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DEFORMATION DURING INTERDIFFUSION

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Abstract—A general theory of stress and deformation during interdiffusion is presented which spans the gap between the Darken analysis of the Kirkendall effect and the recent treatment by Larché and Cahn of the interaction between stress and diffusion. Special consideration is given to the generation of internal stress and vacancy chemical potential, to the contribution of these potentials to the diffusion potentials, to the relaxation of these potentials via plastic deformation and vacancy creation/annihilation, and to convective transport due to deformation induced by diffusion. When the mobilities or the partial molal volumes of the components differ, the coupling of the relaxation equations for plastic strain and vacancy creation to the diffusion equations for the component densities can lead to a change in the rate-limiting step for interdiffusion as a function of the distance scale of the composition and stress profiles. The characteristic lengths at which these changes occur are determined by relations between the mobilities, the viscosity, and the rate constant for vacancy creation. When a relaxation process is rate-limiting, composition penetration profiles have an exponential (rather than error-function) form, and the integrated amount of material transported increases linearly with time (rather than as $t^{1/2}$).

Résumé—Nous présentons une théorie générale de la contrainte et de la déformation pendant l'interdiffusion, qui rapproche l'analyse de l'effet Kirkendall due à Darken, et le traitement récent de l'interaction entre contrainte et déformation proposé par Larché et Cahn. Nous considérons plus particulièrement l'apparition d'un potentiel chimique de contraintes internes et de lacunes, la contribution de ces potentiels aux potentiels de diffusion, la relaxation de ces potentiels par déformation plastique et par annihilation ou création de lacunes et le transport par convection dû à la déformation induite par diffusion. Quand les mobilités ou quand les volumes molaires partiels des composants sont différents, le couplage des équations de relaxation pour la déformation plastique et la création des lacunes avec les équations de diffusion pour les densités des composants peut conduire à un changement due stade qui contrôle l'interdiffusion, fonction de l'échelle des profils de composition et de contrainte. On peut déterminer les longueurs caractéristiques pour lesquelles apparaissent ces changements à l'aide de relations entre les mobilités, la viscosité et la constante de vitesse pour la création des lacunes. Quand un mécanisme de relaxation limite la vitesse, les profils de pénétration de la composition ont une forme exponentielle (plutôt qu'une forme de fonction d'erreur), et la quantité intégrée de matériau transporté croît linéairement avec le temps (plutôt qu'en $t^{1/2}$).

Zusammenfassung—Es wird eine allgemeine Theorie der während der Interdiffusion auftretenden Spannungen und Verformungen vorgelegt, die die Lücke zwischen der Analyse des Kirkendall-Effektes von Darken und der neueren Behandlung der Wechselwirkung zwischen Spannung und Diffusion von Larche' und Cahn füllt. Besonderes beachtet wird die Erzeugung innerer Spannungen und des chemischen Potentials der Leerstellen, der Beitrag dieser Potentiale zu den Diffusionspotentialen, die Relaxation dieser Potentiale durch plastische Verformung und Leerstellenbildung/-annihilation und der konvektive, durch die Diffusion über die Verformung erzeugte Transport. Unterscheiden sich die Beweglichkeiten oder die partialen Molvolumen der Komponenten, dann kann die Kopplung der Relaxationsgleichungen für plastische Dehnung und Leerstellenerzeugung an die Diffusionsgleichungen für die Dichte der Komponenten zu einem Wechsel im ratenbestimmenden Schritt der Interdiffusion in Abhängigkeit von der Abstandsskala in Zusammensetzung und Spannungsprofil führen. Die charakteristischen Abstände, unter denen diese Wechsel auftreten, werden durch die Zusammenhänge zwischen den Beweglichkeiten, der Viskosität und der Ratenkonstanten für die Leerstellenerzeugung festgelegt. Ist ein Relaxationsprozeß der ratenbestimmende Schritt, dann sind die Durchdringungsprofile der Konzentrationsverläufe exponentiell (statt der Fehlerfunktion); in diesem Fall steigt der integrierte Anteil des transportierten Materials linear mit der Zeit an (statt wie $t^{1/2}$).

1. INTRODUCTION

In either amorphous or crystalline solids, the overall interdiffusion process can involve a complex set of interactions between the diffusive transport of each chemical component, the generation of internal stress, and convective transport due to the induced deformation. For example, consider a system which initially has non-uniform composition but is in a state of zero stress. When the components have different partial molal volumes or mobilities, their simultaneous diffusion can give rise to an imbalance in the "volume" transport (i.e. a non-uniform stress-free strain). To accommodate this imbalance, elastic strain and internal stress are generated. The internal stress contributes to the thermodynamic potentials for both diffusion and plastic deformation. The resulting plastic strain tends to relax the stress generated by diffusion, and the overall deformation produces convective transport (the Kirkendall effect [1]). In crystalline substitutional solid solutions, the involvement of vacancies in the diffusion mechanism can lead to additional complications, such as the generation of an internal vacancy chemical potential coupled to deformation through vacancy creation/annihilation at boundaries or extended defects. The effects of this vacancy chemical potential are analogous to those of the internal stress, since both enter into the potentials driving diffusive and convective transport.

Recent fundamental treatments by Larché and Cahn of the generation of internal stress during interdiffusion [2, 3], and of the stress contribution to the diffusion potentials [3–5], focus on the behavior of systems which can reach equilibrium under nonhydrostatic stress, such as the interior of perfect crystals. In these models, stress relaxation and convective transport due to plastic deformation and vacancy creation/annihilation are not allowed, and it is assumed that the lattice remains coherent (i.e. lattice sites are conserved) in order to relate the internal stress distribution to the composition distribution. On the other hand, in the seminal analysis of convective transport during interdiffusion given by Darken [6], the contributions of stress and vacancy chemical potential to the diffusion potentials are neglected. In the Darken analysis it is assumed that the distance scale over which the interdiffusion occurs is sufficiently large such that the time constant for relaxation of these contributions by plastic deformation and vacancy creation/annihilation is small relative to the time constant for diffusion [7]. The purpose of this paper is to develop a treatment of interdiffusion which takes into account both the effects of stress and vacancy chemical potential terms in the diffusion potentials, and also the relaxation of these terms and the resulting convective transport. Such a treatment will be applicable to amorphous and defective crystalline systems at relatively small distance scales, a regime in which one or another of the assumptions used in previous models are not generally valid. A detailed theory is developed first for an amorphous system having internal stress (but no vacancy chemical potential) in which plastic deformation occurs by Newtonian viscous flow. The modifications necessary to apply this model to defective interstitial and substitutional crystalline systems are then considered.

A brief letter has been published elsewhere [8] describing some of the results of the model which is presented in detail here. This model provides a foundation for previous work on spinodal decomposition in amorphous systems [9], primarily by addressing the nature of stress-free strain in a system with no site conservation constraint. The treatment differs from others recently proposed [10, 11], particularly in the relationships used between composition and strain and between stress and the diffusion fluxes.

2. THEORY FOR AN AMORPHOUS SYSTEM

Kinetic equations for interdiffusion in a multicomponent amorphous system are developed below. Diffusion fluxes and strains are first carefully defined, and their relationships to component densities are obtained. Maxwell-solid constitutive relations are used to relate elastic and plastic strain to stress. A new general definition for the stress-free strain coupling diffusion to strain is proposed. Diffusion potentials are derived which include the internal stress. Several basic kinetic equations then determine the evolution of the system: a diffusion equation for each component, and a relaxation equation for plastic strain. These are written as coupled differential equations for the composition variables and the stress.

To demonstrate the behavior predicted by these coupled differential equations, an analytical solution for small composition changes in a two-component system is obtained by linearizing the equations and making a quasi-steady-state approximation. It is found that internal stress effects are important when the product of the partial molal volume and the mobility of one component differs significantly from that of the other. The evolution of the composition is described by a simple Fickian diffusion equation in two limiting cases. In the limit of low viscosity or large distance scale, the interdiffusion coefficient is given by the Darken expression [6]. In the limit of high viscosity or small distance scale, one obtains an interdiffusion coefficient of the Nernst–Planck type [12]. In general, however, the rate-limiting step changes with time as the distance scale of the interdiffusion process changes, and a Fickian diffusion equation does not describe the behavior of the system. The characteristic lengths, at which the rate-limiting step changes from diffusion of the "slower" component, to plastic deformation, to diffusion of the "faster" component, are obtained in terms of products of the viscosity and the mobilities. Graphs are presented showing the qualitative differences between the shapes of composition profiles encountered during various stages of interdiffusion. It is found that the integrated amount of material transported increases linearly with time when plastic deformation is rate-limiting, in contrast to the parabolic ($t^{1/2}$) time dependence obtained when diffusion is rate-limiting.

2.1. Coordinates, densities and fluxes

In general, it is necessary to carefully distinguish between transport due to diffusion and that due to deformation (convection) in order to model interdiffusion in a multicomponent system [6]. This development therefore begins at a fundamental level, so that the definitions of the quantities under discussion are clear. Following the usual practice in continuum mechanics, deformation is modelled here using a material (Lagrangean) coordinate system, imagined as being imbedded in and deforming with the solid. The deformation is defined by the motion of the material coordinate system relative to a fixed spatial (Eulerian) coordinate system [13]. Diffusion fluxes are then defined relative to the material coordinate system. The material coordinate system is similar to the "network" of Larché and Cahn [2–5] in that it defines the total deformation; however, since plastic deformation is allowed here, the total deformation alone does not determine the stress state. It is not necessary at the outset to specify the relationship between the material coordinate system and the atomic structure of the solid. Rather, as in the Darken analysis, it is assumed that species which do not diffuse (e.g. components of negligible mobility or macroscopic inclusions) can in principle serve as "Kirkendall markers" to define the material coordinate system.

The deformation state at time t can formally be described by a one-to-one relation, $\mathbf{X}_t$, between the spatial and material coordinates of every point [13].

$$\mathbf{r} = \mathbf{X}_t(\mathbf{r}'); \quad \mathbf{r}' = \mathbf{X}_t^{-1}(\mathbf{r}). \tag{1a, b}$$

Here an unprimed vector, $\mathbf{r}$, specifies position in the fixed spatial coordinate system, and a primed vector, $\mathbf{r}'$, specifies position in the deforming material coordinate system. Any quantity which is a function of position can be expressed as a function of either $\mathbf{r}$ or $\mathbf{r}'$ without ambiguity, since one determines the other, given the deformation state $\mathbf{X}_t$. For simplicity, no notational distinction is made between the function of $\mathbf{r}$ and that of $\mathbf{r}'$ for a particular quantity.

Gradients and divergences taken with respect to the spatial or material coordinate systems are denoted by unprimed or primed symbols, ∇ or ∇', respectively. As is usual in fluid mechanics, the notations for time derivatives of any quantity a at fixed $\mathbf{r}$ and at fixed $\mathbf{r}'$ are, respectively,

$$\frac{\partial a}{\partial t} \equiv \left.\frac{\partial a}{\partial t}\right|_{\mathbf{r}\ \text{constant}}; \quad \frac{\mathrm{D}a}{\mathrm{D}t} \equiv \left.\frac{\partial a}{\partial t}\right|_{\mathbf{r}'\ \text{constant}}. \tag{2a, b}$$

The time derivative $\mathrm{D}a/\mathrm{D}t$ (often called the substantial derivative [14]) gives the rate of change of a seen at a point which follows the motion of the material coordinate system. The velocity field can be defined as [13]

$$\mathbf{v} \equiv \frac{\mathrm{D}\mathbf{r}}{\mathrm{D}t}. \tag{3}$$

The two time derivatives are related by the expression

$$\frac{\mathrm{D}a}{\mathrm{D}t} = \frac{\partial a}{\partial t} + \mathbf{v}\cdot\nabla a. \tag{4}$$

A system with n chemical components is considered. For simplicity, these components are assumed to be uncharged, and electric field effects are not explicitly considered. (This model can be applied to many problems in ionic systems by appropriate choice of neutral components—see Discussion.) The spatial density of each component, ρ_i, is defined as the local number of moles per unit spatial-coordinate-system volume. Each density is a function of position and time. Likewise each material density, ρ_i', is defined as the local number of moles per unit material-coordinate-system volume. The material densities are introduced because they are the natural variables for the description of diffusion in a deforming system. Instead of separately specifying the component densities, the distribution of the components can equivalently be described by the total spatial density or total material density and $n - 1$ of the composition variables (mole fractions), defined respectively by

$$\rho \equiv \sum_{i=1}^{n} \rho_i; \quad \rho' \equiv \sum_{i=1}^{n} \rho_i', \tag{5a, b}$$

$$c_i \equiv \frac{\rho_i}{\rho} = \frac{\rho_i'}{\rho'} \quad \text{for} \quad i = 1 \text{ to } n. \tag{6}$$

The composition variables do not depend on the volume basis used. Since only $n - 1$ of them are independent, here c_n is taken to be a function of the others.

The total spatial density is assumed to be a function only of the instantaneous composition and stress. This assumption is consistent with the mechanical constitutive relations used below, in which plastic deformation does not produce volume change. The total spatial density at zero stress is denoted by the stress-free density, ρ^{SF}, which is a function only of the c_i. This is the inverse of the molar volume in a system of uniform composition at zero stress. The partial molal volumes in an unstressed system of uniform composition, $\bar{V}_i$, are related to ρ^{SF} by

$$\bar{V}_i = \bar{V}_n - \left(\frac{1}{\rho^{\mathrm{SF}}}\right)^2 \frac{\partial \rho^{\mathrm{SF}}}{\partial c_i} \quad \text{for} \quad i = 1 \text{ to } n - 1, \tag{7a}$$

$$\bar{V}_n = \frac{1}{\rho^{\mathrm{SF}}} + \left(\frac{1}{\rho^{\mathrm{SF}}}\right)^2 \sum_{j=1}^{n-1} c_j \frac{\partial \rho^{\mathrm{SF}}}{\partial c_j}, \tag{7b}$$

where each of the partial derivatives of ρ^{SF} with respect to one of the independent c_i is taken with the remaining $n - 2$ independent c_k held constant.

