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# Vacancy-controlled interdiffusion: Nonlinear effects

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We derive the nonlinear equations governing vacancy-controlled interdiffusion in a two-component noninteracting lattice gas. We observe that when the diffusion constants of the two species are not equal, the problem cannot be reduced to a simple linear diffusion. In order to treat the strongly nonlinear limit of large kinetic asymmetry and small concentration of vacancies, we introduce an adiabatic approximation in which the “fast” species is in an equilibrium state defined by the instantaneous distribution of the “slow” species, which obeys a linear diffusion equation with a renormalized diffusion coefficient. Comparison with numerical solutions of the nonlinear equations shows that the adiabatic approximation captures the essential physics of the diffusion process.

## I. INTRODUCTION

Our purpose is to discuss the role of nonlinearities in the interdiffusion of two species. The most obvious problem is the formation of a diffusion front from a sharp boundary. This involves transport through a region in which relative concentrations vary over a wide range and will therefore, in general, be a highly nonlinear problem. Nonlinearities in the transport coefficients arise both from the concentration dependence of the driving chemical potentials and from that of the transport coefficients. It is far from obvious, *a priori*, that the evolution of the diffusion front can be described adequately by an effective interdiffusion equation for the relative concentration with a suitable interdiffusion constant—as one would like to assume. This paper is an attempt to get some insight into this problem.

Interdiffusion is a complicated process and can be modeled in a variety of ways, depending on the actual physics of the situation in which one is interested. In this paper we focus on the noninteracting random alloy model hereafter referred to as RAM.<sup>1-3</sup> Neglecting the local dynamical correlations we derive the transport equations. We find that they are highly nonlinear and of rather peculiar form. We study the evolution of the diffusion front with these equations.

In the simplest version of the RAM<sup>1-3</sup> one considers the vacancy-controlled interdiffusion of two noninteracting species on a lattice. The local hopping rates of the diffusing atoms in this model depend only on the availability of vacant sites into which an atom can hop. There are no explicit interactions so that the chemical potentials are completely determined by the entropy of mixing. The only interactions between the diffusing species are then of the excluded-volume type, i.e., two atoms cannot simultaneously occupy the same lattice site. Such interactions have no effect on the collective diffusion of a single species.<sup>4</sup> They do, however, affect self-diffusion even in this case and lead to nonlinear transport equations for the interdiffusion problem. Kehr, Binder, and Reulein<sup>3</sup> have recently studied the Onsager transport coefficients

in the RAM in great detail both by analytical methods and by numerical simulations, the latter being necessary due to the importance of short-time local correlations. We are interested in studying the effect of the nonlinearities in the transport equations and shall therefore neglect these correlation effects.

Discussions of interdiffusion in solids in the context of different experiments and physical situations are too numerous to list here. All those we have been able to trace amount to linearizations of the transport equations using heuristic arguments and assuming implicitly that one can indeed absorb the nonlinearities into an effective interdiffusion constant. While our results seem to confirm this feeling, they also show that this assumption is far from trivial and that it is at least conceivable that the nonlinearities can have important qualitative effects in more complex situations—as they frequently do in other problems.

While we only discuss the RAM in the following, we would also like to comment on the adequacy of this model in describing physical situations. This is important since many of the discussions in the literature and, in particular, those in the metallurgical literature, are not consistent with this model. The problem can be traced back to the three conservation laws implied by the RAM. While two of these conservation laws, namely the ones referring to the conservation of the numbers of atoms of the two diffusing species, are clearly necessary, the model also conserves the lattice and therefore the number of lattice sites and the number of vacancies. The fact that lattice sites and vacancies cannot be created or destroyed turns out to be extremely important in coupling the interdiffusion of the two species and dominates the nonlinearities we find. In situations involving kinetic asymmetry and low vacancy concentrations, it implies that the slow species must dominate the evolution of the diffusion front.

The conservation of the number of lattice sites is a topological constraint. While this law need not be rigorously obeyed in real physical situations, it is not trivial to violate such, essentially topological, constraints significantly. For crystals one could, for example, intercalate new lattice planes but this would require the growth or the creation of dislocation loops as part of the interdiffusion process. Even for amorphous systems the implied rearrangements of the

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molecular packing must constitute a significant constraint.

In Sec. II we start from a master equation and derive a nonlinear diffusion equation for this problem using a decoupling approximation for the nonlinear terms in the master equation. We compare this equation with the more general linear response coefficients computed in Ref. 3 which also include local correlations. In Sec. III we discuss the solutions of these equations and their implications for the development of a diffusion front. Since the nonlinearities have a somewhat unusual form we are not able to give a complete rigorous analysis. We do, however, develop a systematic iterative procedure for their solution. We show that it is unlikely that the solutions develop a shock front and that the naive intuitive expectations about the diffusion front cannot be very wrong. We also discuss the role of correlation effects in the development of the diffusion front. In Sec. IV we compare our predictions with numerical solutions of our equations. In Sec. V we summarize our main results and outline directions for future research.

In Appendix A we discuss the effect of the standard diffusion ansatz ( $z = x/\sqrt{t}$ ) on our equations and show that while the partial differential equations can be transformed into ordinary differential equations, the latter are not consistent with the boundary conditions. We illustrate this point for a simple limiting case in Appendix B. In Appendix C we briefly discuss the problems of self-diffusion and tracer diffusion.

