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Correlation factors for atomic diffusion in nondilute multicomponent alloys with arbitrary vacancy concentration

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Vacancy-assisted tracer diffusion in a multicomponent kinetic alloy consisting of $x^{\lambda}N$ atoms with hopping rate J^{λ} (where $\lambda \equiv A,B,C$, etc.) and vN vacancies (where $v=1-\sum_{\lambda}x^{\lambda}$) distributed randomly over a regular d-dimensional (where $d \geq 2$) hypercubic, or close-packed, lattice of N sites is analyzed through a self-consistent renormalization of a recent theory of Tahir-Kheli and Elliott combined with a generalization of concepts introduced by Manning. The result for the tracer-diffusion correlation factor is the following: $f^{\mathrm{tr}}=H''(\mathrm{tr})/[H''(\mathrm{tr})+2J^{0}]$, where J^{0} is the tracer-hopping rate, $H''(\mathrm{tr})$ is a generalized effective vacancy escape frequency, $H''(\mathrm{tr})=[M/(1-v)][J^{0}vf^{\mathrm{tr}}+J^{\mathrm{eff}}]$, where J^{eff} is an effective hopping rate of the background atoms averaged with a weighting factor proportional to x^{λ} and f^{λ}, i.e., $J^{\mathrm{eff}}=\sum_{\lambda}(J^{\lambda}x^{\lambda}f^{\lambda})/\sum_{\lambda}(x^{\lambda}f^{\lambda})$ and $M=-(1+\langle\cos\theta\rangle)/\langle\cos\theta\rangle$. For a single-component alloy, with particle concentration x, $J^{\lambda}=J$, and vacancy concentration $v=1-x$, our theory provides an excellent overall description of the correlation factor as long as $J/J^{0} \gtrsim z^{-2}$. Indeed, even for $J \rightarrow 0$, the calculated results agree with the Monte Carlo estimates, except in the immediate vicinity of the percolation threshold, v_{p}, which is located self-consistently to an accuracy of the order $1/z$.

I. INTRODUCTION

Atomic diffusion in solids has long been known to exhibit correlations[1] which are neglected by random-walk descriptions of the phenomenon. In the limit of vanishing vacancy concentration v, i.e., for a single vacancy in a macroscopic lattice, exact results for the self-diffusion correlation factor in a single-component alloy have been available for several lattices for more than a quarter of a century.[2,3] More recently, the methodology for obtaining these single-vacancy-limit results has been further developed[4] so that exact results can be obtained even when the tracer-hopping characteristics are distinct from those of the background atoms. (Note, this is true only when the macroscopic lattice has a *single* tracer atom.)

In the opposite limit of large vacancy concentration, namely for $(N-1)$ vacancies in a lattice of $N \gg 1$ sites, the treatment of the problem (which now consists of only a single atom) is even simpler. Here, in addition to the diffusion coefficient, the complete frequency- and wave-vector-dependent response $S(\vec{K},\omega)$ can also be exactly calculated.[5]

However, once the system departs from these highly idealized limits, the solution of the problem becomes far from simple. This is true, not only for $S(\vec{K},\omega)$ but also for the simpler quantity embodied in the tracer-diffusion correlation factor f^{tr}. The latter involves knowledge of $S(\vec{K},\omega)$ only in the limit $K \rightarrow 0, \omega \rightarrow 0$.

Several years ago Fedders and Sankey[6,7] (FS) undertook the task of calculating $S(\vec{K},\omega)$ throughout the concentration range. They presented a scheme which summed dominant subsets of an infinite series of diagrams. For uniform lattices their calculations referred to the case where the tracer is identical to the background hopping atoms, i.e., to a single-component alloy with an arbitrary number of vacancies.

Recently Nakazato and Kitahara[8] (NK) have presented a brief account of a treatment employing a projection-operator technique. They found the Laplace transform of the response in the form

$$S(\vec{K},u)=\left[u+\sum_{\mu,\nu}D_{\mu\nu}(u)k_{\mu}k_{\nu}+\cdots\right]^{-1}, \tag{1}$$

where $u=-i\omega$. For small wave vectors this defines the first set of terms in a convergent expansion and using the limit $u \rightarrow 0$ they gave an expression for the tracer-diffusion correlation factor valid for a simple (hyper)cubic lattice of d dimensions. While the NK prediction for the diffusion coefficient was noted to be exact in both the concentration limits, i.e., $v=0$ and 1, no rigorous statements concerning either its rate of change in these limits or its accuracy as a function of the particle concentration and the ratio of the rates of hopping of the background particles and the tracer atom were provided.

Very recently Tahir-Kheli and Elliott[9] (TKE) have presented an equation-of-motion method to calculate $S(\vec{K},\omega)$ at general $\vec{K}$ and ω. With the use of the assumption that the third-order fluctuations may be ignored, TKE solved the integral equation involving the second-order terms (for both hypercubic and close-packed lattices). The neglect of third-order fluctuations in the TKE theory was shown to be justified at both $v=0$ and 1, with the additional statement that in the limit $v \rightarrow 1$, the initial rate of change of the diffusion correlation factor with respect to the particle concentration was also given exactly by such a procedure. For general $\vec{K}$ and ω the predictions of the TKE theory were found to be in excellent agreement with those of a very careful Monte Carlo work[10] available for the face-centered-cubic (fcc) lattice where the tracer-hopping rate J^{0} coincided with that of the background particles J.