Continuity equations can be written in either the spatial or material coordinate system for the corresponding density of each component.

$$\frac{\partial \rho_i}{\partial t} = -\nabla\cdot\mathbf{J}_i \quad \text{for} \quad i = 1 \text{ to } n \tag{8}$$

$$\frac{\mathrm{D}\rho_i'}{\mathrm{D}t} = -\nabla'\cdot\mathbf{j}_i \quad \text{for} \quad i = 1 \text{ to } n. \tag{9}$$

In this model $\mathbf{j}_i$, the flux with respect to the material coordinate system, is the diffusion flux of chemical component i, while $\mathbf{J}_i$, the flux with respect to the fixed spatial coordinate system, contains by diffusive and convective terms. Equation (9) indicates that the material densities at a point on the material coordinate system change solely because of diffusion, and are unaffected by deformation. Likewise, it can be seen that the composition variables at a point on the material coordinate system change solely because of diffusion, by differentiating equation (6) to obtain

$$\frac{\mathrm{D}c_i}{\mathrm{D}t} = \frac{1}{\rho'}\frac{\mathrm{D}\rho'_i}{\mathrm{D}t} - \frac{c_i}{\rho'}\frac{\mathrm{D}\rho'}{\mathrm{D}t} \quad \text{for} \quad i = 1 \text{ to } n. \tag{10}$$

2.2. *Strain and stress*

The definition of the total strain and its subdivision into elastic, plastic, and stress-free strains are carefully considered below so that the coupling between diffusion and internal stress in amorphous systems can be precisely stated. Although increments in elastic strain are small during interdiffusion in many systems of interest, increments in plastic and stress-free strain (and thus total strain) can be large. The analysis is therefore based on large-strain theory. Following standard practice [13], the total strain is defined using the deformation-gradient tensor, $\underline{F}$, given by

$$\underline{F} \equiv \nabla'\mathbf{r}. \tag{11}$$

Since the substantial derivative commutes with ∇', the velocity field is related to $\underline{F}$ by the expression

$$\frac{\mathrm{D}\underline{F}}{\mathrm{D}t} = \nabla'\mathbf{v}. \tag{12}$$

In these equations, the vector product is a dyadic product [14]. The deformation gradient tensor can be uniquely decomposed into an orthogonal rotation tensor, $\underline{R}$, and a symmetric stretching tensor, $\underline{U}$.

$$\underline{F} = \underline{R}\cdot\underline{U}. \tag{13}$$

The Jacobian determinant gives the volume change due to the deformation [13], which can be written as the ratio of the material and spatial densities.

$$\det \underline{U} = \frac{\rho'}{\rho}. \tag{14}$$

There are several strain measures which can be defined from $\underline{U}$. For the present work, the true logarithmic strain [15] is used.

$$\underline{\epsilon}^{\mathrm{TOT}} = \underline{\underline{\log}}\,\underline{U}. \tag{15}$$

Here the tensor logarithm is used, which can be formally defined using a power series expansion such as

$$\underline{\underline{\log}}\,\underline{U} \equiv (\underline{U} - \underline{1}) - \tfrac{1}{2}(\underline{U} - \underline{1})\cdot(\underline{U} - \underline{1}) + \cdots, \tag{16}$$

where $\underline{1}$ is the unit tensor. It can be seen that this definition of the total strain reduces to the standard small-strain measure as $\underline{U}$ approaches $\underline{1}$. Logarithmic strain is particularly appropriate for systems capable of plastic deformation, since increments in strain are referenced to the current deformation state rather than any fixed state. It is used here to simplify the relationship between strain and density. The total dilatation, e^{TOT}, is defined as the mean of the normal total strains by the relation

$$e^{\mathrm{TOT}} \equiv \tfrac{1}{3}\,\mathrm{trace}\,\underline{\epsilon}^{\mathrm{TOT}}. \tag{17}$$

It can be related to the ratio of the material and spatial densities by

$$e^{\mathrm{TOT}} = \tfrac{1}{3}\,\mathrm{trace}\,\underline{\underline{\log}}\,\underline{U} = \tfrac{1}{3}\log\det\underline{U} = \tfrac{1}{3}\log\left(\frac{\rho'}{\rho}\right). \tag{18}$$

The total strain tensor is taken to be the sum of elastic, plastic and stress-free strain tensors, which are individually evaluated below.

$$\underline{\epsilon}^{\mathrm{TOT}} = \underline{\epsilon}^{\mathrm{E}} + \underline{\epsilon}^{\mathrm{P}} + \underline{\epsilon}^{\mathrm{SF}}. \tag{19}$$

Dilatations are defined for the elastic, plastic, and stress-free strain tensors by relations analogous to equation (17). The local pressure, P, is likewise defined as the mean normal compressive stress,

$$P \equiv -\tfrac{1}{3}\,\mathrm{trace}\,\underline{\sigma}, \tag{20}$$

where $\underline{\sigma}$ is the Cauchy stress tensor (force per spatial-coordinate-system area).

In the present model, the constitutive relations of a Maxwell solid [9, 16] are used to relate plastic and elastic strain to stress. These simple, isotropic constitutive relations provide the two physical aspects necessary to the analysis: stored elastic energy and stress relaxation.

$$e^{\mathrm{E}} = -\frac{1-2\nu}{E}P \tag{21}$$

$$\underline{\epsilon}^{\mathrm{E}} = \frac{1+\nu}{E}(\underline{\sigma} + P\underline{1}) + e^{\mathrm{E}}\underline{1} \tag{22}$$

$$e^{\mathrm{P}} = 0 \tag{23}$$

$$\frac{\mathrm{D}\underline{\epsilon}^{\mathrm{P}}}{\mathrm{D}t} = \frac{1}{2\eta}(\underline{\sigma} + P\underline{1}). \tag{24}$$

Here E is Young's modulus, ν is Poisson's ratio, and η is the shear viscosity. For simplicity in evaluating the stress distribution, the elastic coefficients E and ν are assumed to be constants, independent of composition and density. The plastic strain is non-dilatational, and leads to stress relaxation through Newtonian flow. The elastic dilatation relates the spatial density to the stress-free density.

$$e^{\mathrm{E}} = \tfrac{1}{3}\log\left(\frac{\rho^{\mathrm{SF}}}{\rho}\right). \tag{25}$$

This can be derived from equation (18) by considering the effect of applied stress on a system in which no diffusion occurs, so that e^{SF} and ρ' are constant. Beginning in Section 2.5 below, it is assumed that the elastic strain is much smaller than unity. This approximation is not necessary for the analysis, but it leads to significant simplifications in the kinetic equations obtained.

Previous derivations of the stress contributions to the diffusion potentials [2–5] have focussed on systems in which the stress-free strain distribution is completely determined by the composition distribution. For example, in a perfect crystal the stress-free strain can be defined in terms of the change in the density of lattice sites as a function of composition, at zero stress. This definition is based on the assumption that vacant lattice sites are not created or destroyed at internal sources or sinks (e.g. extended defects) during interdiffusion, so that the crystal lattice serves as the material coordinate system.

To model amorphous or imperfectly crystalline systems in which there is no site-conservation constraint, a more general definition of the stress-free strain is needed. For simplicity an isotropic system is considered here, so that the stress-free strain is purely dilatational.

$$\underline{\epsilon}^{\mathrm{SF}} = e^{\mathrm{SF}}\underline{1}. \tag{26}$$

The stress-free dilatation can be expressed in terms of the ratio of the material and stress-free densities through a relation analogous to equations (18) and (25).

$$e^{\mathrm{SF}} = \tfrac{1}{3}\log\left(\frac{\rho'}{\rho^{\mathrm{SF}}}\right). \tag{27}$$

This follows from equations (17)–(19), (23), and (25). It can alternatively be derived from equation (18) directly by considering the effect of accumulation of density in a material-coordinate-system volume element because of diffusion, at zero stress. To compare this general expression for stress-free dilatation with the expression used previously, it is convenient to differentiate equation (27).

$$\frac{\mathrm{D}e^{\mathrm{SF}}}{\mathrm{D}t} = \frac{1}{3\rho'}\frac{\mathrm{D}\rho'}{\mathrm{D}t} - \frac{1}{3\rho^{\mathrm{SF}}}\frac{\mathrm{D}\rho^{\mathrm{SF}}}{\mathrm{D}t}. \tag{28}$$

Only the second term on the right-hand side has been considered in previous treatments [2–5, 9]. For example, the first term is zero in a perfect crystal with substitutional components where vacancies are counted as a component, since ρ' is constant when no vacancy sources or sinks operate. In the present model no site-conservation constraint is imposed, so that the first term is determined only by solution of the separate transport equations for diffusion of each component.

In the second term of equation (28), $\mathrm{D}\rho^{\mathrm{SF}}/\mathrm{D}t$ can be expanded in terms of the independent $\mathrm{D}c_i/\mathrm{D}t$. Equations (7a, b) and (10) then give a somewhat simpler form for equation (28),

$$\frac{\mathrm{D}e^{\mathrm{SF}}}{\mathrm{D}t} = \frac{\rho^{\mathrm{SF}}}{3\rho'}\sum_{i=1}^{n}\left(\bar{V}_i\frac{\mathrm{D}\rho_i'}{\mathrm{D}t}\right). \tag{29}$$

A comparison of this with equations (9) and (10) shows that the change in the stress-free dilatation is determined by the diffusion fluxes, but is not in general determined by the change in composition. This result is one of the major differences between the current model and that developed in a previous article on spinodal decomposition in amorphous systems [9], in which is was assumed that the stress-free dilatation could be expressed as a function of composition.

2.3. *Choice of the undeformed state*

One important aspect of the constitutive relations used is the arbitrary zero of $\underline{\epsilon}^{\mathrm{P}}$ and e^{SF} owing to the unspecified initial state of the material coordinate system. Because of this, the state of the system can be defined to be the undeformed state (i.e. $\underline{\epsilon}^{\mathrm{TOT}} = \underline{0}$, so that the material and spatial coordinate systems coincide) at any particular time. Only the local rate of deformation is significant, rather than the total amount of deformation of some reference state. This is physically reasonable for a system capable of plastic deformation. Whenever the system is undeformed, there is no difference between the value of a gradient, divergence, volume density, or area density taken with respect to the material coordinate system and one taken with respect to the spatial coordinate system. (There is a difference between the values of the time derivatives of these quantities, however; this is the reason for the use of two coordinate systems in the first place.) For the present purpose of developing differential equations for the evolution of the system, it is thus very convenient to stipulate that the system is undeformed at the particular time for which expressions are evaluated. This is equivalent to specifying that $\mathbf{X}_i$ in equations (1a, b) is a "relative deformation function" [13].

One consequence of this choice is that the difference between primed and unprimed gradients, divergences, and densities can generally be ignored, provided that they are not within time derivatives or variations. Likewise, since no distinction need be made in the measurement of area, the relationship between the two fluxes of equations (8) and (9) can be obtained as

$$\mathbf{J}_i = \mathbf{j}_i + \rho_i\mathbf{v} \quad \text{for} \quad i = 1 \text{ to } n, \tag{30}$$

where the second term gives the transport by convection. In addition, the substantial derivatives of $\underline{\epsilon}^{\mathrm{TOT}}$, $\underline{U}$, and $\underline{F}$ can be related by the small-total-strain formula,

$$\frac{\mathrm{D}\underline{\epsilon}^{\mathrm{TOT}}}{\mathrm{D}t} = \frac{\mathrm{D}\underline{U}}{\mathrm{D}t} = \frac{1}{2}\left(\frac{\mathrm{D}\underline{F}}{\mathrm{D}t} + \frac{\mathrm{D}\underline{F}^{\mathrm{T}}}{\mathrm{D}t}\right). \tag{31}$$

Combining the traces of equation (12) and (31), one obtains

$$\frac{\mathrm{D}e^{\mathrm{TOT}}}{\mathrm{D}t} = \tfrac{1}{3}\nabla\cdot\mathbf{v}. \tag{32}$$

2.4. *Stress distribution during interdiffusion*

To determine the stress distribution, the equilibrium relation for force balance is needed in addition to the constitutive relations. For creeping flow in which acceleration is negligible, this is given by

$$\mathbf{0} = \nabla\cdot\underline{\sigma}. \tag{33}$$

In the analysis presented below, it is assumed for simplicity that the spatial average of the pressure is zero. (Adding a constant to the pressure has no effect on the thermodynamic potentials for transport [9].)

First consider an unbounded system with composition and density profiles which vary only in one dimension (the x-direction). The stress distribution for this case is easily obtained because of symmetry [2, 9]. The transverse total strains, $\epsilon_{yy}^{\mathrm{TOT}}$ and $\epsilon_{zz}^{\mathrm{TOT}}$, the longitudinal stress, σ_{xx}, and all off-diagonal tensorial components vanish. It is convenient to define a scalar, $\Delta\epsilon^{\mathrm{P}}$, which determines the tensorial components of the plastic strain through the relations

$$\epsilon_{xx}^{\mathrm{P}} = 2\Delta\epsilon^{\mathrm{P}}, \tag{34a}$$

$$\epsilon_{yy}^{\mathrm{P}} = \epsilon_{zz}^{\mathrm{P}} = -\Delta\epsilon^{\mathrm{P}}. \tag{34b}$$

The stress and strain distributions can then be written in terms of this variable and the stress-free dilatation. The expressions obtained for the stress are [9]

$$P = \frac{2Y}{3}(e^{\mathrm{SF}} - \Delta\epsilon^{\mathrm{P}}), \tag{35a}$$

$$\sigma_{xx} = 0, \tag{35b}$$

$$\sigma_{yy} = \sigma_{zz} = -\tfrac{3}{2}P, \tag{35c}$$

where Y is the combined elastic constant, defined by

$$Y \equiv \frac{E}{1-\nu}. \tag{36}$$

The total dilatation can be written as

$$e^{\mathrm{TOT}} = \frac{1+\nu}{3(1-\nu)}e^{\mathrm{SF}} + \frac{2(1-2\nu)}{3(1-\nu)}\Delta\epsilon^{\mathrm{P}}. \tag{37}$$

For this stress distribution, the constitutive relation for plastic strain, equation (24), can be written as

$$\frac{\mathrm{D}\Delta\epsilon^{\mathrm{P}}}{\mathrm{D}t} = \frac{P}{4\eta}. \tag{38}$$

The stress distribution for an unbounded system with a three-dimensional variation in $\Delta\epsilon^{\mathrm{P}}$ and e^{SF} can be obtained simply by superimposing one-dimensional solutions. Equations (35a) and (37)–(38) remain valid for an appropriately generalized definition of $\Delta\epsilon^{\mathrm{P}}$ [9]. Larché and Cahn [2] have considered stress distributions for various boundary geometries. The relations obtained above remain valid for one-dimensional interdiffusion in a semi-infinite system bounded only by surfaces perpendicular to the transport direction, such as that considered in Section 2.7. In some situations (e.g. diffusion through a finite plate which is unconstrained laterally), the stress distributions obtained lead to behavior which is significantly different from that of the simple case considered here.

