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Continuum basis for diffusion in regions with multiple diffusivity

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A continuum model is proposed to consider diffusion situations where distinct types of structural or point defects contribute to the overall diffusivity. With respect to structural defects, the analysis is motivated by diffusion in the presence of a continuous distribution of high-diffusivity paths, such as grain boundaries and dislocations. With respect to point defects, the analysis is motivated by simultaneous diffusion of vacancies and interstitials, or vacancies and substitutionals. As a result of continuum modeling, the analysis is strictly valid in cases where the distribution of defects can be assumed continuous in space-time. The model is illustrated by detailing an example: dislocation-pipe diffusion under steady-state conditions.

I. INTRODUCTION

A method is proposed to quantify diffusion in certain cases where two distinct diffusion processes take place simultaneously. The analysis is particularly motivated by diffusion problems where distinct types of structural or point defects contribute to the overall diffusivity. In the case of structural defects, we have in mind diffusion problems where grain-boundary or dislocation-pipe diffusion occurs simultaneously with ordinary lattice diffusion. For point defects, we have in mind the simultaneous diffusion of vacancies and interstitials or vacancies and substitutionals.

The present method is based on continuum modeling. As a result, the analysis is strictly valid for situations where the distribution of defects can be considered continuous in space-time. It is well-known that in continuum theories a mathematical point represents an actual infinitesimal material element. Thus, the various phenomenological relationships which are assumed to hold pointwise in the mathematical formulation should be also physically sensible within an elementary infinitesimal volume or "neighborhood." Continuum theories are ad hoc in that they do not specify the dimensions of the "neighborhood." Thus, the appropriateness of continuum formulations is left to physical intuition followed by experimental verification.

Due to the above vagueness we attempt an intuitive description of the notion of "neighborhood" as it relates to the present problem. In the case of simultaneous diffusion of two types of point defects, such as vacancies and substitutionals, it is obvious that the notion of neighborhood is similar to the notion of neighborhood in ordinary diffusion problems. Thus, one can assume that the concentrations of both type of defects are continuous quantities. In the case of structural defects, however, the situation is somewhat different. For example, in the problem of simultaneous lattice and grain-boundary diffusion, the neighborhood should be taken sufficiently large so that it contains several grains. Then it is reasonable to assume that the concentration of the diffusing species at the grain-boundary space is continuous. Of course, if the above condition is fulfilled, it follows that the concentration in the lattice space is also continuous. It turns out

that choosing a neighborhood to ensure a continuous distribution of grain boundaries, it is sufficient to our purposes. In this connection, we also point out that in typical continuum theories of material behavior it is always assumed *a priori* that the distribution of defects, such as vacancies, dislocations, and grain boundaries, is continuous in space-time. Thus, one can conclude that concerning the notion of neighborhood the present diffusion theory enjoys an applicability similar to that of usual continuum theories of material behavior.

Obviously, the present theory cannot model, for example, experiments where two large grains have been grown together and diffusion of a solute along the grain boundary is allowed to take place. For such cases, physicists have developed mathematical models[1-9] to quantify the relevant phenomena. These models are microscopic and discrete in nature. For example, Fisher[2] presented an analysis for grain-boundary diffusion in bicrystals. He assumed the grain boundary to be a thin layer of high-diffusivity material between two grains which have a low diffusivity. It is also assumed that there is no concentration gradient across the grain boundary so that the diffusion is one dimensional within the grain boundary and that the concentration varies continuously in going from the grain-boundary slab to the grain. Fick's first law of diffusion is taken to hold in both regions outside and inside the grain boundary. The diffusion equation for the region outside the grain boundary is Fick's second law of diffusion. A diffusion equation is derived for the region inside the grain boundary by balancing fluxes in an element $\delta \, dy$ where δ is the grain boundary width and dy a differential length in the direction of diffusion along the grain boundary. Thus, the model is reduced to a mixed boundary-value problem in the sense that a solution is sought which will satisfy simultaneously the above diffusion equations in the respective regions and be continuous, or "match up," across the boundary between the slab and the grain.

This type of analysis has withstood the test of experimental confirmation whenever the experiments were designed carefully to meet the basic requirements of the model.