## II. THE NONLINEAR DIFFUSION EQUATION

### A. Derivation from master equation

We are interested in the development of a diffusion front formed when two miscible species A and B, initially separated by a sharp boundary, diffuse into each other. The simplest model is to assume that the two species are only coupled by excluded-volume effects, i.e., two atoms cannot occupy the same site simultaneously and there are no other interactions. Thus, the chemical potentials are controlled by the entropy of mixing (of A, B, and vacancies). This still leaves freedom for the dynamics. If A and B can simply interchange the problem maps on the single-species diffusion equation. One therefore assumes that both A and B can only move into vacant sites with a hopping probability which only depends on the species (A, B) and on the hopping distance; the diffusion is then vacancy-controlled. In the present context this model is usually called the RAM.

We write a master equation on a lattice,<sup>4</sup>

$$\begin{aligned} d\langle n_A^i \rangle / dt &= \sum_j P_{ij}^A [(1 - n_A^i - n_B^i) \cdot n_A^j - n_A^i \cdot (1 - n_A^j - n_B^j)] \\ &= \sum_j P_{ij}^A [(n_A^j - n_A^i) + (n_A^i \cdot n_B^j - n_B^j \cdot n_A^i)] \quad (2.1a) \end{aligned}$$

and similarly

$$\begin{aligned} d\langle n_B^i \rangle / dt &= \sum_j P_{ij}^B [(n_B^j - n_B^i) \\ &\quad - (n_A^i \cdot n_B^j - n_B^i \cdot n_A^j)], \quad (2.1b) \end{aligned}$$

where the site occupation operators ( $n_A^i, n_B^i$ ) have values 0 or 1,  $\langle n_A^i \rangle$  and  $\langle n_B^i \rangle$  are the site occupation probabilities and  $P_{ij}^A$  and  $P_{ij}^B$  are the hopping probabilities which are assumed

to depend only on the hopping species (A or B) and on the distance between sites  $i$  and  $j$ . It is evident that equations (2.1) reduce to a *linear* equation with a concentration-independent diffusion constant for the single species case<sup>4</sup> ( $n_B \equiv 0$ ).

A standard continuum approximation

$$\langle n_A^i \rangle_i = A(r_i, t); \quad \langle n_B^i \rangle_i = B(r_i, t), \quad (2.2)$$

where  $A(r, t)$  and  $B(r, t)$  are the concentrations of the two species, and decoupling of the nonlinear terms in Eqs. (2.1)

$$\begin{aligned} \langle n_A^i \cdot n_B^j - n_B^i \cdot n_A^j \rangle_i &\propto A(r_i, t) \cdot B(r_j, t) \\ &\quad - B(r_i, t) \cdot A(r_j, t), \quad (2.3) \end{aligned}$$

yields the coupled differential equations,

$$(1/D_A) \cdot dA/dt = \nabla^2 A + A \cdot \nabla^2 B - B \cdot \nabla^2 A \quad (2.4a)$$

and

$$(1/D_B) \cdot dB/dt = \nabla^2 B + B \cdot \nabla^2 A - A \cdot \nabla^2 B. \quad (2.4b)$$

The diffusion constants  $D_A$  and  $D_B$  are concentration independent and determined by the hopping probabilities  $P_{ij}^A$  and  $P_{ij}^B$ , respectively. As usual in this context we only keep the lowest order terms in the gradients.

The main approximation in Eqs. (2.4) is the neglect of short-range correlations in the decoupling of the left-hand side of Eq. (2.3) to get the right-hand side of this equation. The results of Ref. 3 show that there can be important corrections because of this and, in particular, nonvanishing off-diagonal Onsager coefficients.

Corresponding to Eqs. (2.4) one can write the equations for the diffusion currents,

$$J_A = D_A \cdot (\nabla A + A \cdot \nabla B - B \cdot \nabla A) \quad (2.5a)$$

and

$$J_B = D_B \cdot (\nabla B + B \cdot \nabla A - A \cdot \nabla B). \quad (2.5b)$$

Using the chemical potentials,

$$\begin{aligned} \mu_A &= \log[A/(1 - A - B)]; \\ \mu_B &= \log[B/(1 - A - B)], \quad (2.6) \end{aligned}$$

one finds the Onsager transport coefficients,

$$\begin{aligned} \Lambda_{AA} &= D_A \cdot A \cdot (1 - A - B), \\ \Lambda_{BB} &= D_B \cdot B \cdot (1 - A - B), \\ \Lambda_{AB} &= \Lambda_{BA} = 0. \quad (2.7) \end{aligned}$$

One can compare this with the results of Ref. 3. As shown there the off-diagonal Onsager coefficients  $\Lambda_{AB}$  do not vanish and can be comparable in magnitude to the diagonal ones. This also results in corrections to the diagonal coefficients through the identities of Ref. 5. It is evident from the derivation that these corrections must result from the correlations in the vacancy distribution around a diffusing particle which are neglected in the decoupling approximation.

### B. Some general properties

We note the following properties of Eqs. (2.4).

1. All time dependence disappears when there are no vacancies,

$$A + B = 1 \quad (2.8)$$

as can easily be seen by substitution in Eq. (2.4).

2. In the dilute case,

$$A, B \ll 1 \quad (2.9)$$

the nonlinear term cannot play any significant role. A and B diffuse essentially independently. The only interesting case is therefore the low vacancy concentration limit,

$$v = 1 - (A + B) \ll 1. \quad (2.10)$$

3. In the static limit,  $D_B = 0$ , Eq. (2.4a) describes the diffusion of A in the free volume  $1 - B(x)$ . One notes that this neglects percolation effects when  $(1 - B)$  becomes small.