In the simple hypercubic lattice, the TKE result for the diffusion coefficient has been found to be identical[11] to the NK result. In addition, for the case $J^0=J$, the TKE expressions for the diffusion coefficient also appear to reduce to those given in the FS work.[6,7]

For general concentrations, the neglect of the third-order fluctuations in the TKE theory is not fully justified. However, using heuristic arguments supplemented by detailed numerical computations, TKE have concluded that in three dimensions (3D) as long as the background-particle hopping rate J is faster than a number approximately equal to J^0/z (z is the coordination number of the lattice), their theory provides an adequate description for the entire response, $S(\vec{K},\omega)$, throughout the concentration range. This is also true in d dimensions with $d \geq 2$.[2] Conversely, when the background is slow, i.e., $J<(J^0/z)$, the TKE theory becomes inadequate at small frequencies, i.e., $\omega \ll (J^0/z)$. However, for larger frequencies, $\omega \sim zJ^0$, the TKE theory remains valid even for the case of a much slower background. Because the behavior at small frequencies and long wavelengths pertains to diffusion, the TKE predictions for the diffusion correlation factor are also inadequate when J falls below about J^0/z. In particular, for the worst case, i.e., $J \rightarrow 0$, the TKE results are quite unsatisfactory for vacancy concentrations of around 50% or smaller for the fcc lattice[11] (excepting, of course, the region $v \rightarrow 0$ where the TKE theory again becomes exact). In lower coordination systems the corresponding figure for the vacancy concentration below which the TKE results for the $J \rightarrow 0$ case would become poor is anticipated to be even higher, about 70% for the quadratic lattice.

The goal of this work is to develop first a procedure which leads to an adequate description of the diffusion correlation factor throughout the concentration range even when the background is relatively slow moving. Second, the goal is to extend such a result to a more general alloy comprising m different types of atoms with finite concentration.

In this connection it should be mentioned that extensive literature already exists on the subject of vacancy-assisted diffusion correlation parameters in a general alloy. However, much like the earlier works relating to single-component alloy,[1-4] these works[13-16] also appear to be restricted to vanishingly small v. On the other hand, quite unlike the single-component alloy where the $v \rightarrow 0$ limit can be solved exactly in terms of an appropriately formulated two-body problem, in the multicomponent alloy even the $v \rightarrow 0$ limit leads to a "many-body" problem. The enormity of the present undertaking is therefore best appreciated by noting, for example, that the dynamical site-percolation problem is already contained within it even when it refers to only a two-component alloy.

Recently Fukai *et al.*[17] and Kutner and Kehr[11] (KK) have reported some preliminary studies of the finite-vacancy two-component alloy by using numerical simulation and Monte Carlo procedures. While the work of Ref. 17 is directed toward the analysis of NMR experiments on hydrogen-deuterium mixtures in niobium, the KK work is directly related to the diffusion correlation parameters f^λ. Unfortunately, however, the KK data for the A-B alloy relates to only a narrow range of concentration, e.g., where x^B is of order 4.6% or less. Also it refers essentially to a single-vacancy concentration, i.e., $v \sim 7\%$, and deals with only one lattice, i.e., the fcc lattice. More extensive Monte Carlo work on the A-B system would therefore be very valuable.

In Sec. II, we present first a brief review of the TKE calculation for the diffusion correlation factor. We are able to identify the primary source of the difficulty which causes the quality of the TKE results for the diffusion correlation parameter to deteriorate when the hopping rate of the host atoms is chosen to be much slower than J^0/z. To correct this problem, we institute a simple but powerful program of recurrent renormalization of the tracer hopping rate as it diffuses through a kinetic sea of background particles.

A compact expression for the tracer-diffusion correlation factor which follows from the new procedure is presented next in Sec. II. It is noted that the self-consistent "dressing" of the tracer propagator becomes progressively more important as J decreases below J^0/z toward zero. In particular, for $J \rightarrow 0$ the self-consistent dressing becomes crucial and its effects are most noticeable when the diffusion is substantially slowed. Of course, this occurs as the concentration of the immobile atoms increases toward the percolation threshold. Accordingly, for finite but small J, the effects of such a renormalization continue to be important throughout the forbidden concentration region (to use a phrase similar to that introduced by Manning[14]) until we reach the close vicinity of $v \rightarrow 0$ where the TKE prediction for f^{tr} once again becomes accurate and the additional dressing of the propagator approaches zero.

In Sec. III an important theorem, relating the diffusion coefficient of a *single* tracer in an alloy with immobile background but arbitrary vacancy concentration to that of a *single* vacancy diffusing in a *two*-component alloy where only one of the species of atoms is immobile, is presented. Thus, on rigorous grounds a common point in the results of Sec. II and those[14] of a binary alloy with $v \rightarrow 0$ is predicted. It is then discovered that such a rigorous prediction, true only for an exact set of results, is also obeyed by the corresponding approximate results that follow, respectively, from the present procedure and that given by Manning[14] in a different context.