However, one may conclude easily that such idealized situations (e.g., accurate knowledge of grain-boundary width and orientation) are not present in typical engineering problems. Furthermore, discrete modeling cannot be considered faithful in the case where one is concerned with diffusion in a metal containing a continuous distribution of high-diffusivity paths. On the other hand, a conventional continuum model based, for example, on Fick's first and second law of diffusion but ignoring the existence of high-diffusivity paths is obviously invalid.

To resolve the above dilemma we propose here an alternative approach which may be thought of as a compromise between discrete and continuum modeling. Thus, we retain the basic features of the continuum model by providing our proposal with the broadness of a field theory. In addition, we take into account the microscopic configuration by postulating that at each point of space (neighborhood) not one but two distinct sets of diffusion fields (e.g., concentrations, concentration gradients, diffusion fluxes) exist. One set is associated with regular paths and the other with high-diffusivity paths. We assume that separate mass balance equations hold for the diffusing species in the regular and high-diffusivity paths. However, in these equations source terms appear which represent the transfer of mass of diffusing species between the two types of diffusion paths. Thus a coupling between the motion of the diffusing species in the regular and high-diffusivity paths is modeled. An additional coupling is introduced in the model by assuming that each diffusion flux is a function of concentrations and concentration gradients of the diffusing species in both types of diffusion paths.

Similarly, in the case of simultaneous diffusion of two types of point defects (for example, vacancies and substitutionals) we assume separate differential equations to express the conservation of each type of defect. The source terms here model the local positive or negative production of vacancies, as well as the amount of substitutionals that is locally trapped or released. Again, we assume that each flux is a function of concentrations and concentration gradients of both type of defects.

While an axiomatic approach to diffusion similar to that adopted previously by Aifantis and Gerberich[10-11] is possible, we prefer to construct the theory along more conventional lines and we follow the approach of Aifantis.[12] In this latter work the diffusion flux was treated as a constitutive function. By applying the techniques of modern constitutive theory (i.e., invariant considerations of frame indifference and symmetry) we found under what conditions Fick's law is valid. A similar point of view is also adopted here and we take the diffusion fluxes to be out fundamental constitutive functions.

For simplicity we assume that only one type of high-diffusivity paths (e.g., grain boundaries or dislocations) or two type of point defects (e.g., vacancies and substitutionals or vacancies and interstitials) are involved. Of course, the case where a multiplicity of structural or point defects contributes to the overall diffusivity can also be handled with similar methods. In particular, such studies should follow

the lines of a theory of "multiporosity" which we have recently developed[13] to treat analogous physical situations.

The plan of the paper is as follows: In Sec. II the basic equations of the present model are listed. Sec. III contains the relevant diffusion theory. Coupled partial-differential equations are derived modeling diffusion in the presence of structural or point defects. Uncoupling of these equations indicates the nonclassical character of the present diffusion theory. It also shows explicitly the points of departure from Fick's model. These points are further illustrated by studying a particular example in Sec. IV, i.e., one-dimensional dislocation-pipe diffusion under steady-state conditions.

In concluding this section, we wish to point out that ideas similar to those contained here have been introduced by the Russian school[14,15] to describe the propagation of heat in heterogeneous media having physically distinct regions with different conductivities as well as the flow of liquids in fissured rocks, i.e., rocks with double porosity.

II. BASIC EQUATIONS

To fix ideas, we consider lattice diffusion in the presence of a continuous distribution of high-diffusivity paths (e.g., grain boundaries or dislocations). We restrict attention to an elementary volume centered about an arbitrary point of the medium and we designate by c_1 and c_2 the mass of the diffusing species in the high-diffusivity and regular paths which are contained in this differential volume. Of course, one recognizes c_1 and c_2 as the concentrations of the diffusing species in the respective regions at the above arbitrary point of the medium. We also denote by j_1 and j_2 the corresponding fluxes of the diffusing species.[16] Finally, with m_1 and m_2 we designate the amount of mass per unit time per unit volume which is produced or lost in the respective regions within the differential volume. Then, a balance of mass for the diffusing species in both types of paths within the differential volume under consideration leads, in the usual way, to the following equations.