4. The symmetric situation

$$D_A = D_B = D \quad (2.11)$$

is special. Writing  $m = A - B$  one obtains

$$dv/dt = D \cdot \nabla^2 v \quad (2.12a)$$

$$dm/dt = D \cdot (v \cdot \nabla^2 m - m \cdot \nabla^2 v). \quad (2.12b)$$

One can therefore solve Eq. (2.12a) for any initial conditions giving a linear partial differential equation with time-dependent coefficients  $[v(x, t)]$  for the concentration difference  $m(x, t)$ . This becomes a simple diffusion equation if one assumes that  $v$  is constant initially,

$$v(x, 0) = v_0$$

so that

$$dm/dt = (v_0 \cdot D) \cdot \nabla^2 m \quad (2.13)$$

with an interdiffusion coefficient ( $v_0 \cdot D$ ) much smaller than the collective (i.e., vacancy) diffusion coefficient for the total concentration ( $D$ ).

5. The really interesting case is clearly the asymmetric situation with a low vacancy concentration, say

$$v \ll 1; \quad D_B/D_A \equiv \eta \ll 1. \quad (2.14)$$

We therefore discuss the solution of Eqs. (2.4) in the limit described by (2.14) and with initial conditions corresponding to the evolution of a diffusion front.

### III. THE DIFFUSION FRONT

We are interested in solutions of the interdiffusion Eqs. (2.4) with initial conditions,

$$A(x, 0) = \begin{cases} 1 - v_0 & x > 0 \\ 0 & x < 0 \end{cases} \quad (3.1a)$$

$$B(x, 0) = \begin{cases} 0 & x > 0 \\ 1 - v_0 & x < 0 \end{cases} \quad (3.1b)$$

and assuming the inequalities (2.14).

At finite times one then expects  $v(x, t)$  to have a minimum on the B side (i.e., for negative  $x$ ) and a maximum on the A side. This follows because at finite times  $A(x, t)$  will be a monotonic increasing function of  $x$  and  $B(x, t)$  a monotonic decreasing function of  $x$ , both with vanishing derivatives asymptotically (for  $x \rightarrow \pm \infty$ ) and, in general, with *different* widths for their diffusion fronts. Irrespective of the detailed shape of these fronts this implies *two* extrema for which

$$-dv/dx = dA/dx + dB/dx = 0. \quad (3.2)$$

Note that the two extrema become degenerate and merge at  $x = 0$  for the symmetric case ( $\eta = 1$ ).

#### A. The adiabatic approximation

Because of (2.14) ( $\eta \ll 1$ ) it seems reasonable to make an adiabatic approximation which gives the equilibrium solution for A when B is frozen in its instantaneous configuration. This assumes that the fast species (A) always fills up the space vacated by the slow species. As long as one can neglect boundary effects due to the finiteness of the system this means that A will have the concentration it has at infinity ( $1 - v_0$ ) in the local free volume available to it,

$$A_{ad} = (1 - v_0) \cdot (1 - B). \quad (3.3)$$

Substituting this in Eqs. (2.4) gives the adiabatic equation for B,

$$dB_{ad}/dt = D_B \cdot v_0 \cdot \nabla^2 B_{ad}. \quad (3.4)$$

In this approximation the diffusion front is controlled by the diffusion of the slow species with a renormalized diffusion constant  $v_0 \cdot D_B$ . This is, of course, what one expects intuitively. A cannot penetrate the B region appreciably before the slow species B has created the space into which it can diffuse. The diffusion front should therefore be controlled by the diffusion constant of B in the A-rich environment. One would therefore guess that the solutions of Eq. (3.4) are essentially correct and do describe the main features of the diffusion front. We shall see that this is confirmed by the numerical results.

There are however problems with this which can be seen in two ways. If one proceeds naively and substitutes the adiabatic ansatz (3.3) on the right-hand side of the equation for A [Eq. (2.4a)], one finds that it vanishes identically (and therefore  $dA/dt \equiv 0$ ) which is of course inconsistent. This is simply a result of the fact that  $A_{ad}(x, t)$  describes the *equilibrium* state for A in the *instantaneous* distribution of B  $[B(x, t)]$ . Qualitatively one expects the adiabatic approximation (3.3) to be valid for positive  $x$  and throughout the diffusion front of B where  $1 - B \gg v_0$ . On the other hand the approximation must break down well inside the B region where A has not had time to equilibrate and is therefore much smaller,

$$A(x, t) \ll A_{ad}(x, t) = (1 - v_0) \cdot [1 - B(x, t)] \\ \simeq v_0(1 - v_0); \quad x \rightarrow -\infty. \quad (3.5)$$

The implication is that there must be a different diffusion front for A in the B-rich region. Since the adiabatic vacancy concentration is small,

$$v_{ad} = v_0 \cdot (1 - B) < v_0 \quad (3.6)$$

this is associated with a minimum in the vacancy concentration and possibly with a bottleneck in the diffusion process. Alternatively and somewhat more precisely, this can be regarded as a position dependence of the effective diffusion constants. Far inside the B region B has its full diffusion constant,

$$D_B^{\text{eff}} \sim D_B; \quad v \sim v_0 \sim A_{ad} \gg A; \quad x \rightarrow -\infty \quad (3.7a)$$

while, as we have seen in Eq. (3.5),

$$D_B^{\text{eff}} \sim v_0 \cdot D_B \ll D_B; \quad A \sim A_{\text{ad}} \quad (3.7b)$$

for positive but finite  $x$ . The transition between these two limits occurs somewhere inside the diffusion front.