By differentiating equation (35a) and using equations (29) and (38), the change in the pressure at a point on the material coordinate system can be written as

$$\frac{\mathrm{D}P}{\mathrm{D}t} = \frac{2Y\rho^{\mathrm{SF}}}{9\rho'}\sum_{i=1}^{n}\left(\bar{V}_i\frac{\mathrm{D}\rho_i'}{\mathrm{D}t}\right) - \frac{Y}{6\eta}P. \tag{39}$$

Since the substantial derivatives of the material densities are simply related to the diffusion fluxes through the continuity equation (9), the above equation explicitly shows the manner in which diffusion and plastic deformation affect the stress distribution. By combining it with diffusion equations for the components which include stress in the diffusion potential, the evolution of the system during interdiffusion is determined.

2.5. *Kinetic equations for the case of small elastic strain*

A kinetic equation can be written for each of the basic transport processes considered: diffusion of each component with respect to the material coordinate system, and plastic deformation of the material coordinate system. The thermodynamic potential for each of these processes is the variational derivative of the free energy functional for the system with respect to a variable associated with that process [17–19]. The kinetic equation for a conserved variable (e.g. a material density) is a diffusion equation; that for a non-conserved variable (e.g. plastic strain) is a relaxation equation. The set of variables must be chosen such that each is directly affected by one and only one basic process. Because of this, cross-terms in the kinetic equations between the various thermodynamic potentials and rates of change of the variables are neglected [20]. In particular, for an amorphous system the diffusion of each of the n components is considered to be an independent process affecting only one of the material densities directly. The processes are coupled indirectly through the effects of composition and stress on the separate thermodynamic potentials and kinetic coefficients (mobilities and viscosity).

For simplicity, kinetic equations are derived here for systems in which the elastic strain is negligible with respect to unity. The free energy functional is given by

$$F = \int_{\infty}(\rho f + \tfrac{1}{2}\underline{\sigma}:\underline{\epsilon}^{\mathrm{E}})\,\mathrm{d}\mathbf{r}, \tag{40}$$

where f is the free energy per mole of an unstressed, uniform system as a function of composition, and the second term is the elastic energy density for small elastic strains. (Gradient energy terms could be added to the integrand to model spinodal decomposition or interdiffusion at small distance scales.) From the stress distribution obtained above for an unbounded system, the integrated elastic energy can be expressed as [9]

$$\int_{\infty}\tfrac{1}{2}\underline{\sigma}:\underline{\epsilon}^{\mathrm{E}}\,\mathrm{d}\mathbf{r} = \int_{\infty}\frac{9P^2}{4Y}\,\mathrm{d}\mathbf{r}. \tag{41}$$

The set of variables which are independently affected by diffusion of each component and plastic deformation are the ρ_i' and $\Delta\epsilon^{\mathrm{P}}$, respectively, provided that variations are taken with respect to the material coordinate system. Inserting equation (41) into equation (40) and changing to material coordinates, one obtains

$$F = \int_{\infty} \left(\rho' f + \frac{\rho'}{\rho}\frac{9P^2}{4Y}\right) \mathrm{d}\mathbf{r}'. \tag{42}$$

The variation in free energy is given by

$$\delta F = \int_{\infty} \left[\rho' \delta f + f \delta \rho' + \frac{\rho'}{\rho}\delta\left(\frac{9P^2}{4Y}\right) + \frac{9P^2}{4Y}\delta\left(\frac{\rho'}{\rho}\right)\right] \mathrm{d}\mathbf{r}'. \tag{43}$$

The variations in the integrand can be expressed in terms of the $\delta\rho'_i$ and $\delta\Delta\epsilon^{\mathrm{P}}$ by comparison with the relations between substantial derivatives.

$$\delta f = \sum_{i=1}^{n-1} \frac{\partial f}{\partial c_i}\delta c_i \tag{44a}$$

$$\delta c_i = \frac{1}{\rho'}\delta\rho'_i - \frac{c_i}{\rho'}\delta\rho' \quad \text{for} \quad i = 1 \text{ to } n-1 \tag{44b}$$

$$\delta\rho' = \sum_{i=1}^{n} \delta\rho'_i \tag{44c}$$

$$\delta\left(\frac{9P^2}{4Y}\right) = 3P(\delta e^{\mathrm{SF}} - \delta\Delta\epsilon^{\mathrm{P}}) \tag{44d}$$

$$\delta\left(\frac{\rho'}{\rho}\right) = \frac{1+\nu}{1-\nu}\delta e^{\mathrm{SF}} + \frac{2(1-2\nu)}{1-\nu}\delta\Delta\epsilon^{\mathrm{P}} \tag{44e}$$

$$\delta e^{\mathrm{SF}} = \frac{\rho^{\mathrm{SF}}}{3\rho'}\sum_{i=1}^{n} \bar{V}_i \delta\rho'_i. \tag{44f}$$

Each of the partial derivatives of f with respect to one of the independent c_i is taken with the remaining $n-2$ independent c_k held constant.

Some simplifications result from the assumption of small elastic strain introduced at equation (40), which implies that P/Y and $(\rho^{\mathrm{SF}} - \rho)/\rho$ are negligible with respect to unity. The last term in the integrand of equation (43) can be neglected, and the variational derivatives can be evaluated as

$$\frac{\delta F}{\delta\rho'_i} = \mu_i^{\mathrm{SF}} + \bar{V}_i P \quad \text{for} \quad i = 1 \text{ to } n, \tag{45}$$

$$\frac{\delta F}{\delta\Delta\epsilon^{\mathrm{P}}} = -3P, \tag{46}$$

where μ_i^{SF} is the chemical potential (partial molal free energy) of component i in an unstressed system of uniform composition, related to f by

$$\mu_i^{\mathrm{SF}} = \mu_n^{\mathrm{SF}} + \frac{\partial f}{\partial c_i} \quad \text{for} \quad i = 1 \text{ to } n-1, \tag{47a}$$

$$\mu_n^{\mathrm{SF}} = f - \sum_{j=1}^{n-1} c_j \frac{\partial f}{\partial c_j}. \tag{47b}$$

Equation (45) for the diffusion potential in an unbounded internally-stressed system with small elastic strain agrees with that obtained in other treatments [2, 4, 21].

The equation for the diffusion flux of each component is written as

$$\mathbf{j}_i = -M_i\rho_i\nabla\left(\frac{\delta F}{\delta\rho'_i}\right) \quad \text{for} \quad i = 1 \text{ to } n. \tag{48}$$

Here M_i is the molar mobility of component i, related to the tracer diffusivity D_i^* by

$$M_i = \frac{D_i^*}{RT} \quad \text{for} \quad i = 1 \text{ to } n, \tag{49}$$

where R is the molar Boltzmann constant and T is the temperature. With the continuity equation (9), this gives a diffusion equation for each material density.

$$\frac{\mathrm{D}\rho'_i}{\mathrm{D}t} = \nabla\cdot M_i\rho_i\nabla(\mu_i^{\mathrm{SF}} + \bar{V}_i P) \quad \text{for} \quad i = 1 \text{ to } n. \tag{50}$$

The relaxation equation for plastic strain is given by equation (38). This can also be written in terms of the variational derivative.

$$\frac{\mathrm{D}\Delta\epsilon^{\mathrm{P}}}{\mathrm{D}t} = -\frac{1}{12\eta}\frac{\delta F}{\delta\Delta\epsilon^{\mathrm{P}}}. \tag{51}$$

The relaxation equation does not contain the divergence and gradient found in the diffusion equations. This leads to qualitatively different behavior when stress relaxation rather than diffusion is the rate-limiting step for interdiffusion.

Although the variables ρ'_i and $\Delta\epsilon^{\mathrm{P}}$ are used to define the variations occurring due to the basic transport processes considered, the variables c_i and P are more convenient for describing the evolution of the system. After eliminating the substantial derivatives of the material densities in equations (10) and (39) using equation (50), one obtains a set of coupled non-linear differential equations in the unknowns c_i and P, given by

$$\frac{\mathrm{D}c_i}{\mathrm{D}t} = \frac{1}{\rho}\nabla\cdot[M_i\rho_i\nabla(\mu_i^{\mathrm{SF}} + \bar{V}_i P)] - \frac{c_i}{\rho}\sum_{j=1}^{n}\{\nabla\cdot[M_j\rho_j\nabla(\mu_j^{\mathrm{SF}} + \bar{V}_j P)]\} \quad \text{for} \quad i = 1 \text{ to } n, \tag{52}$$

$$\frac{\mathrm{D}P}{\mathrm{D}t} = \frac{2Y}{9}\sum_{i=1}^{n}\{\bar{V}_i\nabla\cdot[M_i\rho_i\nabla(\mu_i^{\mathrm{SF}} + \bar{V}_i P)]\} - \frac{Y}{6\eta}P. \tag{53}$$

The kinetic equation for c_n is not independent, leaving n independent equations in n unknowns. Since these equations involve the substantial derivative, a knowledge of the velocity field is also required to determine the spatial evolution of the system. For elastic strains much smaller than unity, equations (29), (32), and (50) give

$$\nabla\cdot\mathbf{v} = \sum_{i=1}^{n}\{\bar{V}_i\nabla\cdot[M_i\rho_i\nabla(\mu_i^{\mathrm{SF}} + \bar{V}_i P)]\}. \tag{54}$$

2.6. *Analytical solution to the linearized equations for a binary system*

The coupled differential equations for the c_i and P can be solved analytically for the case in which the composition and pressure deviations are small, so that higher-order (non-linear) terms, in expansions of these quantities about their average values, can be neglected. This solution shows the fundamental behavior of the general equations (52)–(53). For simplicity, a two-component system is considered below with a single independent composition variable, $c \equiv c_1$.

In the linear approximation, the gradients, fluxes, and velocity field are proportional to small quantities. The product of two of these is negligible, so that the substantial derivative, D/Dt, reduces to the time derivative at fixed spatial position, $\partial/\partial t$. The differential equations for composition and pressure can be written in linearized form as

$$\frac{\partial c}{\partial t} = [(1-c_0)M_{10} + c_0 M_{20}]c_0(1-c_0)f''\nabla^2 c + (\bar{V}_{10}M_{10} - \bar{V}_{20}M_{20})c_0(1-c_0)\nabla^2 P, \tag{55}$$

$$\frac{\partial P}{\partial t} = \frac{2Y}{9}(\bar{V}_{10}M_{10} - \bar{V}_{20}M_{20})\rho_0 c_0(1-c_0)f''\nabla^2 c + \frac{2Y}{9}[\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]\rho_0\nabla^2 P - \frac{Y}{6\eta_0}P. \tag{56}$$

Here c_0 is the average composition, the subscript zeros on M_1, M_2, $\bar{V}_1$, $\bar{V}_2$, ρ, and η indicate evaluation at c_0, and the coefficient f'' is defined by

$$f'' \equiv \left.\frac{d^2 f}{dc^2}\right|_{c_0}. \tag{57}$$

Because of the Gibbs–Duhem relation, only this single parameter is needed to specify the composition dependence of both chemical potentials in a binary system.

To solve equations (55) and (56), it is convenient to express the dimensionless quantities $c(\mathbf{r}, t)$ and $P(\mathbf{r}, t)/Y$ in terms of their Fourier amplitudes. Within the linear approximation, Fourier components of different wavevector do not interact. For appropriate initial conditions, the amplitudes of c and P/Y at a given wavevector are "in phase" at all times, and their phase does not change. It is then sufficient to consider only the real magnitudes, $\hat{c}(\mathbf{k}, t)$ and $\hat{p}(\mathbf{k}, t)$, of the complex amplitudes. The kinetic equations become

$$\frac{\partial \hat{c}}{\partial t} = -[(1-c_0)M_{10} + c_0 M_{20}]c_0(1-c_0)f''k^2\hat{c} - (\bar{V}_{10}M_{10} - \bar{V}_{20}M_{20})c_0(1-c_0)Yk^2\hat{p}, \tag{58}$$

$$\frac{\partial \hat{p}}{\partial t} = -\tfrac{2}{9}(\bar{V}_{10}M_{10} - \bar{V}_{20}M_{20})\rho_0 c_0(1-c_0)f''k^2\hat{c} - \left(\tfrac{2}{9}[\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]\rho_0 Yk^2 + \frac{Y}{6\eta_0}\right)\hat{p}. \tag{59}$$

where k is the wavenumber (the magnitude of the wavevector, $\mathbf{k}$). This set of linear, first-order differential equations is readily solved by matrix methods [22].

From the linearized equations in either real space or Fourier space, one can see immediately that the coupling between the composition and internal stress fields vanishes when the mobilities and partial molal volumes satisfy the relation

$$\bar{V}_{10}M_{10} = \bar{V}_{20}M_{20}. \tag{60}$$

In this case, the interdiffusion of the components leads to no stress-free dilatation. Conversely, large stress effects can be expected when the products in equation (60) are very different.