To exploit the above noted self-consistency, in Sec. IV the results of Sec. II for the diffusion correlation factor of an arbitrary tracer in a single-component alloy with arbitrary concentration of vacancies are cast in a form generally used for calculating the same only in the limit $v \rightarrow 0$. Thus, a more general expression for what is referred to[4,14,15] as the vacancy "escape frequency" is derived. At this juncture a procedure which parallels that of Manning[14] is used to define an "effective escape frequency" for the vacancy which refers to an m-component alloy but with the new feature that the vacancy concentration is now arbitrary. (Once again, this effective escape frequency reduces to that introduced by Manning[14] for an m-component alloy in the limit $v \rightarrow 0$.) With this generalization, the stage is set for the derivation of the diffusion correlation factors in the generalized alloy.

This is done in Sec. V where the expression for the tracer-diffusion correlation factor is presented in a compact form. For $v \rightarrow 0$ this expression reduces to that of Manning.[14]

The paper is concluded by a discussion of the general result. In particular, the results are compared with available Monte Carlo data of KK (Ref. 11) and Kehr, Kutner, and Binder.[18]

II. TRACER DIFFUSION IN A SINGLE-COMPONENT ALLOY

Let us consider first a single distinct tracer atom with hopping rate J^0 in a host system consisting of xN atoms with hopping rate J distributed randomly over a regular d-dimensional (dD) lattice of N sites. (Here $d \geq 2$.) The lattice may be simple hypercubic or close packed. The vacant sites are to be treated as though they were occupied by double occupancy avoiding entities called "vacancies" whose concentration v is therefore equal to $1-x$.

As usual,[4-11] instantaneous but stochastic hopping of atoms to unoccupied sites is assumed. Forbidding multiple atomic occupancy of any site, the following rate equation is used:

$$\frac{d\sigma_i}{dt} = -\sum_j J_{ij}^{\sigma}(\sigma_i V_j - \sigma_j V_i) \ . \tag{2.1}$$

Here $\sigma_i = p_i$ or n_i according to whether the site i is currently occupied by the tracer or one of the host atoms, respectively. Similarly, V_i refers to the vacancy occupation of a site i.

The spatial range of the hopping integrals, J_{ij}^{σ}, is restricted for simplicity to nearest-neighbor separation, i.e.,

$$J_{ij}^{\sigma} = \begin{cases} J^{\sigma} \text{ if } i \text{ and } j \text{ are neighbors} \\ 0, \text{ otherwise} \end{cases} \tag{2.2}$$

and $J^{\sigma} = J^0$ or J depending on whether σ_i refers to p_i or n_i.

Once the tracer and the background-particle occupancy variables have been introduced, the vacancy occupancy is completely specified, i.e.,

$$V_i = 1 - p_i - n_i \ . \tag{2.3}$$

In the TKE formulation[9] the tracer-occupancy-retarded Green's function,

$$G_{gg'}(t) = -2\pi i \Theta(t) \langle p_g(t) p_{g'}(0) \rangle \ , \tag{2.4}$$

and the frequency and the inverse-lattice Fourier transforms,

$$\begin{aligned} G_{gg'} \equiv \langle\langle pg;pg' \rangle\rangle &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} G_{gg'}(t) \exp(i\omega t) d\omega \ , \\ &= (1/N) \sum_K G_K \exp[i\vec{k}\cdot(\vec{g}-\vec{g}\,')] \ , \end{aligned} \tag{2.5}$$

are analyzed. (Here and henceforth the length of the elementary cube edge is chosen to be unity. This in turn also fixes the scale for the inverse-lattice wave vectors.)

As demonstrated by TKE, the mass operator of G_K, i.e.,

$$G_K = [\omega + i\Sigma(\vec{K},\omega)]^{-1} \ , \tag{2.6}$$

$$\Sigma(\vec{K},\omega) = vJ^0 \left[\omega_K - \sum_{\delta} [1 - \exp(i\vec{K}\cdot\vec{\delta})] \rho(\vec{\delta}) \right] \ , \tag{2.7}$$

involves the second-order propagator $\rho(\vec{\delta})$, which refers to a composite pair consisting of a tracer and a neighboring background-particle fluctuation field (henceforth to be called the composite pair), diffusing with relative momentum $\vec{K}$, i.e.,

$$\rho(\vec{\delta}) = \frac{1}{N} \sum_{\vec{K}'} G^{(2)}_{\vec{K}-\vec{K}',\vec{K}'} \exp(-i\vec{K}'\cdot\vec{\delta})/G_{\vec{K}} \ . \tag{2.8}$$

Here $\vec{\delta}$ is a nearest-neighbor vector and

$$\begin{aligned} G^{(2)}_{lj;g'} &\equiv \langle\langle p_l U_j ; p_{g'} \rangle\rangle \\ &= \left[\frac{1}{N}\right]^2 \sum_{\vec{K}_1} \sum_{\vec{K}_2} G^{(2)}_{\vec{K}_1,\vec{K}_2} \exp[i\vec{K}_1\cdot(\vec{l}-\vec{g}\,') \\ &\qquad + i\vec{K}_2\cdot(\vec{j}-\vec{g}\,')] \ , \end{aligned} \tag{2.9}$$

$$U_j = n_j - \langle n_j \rangle = n_j - x \ . \tag{2.10}$$

The remaining notation is as follows:

$$\omega_K = z(1-\gamma_K), \quad \gamma_K = \sum_{\delta} \cos(\vec{K}\cdot\vec{\delta})/z \ , \tag{2.11}$$

where z is the coordination number of the lattice.