$$\frac{\partial c_1}{\partial t} + \operatorname{div} j_1 = m_1, \qquad (2.1)$$

$$\frac{\partial c_2}{\partial t} + \operatorname{div} j_2 = m_2, \qquad (2.2)$$

$$m_1 + m_2 = 0. \qquad (2.3)$$

Restriction (2.3) should be regarded as a statement of total mass balance. This can be easily concluded by adding Eqs. (2.1) and (2.2) and noting that a total concentration and a total flux can be defined as the sums $c_1 + c_2$ and $j_1 + j_2$, respectively. Of course, one does not expect Eq. (2.3) to be valid in the case where a chemical reaction takes place or an amount of the diffusing species is immobilized by absorption or another trapping mechanism. In our formulation, it is assumed that Eqs. (2.1)–(2.3) hold pointwise throughout the medium. This, of course, is sensible whenever the distribution of high-diffusivity paths is continuous; in other words, whenever a sufficient number of high-diffusivity paths exists within the above-mentioned differential volume or neighborhood, so that the concentration of the diffusion species along these paths varies continuously in space.

In the case of point defects, e.g., when simultaneous diffusion of vacancies and substitutionals takes place, Eqs. (2.1) and (2.2) hold obviously pointwise throughout the domain of interest. Of course, $\{c_1, j_1, m_1\}$ represents the concentration, the flux, and the source term of vacancies, while the set $\{c_2, j_2, m_2\}$ corresponds to substitutionals. Also the notion of neighborhood, here, is similar to the notion of neighborhood in classical diffusion problems. However, restriction (2.3) should be regarded now as valid only in very special cases. It is recalled that m_1 represents the local production or destruction of vacancies, while m_2 represents the amount of substitutionals that is locally trapped or released. It follows that condition (2.3) is valid here only if the relevant diffusion mechanism is such that the net production of defects vanishes. Even though condition (2.3) places no essential restriction on the theory, we prefer, for simplicity, to retain (2.3) throughout the subsequent development.

Next, we introduce constitutive equations for the diffusion fluxes which are regarded, in general, as functions of the concentration and concentration gradients.

$$j_1 = \hat{j}_1\,(c_1, c_2, \mathrm{grad}\,c_1, \mathrm{grad}\,c_2), \tag{2.4}$$

$$j_2 = \hat{j}_2\,(c_1, c_2, \mathrm{grad}\,c_1, \mathrm{grad}\,c_2). \tag{2.5}$$

In continuum physics, constitutive equations are restricted by invariance requirements of frame indifference and symmetry.[10-13] In the present case we assume that the diffusion is isotropic. Then, considerations of invariance[12] restrict the form of Eqs. (2.4) and (2.5) as follows:

$$j_1 = -\hat{\alpha}_{11}(c_1, c_2, |\,\mathrm{grad}\,c_1\,|, |\,\mathrm{grad}\,c_2\,|)\,\mathrm{grad}\,c_1$$
$$\quad -\hat{\alpha}_{12}(c_1, c_2, |\,\mathrm{grad}\,c_1\,|, |\,\mathrm{grad}\,c_2\,|)\,\mathrm{grad}\,c_2, \tag{2.6}$$

$$j_2 = -\hat{\alpha}_{21}(c_1, c_2, |\,\mathrm{grad}\,c_1\,|, |\,\mathrm{grad}\,c_2\,|)\,\mathrm{grad}\,c_1$$
$$\quad -\hat{\alpha}_{22}(c_1, c_2, |\,\mathrm{grad}\,c_1\,|, |\,\mathrm{grad}\,c_2\,|)\,\mathrm{grad}\,c_2. \tag{2.7}$$

To conform with the classical diffusion interpretations we assume that the functions $\hat{\alpha}_{11}, \hat{\alpha}_{12}, \hat{\alpha}_{21}$, and $\hat{\alpha}_{22}$ are independent[17] of the magnitudes of concentration gradients $|\mathrm{grad}\,c_1|$ and $|\mathrm{grad}\,c_2|$. Then Eqs. (2.6) and (2.7) take the simpler form

$$j_1 = D_{11}\,\mathrm{grad}\,c_1 - D_{12}\,\mathrm{grad}\,c_2, \tag{2.8}$$

$$j_2 = D_{21}\,\mathrm{grad}\,c_1 - D_{22}\,\mathrm{grad}\,c_2, \tag{2.9}$$

where the coefficients D_{11}, D_{12}, D_{21}, and D_{22} are, in general, functions of concentrations.

