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One-dimensional-particle kinetics in a multicomponent alloy. The asymptotic time dependence of the mean-square displacement

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The mean-square displacement, $\langle r^2(t)\rangle$, of a labeled particle hopping on a linear chain through a multicomponent dynamic background with vacancy concentration v is evaluated in the limit of extremely long times. We find $\langle r^2(t)\rangle = [2va^2/(1-v)^{1/2}](\bar{J}t/\pi)^{1/2}$, where $\bar{J}$ is a collective hopping rate given by $(\sum_\lambda x^\lambda/J^\lambda)^{-1}$. Here J^λ is the hopping rate and x^λ the concentration of the λth atomic species in the background.

I. INTRODUCTION

The kinetics of noninteracting classical particles hopping stochastically on regular lattices are described by the well-known random walk theory.[1] In actual physical systems, the neglect of interactions is rarely justified. At the very least, hard-core repulsion forbidding multiple occupancy must be taken into account.

Unfortunately, the inclusion of interparticle interactions, even with zero range, causes long-range correlations to occur and makes the problem nontrivial to solve. In particular, after protracted motion, the single-particle properties are affected drastically and self-diffusion, which is the hallmark of classical random walk motion, fails to obtain if the lattice is not completely empty (excluding, of course, the tracer atom).

This phenomenon, sometimes referred to as the single filing condition, has received wide attention in several disciplines.[2] In biophysics, Hodgkin and Heynes[3] (see also Heckmann[4]) used the concept in their description of diffusion through very narrow pores in membranes. For finite but random channel lengths comprising N^R background particles, the essence of these findings[5-9] was a greatly reduced tracer diffusion as compared to its uncorrelated random walk value. This reduction, being proportional to $\langle (N^R+1)^{-1}\rangle$, becomes quite significant for long channels and thereby seriously curtails large scale wanderings of the ion under observation.[2,8] In a similar vein, mathematics[10-13] as well as physics[14-16] literature has dealt with single filing problems. In particular, the asymptotic time dependence of the mean-square displacement, $\langle r^2(t)\rangle$, of a tracer with hopping rate J^0 has been evaluated to have the following form:

$$\lim_{J^0 t\to\infty} \langle r^2(t)\rangle = 2\frac{(1-c)a^2}{c}\left(\frac{J^0 t}{\pi}\right)^{1/2} . \tag{1}$$

Here a is the length of the elementary hop and the background atoms, whose concentration c is finite, are assumed to have the same hopping rate as the labeled tracer.

The expression given in (1) is exact at both the concentration limits, i.e., when either the vacancy concentration $v=(1-c)\to 0$ or when the background particle concentration c is vanishing. Moreover, in the intermediate concentration regime it also appears to be substantially corroborated.[2]

Recently, using a theory given by Tahir-Kheli and Elliott[17] (TKE), Tahir-Kheli and El-Meshad[18] (TKEM) extended the above result given in (1), to the case where the background particles hopping rate, J, is arbitrary. In particular, TKEM have shown that in the limit of a rapidly hopping background, i.e., $J >> J^0$, the expression corresponding to Eq. (1) becomes

$$\lim_{J^0 t\to\infty} \langle r^2(t)\rangle = \frac{2va^2}{c}\left(\frac{Jt}{\pi}\right)^{1/2} , \quad \text{for } \eta >> 1 , \tag{2}$$

where $\eta = J/J^0$. In addition, TKEM have conjectured that the relationship (2) should hold more generally, quite possibly for all positive values of η.

The difficulty with the TKEM prediction given in Eq. (2) above is that it is rigorously substantiated only in the designated limit where $\eta >> 1$. For finite η, (2) is proven only in the limit of vanishing vacancy concentration, i.e., when $v\to 0$ or $c\to 1$.

The objective of the present work is twofold. First, it is to reexamine TKE and TKEM with a view to developing a recursive renormalization for the small frequency propagator of the tracer particle. Such considerations were left out in the original TKE formulation. In one dimension, the relevant renormalization turns out to be more substantial than in higher dimensions. In particular, for small frequencies, the renormalization becomes crucially important. Indeed, the serious overestimate of the long-time asymptotics of the tracer (mean-square) displacement away from the $v\to 0$ and/or the $\eta\to\infty$ limits in the original TKE formulation (see Ref. 18) can be directly traced to this neglect.