2.7. Quasi-steady-state pressure distribution

It is useful to consider a quasi-steady-state solution to understand how the rate-limiting step for interdiffusion can change, depending upon the distance scale. Since the elastic constant Y is typically much larger in magnitude than the product $\rho_0 c_0(1-c_0)f''$, the coefficient of $\hat{p}$ in equation (59) is often much larger in magnitude than that of $\hat{c}$. In this case (the "small-chemical-term" limit [9]), the pressure relatively rapidly approaches a quasi-steady-state distribution obtained by setting $\partial\hat{p}/\partial t$ to zero in equation (59).

$$\hat{p} = -\left\{\frac{(\bar{V}_{10}M_{10} - \bar{V}_{20}M_{20})\rho_0 k^2}{\dfrac{3\rho_0}{4\eta_0} + [\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]\rho_0^2 k^2}\right\} \times \frac{\rho_0 c_0(1-c_0)f''}{Y}\hat{c}. \tag{61}$$

The kinetic equation for composition can then be expressed as

$$\frac{\partial \hat{c}}{\partial t} = -\tilde{M}c_0(1-c_0)f''k^2\hat{c}, \tag{62}$$

where the net mobility $\tilde{M}$ is a function of wavenumber given by

$$\tilde{M} = \frac{\left(\dfrac{3\rho_0}{4\eta_0}\right)[(1-c_0)M_{10} + c_0 M_{20}] + M_{10}M_{20}k^2}{\left(\dfrac{3\rho_0}{4\eta_0}\right) + [\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]\rho_0^2 k^2}. \tag{63}$$

These quasi-steady-state expressions are valid after an induction time given by the inverse of the coefficient of $\hat{p}$ in equation (59),

$$t_{\mathrm{QSS}} = \frac{\left(\dfrac{9\rho_0}{2Y}\right)}{\left(\dfrac{3\rho_0}{4\eta_0}\right) + [\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]\rho_0^2 k^2}. \tag{64}$$

As discussed in the previous short article [8], equations (62) and (63) lead to interdiffusion behavior which spans the range between that given by the Darken analysis [6] and that given by a modified Nernst–Planck analysis [12]. In a system in which the viscosity is sufficiently small, stress relaxation occurs relatively rapidly, since the rate constant for plastic deformation is much larger than both of those for diffusion. The net mobility reduces to that given by the Darken analysis, in which stress is neglected and only the convective term couples the two spatial fluxes.

$$\tilde{M}_{\mathrm{D}} = (1 - c_0)M_{10} + c_0 M_{20}. \tag{65}$$

If the components have very different mobilities, the rate-limiting step for composition change in the Darken regime is diffusion of the faster component, since the slower can be transported by deformation. On the other hand, in a system in which the viscosity is sufficiently large, convective transport can be neglected, and only the stress term in the potentials couples the two spatial fluxes. The net mobility is of the Nernst–Planck form,

$$\tilde{M}_{\mathrm{NP}} = \frac{M_{10}M_{20}}{[\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1 - c_0)M_{20}]\rho_0^2}. \tag{66}$$

In the standard Nernst–Planck analysis, a similar result is obtained using an electrostatic potential term rather than a stress term to couple the fluxes. In this case, if the components have similar partial molal volumes but very different mobilities, internal stress builds up to impede diffusion of the faster component and to drive counter-diffusion of the slower component. The rate-limiting step is thus diffusion of the slower component. When equation (60) holds, the Darken and Nernst–Planck expressions for the net mobility are equivalent.

In each of these two limits, the net mobility is not a function of wavenumber, so that the real-space form of equation (62) is given by the simple linear Fickian diffusion equation

$$\frac{\partial c}{\partial t} = \tilde{D}\nabla^2 c. \tag{67}$$

Here the interdiffusion coefficient is related to the net mobility by

$$\tilde{D} = \tilde{M}c_0(1 - c_0)f''. \tag{68}$$

To understand the interdiffusion behavior without making either of these assumptions about the viscosity, it is expedient to cast the quasi-steady-state kinetic equation for composition into dimensionless form by defining a characteristic time and a characteristic wavenumber (inverse length) for the material, given by

$$t_{\mathrm{d}} \equiv \frac{4\bar{V}_{10}^2\rho_0\eta_0}{3(1 - c_0)^2 f''}, \tag{69}$$

$$k_{\mathrm{d}} \equiv \left[\frac{3\rho_0(1 - c_0)}{4\eta_0 M_{20}}\right]^{1/2}. \tag{70}$$

As shown below, the characteristic time t_{d} is the time constant for the relaxation of the stress generated by diffusion, and the characteristic wavenumber k_{d} is the wavenumber for which Nernst–Planck-type interdiffusion has the same time constant as stress relaxation. In terms of the dimensionless variables $\tau \equiv t/t_{\mathrm{d}}$ and $q \equiv k/k_{\mathrm{d}}$, equations (62) and (63) become

$$\frac{\partial \hat{c}}{\partial \tau} = -\Gamma\hat{c}, \tag{71}$$

$$\Gamma = \left\{\frac{[1 + \bar{V}_{10}^2 c_0^2 \rho_0^2 q_{\mathrm{m}}^2] + q^2}{q_{\mathrm{m}}^2 + [1 + \bar{V}_{20}^2(1 - c_0)^2\rho_0^2 q_{\mathrm{m}}^2]q^2}\right\} q^2, \tag{72}$$

where Γ is the dimensionless rate constant and q_{m} is a dimensionless material parameter related to the ratio of the mobilities by

$$q_{\mathrm{m}} \equiv \left[\frac{M_{20}}{\bar{V}_{10}^2 c_0(1 - c_0)\rho_0^2 M_{10}}\right]^{1/2}. \tag{73}$$

Likewise equation (61) becomes

$$\hat{p} = -\left\{\frac{[1 - \bar{V}_{10}\bar{V}_{20}c_0(1 - c_0)\rho_0^2 q_{\mathrm{m}}^2]q^2}{q_{\mathrm{m}}^2 + [1 + \bar{V}_{20}^2(1 - c_0)^2\rho_0^2 q_{\mathrm{m}}^2]q^2}\right\} \times \frac{(1 - c_0)f''}{\bar{V}_{10}Y}\hat{c}, \tag{74}$$

and the quasi-steady-state induction time is given in dimensionless units by

$$\tau_{\mathrm{QSS}} = \left\{\frac{q_{\mathrm{m}}^2}{q_{\mathrm{m}}^2 + [1 + \bar{V}_{20}^2(1 - c_0)^2\rho_0^2 q_{\mathrm{m}}^2]q^2}\right\} \times \frac{9(1 - c_0)^2 f''}{2\rho_0\bar{V}_{10}^2 Y}. \tag{75}$$

Equations (72) and (74)–(75) can be simplified when the parameter q_{m} is sufficiently small such that the terms involving q_{m}^2 within the square brackets are negligible with respect to unity. Provided that neither $\bar{V}_{10}c_0\rho_0$ nor $\bar{V}_{20}(1 - c_0)\rho_0$ has a value close to zero, this approximation is valid under the condition $\bar{V}_{20}M_{20} \ll \bar{V}_{10}M_{10}$. This is the same condition necessary for the Darken and Nernst–Planck net mobilities to differ significantly, i.e. necessary for the behavior predicted by the present model to be interesting. The simplified expressions are given by

$$\Gamma = \left(\frac{1 + q^2}{q_{\mathrm{m}}^2 + q^2}\right)q^2, \tag{76}$$

$$\hat{p} = -\left(\frac{q^2}{q_{\mathrm{m}}^2 + q^2}\right)\frac{(1 - c_0)f''}{\bar{V}_{10}Y}\hat{c}, \tag{77}$$

$$\tau_{\mathrm{QSS}} = \left(\frac{q_{\mathrm{m}}^2}{q_{\mathrm{m}}^2 + q^2}\right)\frac{9(1 - c_0)^2 f''}{2\rho_0\bar{V}_{10}^2 Y}. \tag{78}$$

The approximation that q_{m} is sufficiently small (denoted simply by $q_{\mathrm{m}}^2 \ll 1$ below) is used in obtaining the simple asymptotic expressions (79)–(85) and (87)–(89), although the complete equations (72) and (74) are used in calculating the curves in Figs 1–4.

The rate constant Γ of equations (71)–(72) is plotted against dimensionless wavenumber in Fig. 1,

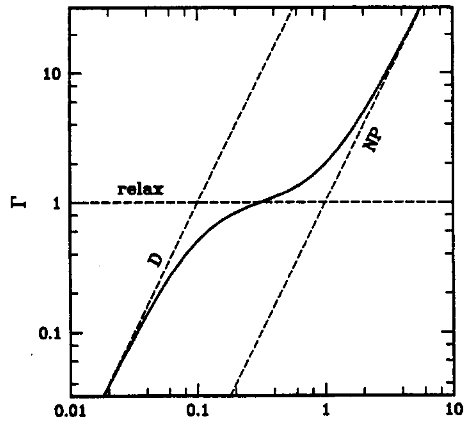

Fig. 1. Solid curve: the dimensionless rate constant Γ as a function of dimensionless wavenumber q, for a binary amorphous system. Dashed lines: the Darken, Nernst–Planck and deformation-limited asymptotes.

using logarithmic scales. The values of the dimensionless material paramters q_m, c_0, and $\bar{V}_{10}\rho_0$ used in calculating Fig. 1 are given in Table 1, along with $\bar{V}_{20}\rho_0$ and the mobility ratios implied by these values. From the breaks in the slope of Γ, one can see that the rate-limiting step for interdiffusion changes as a function of wavenumber. Three regimes can be distinguished. For q much smaller than q_m, diffusion of the faster component 1 is rate-limiting (the Darken regime). For q much larger than unity, diffusion of the slower component 2 is rate-limiting (the Nernst–Planck regime). For q between q_m and unity, plastic deformation is rate-limiting, since it partially relaxes the internal stress due to the imbalance in the diffusion fluxes. In this regime, the rate constant does not have the strong dependence on wavenumber characteristic of diffusion; rather, it shows the wavenumber-independence of a relaxation process.

Table 1. Material parameters for Figs 1–4

$q_m = 0.1$	$\bar{V}_{20}\rho_0 = 1$
$c_0 = 0.5$	$M_{10}/M_{20} = 400$
$\bar{V}_{10}\rho_0 = 1$	$\tilde{M}_D/\tilde{M}_{NP} \simeq 100$

The width of the deformation-limited regime is given by the square-root of the ratio of the Darken and Nernst–Planck net mobilities. When the dimensionless wavenumber range of interest includes this regime, in a system for which the net mobilities differ significantly, a simple Fickian diffusion equation does not describe the interdiffusion behavior.

Also shown in Fig. 1 are dashed lines corresponding to simple asymptotic forms for the rate constant in the Darken, Nernst-Planck, and deformation-limited regimes. Under the condition $q_m^2 \ll 1$, these are, respectively,

$$\Gamma_D = \frac{q^2}{q_m^2}, \quad \text{for} \quad q^2 \ll q_m^2, \tag{79}$$

$$\Gamma_{NP} = q^2, \quad \text{for} \quad 1 \ll q^2, \tag{80}$$

$$\Gamma_{relax} = 1, \quad \text{for} \quad q_m^2 \ll q^2 \ll 1. \tag{81}$$

The full solution approaches these asymptotes more closely for smaller values of q_m. Each asymptotic form can be associated with a rate constant for one of the three basic processes (diffusion of the faster component 1, diffusion of the slower component 2, and plastic deformation, respectively). One can see that, in each of the asymptotic regimes, the rate-limiting step is always the next-to-slowest of the three processes.

The effects of the complicated wavenumber dependence of the rate constant on the evolution of real-space composition and pressure profiles can easily be seen in the case of one-dimensional interdiffusion into a semi-infinite system. Consider a system, initially of uniform composition c_∞ and zero

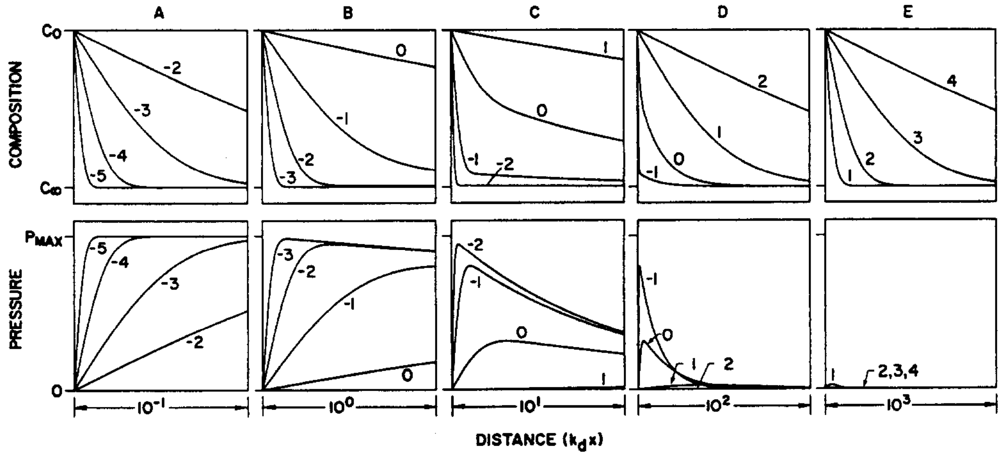

Fig. 2. Composition and pressure profiles as a function of dimensionless distance $l \equiv k_d x$, at various times after the surface composition is changed. The sequence is shown using five spatial magnifications A–E. The dimensionless time corresponding to each curve is indicated by the value of $\log_{10} \tau$ shown near the curve.