Within the simplest mean-field approximation (MFA), the second-order propagator $\rho(\vec{\delta})$ is neglected and thus

$$\Sigma(\vec{K},\omega) \underset{\text{MFA}}{\sim} vJ^0\omega_K \ . \tag{2.12}$$

For long wavelengths the tracer motion is easily identified with random-walk diffusion since $\omega_K \sim K^2$. Thus the uncorrelated diffusion coefficient D of the tracer is simply equal to vJ^0,

$$D \underset{\text{MFA}}{\sim} vJ^0 = D_0 \ . \tag{2.13}$$

If correlations were to be taken into account, the diffusion coefficient of the tracer would, in general, be reduced, i.e.,

$$D = \lim_{\omega \rightarrow 0, K^2/\omega \rightarrow 0} [\Sigma(\vec{K},\omega)/K^2] \equiv D_0 f^{\text{tr}} \ , \tag{2.14}$$

and the diffusion correlation parameter $f^{\text{tr}} \leq 1$ would depend on both the lattice structure as well as the details of the host alloy.

In order to take account of the correlations TKE analyzed the equation of motion of the second-order propagator $G^{(2)}$. Such an equation in turn involves $G^{(3)}$,

$$G^{(3)} \underset{1 \neq 2 \neq 3}{=} \langle\langle p_1 U_2 U_3 ; p_{g'} \rangle\rangle \ , \tag{2.15}$$

which refers to diffusion of larger composites. Because in $d \geq 2$ dimensions, these terms are strictly of order $v^2x^2G_K$, their neglect relative to the $G^{(2)}$ terms is rigorously justified at both the concentration limits, namely, $v \rightarrow 0$ and 1.

Ignoring third-order fluctuations TKE were able to solve the remaining set of equations in a compact form, i.e.,

$$\rho(\vec{\delta})=\Phi(\vec{\delta})+\sum_{\vec{\delta}'}\rho(\vec{\delta}')\{\alpha[P(\vec{\delta}-\vec{\delta}')-P(\vec{\delta})]$$
$$+\beta[P(\vec{\delta}+\vec{\delta}')-P(\vec{\delta}-\vec{\delta}')]\}\ , \tag{2.16a}$$

$$\Phi(\vec{\delta})=(i\beta/N)\sum_{\vec{K}'}\exp(i\vec{K}'\cdot\vec{\delta})[\omega_{\vec{K}+\vec{K}'}-\omega_{\vec{K}'}]/E(\vec{K}')\ , \tag{2.16b}$$

$$E(\vec{K}')=\omega+i[J\omega_{\vec{K}'}+vJ^0\omega_{\vec{K}+\vec{K}'})\ , \tag{2.16c}$$

$$P(\vec{r})=(1/N)\sum_{\vec{K}'}\exp(i\vec{K}'\cdot\vec{r})/E(\vec{K}')\ , \tag{2.16d}$$

$$\alpha=J+vJ^0,\ \ \beta=xJ^0\ . \tag{2.16e}$$

The δ' sum on the right-hand side of Eq. (2.16a) is taken over z nearest-neighbor vectors. This makes Eq. (2.16a) equivalent to a simple set of z simultaneous linear equations in the z unknowns $\rho(\delta')$.

The following aspects of these simultaneous linear equations are of special interest here. First, the coefficients involve inverse-lattice sums $P(\vec{r})$ and $\Phi(\vec{\delta})$, both of which have the same denominator $E(K')$. Second, these sums can all be carried out analytically in the diffusive regime of interest, that is, when $K^2 \to 0, \omega \to 0$. Third, and most important, in this regime all the coefficients depend uniquely on two specific combinations of the rate parameters, namely, α and β, and also $E(K')$ can be replaced by $i\alpha\omega_{K'}$.

The physical roles played by the parameters α and β are quite distinct. Whereas α provides the signature of the composite-pair diffusion [e.g., in the denominators on the right-hand side of (2.16a)], β plays no such corresponding role. In this connection we also note that the signature of the diffusing tracer (without an accompanying background field) is provided by the rate factor vJ^0.

In the TKE formulation, all correlations altering the tracer-diffusion rate within the composite pair were totally ignored. This is clearly justified for $d \geq 2$, when either $x \to 0$ or $v \to 0$, because such effects are vanishingly small in these limits. On the other hand, for finite x (or finite v), the effect of correlations on the tracer diffusion both *without* and *within* the composite pair must be taken into account. Moreover, if possible, this should be done self-consistently.

The new procedure, therefore, is the following. Calculate f^{tr} as in TKE. Introduce this f^{tr} into the diffusion coefficient of the composite pair by replacing α by its *correlated value* α' such that

$$\alpha'=J+vJ^0f^{\text{tr}}\ . \tag{2.17}$$

Repeat the cycle until no further changes in f^{tr} occur.

The TKE expression for f^{tr} as evaluated from Eq. (2.16a) without renormalizing the composite-pair diffusion was as follows:

$$f^{\text{tr}}_{\text{TKE}}=\left[1-\frac{2\beta\langle\cos\theta\rangle}{\alpha(1+\langle\cos\theta\rangle)}\right]^{-1}\ . \tag{2.18}$$

Therefore a fully iterated self-consistent treatment of tracer diffusion both *outside* and *inside* the composite pair is contained in the following:

$$f^{\text{tr}}=\left[1-\frac{2\beta\langle\cos\theta\rangle}{\alpha'(1+\cos\theta\rangle)}\right]^{-1}\ . \tag{2.19}$$

The nature of the approximation involved in (2.18) is quite different from that inherent in (2.19). Equation (2.19) assumes the third- and higher-order propagators have much the *same* effect on the tracer diffusion *within* the composite pair as the second-order propagators have on the tracer diffusion of the tracer by itself. In contrast, Eq. (2.18) ignores all contributions from third- and higher-order propagators, especially on the diffusing composite pair.