The tail in the front of the fast species (A) [Eq. (3.7a)] is of course also the place where one expects the corrections to the decoupling approximation [Eq. (2.3)] to become important. Since  $D_B$  is small and the free volume  $(1 - B)$  available to A is also small (dynamic) percolation effects can become important.<sup>6-8</sup>

Qualitatively, the criterion for this is

$$1 - B < p_{\text{perc}}, \quad (1 - B) \gg \eta. \quad (3.8)$$

The diffusion of A is then dominated by the diffusion of vacancies and vanishes in the limit  $D_B \rightarrow 0$ . To lowest order this effect shows up in the off-diagonal Onsager constant  $\Lambda_{AB} \propto D_B$  (see Ref. 3). The “effective” diffusion constant of A can then actually be much smaller than  $v_0 \cdot D_A$ .

One has a situation where the effective diffusion constant of both species *decreases* with their respective concentrations across the diffusion front. The diffusion current of A [ $J_A$ , Eq. (2.5)] is negative and the effective diffusion constant of A also decreases in this direction (from  $D_A$  to  $v_0 \cdot D_A$ ). The same holds for B in the direction of  $J_B$ . Potentially such a situation could lead to dramatic changes in the shape of the front—e.g., by creating a shock front. To see if this can actually happen for solutions of the nonlinear diffusion Eqs. (2.4), we try to go beyond the adiabatic approximation.

## B. Corrections to the adiabatic approximation

We want to expand around the adiabatic approximation by successive approximations,

$$\begin{aligned} A_n &= A_n[B_{n-1}] = A_{n-1} + a_n; \\ B_n &= B_n[A_n] = B_{n-1} + b_n. \end{aligned} \quad (3.9)$$

We start from the adiabatic approximation for A [Eq. (3.3)],

$$A_{\text{ad}} = (1 - v_0) \cdot (1 - B_{\text{ad}})$$

so that [Eq. (3.4)]

$$(1/D_B) \cdot dB_{\text{ad}}/dt = v_0 \cdot \nabla^2 B_{\text{ad}}.$$

It is convenient to define

$$\tilde{a}_1(x, t) = a_1(x, t) + v_0 \cdot (1 - v_0) \cdot \eta. \quad (3.10)$$

Thus  $\tilde{a}_1$  obeys the homogeneous diffusion equation,

$$\begin{aligned} (1/D_A) \cdot d\tilde{a}_1(x, t)/dt &= [1 - B_{\text{ad}}(x, t)] \cdot \nabla^2 \tilde{a}_1(x, t) \\ &+ \tilde{a}_1(x, t) \cdot \nabla^2 B_{\text{ad}}(x, t), \end{aligned} \quad (3.11)$$

where  $B_{\text{ad}}(x, t)$  is the solution of Eq. (3.4)—in essence an error function in the variable

$$z = x/\sqrt{(v_0 \cdot D_B \cdot t)}. \quad (3.12)$$

Since  $A_{\text{ad}}(x, t)$  does not obey the proper boundary conditions at  $x = -\infty$  [Eq. (3.1)] one requires for  $\tilde{a}_1$

$$\tilde{a}_1(x, 0) = \begin{cases} -(1 - \eta) \cdot v_0 \cdot (1 - v_0) & x < 0 \\ \eta \cdot v_0 \cdot (1 - v_0) & x > 0 \end{cases}. \quad (3.13)$$

Thus, the required solution of the equation for  $\tilde{a}_1$  is in the

same category as that of the original diffusion problem. The equation is homogeneous and the required solution does not vanish because of the step-function initial conditions. The solution of this equation is not as straightforward as would seem because its transformation into an ordinary differential equation by the standard variable transformations for the diffusion equation ( $z = x/\sqrt{t}$ ) is not consistent with the boundary conditions. We discuss this in Appendix A. Therefore, to obtain  $\tilde{a}_1$  one has to solve a partial differential equation with time-dependent coefficients [Eq. (3.11)].

All the higher order corrections obey inhomogeneous diffusion equations with inhomogeneous terms confined to the diffusion front. They also vanish at infinity. We only write down the equation for  $b_1$ ,

$$\begin{aligned} (1/D_B) \cdot db_1/dt &- [v_0 + (1 - v_0) \cdot B_{\text{ad}} - a_1] \cdot d^2 b_1/dx^2 \\ &- b_1 \cdot [d^2 a_1/dx^2 - (1 - v_0) d^2 B_{\text{ad}}/dx^2] \\ &= B_{\text{ad}} \cdot d^2 a_1/dx^2 - a_1 \cdot d^2 V_{\text{ad}}/dx^2, \end{aligned} \quad (3.14)$$