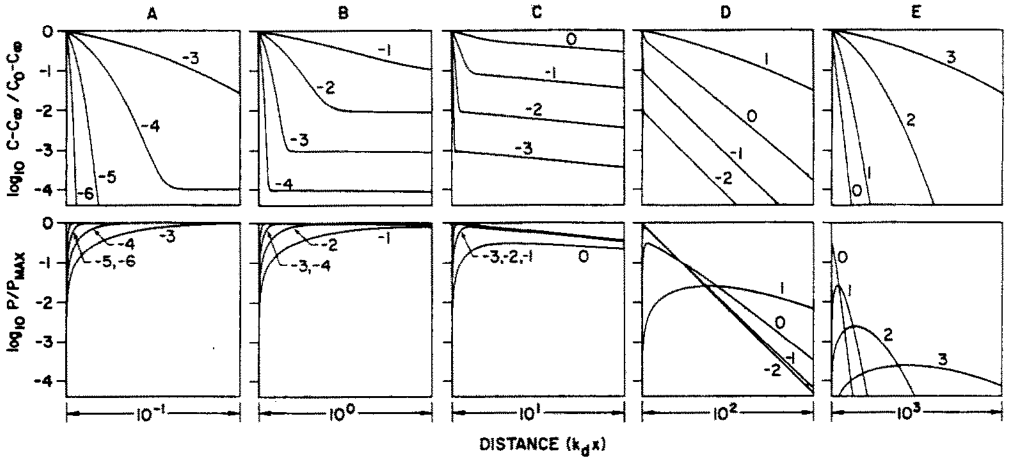

Fig. 3. Composition and pressure profiles as in Fig. 2, plotted on logarithmic scales as a function of linear distance. The non-Fickian exponential form of the profiles in the deformation-limited regime is evident.

stress, in which the composition at the surface $x = 0$ is instantaneously brought to a new value c_0 at time $t = 0$ and maintained there. Figure 2 shows composition and pressure as a function of distance at specific times, calculated from the linearized quasi-steady-state solution to the model developed above, equations (71)–(74), by numerically computing the real-space profiles from the Fourier-space solution using the parameter values in Table 1. The five pairs of graphs show profiles at five different spatial magnifications, plotted in terms of dimensionless distance and time variables, l and τ. The length of the displayed portion of the profiles is shown below each pair of graphs, expressed as a value of $l \equiv k_d x$, where x is the distance along the transport direction. This displayed length changes by an order of magnitude between each pair. The logarithm of the dimensionless time, $\log_{10} \tau$, corresponding to each composition and pressure profile is shown near the curve. The profiles shown span nine orders of magnitude in time.

Since different portions of the kinked rate-constant spectrum shown in Fig. 1 are applicable to each of the pairs of graphs shown in Fig. 2, the shapes of the real-space composition profiles change fundamentally from graph to graph. This can be seen even more strikingly in Fig. 3, in which the logarithm of the composition or pressure is plotted against (linear) distance. To take advantage of the logarithmic scales, the range of times shown has been shifted by one decade between Figs 2 and 3; otherwise, the parameters used to calculate the curves in the two figures are identical. One can see that the composition profiles, initially of error-function form, develop increasingly prominent exponential tails and then finally revert back to error-function form.

This behavior can be understood by considering the aysmptotic forms for the quasi-steady-state composition and pressure profiles in each of the three regimes. These can be simply expressed in dimensionless variables in the limit $q_m^2 \ll 1$. At the largest distance scale (graph E), the system is primarily in the Darken regime, in which the stress is completely relaxed and diffusion of the faster component 1 is rate-limiting. The composition profile is of the well-known error-function form obtained by solving the simple linear diffusion equation (67).

$$\frac{c - c_\infty}{c_0 - c_\infty} = 1 - \mathrm{erf}\left(\frac{q_m l}{2\tau^{1/2}}\right) \tag{82a}$$

$$P = 0. \tag{82b}$$

These asymptotes for the Darken regime are valid in the limit

$$1 \ll \tau. \tag{82c}$$

At the smallest distance scale (graph A), the system is primarily in the Nernst–Planck regime, in which stress relaxation is negligible and diffusion of the slower component 2 is rate-limiting. The composition and pressure profiles are both of the error-function form.

$$\frac{c - c_\infty}{c_0 - c_\infty} = 1 - \mathrm{erf}\left(\frac{l}{2\tau^{1/2}}\right) \tag{83a}$$

$$\frac{P}{P_{\mathrm{MAX}}} = \mathrm{erf}\left(\frac{l}{2\tau^{1/2}}\right). \tag{83b}$$

These asymptotes for the Nernst–Planck regime are valid in the limit

$$\tau \ll 1 - \mathrm{erf}\left(\frac{l}{2\tau^{1/2}}\right). \tag{83c}$$

For $q_m^2 \ll 1$, the maximum pressure is given by

$$P_{\mathrm{MAX}} = \frac{(1 - c_0)f''}{\bar{V}_{10}}(c_0 - c_\infty). \tag{84}$$

At intermediate distance scales (graphs B, C, and D), the profiles show aspects of both diffusive and relaxational kinetics. When plastic deformation is rate-limiting, the composition and pressure profiles decay exponentially with distance and appear as straight lines in Fig. 3. The asymptotic solutions can be obtained by solving equations (55)–(56) in the limit that terms containing $\nabla^2 c$ are negligible.

$$\frac{c-c_\infty}{c_0-c_\infty}=\tau\exp(-q_\mathrm{m}l) \tag{85a}$$

$$\frac{P}{P_\mathrm{MAX}}=\exp(-q_\mathrm{m}l). \tag{85b}$$

These asymptotes for the deformation-limited regime are valid in the limit

$$1-\operatorname{erf}\left(\frac{l}{2\tau^{1/2}}\right)\ll\tau \quad\text{and}\quad \tau\ll 1. \tag{85c}$$

From the asymptotic forms obtained for the three regimes, it can be seen that the time exponent characterizing the extent of interdiffusion changes depending upon whether diffusion or plastic deformation is the rate-limiting step. The extent of interdiffusion can be defined as

$$\xi\equiv\int_0^\infty\frac{c-c_\infty}{c_0-c_\infty}\,\mathrm{d}l. \tag{86}$$

This quantity is plotted against dimensionless time in Fig. 4, calculated from the same solution used to generate the curves in Figs 1–3. The asymptotic expressions for ξ obtained by integrating equations (82a), (83a), and (85a) are respectively given by

$$\xi_\mathrm{D}=\left(\frac{4}{\pi}\right)^{1/2}\frac{\tau^{1/2}}{q_\mathrm{m}}\quad\text{for}\quad 1\ll\tau, \tag{87}$$

$$\xi_\mathrm{NP}=\left(\frac{4}{\pi}\right)^{1/2}\tau^{1/2}\quad\text{for}\quad \tau\ll q_\mathrm{m}^2, \tag{88}$$

$$\xi_\mathrm{relax}=\frac{\tau}{q_\mathrm{m}}\quad\text{for}\quad q_\mathrm{m}^2\ll\tau\ll 1. \tag{89}$$

These three asymptotes are plotted as dashed lines in Fig. 4. Once again, the full solution approaches these asymptotes more closely for smaller values of q_m. The linear time dependence found when deformation is rate-limiting differs fundamentally from the parabolic time dependence of the diffusion-limited regimes.

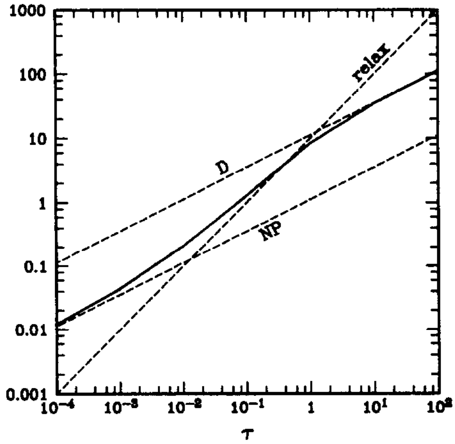

Fig. 4. Solid curve: the extent of interdiffusion ξ as a function of dimensionless time τ, for the composition profiles shown in Figs 2–3. Dashed lines: the Darken, Nernst–Planck and deformation-limited asymptotes.

2.8. System with one immobile component

It is of interest to consider an amorphous system in which the mobility of component n is negligible, since a component which does not diffuse serves to physically define the material coordinate system. In this case interdiffusion occurs by the diffusion of components 1 to $n-1$ in the interstices of a deforming network of component n. An example of such an immobile component is a heavily cross-linked "backbone" in a polymer or oxide glass system, or an inert component introduced as dispersed macroscopic inclusions to provide Kirkendall markers for the measurement of deformation. As discussed below, this case is also applicable to an interstitial crystalline solid solution.

For such an interstitial system, it is convenient to use $n-1$ composition variables, χ_i, based on unit density of the non-diffusing component,

$$\chi_i\equiv\frac{\rho_i}{\rho_n}=\frac{c_i}{c_n}\quad\text{for}\quad i=1\text{ to }n-1. \tag{90}$$

Likewise, it is convenient to use the stress-free density of the non-diffusing component, ρ_n^SF, and the free energy per mole of the non-diffusing component, f_n, defined by

$$\rho_n^\mathrm{SF}\equiv c_n\rho^\mathrm{SF}, \tag{91}$$

$$f_n\equiv\frac{f}{c_n}. \tag{92}$$

The partial molal quantities can be simply expressed in terms of these variables as

$$\bar V_i=-\left(\frac{1}{\rho_n^\mathrm{SF}}\right)^2\frac{\partial\rho_n^\mathrm{SF}}{\partial\chi_i}\quad\text{for}\quad i=1\text{ to }n-1, \tag{93a}$$

$$\bar V_n=\frac{1}{\rho_n^\mathrm{SF}}+\left(\frac{1}{\rho_n^\mathrm{SF}}\right)^2\sum_{j=1}^{n-1}\chi_j\frac{\partial\rho_n^\mathrm{SF}}{\partial\chi_j}, \tag{93b}$$

$$\mu_i^\mathrm{SF}=\frac{\partial f_n}{\partial\chi_i}\quad\text{for}\quad i=1\text{ to }n-1, \tag{94a}$$

$$\mu_n^\mathrm{SF}=f_n-\sum_{j=1}^{n-1}\chi_j\frac{\partial f_n}{\partial\chi_j}. \tag{94b}$$

Here each of the partial derivatives with respect to one of the χ_i is taken with the $n-2$ remaining χ_k held constant. The model developed above can be rewritten using the χ_i, ρ_n^SF, and f_n instead of the c_i, ρ^SF, and f. In particular, the change in the stress-free dilatation, equation (28), can be written as

$$\frac{\mathrm{D}e^\mathrm{SF}}{\mathrm{D}t}=\frac{1}{3\rho_n'}\frac{\mathrm{D}\rho_n'}{\mathrm{D}t}-\frac{1}{3\rho_n^\mathrm{SF}}\frac{\mathrm{D}\rho_n^\mathrm{SF}}{\mathrm{D}t}. \tag{95}$$

When the mobility of component n is negligible, the continuity equation implies that the first term on the right-hand side of equation (95) can be neglected. The change in the stress-free dilatation is then determined by the change in ρ_n^{SF}, which is a function only of the composition variables. An especially simple expression can be written using the χ_i.

$$\frac{\mathrm{D}e^{\mathrm{SF}}}{\mathrm{D}t} = \frac{\rho_n^{\mathrm{SF}}}{3} \sum_{i=1}^{n-1} \bar{V}_i \frac{\mathrm{D}\chi_i}{\mathrm{D}t}. \tag{96}$$

The coupled equations for composition, pressure, and the velocity field are also simpler when the mobility of component n is negligible than in the general case.

$$\frac{\mathrm{D}\chi_i}{\mathrm{D}t} = \frac{1}{\rho_n} \nabla \cdot [M_i \rho_i \nabla(\mu_i^{\mathrm{SF}} + \bar{V}_i P)] \quad \text{for} \quad i = 1 \text{ to } n-1 \tag{97}$$

$$\frac{\mathrm{D}P}{\mathrm{D}t} = \frac{2Y\rho_n}{9} \sum_{i=1}^{n-1} \bar{V}_i \frac{\mathrm{D}\chi_i}{\mathrm{D}t} - \frac{Y}{6\eta} P \tag{98}$$

$$\nabla \cdot \mathbf{v} = \sum_{i=1}^{n-1} \bar{V}_i \frac{\mathrm{D}\chi_i}{\mathrm{D}t}. \tag{99}$$

The linearized equations for a binary system ($n = 2$) with one immobile component are given by

$$\frac{\partial \chi}{\partial t} = M_{10}\chi_0(f_2'' \nabla^2 \chi + \bar{V}_{10} \nabla^2 P), \tag{100}$$

$$\frac{\partial P}{\partial t} = \frac{2Y\rho_{20}}{9} \frac{\partial \chi}{\partial t} - \frac{Y}{6\eta_0} P, \tag{101}$$

with $\chi \equiv \chi_1$ and

$$f_2'' \equiv \left.\frac{\mathrm{d}^2 f_2}{\mathrm{d}\chi^2}\right|_{\chi_0} = (1 - c_0)^3 f''. \tag{102}$$

To compare these results with equations (55)–(56), the relation between the linearized composition variables is

$$\chi - \chi_0 = \frac{c - c_0}{(1 - c_0)^2}. \tag{103}$$

Equations (100)–(101) are equivalent to those used in a previous article on spinodal decomposition in amorphous systems [9].