Note, the quantity $\langle\cos\theta\rangle$ mentioned in Eqs. (2.18) and (2.19) is the well-known average cosine of the angle between the directions of successive vacancy-tracer interchanges,

$$\langle\cos\theta\rangle=\begin{cases}-0.209\,841\,70, & \text{sc}\\ -0.157\,947\,42, & \text{bcc}\\ -0.122\,680\,07, & \text{fcc}\\ -0.363\,380\,23, & \text{quadratic lattice}\ .\end{cases}$$

Clearly for $v \to 0$ the replacement of α with α' does not affect the results. Away from this limit, we write schematically

$$f^{\text{tr}}\sim f^{\text{tr}}_{\text{TKE}}+\Delta\ , \tag{2.20}$$

and hence

$$\Delta\sim-2xv(f^{\text{tr}}f^{\text{tr}}_{\text{TKE}})^{-1}\frac{\langle\cos\theta\rangle}{(1+\langle\cos\theta\rangle)}\frac{(f^{\text{tr}}-1)}{(v+\eta)(vf^{\text{tr}}+\eta)}\ , \tag{2.21}$$

where

$$\eta=J/J^0\ . \tag{2.22}$$

Therefore, when x is small or when η is large, the new formulation reduces to TKE. Any differences Δ between the two are important only when η is small compared to unity. Moreover, this is especially true for that range of vacancy concentration where $f^{\text{tr}} \ll 1$. As is well known, the latter occurs in the "forbidden" range of concentrations[14] (where for $\eta \to 0, f^{\text{tr}} \to 0$).

The new equation for f^{tr} given in (2.19) has a simple solution. This is especially the case when the background is immobile, i.e., $J=0$,

$$f^{\text{tr}}=1+2x\langle\cos\theta\rangle/[v(1+\langle\cos\theta\rangle)]\ . \tag{2.23}$$

This gives a physically acceptable (that is, "positive") value for f^{tr} until the vacancy concentration falls to the percolation threshold v_P,

$$v_p=2\langle\cos\theta\rangle/(\langle\cos\theta\rangle-1)\ , \tag{2.24}$$

where $f^{\text{tr}} \to 0$. Below v_p, the tracer cannot diffuse at all, hence the forbidden vacancy concentration region, i.e., $v_p < v \leq 0$.

In Fig. 1, f^{tr} given by (2.23) is plotted (as continuous

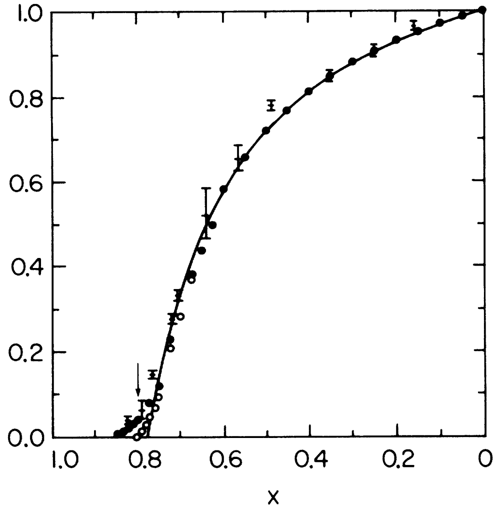

FIG. 1. Tracer-diffusion correlation factor f^{tr} is given as a function of the background-particle concentration x. The lattice is fcc and the background particles, which are assumed to be immobile, are considered to be randomly distributed. Solid curve represents (2.23) of the text. Data marked I are taken from KK's Monte Carlo work (see Ref. 11, Fig. 7). Both the open and closed circles represent different sets of Monte Carlo results for the same quantity (see Sec. III of the text) as given by Murch and Rothman (see Fig. 1 of Ref. 16).

curve) versus the immobile-particle concentration x. The corresponding Monte Carlo data of KK (Ref. 11) are signified by the symbol I. Closed and open circles represent an equivalent set of data given by Murch and Rothman[16] which will be discussed later in Sec. III.

III. THEOREM

It is interesting to examine the equations of motion and hence the diffusion characteristics of *a tracer* atom hopping through a background consisting of Nx completely immobile atoms distributed randomly over a lattice of N sites and to compare it with the corresponding diffusion characteristics of *a single vacancy* hopping through the same lattice with the same configuration of Nx completely blocked sites (on which immobile atoms reside) while all the remaining sites are occupied with mobile atoms that can hop via the vacancy-exchange mechanism. These two sets of equations of motion as well as their complete hierarchy are found to be identical, thus proving the equality of the two diffusion coefficients.