where

$$b_1(\mp \infty) = 0. \quad (3.15)$$

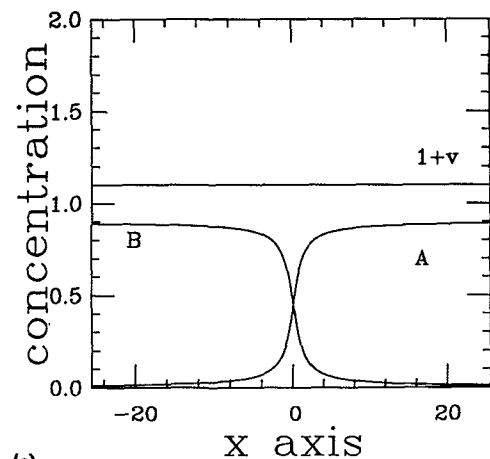
One would expect this procedure to converge nicely. It is evident that  $a_1$  is continuous and relatively small everywhere. Because of the shape of  $B_{\text{ad}}(x, t)$  it should be similar to the solution for a static step function (see Appendix B) for both large positive and negative  $x$  but with a smooth transition through the diffusion front.

## IV. NUMERICAL RESULTS

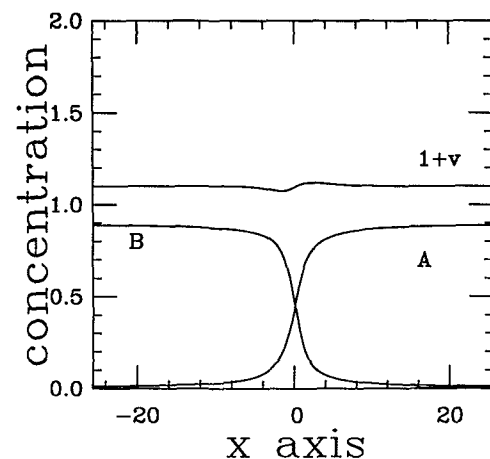
We solve the system of nonlinear Eqs. (2.4) by numerically integrating the equations, starting from the one-dimensional (along the  $x$  axis) initial concentration profiles given in Fig. 1(a). The choice of smooth rather than step-like initial data ensures that the second derivatives of the concentrations are everywhere finite so that all the derivatives in Eqs. (2.4) are well-defined. The initial concentration of vacancies is constant in space. Since we are interested in the strongly nonlinear limit of the equations we consider the case of a small concentration of vacancies ( $v_0 = 0.1$ ) and strongly asymmetric diffusion coefficients ( $D_A \gg D_B$ ).

The concentration profiles at time  $t = 2$  (in arbitrary units) are shown in Fig. 1(b). While there is not yet an appreciable change of the concentrations of the two components compared to the initial profiles, the vacancy concentration develops a maximum and a minimum on the “fast” and the “slow” sides of the interface, as expected from the discussion following Eqs. (3.1). Notice that Fig. 1(b) pertains to the short-time regime in which the finite size of the system (see below) doesn’t play an important role. The situation is quite different at later times, e.g.,  $t = 190$  [Fig. 1(c)]. Now, finite size effects on the concentration of the fast species (A) are clearly manifested in the depletion of its initial concentration profile and the subsequent buildup of the A concentration within the B-rich domain, and in the disappearance of the maxima and the minima in the concentration of vacancies.

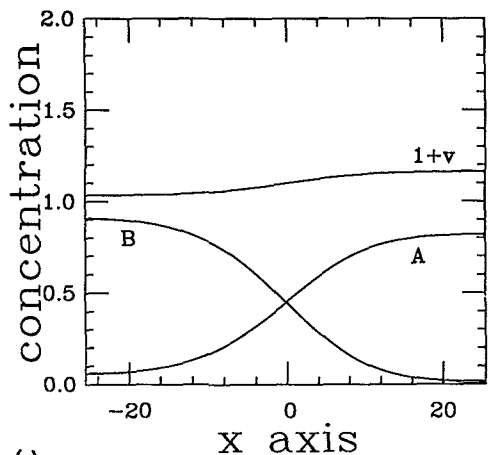
In Fig. 2 we plot the deviation from the adiabatic concentration profile,  $A - A_{\text{ad}}$ , as a function of the  $x$  position for  $D_A = 10$ ,  $D_B = 1$ , and  $v_0 = 0.1$ . At  $t = 0$  the adiabatic pro-



(a)



(b)



(c)

FIG. 1. (a) The initial ( $t = 0$ ) concentration profiles of the “fast” A and the “slow” B species and the concentration of vacancies  $v$  (shifted by unity for clarity of presentation) are plotted as a function of position  $x$ , for  $D_A = 10$ ,  $D_B = 1$ , and  $v_0 = 0.1$ . (b) Same as in (a), at time  $t = 2$ . (c) Same as in (a), at time  $t = 190$ .

file given by Eq. (3.3) is nearly exact within the A-rich domain and overestimates the A concentration within the B-rich domain. Although, based on the discussion in Sec. III A, we expect the adiabatic approximation to improve with time, a naive application of Eq. (3.3) shows that while