A solution can be obtained using the quasi-steady-state pressure distribution which is equivalent to equations (61)–(63) with M_{20} set to zero.

$$\hat{p} = -\left(\frac{\bar{V}_{10} M_{10} \rho_{20} k^2}{\frac{3\rho_{20}}{4\eta_0} + \bar{V}_{10}^2 \chi_0 M_{10} \rho_{20}^2 k^2}\right) \frac{\rho_{20}\chi_0 f_2''}{Y} \hat{\chi} \tag{104}$$

$$\frac{\partial \hat{\chi}}{\partial t} = -\left(\frac{\frac{3\rho_{20}}{4\eta_0} M_{10}}{\frac{3\rho_{20}}{4\eta_0} + \bar{V}_{10}^2 \chi_0 M_{10} \rho_{20}^2 k^2}\right) \chi_0 f_2'' k^2 \hat{\chi}. \tag{105}$$

From the form of the net mobility in equation (105), one can see that only the Darken and deformation-limited regimes are found in a binary system when component 2 is immobile. The wavenumber at which the rate-limiting step changes from diffusion of component 1 to plastic deformation is the same as that obtained in Section 2.7 above. It is given by $k_c \equiv q_m k_d$, or equivalently

$$k_c = \left(\frac{3}{4\eta_0 \bar{V}_{10}^2 \chi_0 M_{10} \rho_{20}}\right)^{1/2}. \tag{106}$$

In a ternary system with one immobile component, one can expect a Nernst–Planck-type regime to occur as well, although the solution is more complex than those developed above for binary systems because two composition variables and chemical potential gradients are independent.

3. THEORY FOR CRYSTALLINE SYSTEMS

In this section, the above treatment is extended to defective crystalline systems capable of plastic deformation. Although much of the model for amorphous systems is equally applicable to crystalline systems, a few of the assumptions made must be reconsidered. In addition, different assumptions are typically appropriate for crystalline systems with different dominant point defects. Two simple cases are considered: an interstitial solid solution, and a substitutional solid solution with vacancies. The behavior predicted for defective crystalline systems is found to be qualitatively similar to that for amorphous systems. In both, the rate-limiting step for interdiffusion can change between a relaxation process and a diffusion process as the distance scale changes.

A detailed treatment of deformation during interdiffusion is inherently more complex for a crystalline system than for an amorphous system. The amorphous system is modelled above as a Maxwell solid, in which plastic deformation can occur by viscous flow at every point in the system. In a crystalline system, plastic deformation is expected to occur only at extended lattice defects such as dislocations or grain boundaries. Thus the mechanical constitutive relations appropriate for a crystalline system are non-uniform in detail; to fully model microscopic behavior, regions at extended defects must be treated differently than the regions of perfect lattice in between. Likewise, in the model for amorphous systems, the change in the total material density contributes to the stress-free dilatation at every point in the system. In a substitutional crystalline system with vacancies, this contribution occurs only through the creation/annihilation of vacancies at extended defects. In addition, the stress-free strain is assumed to be purely dilatational in the amorphous-system model. The stress-free strain associated with the occupation of a site in a crystalline lattice can have deviatoric components, and the alignment of this anisotropy with the lattice can lead to collective effects. These complications of non-uniformity and anisotropy are not addressed here. Rather, the isotropic continuum equations are retained, with the understanding that they involve an average over distance scales of the order of the extended-defect spacing, and over all orientations of anisotropic sites.

3.1. Interstitial crystalline system

A crystalline interstitial solid solution with a deformable host lattice can be treated in a manner very similar to an amorphous system. Consider a system in which components 1 to $n-1$ occupy interstitial sites in a host lattice of component n. For simplicity, diffusion of the host component and creation/annihilation of vacancies on the host lattice are neglected, although it is assumed that the lattice can undergo plastic deformation (e.g. through dislocation glide). Since vacant interstitial sites are not considered to be a component, diffusion of each of the $n-1$ interstitial components is an independent process affecting only one of the material densities directly. Within the Maxwell solid approximation, the treatment for this case is identical to that for an amorphous system with one immobile component, equations (96)–(106). The host lattice serves as the material coordinate system, and the stress-free strain depends only on the composition. The non-Fickian behavior which occurs when plastic deformation is the rate-limiting step for interdiffusion can thus be expected in a deformable interstitial crystalline system.

3.2. Substitutional crystalline system with vacancies

For a substitutional crystalline solid solution in which diffusion occurs by a vacancy mechanism, a model for interdiffusion must take into account both the creation/annihilation of vacancies at extended defects and the contribution of the vacancy chemical potential to the diffusion potentials. This leads to some significant differences with the treatment for amorphous systems. In particular, vacancies must be considered to be a component, and the continuity equation for vacancies must be modified to include a source term. If vacancies are component n, one obtains

$$\frac{\partial \rho_n}{\partial t} = -\nabla\cdot \mathbf{J}_n + s, \tag{107}$$

$$\frac{\mathrm{D}\rho'_n}{\mathrm{D}t} = -\nabla'\cdot \mathbf{j}_n + s, \tag{108}$$

where s is the rate of creation of vacancies per unit volume. The continuity equations for components 1 to $n-1$ do not contain this source term.

Since diffusion occurs only by the exchanges of vacancies with other components, the diffusion fluxes obey the constraint

$$\mathbf{0} = \sum_{i=1}^{n} \mathbf{j}_i, \tag{109}$$

which implies that the change in the total material density is determined by the vacancy creation rate.

$$\frac{\mathrm{D}\rho'}{\mathrm{D}t} = s. \tag{110}$$

The change in the stress-free dilatation can then be written as

$$\frac{\mathrm{D}\rho^{\mathrm{SF}}}{\mathrm{D}t} = \frac{1}{3\rho'}s - \frac{1}{3\rho^{\mathrm{SF}}}\frac{\mathrm{D}\rho^{\mathrm{SF}}}{\mathrm{D}t}. \tag{111}$$

When the second term is expanded in the composition variables, one obtains

$$\frac{\mathrm{D}e^{\mathrm{SF}}}{\mathrm{D}t} = \frac{\rho^{\mathrm{SF}}}{3\rho'}\left[\bar{V}_n s + \sum_{i=1}^{n-1}(\bar{V}_i - \bar{V}_n)\frac{\mathrm{D}\rho'_i}{\mathrm{D}t}\right]. \tag{112}$$

To derive the thermodynamic potentials for the kinetic equations, a set of variables which are independently affected by each basic process considered must be used in the variational derivatives of the free energy functional. The set for a substitutional crystalline system with vacancies differs from that for an amorphous or interstitial crystalline system, so the potentials obtained differ. Only $n-1$ independent diffusion processes occur: the exchange of vacancies with each of the other components. In addition to these, vacancy creation/annihilation and plastic deformation are the basic processes considered. An appropriate set of variations for these processes are $\delta\rho'_i$, for $i = 1$ to $n-1$, $\delta\rho'$, and $\delta\Delta\epsilon^{\mathrm{P}}$, respectively. The integrand of equation (43) can be expressed in terms of these variations using equations (44a, b, d, e) and

$$\delta e^{\mathrm{SF}} = \frac{\rho^{\mathrm{SF}}}{3\rho'}\left[\bar{V}_n\delta\rho' + \sum_{i=1}^{n-1}(\bar{V}_i - \bar{V}_n)\delta\rho'_i\right]. \tag{113}$$

The variational derivatives can be evaluated as

$$\frac{\delta F}{\delta\rho'_i} = \mu_i^{\mathrm{SF}} - \mu_n^{\mathrm{SF}} + (\bar{V}_i - \bar{V}_n)P \quad \text{for} \quad i = 1 \text{ to } n-1, \tag{114}$$

$$\frac{\delta F}{\delta\rho'} = \mu_n^{\mathrm{SF}} + \bar{V}_n P, \tag{115}$$

$$\frac{\delta F}{\delta\Delta\epsilon^{\mathrm{P}}} = -3P. \tag{116}$$

As found in previous treatments [2–5], the diffusion potentials for substitutional crystals contain only differences between the chemical potentials (or partial molal volumes) of components 1 to $n-1$ and vacancies.

As in the amorphous case, equation (48) is used to obtain the diffusion fluxes of components 1 to $n-1$, and cross-terms between potential gradients and fluxes of different components are neglected. This may be a more restrictive approximation here than in the amorphous case, since "vacancy wind" effects can occur [23, 24]. The coupled equations for composition, pressure, and the velocity field can then be written as

$$\frac{\mathrm{D}c_i}{\mathrm{D}t} = \frac{1}{\rho}\nabla\cdot\{M_i\rho_i\nabla[\mu_i^{\mathrm{SF}} - \mu_n^{\mathrm{SF}} + (\bar{V}_i - \bar{V}_n)P]\} - \frac{c_i}{\rho}s \quad \text{for} \quad i = 1 \text{ to } n-1, \tag{117}$$

$$\frac{\mathrm{D}P}{\mathrm{D}t} = \frac{2Y}{9}\left[\bar{V}_n s + \sum_{i=1}^{n-1} (\bar{V}_i - \bar{V}_n) \cdot \nabla\{M_i \rho_i \nabla[\mu_i^{\mathrm{SF}} - \mu_n^{\mathrm{SF}} + (\bar{V}_i - \bar{V}_n)P]\}\right] - \frac{Y}{6\eta}P, \tag{118}$$

$$\nabla \cdot \mathbf{v} = \bar{V}_n s + \sum_{i=1}^{n-1} (\bar{V}_i - \bar{V}_n) \cdot \nabla\{M_i \rho_i \nabla[\mu_i^{\mathrm{SF}} - \mu_n^{\mathrm{SF}} + (\bar{V}_i - \bar{V}_n)P]\}. \tag{119}$$

In addition, a kinetic equation for the vacancy creation rate is needed. To be consistent with the Maxwell-solid constitutive relations used for the plastic strain rate, a simple relaxation equation is appropriate.

$$s = -L(\mu_n^{\mathrm{SF}} + \bar{V}_n P). \tag{120}$$

Here L is a rate constant for vacancy creation/annihilation.

A quasi-steady-state vacancy chemical potential distribution can be obtained by considering the vacancy continuity equation. Because the mole fraction of vacancies is typically very small, the vacancy chemical potential is relatively sensitive to changes in vacancy density. This in turn makes the two terms on the right-hand side of equation (108), the divergence of the vacancy diffusion flux and the vacancy creation rate, relatively sensitive to the vacancy density distribution. The quasi-steady-state vacancy chemical potential is obtained by setting the change in the vacancy material density to zero, so that the two sensitive terms balance. This gives

$$s = \sum_{i=1}^{n-1} \nabla \cdot \{M_i \rho_i \nabla[\mu_i^{\mathrm{SF}} - \mu_n^{\mathrm{SF}} + (\bar{V}_i - \bar{V}_n)P]\}. \tag{121}$$

When this is substituted into equations (117)–(119), they take on forms very similar to those for an amorphous system, equations (52)–(54), with $n - 1$ components. The only difference is that the vacancy chemical potential and partial molal volume are present in each of the diffusion potentials. In general, this net vacancy potential can be evaluated using the differential equation obtained from the two expressions for s, equations (120)–(121).

It is interesting to consider in passing the limit in which the rate constant for vacancy creation/annihilation, L, is very large. In this case the net vacancy potential must tend to zero.

$$0 = \mu_n^{\mathrm{SF}} + \bar{V}_n P. \tag{122}$$

The kinetic equations for a substitutional crystalline system with n components (including vacancies) then reduce directly to those for an amorphous system with $n - 1$ components. The treatment developed above for an amorphous system is thus equivalent to that for a substitutional crystalline system in which the vacancy chemical potential is always in local equilibrium.

As in the section on amorphous systems, an analytical solution can be obtained to the coupled equations (117)–(121) by expressing the linearized equations for a binary system (two components besides vacancies; $n = 3$) in Fourier space and making a quasi-steady-state approximation for the pressure distribution. Since the mole fraction of vacancies is small, only the single composition variable $c \equiv c_1$ is used, and only the single parameter f'' is needed to express the composition dependence of μ_1^{SF} and μ_2^{SF}. It is once again expedient to cast the equations for the composition and pressure into dimensionless form using the same characteristic time, t_{d}, and wavenumber, k_{d}, defined above in the treatment for amorphous systems. In addition to q_{m}, a dimensionless material parameter related to the ratio of the vacancy creation/annihilation and plastic deformation rate constants is needed.

$$q_{\mathrm{s}} \equiv \left(\frac{4\bar{V}_{10}^2 \eta_0 L_0}{3}\right)^{1/2}. \tag{123}$$

The kinetic equation for composition can again be expressed as equation (71) with a dimensionless rate constant, Γ. To save space, the exact expressions for Γ, $\hat{p}$, and τ_{QSS} are not reproduced here. They can be simplified in the limit $q_{\mathrm{m}}^2 \ll 1$ (as defined above), to give

$$\Gamma = \left\{\frac{q_{\mathrm{s}}^2(1 + q^2) + \bar{V}_{10}^2 \rho_0^2 q^2}{q_{\mathrm{s}}^2(q_{\mathrm{m}}^2 + q^2) + [1 + (\bar{V}_{10}\rho_0 - 1)^2 q^2]q^2}\right\} q^2, \tag{124}$$

$$\hat{p} = -\left\{\frac{q_{\mathrm{s}}^2 q^2 + \bar{V}_{10}\rho_0(\bar{V}_{10}\rho_0 - 1)q^4}{q_{\mathrm{s}}^2(q_{\mathrm{m}}^2 + q^2) + [1 + (\bar{V}_{10}\rho_0 - 1)^2 q^2]q^2}\right\} \times \frac{(1 - c_0)f''}{\bar{V}_{10} Y}\hat{c}, \tag{125}$$

$$\tau_{\mathrm{QSS}} = \left\{\frac{q_{\mathrm{s}}^2 q_{\mathrm{m}}^2 + q^2}{q_{\mathrm{s}}^2(q_{\mathrm{m}}^2 + q^2) + [1 + (\bar{V}_{10}\rho_0 - 1)^2 q^2]q^2}\right\} \times \frac{9(1 - c_0)^2 f''}{2\rho_0 \bar{V}_{10}^2 Y}. \tag{126}$$

One can see that these equations reduce directly to equations (76)–(78) for an amorphous system in the limit of large q_{s}.

