],$$

$$J_2 = nv_R[-(g+g^2)F_1 + g^2 F_2],$$

$$L_{12} = nv_R(g-g^2), \tag{26}$$

$$L_{21} = -nv_R(g+g^2),$$

where $g = -b_0/a_0 v_R$. The L matrix is not symmetric and Onsager's relations are *not* satisfied.

In the limit that $D\to 0$ and $h\to\infty$, we find $x_r\to x_S$ and this model becomes the "without solute drag" version of the continuous growth model. From physical considerations this limit appears to be meaningful. Furthermore, the linear flow equations in Eq. (26) are equal to those in Eq. (23) [Eq. 4.26 of paper I] plus a constant times the homogeneous equations for F_1 and F_2 given in Eq. (4.25) of paper I. One can add any multiple of Eq. (4.25) to Eq. (13) since to first order Eq. (4.25) is zero. This demonstrates a continuity of the L matrix in this limit. Note, however, that the solution space changes discontinuously at $D/h=0$ from one where all fluctuations are allowed (F_1 and F_2 independent) to a restricted one (shown in Fig. 2) where only a very limited set of fluctuations is allowed. This discontinuity may make the drawing of any meaningful conclusions from this limit questionable.

The version of the diffusion model that reduces to the continuous growth model "with solute drag" in the limit $D\to 0$ and $h\to\infty$ is obtained by substituting Eq. (14) for Eq. (21) in the aforementioned analysis. This version turns out not to yield any new behavior. Even with diffusion, in this form of the model, the forces are dependent to first order.

VI. DISCUSSION

Caroli et al.[11] suggest that the premature inclusion of the homogeneous dependence of the fluxes [Eqs. (4a) and (4b)] that is inherent in solidification without solid diffusion will lead to errors when applying Onsager's relations. The discussion in Sec. II shows that in general this is not the case. The proof by DeGroot and Mazur[25] shows that as long as the forces remain independent even if the fluxes are homogeneously dependent, Onsager's relations hold. Furthermore, including solid diffusion to remove the dependency among the fluxes is no guarantee that Onsager's relations are applicable. In Sec. V it was found that including solid diffusion in the CGM with solute drag still led to a system in which the forces were dependent near equilibrium and Onsager's relations could not be used. It was also found that the generalization of the CGM without solute drag to include solid diffusion resulted in a model in which the fluxes and forces are independent and Onsager's theo-

rem applies. Therefore, whether or not solid diffusion is included is not the key issue when applying Onsager's theorem. It is the structure of the solution space (see Fig. 2) that determines whether or not Onsager's theorem is applicable.

We have employed three different ways to evaluate the L matrix for the CGM models: by expanding the fluxes in terms of the forces at equilibrium, by taking the partial derivatives of the fluxes with respect to the forces near equilibrium and then taking the limit as equilibrium is approached, and by taking the $D/h \to 0$ limit of the model generalized to include diffusion in the solid. The three methods give different L matrices, which has been a cause for considerable consternation in the past. Here it is shown why all three matrices are equally valid and give identical physical behavior. As a result of the linear dependency of the forces, any one of the L matrices can be obtained from any other by the addition of a constant times the linear dependency condition for the forces, Eq. (11), to the rows of L.

VII. SUMMARY

(1.) If the driving forces and fluxes are independent and are defined according to Onsager's prescription. Onsager's relations require a certain symmetry for the matrix of phenomenological coefficients of the linear flow equations, L, near equilibrium. As has been shown in paper I, the proper definition is derived from the partial derivatives of the entropy itself and not the entropy production rate.

(2.) It has been known for some time[25] that the independence of both the fluxes *and* the forces is not necessary. As long as the forces remain independent, a linear homogeneous dependency amongst the fluxes does not rule out the use of Onsager's relations. We have shown here, however, that a dependency among the forces as in Eq. (11) means the L matrix is not unique and Onsager's theorem does not place any requirements on its symmetry.

(3.) The equations of the CGM, both with and without solute drag, lead to a linear homogeneous dependency between the thermodynamic driving forces. The velocity-driving force relations and the kinetic equations for solute partitioning, combined with the constitutive relations for the thermodynamics of the phases and the requirement that the concentrations approach their equilibrium values continuously, necessarily restrict the fluctuations of the forces in the neighborhood of equilibrium. The dependency of the fluxes, Eqs. (4a) and (4b), is not responsible for this behavior. The force dependency is not apparent when the full set of equations for a model, including the constitutive relations, are not considered. Since the L matrix is not uniquely defined by dependent forces, Onsager's theorem yields no conclusions about the validity of either version of the CGM.

(4.) Because the forces are also linearly dependent in Ågren's model, Onsager's relations impose no requirement on the symmetry of the L matrix therein.

(5.) When the CGM "with solute drag" is generalized to include diffusion in the solid phase, the forces remain dependent to first order and Onsager's relations do not apply.

(6.) When the CGM "without solute drag" is generalized to include diffusion in the solid phase, the forces (and fluxes) become independent. In this case, the resulting L matrix is not symmetric, violating Onsager's theorem, and thus this model is not valid.

(7.) It is not clear that this last conclusion can be extended to the corresponding (no solid diffusion) CGM "without solute drag." Taking the limit $D/h \to 0$ yields an asymmetric L matrix which is one of the infinite possibilities [a constant times Eq. (11) can always be added to the rows of L] obtained by a direct analysis of the no-diffusion CGM model. From physical considerations, the limit appears to be meaningful, and it is therefore tempting to eliminate this model also. However, the solution space changes discontiuously at $D/h = 0$, and therefore drawing conclusions from this limit analysis is questionable.

(8.) For the CGM models, there are at least three ways of evaluating the L matrix and they all lead to different results. It has been shown that they are all equally valid (i.e., yield identical physical behavior) and are related to one another through the linear dependency in the forces, Eq. (11).

(9.) For any model with dependent forces, whether the dependency is due to simplifying assumptions in the model or an implicit physical constraint associated with the maintenance of the interface region in steady-state solidification, the conclusion remains the same: Onsager's theorem yields no information about the validity of such a model.

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