Statements (2.8) and (2.9) can be regarded as a generalization of Fick's law as it applies to the present situation. It is interesting to note that we proved these statements by starting with the more general relations (2.4) and (2.5).

Motivated by the previous discussion we find it natural to take the source terms m_1 and m_2 as functions of concentrations and write

$$m_1 = -m_2 \equiv m = \hat{m}\,(c_1, c_2), \tag{2.10}$$

where Eqs. (2.3) has been taken into account. A diffusion theory based on Eqs. (2.1), (2.2), and (2.8)–(2.10) is now possible. However, in this phase of development we found it instructive to illustrate the theory by making further assumptions. These assumptions and the diffusion theory to which they lead are presented in Sec. III.

III. DIFFUSION THEORY

In this section we introduce some simplifying assumptions into the basic structure of Sec. II and we derive a relatively simple diffusion theory. Thus, we assume that the coefficients of the cross terms (D_{12} and D_{21}) in Eqs. (2.8) and (2.9) vanish and that the diffusion coefficients (D_{11} and D_{22}) are constant, i.e.,

$$D_{12} = D_{21} = 0; \qquad D_{11} \equiv D_1; \qquad D_{22} \equiv D_2. \tag{3.1}$$

We further suppose that the source term m in Eq. (2.10) is a linear function of the concentrations, i.e.,

$$m = \hat{m}(c_1, c_2) = -\kappa_1 c_1 - \kappa_2 c_2, \tag{3.2}$$

where κ_1 and κ_2 are constants. While the previous assumptions of this section are not considered to be very restrictive, we regard assumption (3.2) as a model of very special situations.

Next, we introduce Eqs. (2.8), (2.9), (3.1), and (3.2) into Eqs. (2.1) and (2.2) to obtain

$$\frac{\partial c_1}{\partial t} = D_1 \nabla^2 c_1 - \kappa_1 c_1 - \kappa_2 c_2, \tag{3.3}$$

$$\frac{\partial c_2}{\partial t} = D_2 \nabla^2 c_2 + \kappa_1 c_1 + \kappa_2 c_2. \tag{3.4}$$

We regard Eqs. (3.3) and (3.4) as the fundamental differential equations which describe simultaneous diffusion through high-diffusivity and regular diffusion paths, or simultaneous diffusion of vacancies and substitutionals. To specify the concentrations c_1 and c_2 we need to solve Eqs. (3.3) and (3.4) under appropriate boundary conditions.

The solution of Eqs. (3.3) and (3.4) can be facilitated sometimes if one can uncouple the system (3.3)-(3.4) to derive a single higher-order differential equation for both c_1 and c_2. Toward this aim we add Eqs. (3.3) and (3.4) to obtain

$$\frac{\partial c_1}{\partial t} + \frac{\partial c_2}{\partial t} = D_1 \nabla^2 c_1 + D_2 \nabla^2 c_2. \tag{3.5}$$

Next we apply the ∇^2 operator in both sides of Eqs. (3.3) and combine the resultant equation with Eq. (3.5). The result reads

$$D_1 D_2 \nabla^4 c_1 = D_2 \frac{\partial}{\partial t}\nabla^2 c_1 + (\kappa_1 D_2 - \kappa_2 D_1)\nabla^2 c_1$$

$$+ \kappa_2 \frac{\partial}{\partial t}(c_1 + c_2). \tag{3.6}$$

We differentiate Eq. (3.3) with respect to time and we use this result to replace $\partial c_2/\partial t$ in Eq. (3.6). We obtain

$$\frac{\partial^2 c_1}{\partial t^2} + (\kappa_1 - \kappa_2)\frac{\partial c_1}{\partial t} - (D_1 + D_2)\frac{\partial}{\partial t}\nabla^2 c_1$$
$$+ D_1 D_2 \nabla^4 c_1 = (\kappa_1 D_2 - \kappa_2 D_1)\nabla^2 c_1 = 0. \tag{3.7}$$