Figures 5, 6 and 7 show the behavior of the rate constant Γ as a function of wavenumber for three values of q_{s}. The parameter values used in calculating the three curves are given in Table 2; the exact

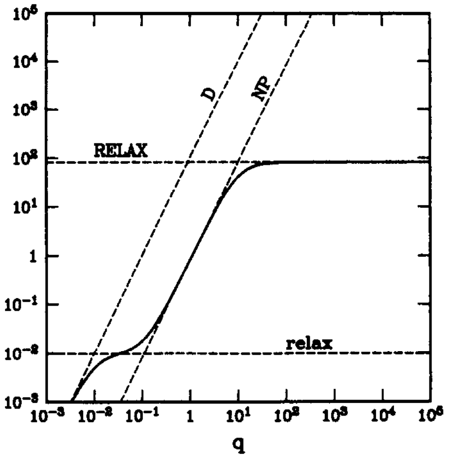

Fig. 5. Solid curve: the dimensionless rate constant Γ as a function of dimensionless wavenumber q, for a binary substitutional crystal with $q_s = 0.1$. Dashed lines: the Darken, Nernst–Planck and two relaxation-limited asymptotes.

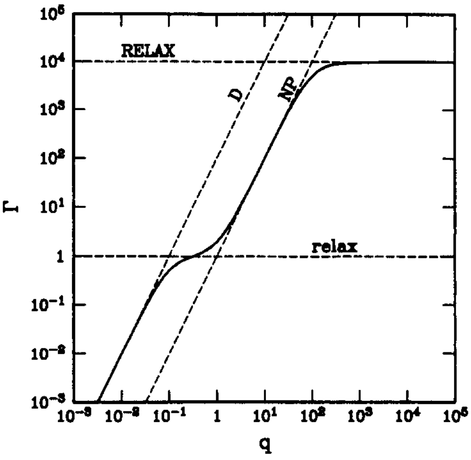

Fig. 7. Solid curve: the dimensionless rate constant Γ as a function of dimensionless wavenumber q, for a binary substitutional crystal with $q_s = 10$. Dashed lines: the Darken, Nernst–Planck and two relaxation-limited asymptotes.

expression for Γ is used, rather than the approximate equation (124). The behavior is somewhat more complicated than in the amorphous case, because the effects of differences in mobility and in partial modal volume are separate when q_s is not infinite. From the breaks in the slopes of each of the curves, four regimes can generally be distinguished. The rate-limiting step for interdiffusion is different in each regime. As in the amorphous case, at the smallest wavenumbers the rate-limiting step is diffusion of the faster component 1 (the Darken regime), since the slower component 2 is transported convectively. In the second regime encountered as wavenumber is increased, the rate-limiting step is the slower of the two relaxation processes, plastic deformation or vacancy creation/annihilation, as determined by the value of q_s. Both are involved in the convective transport of component 2. The third regime encountered is the Nernst–Planck regime, in which diffusion of the slower component 2 is rate-limiting. Finally, when the partial molal volumes differ, the rate-limiting step at the largest wavenumbers is the faster of the two relaxation processes, since either can relax the internal stress generated by the misfit.

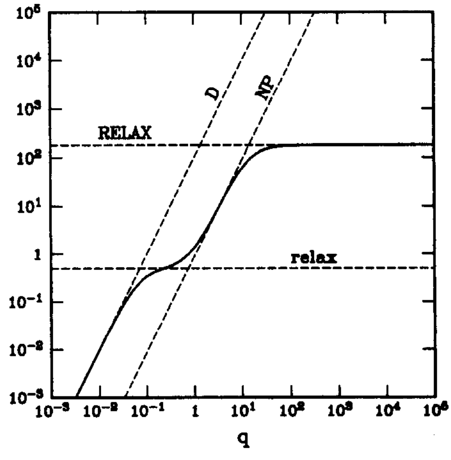

Fig. 6. Solid curve: the dimensionless rate constant Γ as a function of dimensionless wavenumber q, for a binary substitutional crystal with $q_s = 1$. Dashed lines: the Darken, Nernst–Planck and two relaxation-limited asymptotes.

These regimes correspond to four asymptotic forms for Γ in the limit $q_m^2 \ll 1$, given by

$$\Gamma_D = \frac{q^2}{q_m^2}, \quad \text{for} \quad q^2 \ll \frac{q_s^2 q_m^2}{1 + q_s^2}, \tag{127}$$

$$\Gamma_{\text{relax}} = \frac{q_s^2}{1 + q_s^2},$$

$$\text{for} \quad \frac{q_s^2 q_m^2}{1 + q_s^2} \ll q^2 \ll \frac{q_s^2}{\bar{V}_{10}^2 \rho_0^2 + q_s^2}, \tag{128}$$

$$\Gamma_{\text{NP}} = \left(\frac{\bar{V}_{10}^2 \rho_0^2 + q_s^2}{1 + q_s^2} \right) q^2,$$

$$\text{for} \quad \frac{q_s^2}{\bar{V}_{10}^2 \rho_0^2 + q_s^2} \ll q^2 \ll \frac{1 + q_s^2}{(\bar{V}_{10}\rho_0 - 1)^2}, \tag{129}$$

$$\Gamma_{\text{RELAX}} = \frac{\bar{V}_{10}^2 \rho_0^2 + q_s^2}{(\bar{V}_{10}\rho_0 - 1)^2}, \quad \text{for} \quad \frac{1 + q_s^2}{(\bar{V}_{10}\rho_0 - 1)^2} \ll q^2. \tag{130}$$

These asymptotes are plotted as dashed lines along with each of the curves in Figs 5–7. Each asymptotic

Table 2. Material parameters for Figs 5–7

$q_m = 0.1$			$\bar{V}_{20}\rho_0 = 1.1$
$c_0 = 0.5$			$M_{10}/M_{20} \simeq 494$
$\bar{V}_{10}\rho_0 = 0.9$			$\tilde{M}_D/\tilde{M}_{NP} \simeq 100$
Figure	5	6	7
q_s	0.1	1	10

form can be associated with a rate constant for one of the four basic processes. As in the amorphous case, diffusion of the faster component 1 and slower component 2 are associated with Γ_{D} and Γ_{NP}, respectively. Of the two relaxation processes (plastic deformation and vacancy creation/annihilation), the slower is associated with Γ_{relax} and the faster with Γ_{RELAX}, as determined by the value of q_s. In each of the regimes, the net rate constant Γ is always approximated by the asymptote with the next-to-smallest value.

3.3. *Comparison of perfect-crystal and large-viscosity amorphous systems*

The results of previous models for perfect crystals [2–5] can be obtained from the models developed above for defective crystalline systems by considering the limits in which plastic deformation and vacancy creation/annihilation are negligible. In these limits the quasi-steady state approximations for the pressure distributions derived above are not valid for binary systems; the pressure distributions must instead be obtained directly from the general equations. For comparative purposes, an amorphous system in the limit of negligible plastic deformation is first considered. The essential differences between models for perfect crystals and for an amorphous system with large viscosity are reflected by the manner in which different terms in the diffusion potentials are evaluated. For simplicity, linearized equations for binary systems will be compared.

A stress term enters into the diffusion potentials in all cases, amorphous and crystalline. From equations (35a–c) it can be seen that the stress is always determined by the stress-free dilatation in the large-viscosity limit, since no plastic deformation occurs. In an amorphous system the components are not constrained to occupy a lattice of sites, so that the stress-free dilatation (and the stress) are not determined by the composition. Instead, the stress approaches a quasi-steady-state distribution which produces balanced "volume" transport. For the large-viscosity limit, the quasi-steady-state pressure gradient can be obtained from equation (56) as

$$\nabla P = -\frac{(\bar{V}_{10}M_{10} - \bar{V}_{20}M_{20})}{[\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]} \times c_0(1-c_0)f''\nabla c. \quad (131)$$

This can be substituted into equation (55) to give the diffusion equation for an amorphous system in the Nernst–Planck limit,

$$\frac{\partial c}{\partial t} = \frac{M_{10}M_{20}}{[\bar{V}_{10}^2 c_0 M_{10} + \bar{V}_{20}^2(1-c_0)M_{20}]\rho_0^2} \times c_0(1-c_0)f''\nabla^2 c. \quad (132)$$

In an interstitial crystal, the stress-free dilatation is determined by the composition, because the component on the host lattice is immobile. For the large-viscosity limit, the pressure gradient is simply a function of the composition gradient. From equation (101) with a boundary condition of uniform pressure at uniform composition, one obtains

$$\nabla P = \frac{2Y\rho_{20}}{9}\bar{V}_{10}\nabla\chi. \quad (133)$$

This can be substituted into equation (100) to give the diffusion equation

$$\frac{\partial \chi}{\partial t} = M_{10}\chi_0(f_2'' + \tfrac{2}{9}Y\rho_{20}\bar{V}_{10}^2)\nabla^2\chi. \quad (134)$$

This solution is equivalent to those obtained in previous models for binary perfect crystals [2–5]. The partial-molal-volume term tends to drive the system to uniformity. The quasi-steady-state approximation for the pressure is not useful for a binary perfect interstitial crystal. No diffusion occurs at quasi-steady-state, since one component is immobile; rather, all diffusion occurs during the "induction time". (For multicomponent perfect interstitial crystals, diffusion can occur at quasi-steady-state even when partial molal volumes are large, provided that the individual terms in the pressure gradient tend to cancel.)

In a substitutional crystal, the diffusion potentials contain both a stress term and a vacancy chemical potential term. When the vacancy creation rate is negligible, the stress-free dilatation is determined by the composition, as in an interstitial crystal. For the large-viscosity limit of a binary perfect substitutional crystal (two components besides vacancies; $n = 3$), with a boundary condition of uniform pressure at uniform composition, the pressure gradient can be obtained from equation (118) as

$$\nabla P = \frac{2Y\rho_0}{9}(\bar{V}_{10} - \bar{V}_{20})\nabla c. \quad (135)$$

The quasi-steady-state condition for the vacancy chemical potential, equation (121), reduces to

$$\nabla\mu_3^{\mathrm{SF}} = \frac{(M_{10} - M_{20})c_0(1-c_0)f''\nabla c + [\bar{V}_{10}c_0M_{10} + \bar{V}_{20}(1-c_0)M_{20}]\nabla P}{c_0M_{10} + (1-c_0)M_{20}} - \bar{V}_{30}\nabla P. \quad (136)$$

These yield the diffusion equation

$$\frac{\partial c}{\partial t} = \frac{M_{10}M_{20}}{c_0M_{10} + (1-c_0)M_{20}}c_0(1-c_0) \times [f'' + \tfrac{2}{9}Y\rho_0(\bar{V}_{10} - \bar{V}_{20})^2]\nabla^2 c. \quad (137)$$

This agrees with the expressions obtained in previous models for binary perfect crystals [2–5], although here the net mobility is obtained in terms of the component mobilities.

The Nernst–Planck-type mobility factor in equation (137) is similar to its counterpart in equation (132) for an amorphous system; in particular, the two equations are equivalent when the partial molal volumes do not differ. However, the quasi-steady-state approximation used for equation (137) is different than its counterpart for equation (132), since it is based on an approximate vacancy chemical potential rather than pressure distribution. In the amorphous model, the stress which couples the fluxes arises only because of differences between the products $\bar{V}_i M_i$ for each species. In the substitutional perfect-crystal model, the effect of partial molal volume differences is separate from the effect of mobility differences. The stress term in equation (137) is similar to that in equation (134) for the binary perfect interstitial crystal.

4. DISCUSSION

4.1. New assumptions and predictions

As outlined in the previous short article [8], each of the models developed above is essentially a synthesis of the Darken analysis for the convective and diffusive transport contributions to interdiffusion [6] with more recent work on stress effects during diffusion [2–5]. In order to separate the transport due to deformation from that due to diffusion, the material coordinate system of continuum mechanics is introduced at the outset. It is assumed that mechanical constitutive relations govern the motion of the material coordinates relative to fixed spatial coordinates, and that diffusion equations govern transport relative to the deforming material coordinate system. Explicit constitutive relations between stress, diffusion, and the various strain terms, equations (21)–(24) and (29), are used to obtain equation (39) for the evolution of the stress in an unbounded or one-dimensional system due to diffusion and plastic deformation. Stress terms appropriate for a system in which the elastic strain is small are then included in the diffusion potentials. The resulting coupled differential equations for the evolution of the composition and stress distributions are given by equations (52)–(54), (97)–(99), or (117)–(120), for amorphous, interstitial crystalline, or substitutional crystalline systems, respectively.

The behavior of the composition distribution predicted by these coupled equations can differ fundamentally from that predicted by the Fickian diffusion equation obtained from a Darken or Nernst–Planck-type analysis [8]. The differences in behavior are highlighted above by considering binary systems in the simple linear case, in which the composition and pressure are sufficiently uniform such that non-linear effects unrelated to the issues at hand (due to composition or pressure dependence of material parameters) can be neglected. From the quasi-steady-state analytical solutions obtained, it can be seen that the rate-limiting step for interdiffusion can change as a function of the distance scale of the composition profile, since the time constants for relaxation processes such as plastic deformation and vacancy creation/annihilation are independent of distance scale, while the time constants for diffusion depend strongly on distance scale. Thus the shape of the composition profile for interdiffusion into a uniform semi-infinite amorphous system shown in Figs 2 and 3 can change qualitatively during the course of the process, and the time dependence of the extent of interdiffusion shown in Fig. 4 can vary between parabolic and linear.

Such behavior cannot be obtained from a Fickian diffusion equation, in which the diffusion potential gradient is expressed solely in terms of the composition gradient. Although this is analytically demonstrated above only for the linear case in which composition deviations are small, it is true even in the general non-linear case. When the interdiffusion coefficient is allowed to be an arbitrary function of composition, the Fickian diffusion equation for a binary system is given by [8]

$$\frac{\partial c}{\partial t} = \frac{1}{\rho^2} \nabla \cdot (\rho^2 \tilde{D} \nabla c). \tag{138}$$

It has long been known that composition profiles obtained from the general Fickian diffusion equation (138) for various times during interdiffusion into a uniform semi-infinite system can be plotted on a single curve by using the Boltzmann transformation $z \equiv x/t^{1/2}$, and that the time dependence of the extent of interdiffusion is always parabolic [25]. In contrast, solutions to the coupled equations such as (52)–(54) will always show the qualitatively different behavior described above when a relaxation process is rate-limiting, whether or not complications due to composition- or pressure-dependent material parameters are considered.