Let the set of Nx blocked sites be denoted as $\{b_l\}$. Here $0 \leq x \leq 1$. These sites are shown schematically in Figs. 2(a) and 2(b) as closed circles. Let the tracer p_i be at position i [see Fig. 2(a) where the tracer is denoted by the symbol T]. All the remaining sites in Fig. 2(a) are vacant (denoted as open circles). The tracer can hop through the unblocked channels with the equation of motion

$$\frac{dp_i}{dt} = -\sum_j{}' J_{ij}^0(p_i - p_j) . \tag{3.1}$$

This equation of motion is linear because the set of sites over which "j" ranges are those with vacancies. (These sites are the subtraction from "N" of the set $\{b_l\}$ on which immobile atoms reside. This fact is denoted by adding a prime to the summation symbol.)

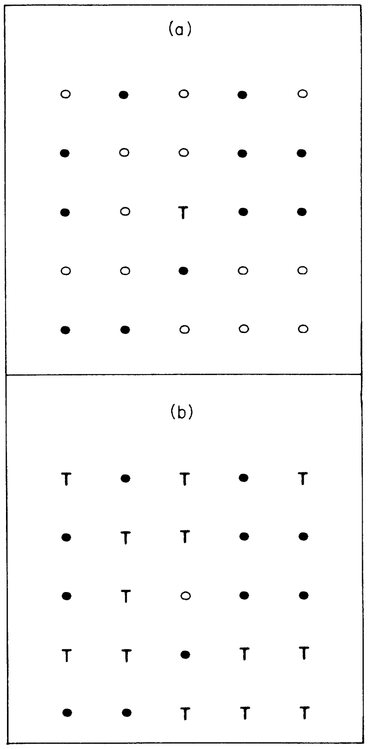

FIG. 2. To illustrate the argument of Sec. III, two equivalent atomic configurations are shown. The tracer (indicated by T) diffusion for configuration (a) is identical to the vacancy (indicated by open circles) diffusion for configuration (b). Closed circles represent immobile atoms.

Let us compare Eq. (3.1) with the equation of motion for the single vacancy V_i, shown schematically in Fig. 2(b). Again, the same set of Nx sites $\{b_l\}$ have been blocked off by immobile atoms. However, all the remaining sites are considered to have atoms that are identical to the tracer of Fig. 2(a). Therefore, we have

$$\frac{dV_i}{dt} = -\sum_j{}' J_{ij}^0(V_i - V_j) . \tag{3.2}$$

[Note the prime on the j sum in Eq. (3.2).] Not only are Eqs. (3.1) and (3.2) identical, even the variables are related, i.e.,

$$V_k = 1 - p_k , \tag{3.3}$$

where k ranges over i (or j not contained in $\{b_l\}$). Thus the diffusion coefficient as well as the entire response function of the *tracer* self-correlation function of the system shown schematically in Fig. 2(a) is *identical* to those for the *vacancy* in the system shown in Fig. 2(b).

As mentioned in the preceding section, the recent Monte Carlo work of KK (Ref. 11) provides estimates for the tracer-diffusion coefficient in a system such as that shown in Fig. 2(a) as a function of the immobile particle concentration x. Through a helpful coincidence accurate Monte Carlo work[16] for the vacancy diffusion coefficient in a system such as shown in Fig. 2(b) is also available. According to the relationship demonstrated in this section these two seemingly different diffusion coefficients are in fact identical. This is confirmed in Fig. 1, where both the closed and the open circles represent Monte Carlo results for the vacancy diffusion in a system as shown in Fig. 2(b). Here the solid line indicates the results given by our renormalized theory explained in Sec. II whereas the data points marked $\mathbf{\Xi}$ are those supplied by KK (Ref. 11) for tracer diffusion in a corresponding system of the type shown schematically in Fig. 2(a).

There is yet another helpful coincidence to report. The celebrated work of Manning[11] on tracer diffusion in a multicomponent alloy with only a single vacancy is readily applied to a binary alloy where one set of atoms is immobile. The vacancy diffusion in this alloy then corresponds to Fig. 2(b) and is thus identical to tracer diffusion in a system such as described in 2(a) for which our theory of Sec. II yields the result given in Eq. (2.23). As it happens, for this particular limit Manning's result also reduces[15,16] to that given in Eq. (2.23).

The foregoing implies a certain self-consistency between the predictions of the extended TKE procedure discussed in Sec. II and that of Manning[11] in the sense that for the *only point* at which their relevant physical systems "overlap," the two sets of necessarily *approximate* results are (like the corresponding *exact* ones) identical.

IV. EFFECTIVE ESCAPE FREQUENCY FOR THE VACANCY IN A SINGLE-COMPONENT ALLOY

One of the traditional approaches to discussing the tracer-diffusion correlation factor f^{tr} in a single-component alloy with vanishing vacancy concentration is to write[4,13–16]

$$f^{\text{tr}} \underset{v=0}{=} H(\text{tr})/[H(\text{tr})+2J^0] \; , \tag{4.1}$$

where J^0 is the hopping rate of the tracer (to one of the neighboring vacant sites, that is). The quantity $H(\text{tr})$ is referred to as the effective escape frequency of the vacancy from a neighboring site of the tracer. For a single-component system with $v=0$, $H(\text{tr})$ is well known,[14] i.e.,

$$H(\text{tr})=JM \; , \tag{4.2}$$

where

$$M=-(1+\langle\cos\theta\rangle)/\langle\cos\theta\rangle \tag{4.3}$$

and J is the hopping rate of the background atoms. Thus $H(\text{tr})$ depends on the crystal structure as well as the background atom-vacancy exchange rate J.