Using a fully self-consistent renormalization, in Sec. II the TKEM results are corrected and their intuitive conjecture is fully corroborated for all $\eta > 0$ both in the $v\to 0$ and the $c\to 0$ limits.

Our second objective here is considerably more grand: namely, to obtain the long-time asymptotics of the tracer (mean-square) displacement for a general, many-component dynamical alloy. Such an alloy would have a concentration x^λ of the λth type of atoms with hopping rate J^λ. Moreover, we shall continue to assume the existence of an arbitrary vacancy concentration v, i.e., subject only to the condition

$$v = 1 - \sum_\lambda x^\lambda . \tag{3}$$

In (3), λ is summed over all the atomic species present, e.g., $A,B,C,\ldots$, etc. Of course, the single tracer atom is itself also arbitrary and can, if so desired, be made identical to any species of the atoms present in the background stream.

II. LOW-FREQUENCY RENORMALIZATION—SINGLE-COMPONENT SYSTEM

Making the usual assumptions[2,14–20] regarding the stochasticity and the instantaneous nature of the hops which are allowed only across the nearest-neighbor separation to lattice positions that are currently unoccupied, we get the following equations of motion for the occupancy variables of the tracer, p_i, and those of the host atoms of the alloy, n_j^λ (note, i and j are lattice positions):

$$\frac{dp_i}{dt}=-\sum_j J_{ij}^0(p_iV_j-p_jV_i) \quad , \tag{4a}$$

$$\frac{dn_i^\lambda}{dt}=-\sum_j J_{ij}^\lambda(n_i^\lambda V_j-n_j^\lambda V_i) \quad , \tag{4b}$$

where V_i is the vacancy variable

$$V_i=1-p_i-\sum_\lambda n_i^\lambda \quad . \tag{5}$$

To make contact with the TKE and the TKEM works, let us first consider a single-component system such that the host alloy consists of only one variety of atoms (plus, of course, an appropriate number of vacancies which reside on all unoccupied sites). For this system we can dispense with the superscript λ, thus writing J and n_i, instead of J^λ and n_i^λ.

The basic function of interest is the retarded Green's function for the tracer occupancy variable, i.e.,

$$G_{gg'}(t)=\Theta(t)\langle p_g(t)p_{g'}(0)\rangle=\langle\langle p_g;p_{g'}\rangle\rangle \quad , \tag{6a}$$

or equivalently its Laplace transform $\tilde{G}_{gg'}(s)$. As is well known[2,14] the long-wavelength Fourier transform $\tilde{G}_k$, where

$$G_{gg'}(s)=\frac{1}{2\pi}\int_{-\pi/a}^{+\pi/a}dk\, e^{i\vec{k}\cdot(\vec{g}-\vec{g}')}\tilde{G}_k(s) \quad , \tag{6b}$$

is related directly to the Laplace transform of the tracer mean-square deviation. That is, if $\tilde{G}_k(s)$ is written as

$$\tilde{G}_k(s)=[s+\Sigma(\vec{k},s)]^{-1} \quad , \tag{7a}$$

then

$$\tilde{d}(s)=\langle r^2(t)\rangle_{(s)}=\left(\frac{2}{s^2}\frac{\Sigma(\vec{k},s)}{k^2}\right)_{k\to 0} \quad . \tag{7b}$$

Within the TKE theory, the equation of motion for $G_{gg'}(t)$ is written down first. This involves, in addition to the mean-field terms proportional to G, higher-order terms of the form

$$G_{lj;g'}^{(2)}(t)=\langle\langle p_lu_j;p_{g'}\rangle\rangle \quad , \quad l\neq j \quad , \tag{8a}$$

where

$$u_j=n_j-\langle n_j\rangle=n_j-c \quad . \tag{8b}$$

When the fluctuations from the mean field become important—which is always the case in one dimension outside the rather trivial short-time regime—the second-order terms proportional to $G^{(2)}$ cannot be ignored. To take a proper accounting of these fluctuations, TKE consider next the equation of motion of $G^{(2)}$ which in turn involves higher-order fluctuation terms of the form

$$G^{(3)}=\langle\langle p_1u_2u_3;p_{g'}\rangle\rangle \quad , 1\neq 2\neq 3 \quad . \tag{8c}$$

These terms, however, are of the order of

$$\langle u_2^2u_3^2\rangle G_{1g'}\sim v^2c^2G_{1g'} \quad , \tag{8d}$$

and their neglect relative to the second-order terms is justified only as long as Taylor expansions in the limits of small concentration of background particles, i.e., $c\to 0$, and small concentration of vacancies, i.e., $v\to 0$, are valid. However, for finite concentrations, the TKE procedure is not exact and its usefulness lies in the fact that for $J\gtrsim J^0/z$ (where z is the coordination number of the lattice) it appears to incorporate all the dominant fluctuations from the mean field and thus produces a useful approximation for the entire concentration range.