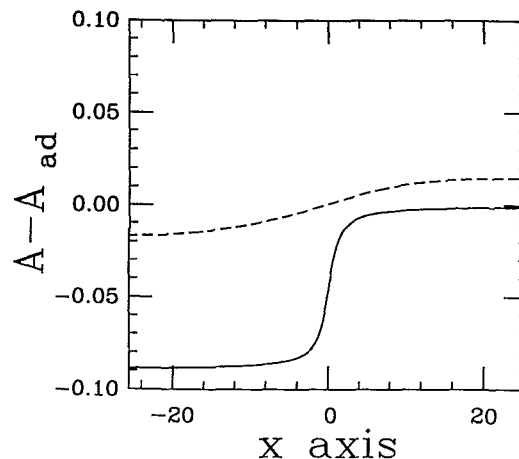


FIG. 2. The difference between the exact [from numerical integration of Eqs. (2.4)] concentration of the “fast” species (A) and the adiabatic approximation results ( $A_{ad}$ ) is plotted as a function of position  $x$ , for  $t = 0$  (solid line) and for  $t = 190$  (dashed line), using Eqs. (3.3) and (4.1), respectively. The diffusion coefficients and the initial vacancy concentration are the same as in Fig. 1.

it does improve in the B-rich domain, it becomes much worse on the A-rich side. The problem can be traced back to the derivation of Eq. (3.3) where we implicitly assumed that the concentration of the A species well inside the A-rich domain (at  $x = \infty$ ) remains unaffected for all finite times,  $A(\infty, 0) = A(\infty, t)$ . This condition is violated after a *finite* time in a *finite* system, due to the diffusion of the A species to the B-rich side. Assuming that initially A and B occupy a volume  $V$  each and equating the adiabatic concentration of A in the local free volume available to it [ $A_{ad}/(1 - B)$ ] with the ratio of the total number of A sites [ $V \cdot (1 - v_0)$ ] to the total number of free sites [ $2V - V \cdot (1 - v_0)$ ], we obtain the long-time/finite-size adiabatic approximation

$$A_{ad} = (1 - B) \cdot (1 - v_0) / (1 + v_0). \quad (4.1)$$

The difference between the calculated long-time ( $t = 190$ ) concentration and this adiabatic solution is plotted in Fig. 2. Although the adiabatic approximation still deviates from the exact result, the improvement is manifested in the fact that the deviation is now of the same magnitude on both sides of the interface. Using this equation we can also obtain the long-time adiabatic diffusion coefficient (corrected for finite size effects),

$$D_B^{eff} = D_B \cdot 2v_0 / (1 + v_0). \quad (4.2)$$

Encouraged by the semiquantitative success of the adiabatic approximation to the full nonlinear diffusion problem we would like to consider the question of interdiffusion and ask whether these coupled nonlinear equations can be replaced by a single linear diffusion equation for the difference of concentrations,  $m = A - B$ , of the form

$$dm/dt = D_{A-B} \cdot \nabla^2 m. \quad (4.3)$$

While such an equation cannot be exact because of the non-trivial coupling between  $m$  and  $v$ , application of the long-time adiabatic approximation does give rise to an equation of the above form, with an interdiffusion coefficient

$$D_{A-B} = D_B \cdot 2v_0 / (1 + v_0). \quad (4.4)$$

In order to compare this approximation with our numerical results we choose a point  $x$  in space, calculate the time and spacial derivatives of the function  $m(x, t) = A(x, t) - B(x, t)$  at this point, and define the corresponding interdiffusion coefficient as

$$D_{A-B} = (dm/dt) / (d^2m/dx^2). \quad (4.5)$$

Although, in principle, this definition gives a diffusion coefficient that depends on the chosen location on the diffusion front, we find that in the long-time limit its value becomes independent of this choice. A typical time dependence of the interdiffusion coefficient calculated at two different points,  $x = 0$  and  $-5$ , is shown in Fig. 3, for  $D_A = 16$ ,  $D_B = 1$ , and  $v_0 = 0.1$ .

In Fig. 4 we plot the long-time ( $t = 150$ ) limits of the interdiffusion coefficients as a function of  $D_A$ , for  $D_B = 1$ , and  $v_0 = 0.1, 0.2$ , and  $0.4$ . The corresponding predictions based on Eq. (4.4) are also shown. As expected, the adiabatic approximation is approached for  $D_A \gg D_B$  and  $v_0 \ll 1$ ; significant deviations are observed when the diffusion coefficients become nearly equal and when the concentration of vacancies is increased.

## V. DISCUSSION

We have derived and studied the nonlinear diffusion equations describing vacancy-controlled interdiffusion away from equilibrium, in a noninteracting lattice gas of species A and B. We have found that in the case of large kinetic asymmetry ( $D_A \gg D_B$ ) and small concentration of vacancies, the process of interdiffusion involves the formation of gradients in the vacancy concentration field, a point that was noticed in recent simulations of the random alloy problem.<sup>9</sup> Interestingly, this result violates the assumption of constant vacancy concentration often made in the metallurgical literature, in discussions of the Kirkendall effect.<sup>10-12</sup> The origin of the discrepancy is related to a fundamental difference between the models: while we assume that the concentration of vacancies changes only by the hopping of the A and B atoms,

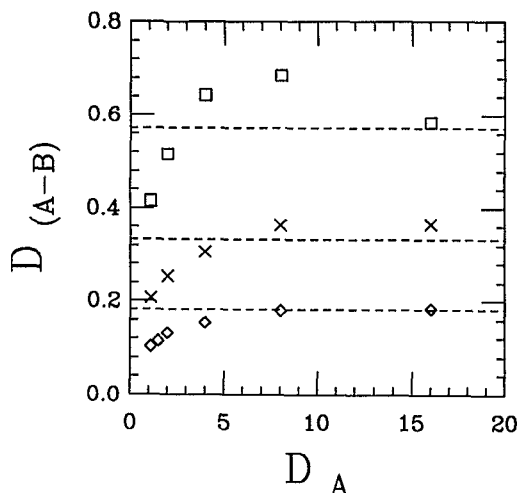


FIG. 4. The long-time limit of the interdiffusion coefficient  $D_{A-B}$  is plotted as a function of the “fast” diffusion coefficient  $D_A$ , for  $D_B = 1$  and  $v_0 = 0.1$  ( $\diamond$ ),  $0.2$  ( $\times$ ), and  $0.4$  ( $\square$ ), respectively. The corresponding adiabatic approximation results corrected for finite size effects [Eq. (4.1)] are given by the dashed lines.