By an analogous procedure one can derive a similar equation for c_2, i.e.,

$$\frac{\partial^2 c_2}{\partial t^2} + (\kappa_1 - \kappa_2)\frac{\partial c_2}{\partial t} - (D_1 + D_2)\frac{\partial}{\partial t}\nabla^2 c_2$$

$$+ D_1 D_2 \nabla^4 c_2 - (\kappa_1 D_2 - \kappa_2 D_1) \nabla^2 c_2 = 0. \qquad (3.8)$$

If the inertia terms $\partial^2 c_1/\partial t^2$ and $\partial^2 c_2/\partial t^2$ are considered unimportant,[18] then Eqs. (3.7) and (3.8) are reduced to

$$\frac{\partial c_\alpha}{\partial t} = \left(\frac{\kappa_1 D_2 - \kappa_2 D_1}{\kappa_1 - \kappa_2} \right) \nabla^2 c_\alpha - \left(\frac{D_1 D_2}{\kappa_1 - \kappa_2} \right) \nabla^4 c_\alpha$$

$$+ \left(\frac{D_1 + D_2}{\kappa_1 - \kappa_2} \right) \frac{\partial}{\partial t} \nabla^2 c_\alpha, \qquad (3.9)$$

where $\alpha = 1, 2$.

It is interesting to observe that if one defines the total concentration c as

$$c = c_1 + c_2, \qquad (3.10)$$

then it follows from Eqs. (3.7) and (3.8) that c obeys the differential equation

$$\frac{\partial^2 c}{\partial t^2} + (\kappa_1 - \kappa_2) \frac{\partial c}{\partial t} - (D_1 + D_2) \frac{\partial}{\partial t} \nabla^2 c$$

$$+ D_1 D_2 \nabla^4 c - (\kappa_1 D_2 - \kappa_2 D_1) \nabla^2 c = 0. \qquad (3.11)$$

By neglecting $\partial^2 c/\partial t^2$ we have

$$\frac{\partial c}{\partial t} = \left(\frac{\kappa_1 D_2 - \kappa_2 D_1}{\kappa_1 - \kappa_2} \right) \nabla^2 c - \left(\frac{D_1 D_2}{\kappa_1 - \kappa_2} \right) \nabla^4 c$$

$$+ \left(\frac{D_1 + D_2}{\kappa_1 - \kappa_2} \right) \frac{\partial}{\partial t} \nabla^2 c. \qquad (3.12)$$

For simplicity, we interpret Eq. (3.12) for the case of diffusion in high-diffusivity paths, and we establish the following result. If one is interested in knowing the concentrations in the high-diffusivity and the ordinary diffusion paths separately, then Eqs. (3.3) and (3.4) should be solved simultaneously. This solution can be facilitated if one finds the general solution of Eq. (3.7) or (3.8) and use this information in connection with Eqs. (3.3) and (3.4). In the problem just described initial and boundary conditions for both c_1 and c_2 should be provided. However, in some cases one may not be interested in details concerning the local distribution of concentrations and a knowledge of the average concentration $c = c_1 + c_2$ may be sufficient. Then Eq. (3.11) should be solved. In this problem initial and boundary conditions for the total concentration c are sufficient. Moreover, we see that the total concentration c does not obey Fick's second law of diffusion, as it would be the case if one was neglecting the existence of high-diffusivity paths. Instead, the higher-order differential equation (3.11) is obeyed. This result can be put on a philosophical basis as follows: Consideration of microstructural parameters within a framework of continuum theory leads, in general, to more complex phenomenological equations. Specifically, the effect of microstructure (in the present case of high-diffusivity paths) is modeled phenomenologically by new correcting terms (in the present case $\partial^2 c/\partial t^2$, $\partial \nabla^2 c/\partial t$, and $\nabla^4 c$) in the equations which describe the phenomenon when the microstructure is neglected (in the present case Fick's second law of diffusion).