It is therefore instructive to recast the renormalized extended result for f^{tr} given in Eq. (2.19) into an analogous form, i.e.,

$$f^{\text{tr}}=H'(\text{tr})/[H'(\text{tr})+2J^0] \; , \tag{4.4}$$

where

$$H'(\text{tr})=\frac{M}{1-v}(vJ^0 f^{\text{tr}}+J) \; . \tag{4.5}$$

Of course, as $v\rightarrow 0$, these reduce to (4.1) and (4.2).

The quantity $H'(\text{tr})$ is the effective escape frequency for the vacancy in the more general system with arbitrary vacancy concentration. As is clear from the discussion presented in Sec. II, $H'(\text{tr})$ is exact not only in the limit $v\rightarrow 0$ but also for $v\rightarrow 1$. Also, in the intermediate concentration, $H'(\text{tr})$ gives an extremely accurate estimate for the effective escape frequency whenever $J>(J^0/z^2)$, thereby implying that when the background is not *too* slow, the renormalized theory works well.

V. TRACER DIFFUSION IN A MULTICOMPONENT ALLOY

On its own the derivation of the effective escape frequency for the vacancy given in the preceding section, i.e., $H'(\text{tr})$, is of no particular physical interest. However, it enables us to achieve an important objective of generalizing a procedure previously employed by Manning[14] for calculating the tracer diffusion in a multicomponent system with only vanishing vacancy concentration.

To this end, let us define a generalized escape frequency for the vacancy $H''(\text{tr})$ in a multicomponent alloy through the introduction of an "effective hopping rate" J^{eff} for the background atoms,

$$H''(\text{tr})=\frac{M}{1-v}(vJ^0 f^{\text{tr}}+J^{\text{eff}}) \; . \tag{5.1a}$$

This expression is similar to that for $H'(\text{tr})$ given in (4.5) except for the as yet undefined hopping rate parameter J^{eff}, which for a single-component alloy is simply equal to J (the hopping rate of the background atoms). Next, let us introduce the physically reasonable assumption that J^{eff} is a *weighted average* over the background with the weighting being proportional to the concentration x^λ as well as the effective diffusion correlation factor of each of the components, i.e.,

$$J^{\text{eff}}=\sum_\lambda J^\lambda(x^\lambda f^\lambda)\Big/\sum_\lambda(x^\lambda f^\lambda) \; . \tag{5.1b}$$

It is clear that for $v\rightarrow 0$ this will lead to Manning's result referred to earlier.

Thus, for a generalized multicomponent alloy the tracer-diffusion correlation factor is

$$f^{\text{tr}}=H''(\text{tr})/[H''(\text{tr})+2J^0] \; , \tag{5.1c}$$

where $H''(\text{tr})$ is as given in (5.1a) and J^{eff} as in (5.1b). The unknown diffusion-correlation parameters f^λ are easily found by assuming the tracer to belong to each of the m species of atoms (one at a time, that is), i.e., by setting $J^0=J^\mu$ and $f^{\text{tr}}=f^\mu$, and solving the set of m equations so obtained in terms of the corresponding m unknowns f^μ. Once this is done, f^{tr} for an arbitrary tracer is given by Eq. (5.1c) where J^{eff} is now a known parameter.

VI. RESULTS AND CONCLUDING REMARKS

The equivalence of the diffusion-correlation factors of a *single* tracer, diffusing through a concentration x of immobile sites, and a *single* vacancy, diffusing through the same lattice with the same configuration of blocked sites

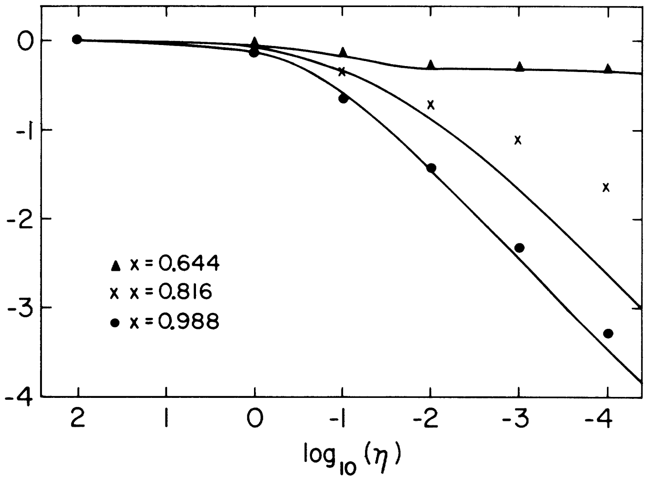

FIG. 3. Monte Carlo data of Kehr, Kutner, and Binder for the fcc lattice (see Ref. 18, Fig. 3) are shown as a function of the ratio η. The ordinate represents $\log_{10} f^{\,\mathrm{tr}}$ and the abscissa $\log_{10}\eta$. Solid curves follow from Eq. (2.19) of the text for the three concentrations $x = 0.644$, 0.816, and 0.988.