the metallurgical models assume that vacancies can be created and annihilated subject only to the constraint that they are everywhere maintained in local equilibrium. The question of which of the two assumptions is better suited to describe a given experimental situation appears to be related to the kinetics of formation of lattice dislocations.

We have developed an adiabatic approximation in which the fast species are assumed to relax to their equilibrium concentration, determined by the instantaneous concentration of the slow species. In the long-time limit this approximation was shown to be in reasonably good agreement with brute-force numerical solutions of the nonlinear diffusion equations, indicating that the usual modeling of the interdiffusion process by a linear diffusion equation for the difference between the local concentrations of the diffusing species (with an appropriate interdiffusion coefficient), gives a qualitatively correct description of the essential physics. Although qualitatively our results appear to agree with the simulations of diffusion fronts in Ref. 9, a quantitative comparison was not attempted because of the neglect of correlation effects leading to off-diagonal Onsager coefficients and percolation effects, in our work.

We would like to comment on future extensions of the present work. One possible direction is to consider interdiffusion in more complex systems, such as polymers, in which the slow time scales make the process amenable to direct experimental observation.<sup>13,14</sup> Another interesting direction of research is suggested by the observation that both our numerical results and analytical approximations indicate that the nonlinearity of the diffusion equations does not give rise to “interesting” phenomena such as instabilities, shock waves, etc., and that the solutions of the equations have a “diffusive” character. Such “catastrophic” behavior can still occur if we were to add new types of nonlinearities, for example, terms proportional to higher powers of concentration gradients. These terms can arise from nearest-neighbor in-

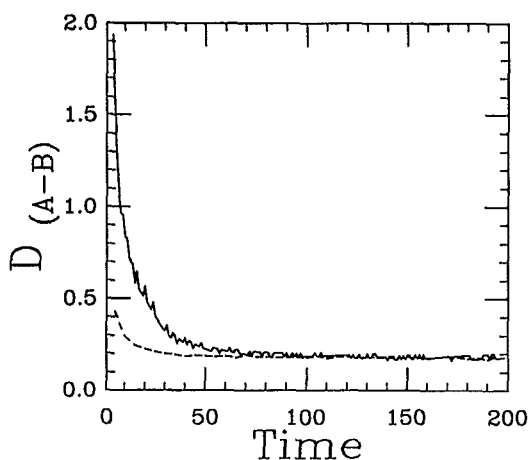


FIG. 3. The interdiffusion coefficient  $D_{A-B}(t)$  as calculated from Eq. (4.5) at positions  $x = 10$  (solid line) and  $-5$  (dashed line), is plotted vs time  $t$ , for  $D_A = 16$ ,  $D_B = 1$ , and  $v_0 = 0.1$ .

teractions between the diffusing species and we are currently attempting to generalize our athermal theory to accommodate such interactions and consequently, to include phase-diagram-type effects.<sup>15</sup>

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## APPENDIX A: THE STANDARD TRANSFORMATION

The usual approach to a diffusion equation is to transform it to an ordinary differential equation. This uses the symmetry of the diffusion equation which has only one, time dependent length scale  $[\sqrt{(Dt)}]$ . This is not possible in the present case because there are two diffusion constants and therefore two length scales. It is however interesting to see how this transformation breaks down. Defining

$$z = x/\sqrt{t} \quad (\text{A1})$$

and

$$A(x, t) = f(z); \quad B(x, t) = g(z) \quad (\text{A2})$$

substitution in Eq. (2.4) leads to the coupled ordinary equations,

$$\begin{aligned} (1/2D_A) \cdot z \cdot f' &= f'' + f \cdot g'' - g \cdot f'', \\ (1/2D_B) \cdot z \cdot g' &= g'' + g \cdot f'' - f \cdot g''. \end{aligned} \quad (\text{A3})$$

One therefore has two coupled equations with one dimensionless parameter ( $\eta = D_B/D_A$ ). This seems plausible and innocent. We have to show that equations (A3) cannot have a solution satisfying the required boundary conditions.

One notes first that Eqs. (A3) imply a symmetry for the solutions which is not at all obvious in the original equations, which results from the fact that the ansatz (A1) for  $z$  requires a unique choice of origin ( $x = 0$ ). In Eqs. (A3) the left-hand side vanishes for  $z = 0$  and therefore

$$f''(0) + g''(0) = 0 \quad (\text{A4})$$

and

$$f''(0) \cdot \{1 - [f(0) + g(0)]\} = 0. \quad (\text{A5})$$

Since  $f + g = 1$  implies that there is no diffusion current across this point the only acceptable solution is  $f'' = g'' = 0$  for  $z = 0$ . Returning to the original equations it can be seen that this also implies that the concentrations at  $x = 0$  are time independent and both have an inflection point there,

$$\begin{aligned} d^2A(0, t)/dx^2 &= dA(0, t)/dt = d^2B(0, t)/dx^2 \\ &= dB(0, t)/dt = 0 \end{aligned} \quad (\text{A6})$$

in spite of the asymmetry in the diffusion constants.