The foregoing argument holds for both two (2D) and three dimensions (3D). However, in one dimension (1D), it breaks down because the concentration-dependent Taylor expansion of the mass operator does not obtain for $c\to 0$.[18] The fact that in the opposite limit, i.e., $v\to 0$, the Taylor expansion continues to be valid even in 1D is of only marginal usefulness because the essential feature necessary for the adequacy of the TKE results at general concentrations is its exactness at both the opposite concentration limits.

In order to identify the source of this difficulty in the TKE formulation, let us recast their result for the mass operator in the limit of long wavelengths. We can write (compare also Ref. 18)

$$\lim_{ka\to 0}[\Sigma(k,s)/(ka)^2]=(vJ^0)R(\alpha,\beta,s) \quad , \tag{9a}$$

where

$$\alpha=J+vJ^0 \quad ; \quad \beta=cJ^0 \quad . \tag{9b}$$

This is a rigorous statement which follows readily after simple rearrangement of the TKE mass operator.

Physically, what Eq. (9a) implies is the following. For small wave vectors, the average tracer hopping rate in the mean-field approximation is equal to vJ^0. Accordingly, the mean-field value of R is unity. If fluctuations are taken into account, the average hopping rate is renormalized by a factor R, where R is a function only of α, β, and the Laplace frequency s. Upon evaluation in 1D,[14,18] the renormalization factor R is found to be greatly diminished from unity, especially for small frequencies (or, equivalently, for long times), i.e.,

$$\lim_{s\to 0}R=(\alpha s)^{1/2}/2\beta \quad . \tag{10}$$

So far, this reduction of the tracer motion has resulted entirely from a single iterative step, namely, by the influence of the second-order propagators upon that of the first order. If a simple perturbative scheme for the mass operator based upon a concentration expansion were valid, any renormalization of the second-order propogators themselves (due to the influence of the third-order propagators) could be neglected to the dominant order in concentration. However, as is clear from Eq. (10), the $c\to 0$ limit for the mass operator is divergent, therefore the renormalization coefficient R has of necessity to be evaluated through a self-consistently "dressed" set of propagators (rather than "bare" ones which were truncated in the TKE theory at the second iterative level).

All correlated propagators, beginning with $G^{(2)}$, involve in addition to the tracer at least one fluctuating background particle field u_i. The signature of the propagation of such a composite is not (vJ^0) but α. [Note that (vJ^0) is the signature of the tracer propagation at the first level.] Thus, the correct procedure for iterative dressing of the tracer hopping is to solve an integral equation where $\alpha = (J + vJ^0)$ is replaced instead by a renormalized α', i.e.,

$$\alpha \rightarrow \alpha' = J + vJ^0R \quad . \tag{11}$$

In such a recursive process, no alteration of the β's is undertaken. The presence of β's is not directly owed to the propagation of a correlated composite pair consisting of a tracer and a background particle fluctuation field. {It is interesting to note that a seemingly different dressing procedure employed by Fedders[15] [see his Eqs. (43)–(50)] for the evaluation of the renormalization factor for the $J^0 = J$ system, sums a similar set of diagrams to that given in (11) above. The apparent differences in the two procedures arise only because of the vastly different formulations being employed.} Thus for zero frequency, i.e., $s \rightarrow 0$, we get the following simple relationship for a fully dressed value of the renormalization parameter R

$$R = s^{1/2}(J + vJ^0R)^{1/2}/2\beta \quad , \tag{12a}$$

which gives

$$\lim_{s \rightarrow 0} R = (Js)^{1/2}/2\beta \quad . \tag{12b}$$

Similarly, at large frequencies, this procedure readily leads to the result $R = 1$ thereby leaving the TKE theory intact away from the small frequency regime. Moreover, Eq. (12) not only agrees with the well-known result[2,15] for $J^0 = J$, it also corroborates the TKEM conjecture[18] which is equivalent to Eq. (12), and puts it on relatively firm theoretical grounds.