IV. DISLOCATION-PIPE DIFFUSION

In this section we illustrate the general theory of Sec. III by considering a simple example. Specifically, we study the one-dimensional counterpart of the theory summarized by Eqs. (3.3), (3.4), (3.7), (3.8), and (3.11) as it applies to the case of steady-state dislocation-pipe diffusion.

To fix ideas consider a typical cylindrical diffusion specimen made up from a metal which, in addition to the ordinary interstitial spaces, contains a set of dislocations oriented along the axial direction. Further suppose that steady-state diffusion of a solute takes place in the direction of the axis of the cylinder. Without loss of generality one may assume that the cylinder extends from 0 to 1 in the axial direction. The problem then is to determine the concentration profile from 0 to 1 for the solute diffusing along dislocations, the solute diffusing through regular interstitial spaces, and the total solute concentration, provided that appropriate boundary conditions are given at the flat ends of the cylinder, i.e., at the points 0 and 1.

This problem will be solved by considering the one-dimensional steady-state counterpart of the diffusion theory presented in Sec. III. In particular, the analysis is based on the equations

$$D_1 \frac{\partial^2 c_1}{\partial x^2} - \kappa_1 c_1 - \kappa_2 c_2 = 0,$$

$$D_2 \frac{\partial^2 c_2}{\partial x^2} + \kappa_1 c_1 + \kappa_2 c_2 = 0, \qquad (4.1)$$

and

$$D_1 D_2 \frac{\partial^4 c}{\partial x^4} - (\kappa_1 D_2 - \kappa_2 D_1) \frac{\partial^2 C}{\partial x^2} = 0, \qquad (4.2)$$

where c_1 and c_2 denote the concentrations of the solute in the dislocations and ordinary interstitial spaces, and c is the total solute concentration. We note that, in accord with Eqs. (3.7) and (3.8), Eq. (4.2) is also satisfied by c_1 and c_2. In the following we assume that the constants D_1, D_2, κ_1, and κ_2 are given to us. For convenience we denote derivatives with respect to x by assigning primes to the appropriate functions. Thus Eqs. (4.1) are written as

$$D_1 c_1'' - \kappa_1 c_1 - \kappa_2 c_2 = 0, \qquad (4.3)$$

$$D_2 c_2'' + \kappa_1 c_1 + \kappa_2 c_2 = 0. \qquad (4.4)$$

By adding Eqs. (4.3) and (4.4) we obtain

$$D_1 c_1'' + D_2 c_2'' = 0, \qquad (4.5)$$

which by double integration with respect to x yields

$$D_1 c_1 + D_2 c_2 = Ax + B, \qquad (4.6)$$

where A and B are arbitrary constants to be determined by boundary conditions. We assume that c_1 and c_2 are given at $x = 0$ and $x = 1$. For convenience, and without loss of generality, we take

$$c_1(0) = c_2(0) = 0, \quad c_1(1) = 1/2D_1, \quad c_2(1) = 1/2D_2, \quad (4.7)$$

which are regarded as the appropriate boundary conditions. Introducing Eqs. (4.7) into Eq. (4.6) we find

$$B = 0, \quad A = 1, \qquad (4.8)$$

and therefore

$$D_1c_1 + D_2c_2 = x. \tag{4.9}$$

We insert Eq. (4.9) into (4.3) to obtain

$$c_1'' - \left(\frac{\kappa_1 D_2 - \kappa_2 D_1}{D_1 D_2} \right)c_1 - \left(\frac{\kappa_2}{D_1 D_2} \right)x = 0. \tag{4.10}$$

For convenience, we define[19]

$$\frac{\kappa_1 D_2 - \kappa_2 D_1}{D_1 D_2} \equiv \lambda^2, \qquad \frac{\kappa_2}{\kappa_2 D_1 - \kappa_1 D_2} \equiv \mu_1. \tag{4.11}$$