This could either mean that the symmetry is forced by the ansatz and that the resulting Eqs. (A3) have *no solution* consistent with the required boundary conditions or that the proper solutions of Eqs. (2.4) do indeed have this symmetry which is not apparent in their structure.

Consider the way the expansion of Sec. II shows up if we make the ansatz (A1). We require a solution of the equation resulting from Eq. (3.11),

$$\begin{aligned} (1/2D_A) \cdot z \cdot f'_1(z) &= [1 - g_{ad}(z)] \cdot \nabla^2 f_1(z) \\ &+ f_1(z) \cdot \nabla^2 g_{ad}(z). \end{aligned} \quad (\text{A7})$$

This should be solved with the boundary conditions corresponding to Eq. (3.13) at infinity,

$$\begin{aligned} f_1(-\infty) &= -(1 - \eta) \cdot v_0 \cdot (1 - v_0); \\ f_1(+\infty) &= \eta \cdot v_0 \cdot (1 - v_0). \end{aligned} \quad (\text{A8})$$

It is simplest to integrate out from  $x = 0$  in both directions where the only freedom one has is the choice of  $f_1(0)$  and  $f'_1(0)$ . It is easy to see that these boundary conditions (at  $x = 0$ ) are uniquely determined by each of the two conditions at infinity—Eq. (A8)—separately. They cannot be chosen to satisfy both boundary conditions simultaneously. Thus Eq. (A7) has no continuous solutions satisfying the boundary conditions. It is instructive to look at the example in Appendix B to see how this works.

## APPENDIX B: THE $D_B = 0$ LIMIT

Consider the static problem,

$$B = \begin{cases} 0 & x > 0 \\ 1 - v_0 & x < 0 \end{cases} \quad (\text{B1})$$

and therefore, taking  $D_A = 1$ ,

$$dA/dt = \begin{cases} v_0 \cdot \nabla^2 A; & J_A = v_0 \cdot \nabla A & x < 0 \\ \nabla^2 A; & J_A = \nabla A & x > 0 \end{cases} \quad (\text{B2})$$

At  $x = 0$  we must have equal concentrations in the space available and equal currents. Thus,

$$\begin{aligned} A(0) &= A_-(0)/v_0 = A_+(0); \\ v_0 \cdot (\nabla A)_- &= v_0^2 \cdot (\nabla A) = (\nabla A)_+. \end{aligned} \quad (\text{B3})$$

We now try the usual type of solution for the diffusion equation,

$$dA/dx = (C_+/\sqrt{t}) \cdot \exp(-x^2/t); \quad x > 0 \quad (\text{B4a})$$

$$dA/dx = (C_-/\sqrt{t}) \cdot \exp(-x^2/v_0 t); \quad x < 0 \quad (\text{B4b})$$

and therefore from the continuity of currents,

$$C_- \cdot v_0^2 = C_+ \quad (\text{B5})$$

and integrating the Gaussian,

$$(\pi/2)^{1/2} \cdot (v_0^{1/2} \cdot C_- + C_+) = 1 - v_0. \quad (\text{B6})$$

Thus, one obtains the solution

$$C_+ = (2v_0^3/\pi)^{1/2} \cdot (1 - v_0)/(1 + v_0^{3/2}) \quad (\text{B7})$$

and

$$A_+(0) = (1 - v_0)/(1 + v_0^{3/2}) = A_-(0)/v_0 \quad (\text{B8})$$

and therefore the density  $A$  is discontinuous at the origin.

This is clearly not an acceptable solution of the diffusion problem [Eq. (B2)] which we tried to solve by the ansatz (A1) above. This is even clearer if one thinks of solutions with a smooth transition region of  $B$  over a limited region.



## APPENDIX C: SELF-DIFFUSION AND TRACER DIFFUSION

Consider first the self-diffusion problem for a single species  $A$ . We look at the diffusion of a labeled particle which was at the origin at time  $t = 0$ . The situation is still described by Eqs. (2.4) where we have labeled the particle at the origin by  $B$ . Furthermore, since the diffusion constants of  $A$  and  $B$  are now identical ( $D$ ) one obtains Eqs. (2.12). They have to be solved with the initial conditions

$$v(\mathbf{r}) = 0; \quad m(\mathbf{r}) = -1 \text{ for } \mathbf{r} = 0$$

$$v(\mathbf{r}) = v_0; \quad m(\mathbf{r}) = 1 - v_0 \text{ otherwise.} \quad (\text{C1})$$

Thus, the self-diffusion constant is clearly renormalized  $-v_0 D$ . Moreover, because of the hole at the origin in  $v$  in the initial conditions, there is a correction term in the solution of Eq. (2.12a) described by the Green's function for the diffusion problem with diffusion constant  $D$ . This has a small effect on the solution at short times.

In order to describe the diffusion of a general tracer labeled  $T$  in a two-component mixture ( $A/B$ ) we have to generalize Eqs. (2.4) to the three-component case. This generalization is straightforward with initial conditions analogous

to Eq. (C1) but the resulting problem is always more complex than the two component interdiffusion problem. The details obviously depend on the three diffusion constants,  $D_A$ ,  $D_B$ , and  $D_T$ .

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