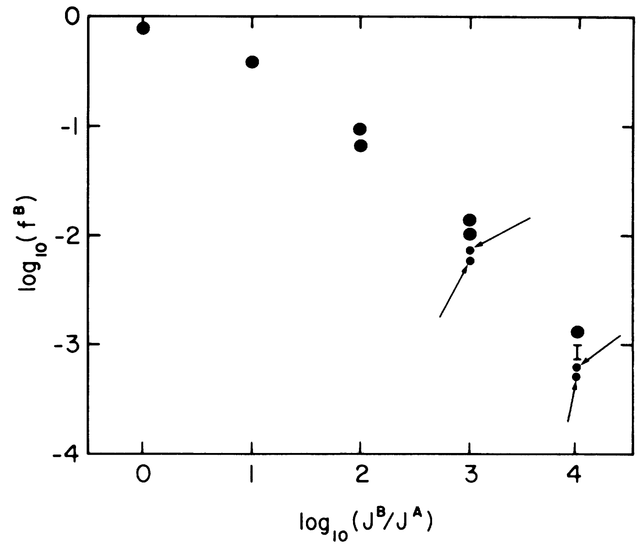

FIG. 4. KK's (Ref. 11) Monte Carlo data (large closed circles and the symbol **I**) are compared with the results obtained from Eqs. (5.1a)–(5.1c) of the text (small closed circles). A binary alloy, with concentrations x^A and x^B of A- and B-type atoms and vacancies $v = 1 - x^A - x^B$, is modeled on an fcc lattice. The tracer belongs to the B species of atoms. For $J^B/J^A = 1$, 10, and 100, our results lie within the large circles provided by KK (see Fig. 6, Ref. 11). The ratio $W = J^B/J^A$ and the concentrations x^A and x^B relating to the eight data points supplied by KK are as follows: $W = 1, x^A = 0.875, x^B = 0.04625$; $W = 10, x^A = 0.875, x^B = 0.04625$; and $x^A = 0.9155, x^B = 0.00575$. (Both sets of concentrations for $W = 10$ lead to the "same" result. Moreover, our calculations for both these concentrations also fit within the single closed circle given by KK.) For $W = 100$, the upper circle relates to $x^A = 0.875, x^B = 0.04625$, whereas the lower circle refers to $x^A = 0.9155, x^B = 0.00575$. Our results lie within the shown circles. For $W = 1000$, the upper circle refers to $x^A = 0.8935, x^B = 0.02755$, whereas the lower one is for $x^A = 0.91925, x^B = 0.0095$. Our results lie somewhat below these (shown by smaller circles). Finally for $W = 10\,000$, the upper result is for $x^A = 0.912, x^B = 0.00925$ and the lower one (shown by the symbol **I**) for $x^A = 0.9155, x^B = 0.00575$. Again our predictions lie somewhat lower.

while the rest of the sites are occupied by atoms similar to the tracer, was demonstrated in Sec. III. The corresponding Monte Carlo results also corroborate this fact (see Fig. 1). What is even more interesting, however, is that the predictions of Eq. (2.19), or more conveniently of Eq. (2.23) of the text (shown as the solid line in Fig. 1), are roughly as accurate as the Monte Carlo data they are being compared with. Nevertheless, discrepancies appear near the percolation threshold.

This fact is further elaborated in somewhat greater detail in Fig. 3, again referring to the fcc lattice, where $\log_{10} f^{\,\mathrm{tr}}$ is plotted as a function of $\log_{10}\eta$ with η as defined in (2.22). For a concentration $x = 0.644$, which is well *above* where the original TKE theory begins to fail, namely, $x \sim 0.45$, but which is well below the percolation concentration, $x_p \sim 0.816$, the results are excellent[18] down to $\eta = 10^{-4}$ and indeed to $\eta \to 0$ (see Fig. 1). A somewhat similar level of accuracy is available for small vacancy concentration, i.e., $v = 0.012$ (note that for this one-component system the results are exact in the limit $v \to 0$). In dramatic contrast to the above, at the percolation threshold the predictions of this paper noticeably depart from those given by Monte Carlo methods when $\eta < 1/(2z)$.

Finally, in Fig. 4, our calculations for a genuine binary system are compared with those provided by KK's Monte Carlo work. Here the vacancy concentration, $v \sim 7\%$, is well within the forbidden region. (Note that $v \sim 0.07$ is completely outside the *small*-vacancy regime.) We notice that for $\eta \gtrsim z^{-2}$, the results are very good. (Note that here η refers to J^A/J^B since one of the B atoms is acting as the tracer, but discrepancies arise when η is lowered toward z^{-3} and below.)

Thus we anticipate that in 3D our theory would provide an excellent treatment of the single-component alloy as long as the relevant ratio of the hopping integrals involved (i.e., η) is greater than about z^{-3}, and moreover if the system is well removed from the forbidden concentration regime. Inside the forbidden concentration regime (but away from the percolation threshold) the accuracy of our results appears to be of order z^{-2}. In contrast, at or near the percolation threshold the corresponding ratio must not be much smaller than z^{-1}. (After all this threshold itself is located only to within such an accuracy.) In lower dimensions, namely, $d = 2$, similar but somewhat more stringent conditions would apply.

Another point worth making is the following. As noted previously, for a multicomponent alloy (with at least two species of atoms with *finite* concentrations), the present theory reduces to that of Manning's in the limit when $v \to 0$. And Manning's theory has been tested extensively for binary systems by Monte Carlo methods[14–16] with the conclusion that is consistent with the statements given above regarding the accuracy of the present theory. In short, the present theory provides a useful extension of Manning's work to general vacancy concentration.

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