III. MULTICOMPONENT SYSTEM: THE DIFFICULTY

The application of the TKE theory to a many-component dynamic alloy is quite involved. Not only is the algebra cumbersome, but also the accuracy of the procedure is inferior[21] to that of the single-component theory.[17] This loss of accuracy arises somewhat as follows: For the general case, the second-order propagators refer to coupled propagation of the tracer with different components of the alloy and the equations of motion of these propagators depend in turn on higher-order fluctuation terms of the form

$$G^{(3)} = \langle \langle p_1 u_2^\lambda u_3^\lambda ; p_{g'} \rangle \rangle \quad , \tag{13a}$$

where

$$u_i^\lambda = n_i^\lambda - \langle n_i^\lambda \rangle = n_i^\lambda - x^\lambda \quad . \tag{13b}$$

Thus, unlike in (8c) and (8d), the neglect of the third-order fluctuation for a multicomponent system is not exactly justified in the limit $v \rightarrow 0$ unless all but one of the components have small concentrations and the dimensionality is two or three. Moreover in 1D, even the small concentration limit offers difficulty.

In 2D (or 3D), the occurrence of this difficulty is expected on general grounds. Here an exact solution of the kinetic equations, even in the limit $v \rightarrow 0$, contains information about the dynamics of the "many-body" system. In particular, it includes all the information needed for the solution of the 2D (or 3D) dynamical percolation problem. In contrast, the corresponding exact solution for a single-component system in 2D (or 3D) for the limit $v \rightarrow 0$ contains[17] only the well-known "two-body" solution for the tracer diffusion correlation factor.[22]

The difficulties encountered in 1D are similarly insurmountable. Moreover, the lack of a convenient small concentration expansion in 1D is a further handicap.

IV. MULTICOMPONENT SYSTEM—AN EFFECTIVE SINGLE-COMPONENT PICTURE

In view of the difficulties enumerated above, we propose an approximate treatment for the multicomponent system in terms of an "effective" single-component picture. To this end, it is convenient to recast Eq. (12a) in the following form

$$R^\sigma = \frac{s^{1/2}[J^{\text{eff}} + vR^\sigma J^\sigma]^{1/2}}{2J^0(1-v)} \quad , \tag{14}$$

where

$$\lim_{(ka) \rightarrow 0} \Sigma^\sigma(k,s)/(ka)^2 = (vJ^\sigma)R^\sigma \quad . \tag{15}$$

The superscript σ implies either a distinct tracer, when $\sigma \equiv 0$, or a tracer which is identical to one of the species of particles in the host alloy, say λ, i.e., $\sigma \equiv \lambda$. The parameter J^{eff} is determined by the constitutents of the alloy, their hopping rates and the frequency.

The most obvious choice for J^{eff} is a weighted average over all the background particles. This average, however, must reflect, rather than just the bare weighting proportional only to the concentration, a fully dressed weighting which takes account of both the concentration, x^λ, and the relevant kinetic renormalization parameter, R^R, of each of the background components when acting as tracers, i.e.,

$$J^{\text{eff}} \approx \sum_\lambda (J^\lambda x^\lambda R^\lambda) / \sum_\lambda (x^\lambda R^\lambda) \quad . \tag{16}$$

The set of Eqs. (14)–(16) completely specify the behavior of the mean-square displacement of the tracer in the long-time limit. Of course, a similar procedure can also be carried out for short times. However, this is quite uninteresting in that the relevant renormalization parameters, R, are close to unity for large frequencies and the results are unchanged from those given by the use of the unembellished TKE procedure.[21]

In the time domain, Eqs. (14)–(16) readily lead to the following simple result for the mean-square displacement of the tracer

$$\lim_{\tilde{J}t \rightarrow \infty} \langle r^2(t) \rangle = \frac{2va^2}{(1-v)^{1/2}} \left(\frac{\tilde{J}t}{\pi} \right)^{1/2} \quad , \tag{17}$$

where $\tilde{J}$ defines a "collective hopping" rate, i.e.,

$$\tilde{J} = \left(\sum_\lambda \frac{x^\lambda}{J^\lambda} \right)^{-1} \quad . \tag{18}$$

Thus the displacement is determined largely by the slowest set of particles in the background.

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