4.2. Relation between the viscosity and the mobilities in an amorphous system

In an amorphous system, the range of distance scales for which interdiffusion is rate-limited by deformation is determined by products of the viscosity and the mobilities. Expressed in terms of wavenumber, the boundaries of the deformation-limited regime for the analytical solution obtained above are determined by the characteristic wavenumber k_{d} and the dimensionless material parameter q_{m}.

$$q_{\mathrm{m}}^2 k_{\mathrm{d}}^2 \ll k^2 \ll k_{\mathrm{d}}^2. \tag{139}$$

The distance scale of a composition gradient can be written as the inverse of the wavenumber. Expanding relation (139), the boundaries of the deformation-limited regime can be expressed in terms of distance scale as

$$\left(\frac{\bar{V}_{10}^2 c_0 \rho_0^2}{(1-c_0)} \frac{4\eta_0}{3\rho_0} \tilde{M}_{\mathrm{NP}}\right)^{1/2} < k^{-1} < \left(\frac{\bar{V}_{10}^2 c_0 \rho_0^2}{(1-c_0)} \frac{4\eta_0}{3\rho_0} \tilde{M}_{\mathrm{D}}\right)^{1/2}, \quad (140)$$

where expressions for $\tilde{M}_{\mathrm{NP}}$ and $\tilde{M}_{\mathrm{D}}$ appropriate for the $q_{\mathrm{m}}^2 \ll 1$ limit have been used.

The physical significance of these boundaries can be seen by expressing the viscosity in terms of a mobility and a length through a generalized Stokes–Einstein relation [26],

$$\eta_0 = \frac{\rho_0 d_{\mathrm{SE}}^2}{C \tilde{M}_{\mathrm{SE}}}. \quad (141)$$

Here d_{SE} is the length over which components diffuse during the local rearrangements involved in the plastic deformation process, $\tilde{M}_{\mathrm{SE}}$ is the net mobility of these components, and C is a geometrical constant of order 10. The characteristic wavenumber can then be expressed as

$$k_{\mathrm{d}} = \left(\frac{3C(1-c_0)}{4\bar{V}_{10}^2 c_0 \rho_0^2}\right)^{1/2} \left(\frac{\tilde{M}_{\mathrm{SE}}}{\tilde{M}_{\mathrm{NP}}}\right)^{1/2} d_{\mathrm{SE}}^{-1} \quad (142)$$

in the limit $q_{\mathrm{m}}^2 \ll 1$. In many systems the first factor is of order unity and can be neglected. The boundaries of the deformation-limited regime are then given approximately by

$$\left(\frac{\tilde{M}_{\mathrm{NP}}}{\tilde{M}_{\mathrm{SE}}}\right)^{1/2} d_{\mathrm{SE}} < k^{-1} < \left(\frac{\tilde{M}_{\mathrm{D}}}{\tilde{M}_{\mathrm{SE}}}\right)^{1/2} d_{\mathrm{SE}}. \quad (143)$$

Since all components must take part in the local rearrangements involved in plastic deformation, in a binary system it is appropriate to associate $\tilde{M}_{\mathrm{SE}}$ with the Nernst–Planck net mobility $\tilde{M}_{\mathrm{NP}}$. The characteristic wavenumber in a binary system is then given approximately by the inverse of the Stokes–Einstein length, d_{SE}^{-1}. In amorphous materials, the Stokes–Einstein length is expected to be a molecular diameter. Thus, for a binary amorphous system, the predictions for wavenumbers larger than k_{d} (i.e. $q > 1$) are not meaningful, and only the Darken and deformation-limited regimes should be observed. In this case the deformation-limited regime extends to distance scales up to $(\tilde{M}_{\mathrm{D}}/\tilde{M}_{\mathrm{NP}})^{1/2}$ times a molecular diameter. If more than two components are present, then it is appropriate to associate $\tilde{M}_{\mathrm{SE}}$ with the mobility of the "slowest" of the components. For pseudo-binary interdiffusion of two other components in a multicomponent amorphous system, k_{d} could be significantly smaller than d_{SE}^{-1}, and the possibility exists of observing a Nernst–Planck-type regime as well. Of course, some modifications of the binary-system solution discussed here would be necessary to treat a multicomponent system.

4.3. *Relations between η, L and the M_i in a substitutional crystalline system*

The generalized Stokes–Einstein relation (141) can also be used for the viscosity of a defective crystalline system due to diffusional creep [27]. For a substitutional crystalline system with vacancies, this relation is derived by considering the rate of diffusion of vacancies between extended defects at which they are created or annihilated. The gradient in vacancy chemical potential is calculated from the deviatoric component of the stress, which produces differences in the resolved forces on extended defects of different orientation, and thus differences in the nearby equilibrium vacancy densities. The Stokes–Einstein length, d_{SE}, then corresponds to the average distance between extended defects in a crystalline system. Likewise, an expression for the rate for vacancy creation/annihilation, L_0, can be obtained by considering the rate of diffusion of vacancies between regions of perfect lattice and extended defects. Here the gradient in vacancy chemical potential is calculated from the hydrostatic component of the stress, which determines the average equilibrium vacancy density near an extended defect, for comparison with the average vacancy density in the lattice. One obtains

$$L_0 = \frac{C' \tilde{M}_{\mathrm{SE}} \rho_0}{d_{\mathrm{SE}}^2}, \quad (144)$$

where C' is a geometrical constant of order 10. The simple relaxation equations used here for the plastic deformation and vacancy creation rates are expected to be quantitative only for distance scales larger than d_{SE}. (For interdiffusion over smaller distance scales, a perfect-crystal model with appropriate surface boundary conditions can be used.)

Substituting the above relations for η_0 and L_0 into equation (123) gives

$$q_{\mathrm{s}} = \left(\frac{4\bar{V}_{10}^2 \rho_0^2 C'}{3C}\right)^{1/2}. \quad (145)$$

The material parameter q_{s} is therefore expected typically to be of order unity. From equation (128), one can see that the relaxation-limited regime corresponding to Γ_{relax} occurs at distance scales given by relation (143), where d_{SE} now corresponds to the extended-defect spacing. In a binary system, where $\tilde{M}_{\mathrm{SE}}$ corresponds to $\tilde{M}_{\mathrm{NP}}$, this relaxation-limited regime extends to distance scales up to $(\tilde{M}_{\mathrm{D}}/\tilde{M}_{\mathrm{NP}})^{1/2}$ times the extended-defect spacing. For psuedo-binary interdiffusion on one sublattice of a crystalline compound, plastic deformation and vacancy equilibration can be rate-limited by transport of the component on the other sublattice, so that the mobility ratio $(\tilde{M}_{\mathrm{NP}}/\tilde{M}_{\mathrm{SE}})^{1/2}$ in relation (143) can be very large. In such cases both a relaxation-limited regime corresponding to Γ_{relax} and a Nernst–Planck regime can occur at distance scales larger than the extended-defect spacing.

If the partial molal volumes of the interdiffusing components differ in substitutional crystals with $(\tilde{M}_{\rm NP}/\tilde{M}_{\rm SE})^{1/2} \gg 1$, such as compounds, a second relaxation-limited regime corresponding to $\Gamma_{\rm RELAX}$ can occur at distance scales larger than $d_{\rm SE}$, which from equation (130) is given by

$$k^{-1} < \left(\frac{\tilde{M}_{\rm NP}}{\tilde{M}_{\rm SE}}\right)^{1/2} |(\bar{V}_{10}\rho_0 - 1)| d_{\rm SE}. \qquad (146)$$

Although the above expressions for the asymptotes are obtained in the limit $q_{\rm m}^2 \ll 1$, one can verify that equation (130) for $\Gamma_{\rm RELAX}$ is valid in general. In crystalline compounds, interdiffusion on one sublattice can thus be rate-limited by relaxation of misfit even when the mobilities of the interdiffusing components are equal.

4.4. *Evidence for relaxation-limited interdiffusion and applications*

The considerations addressed above can be important in a wide variety of problems involving interdiffusion. Distinct deformation-limited regimes are expected to occur for solutes of interstitial nature with non-zero partial molal volume in either amorphous or defective crystalline systems, since the mobility of the interstitial compondents is typically much larger than that of the host component. In substitutional crystals, interdiffusing components often have similar mobilities, so that the Darken and Nernst–Planck-type net mobilities do not differ greatly and the anomalies in the transition regime are not large. However, as shown by equation (146), even small differences in partial molal volume can produce a distinct relaxation-limited regime during interdiffusion on one sublattice of a compound, if the component on the other sublattice is sufficiently immobile. In formulating kinetic laws for transport-limited processes such as spinodal decomposition, nucleation, growth, and interfacial reactions, one must consider whether interdiffusion is rate-limited by a diffusion or a relaxation process at the distance scales of interest.

The experimental and theoretical literature on non-Fickian ("Case II") interdiffusion during the penetration of polymers by liquids is mature and extensive [10, 11, 25, and references therein]. Experiments show that the time exponent of the extent of interdiffusion can vary between 1/2 and 1, with non-Fickian behavior often associated with polymers of high viscosity and penetrants of non-zero partial molal volume. Similar behavior has been found for the interdiffusion of water into silicate glass [28]. Many theories to explain this behavior simply propose composition-, stress-, and time-dependent mobilities. The above treatment for amorphous systems suggests that, to understand this behavior, one must consider: (i) the generation of internal stress due to imbalance in the diffusion fluxes; (ii) the contribution of the stress to the diffusion potentials; and (iii) the relaxation of the stress through plastic deformation. Recently, Thomas and Windle [10] and Stanley [11] have incorporated similar ideas into theories for interdiffusion in polymers. From the present work, one can see that the non-Fickian behavior which results when plastic deformation is the rate-limiting step for interdiffusion can occur in any amorphous or defective crystalline system in which the mobilities or partial molal volumes of the components differ.

It has long been recognized that stress can be generated during ion exchange in oxide glass systems [29]. Recently, stress relaxation during ion exchange has been considered [30]. Evidence for relaxation-limited interdiffusion in alkali-silicate glasses has also been obtained from analysis of the evolution of small-angle X-ray scattering from composition inhomogeneities during the early stage of spinodal decomposition [31]. In order to apply the model developed above to ionic systems, the effects of charged components must be treated. It is straightforward to include an electrostatic potential term in the diffusion potentials, and to use Poisson's equation to relate this potential to the densities of the components. It is generally found that local electroneutrality is violated significantly only for very short wavelengths [32]. One can then use a flux-neutrality condition to solve for the quasi-steady-state electric field, as is done in the standard Nernst–Planck analysis of interdiffusion in ionic systems [12]. In a system of n components, this leads to effective mobilites and potentials for $n - 1$ diffusion processes which do not involve charge transport [20]. For example, consider a mixed-alkali silicate system $\rm A_2O$–$\rm B_2O$–$\rm SiO_2$. Assume that the tracer diffusivities of the ions obey the relations $D^*_{\rm A} \gg D^*_{\rm B} \gg D^*_{\rm O} \gg D^*_{\rm Si}$. One can model interdiffusion in this system using three diffusion processes: exchange of A and B ions, governed by a mobility $M_{\rm AB} \simeq D^*_{\rm B}/RT$; diffusion of alkali oxide, governed by a mobility $M_{\rm R_2O} \simeq D^*_{\rm O}/RT$; and diffusion of silicon oxide, governed by a mobility $M_{\rm SiO_2} \simeq D^*_{\rm Si}/RT$. Sane and Cooper [30] have recently reported stress profiles measured after various amounts of K/Na exchange in a silicate glass. These stress profiles are initially sharply peaked at the surface. The peak subsequently shifts in from the surface, decays in amplitude, and broadens, in a manner similar to that shown above in Fig. 2, graphs C and D. The above analysis indicates that the peak shifts because the stress buildup from K/Na exchange is relaxed not only by plastic deformation, but also by a second, slower diffusion process, such as net outward diffusion of alkali oxide near the surface.

Experimental evidence for relaxation-limited interdiffusion in crystalline systems is less common than in amorphous systems. From the above model, a deformation-limited regime can be expected during interdiffusion of interstitial components such as hydrogen or carbon in metals at temperatures where plastic deformation can occur. It has been recognized that deviations from the equilibrium density of cation vacancies can occur during interdiffusion in oxide crystals with cations of different mobility, making the Darken analysis inapplicable [33]. As outlined above, the relaxation of misfit due to differences in cation partial molal volume may also produce non-Fickian interdiffusion behavior at small distance scales in polycrystalline oxide solid solutions.

Although not considered in the linearized solutions obtained above, the relatively strong composition dependences of material parameters found in many systems can have large effects of the shapes of the composition and pressure profiles. In substitutional crystalline systems, the mobilities are proportional to the vacancy density. Since the vacancy density may not be at its stress-free equilibrium value during diffusion over short distance scales, care must be taken to extract the vacancy density dependence explicitly when using measured tracer diffusivities. Likewise, history dependence of material parameters (owing to structural relaxation in amorphous systems, for example) has not been considered. Solutions using composition- or history-dependent viscosity and mobilities can be obtained by numerically integrating the general equations. More complicated mechanical constitutive relations can also be incorporated into the above analysis.

5. SUMMARY

The relaxation of internal stress and/or vacancy chemical potential generated by unbalanced diffusion fluxes can become the rate-limiting step for interdiffusion. Since the rate constant of a relaxation equation is independent of wavenumber, but the rate constant of a diffusion equation depends strongly on wavenumber, the rate-limiting step can change depending on the distance scale over which interdiffusion is occurring. When a relaxation process such as plastic deformation or vacancy creation/annihilation is rate-limiting, linearized composition profiles have an exponential (rather than error-function) form, and the extent of interdiffusion increases linearly with time (rather than as $t^{1/2}$).

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