Then, the general solution of Eq. (4.10) reads

$$c_1 = A_1 \sinh\lambda x + A_2 \cosh\lambda x + \mu_1 x. \tag{4.12}$$

We determine the constants A_1 and A_2 by using the boundary conditions (4.7). Thus we find

$$c_1 = \mu_1 x + \mu_1^* \sinh\lambda x, \tag{4.13}$$

where

$$\mu_1^* \equiv \frac{1 - 2\mu_1 D_1}{2D_1 \sinh\lambda}. \tag{4.14}$$

Intorducing Eq. (4.13) into Eq. (4.9) we find

$$c_2 = \mu_2 x + \mu_2^* \sinh\lambda x. \tag{4.15}$$

where

$$\mu_2 \equiv \frac{\kappa_1}{\kappa_1 D_2 - \kappa_2 D_1}, \qquad \mu_2^* \equiv \frac{1 - 2\mu_2 D_2}{2D_2 \sinh\lambda}. \tag{4.16}$$

Solutions (4.13) and (4.15) indicate that the concentration profiles are not linear as it would be the case if Fick's law was assumed to hold and the coupling of the diffusion process in the "regular" and "dislocated" space was neglected.

It is also interesting to note that addition of Eqs. (4.13) and (4.15) yields the following solution for the total concentration:

$$c = \mu x + \mu^* \sinh\lambda x, \tag{4.17}$$

where

$$\mu = \mu_1 + \mu_2, \qquad \mu^* = \mu_1^* + \mu_2^*. \tag{4.18}$$

Obviously, if the microstructure (in the form of the dislocated regions as described above) is neglected, then one can only predict (based on a Fick's analysis) a linear dependence of c on x. Solution (4.17) suggests that the effect of the microstructure on our phenomenological description enters through the correcting nonlinear term $\mu^* \sinh\lambda x$.

Identical results are established if one finds the general solution of Eq. (4.2), i.e.,

$$c = B_1 \sinh\lambda x + B_2 \cosh\lambda x + B_3 x + B_4. \tag{4.19}$$

We note that Eq. (4.19) holds for c_1, c_2, and c. Suppose that Eq. (4.19) represents the general solution for c_1. Then introducing Eq. (4.19) into Eq. (4.1)$_1$, we find

$$c_2 = B_1 \left(\frac{D_1 \lambda^2 - \kappa_1}{\kappa_2} \right) \sinh\lambda x$$

$$+ B_2 \left(\frac{D_1 \lambda^2 - \kappa_1}{\kappa_2} \right) \cosh\lambda x$$

$$- B_3 \frac{\kappa_1}{\kappa_2} x - B_4 \frac{\kappa_1}{\kappa_2}. \tag{4.20}$$

Inserting the boundary conditions (4.7) into Eqs. (4.20) and (4.19) with $c = c_1$ we find

$$B_2 = B_4 = 0, \qquad B_1 = \mu_1, \qquad B_3 = -\mu_1^*. \tag{4.21}$$

Thus, both methods lead to identical results as it is expected. The second procedure, however, is more instructive and it should be preferred in more general situations.

If one is not interested in the detailed distribution of the concentration c_1 and c_2 but a knowledge of the average total concentration c is sufficient, then Eq. (4.2) should be solved. The general solution of this equation is given by Eq. (4.19). In this case the constants B_1, B_2, B_3, and B_4 are specified by prescribing not only the values of c but also the slopes of c at the end points.

It should be kept in mind that the above example was only considered to illustrate the theory and provide some insight in the results that should be expected from these type of analyses. It might be thought that a study of more realistic example cases, such as one-dimensional simultaneous diffusion of vacancies and interstitials, is also desirable. More realistic boundary conditions should be also considered. However, such types of detailed studies, as well as a contact of the present theory with existed discrete models and experimental data, are left to a future work.

ACKNOWLEDGMENT

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[16] j_1 and j_2 should be regarded as relative quantities since the diffusion velocities are measured with respect to the velocity of the matrix which, for simplicity, it is assumed to vanish.

[17] A formal justification of this fact can be provided by assuming that j_1 and j_2 are linear and $\hat{\alpha}_{11}$, $\hat{\alpha}_{12}$, $\hat{\alpha}_{21}$, and $\hat{\alpha}_{22}$ are analytic with respect to concentration gradients.

[18] This is a common practice in classical diffusion theories.

[19] Without loss of generality we may take $\kappa_1 > 0$ and $\kappa_2 < 0$. Then since $D_1 > 0$ and $D_2 > 0$, it follows that $\lambda^2 > 0$ and $\mu > 0$.

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