Correlated random walks on two-sublattice systems. II. Monte Carlo simulations

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(Received 21 February 1986)

Correlated random walks on two-sublattice systems, with a potential difference between the sublattices resulting in site-dependent hopping rates, are studied by Monte Carlo simulation techniques. Large effective samples, consisting of approximately a million particles each, are used. Equally important, the systems are monitored over long effective times, e.g., up to 1000 Monte Carlo steps per particle (MCS's/P) for the three-dimensional lattices of NaCl and CsCl types, and up to 2500 MCS's/P for their two-dimensional analogs. The data are analyzed to accurately estimate the labeled-particle diffusion rates. These high-precision Monte Carlo estimates are compared with the predictions of the theory described in the preceding paper. Qualitative agreement between the two sets of results obtains over a wide range of effective potential differences between the two sublattices. Quantitatively, however, the agreement is found to be reasonable only as long as the effective-potential differences, reflected through the intersublattice hopping rates ratio σ, are not too large, or, equivalently, as long as σ lies within the restricted range $(Z-2)>\sigma>1/(Z-2)$. (Here Z is the coordination number for the relevant particle hops.)

I. INTRODUCTION

Simple rate equations, describing stochastic hopping motion of classical particles, have been used to describe transport phenomena in a wide class of physical systems. Examples include ionic motion in fast-ion conductors,[1] diffusion of hydrogen and its isotopes in various metal hydrides,[2] and tracer atom diffusion in hot solids via the vacancy mechanism.[3] Relevant aspects of the microscopic motion are investigated by NMR,[4] incoherent scattering of slow neutrons,[5] and tracer diffusion measurement techniques.

Theoretically, the rate equations have been studied by several different methods.[6–10] In view of the precision inherent in the theoretical predictions, and the relative complexity of the actual physical systems,[11] the cleanest test of the theories is provided by Monte Carlo simulation procedures.[12–15] Most of the existing[6–15] theoretical and numerical works deal with spatially uniform lattices. Two sublattice systems are not only more complex to treat theoretically,[16–18] generally less is known about them either from laboratory or numerical experiments.[18,19]

It is therefore of interest to study, by computer simulation techniques, the dynamics of tracer diffusion in two sublattice systems. In particular, the following three salient features observed in the course of the theoretical work presented in the preceding paper (henceforth to be referred to as I) would at first appear to be worth examining. The detailed notation follows that in I. These are the following.

(a) As the effective potential difference between the sublattices increases, giving rise to either an increase in σ, the ratio of the intersublattice hopping rates, beyond its uniform lattice value of unity, or equivalently a decrease in σ below the value 1, a dip in the tracer diffusion correlation factor, $f^{\rm tr}$, is occasioned whenever the case of half-filled lattice is approached.

(b) The frequency-dependent response of the tracer is found to embody two characteristic frequencies: namely J^0z and σJ^0z. Superficially, this situation is reminiscent of the occurrence of the two distinct time scales in the Richard's model[11] of tracer diffusion in hydrogen-concentrated metal hydrides. However, in detail there are essential physical differences between the two problems. Nevertheless, it would be interesting to gain some insight into this aspect of the phenomenon.

(c) Finally, the wave-vector dependent correlation factor $F(\mathbf{k},0)$, which is related to the tracer response $G_k^{\pm}$ [see Eqs. (5.2)–(5.6) of I], is found not only to undergo a change in its behavior as the average vacancy concentration V spans from 1 to 0, but additionally it is found that for larger V values, a characteristic dip also appears halfway across the k range whenever σ is large (or equivalently "small") compared to unity. Note that this behavior is to be contrasted with the corresponding uniform lattice case (i.e., where $\sigma=1$), which portrays only a transition from a minimum to a less pronounced maximum at the center of the k range without any hint of an additional characteristic dip.

Of these three features of the theory, historically the one most susceptible to error has related to the hydrodynamic limit where the wave vector $\mathbf{k}$ and the frequency ω are both vanishingly small. Indeed, for the uniform lattice case, where both the strengths and the weaknesses of the Tahir-Kheli and Elliot (TKE) decoupling have been extensively studied,[15,20–21] it has been found, by comparison with precision Monte Carlo data and some exact results available in one dimension, that the TKE does best

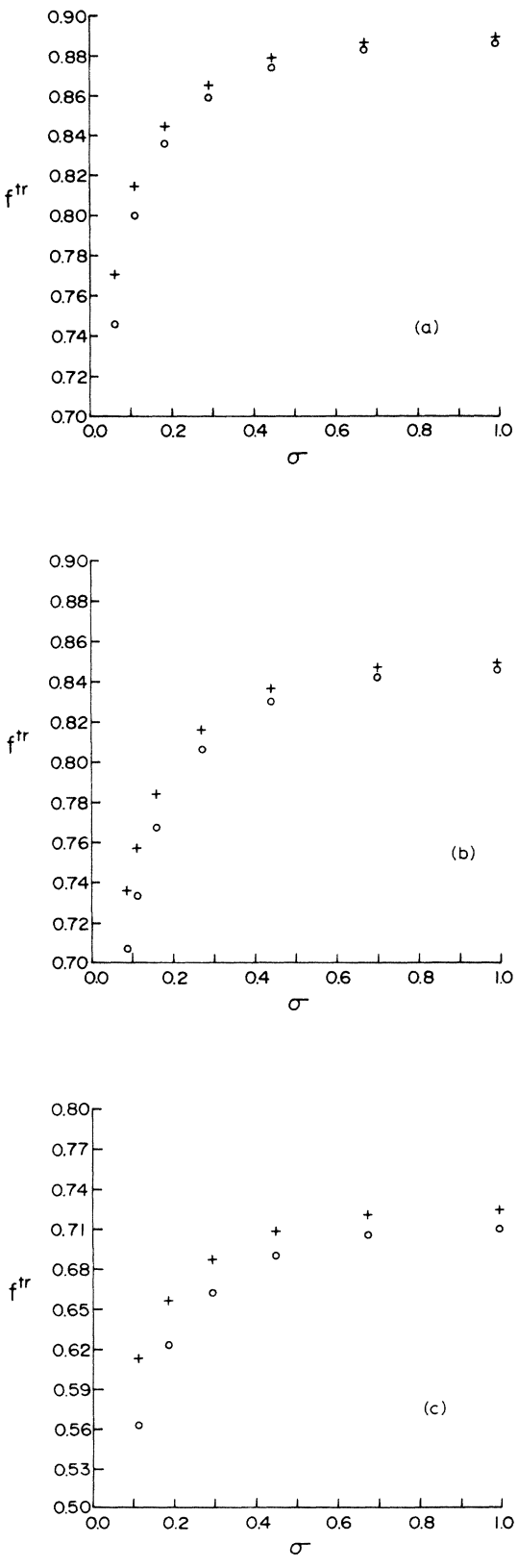

FIG. 1. f^{tr} (theory, +; simulation, ○) is plotted against σ for fixed vacancy concentration $V=0.5$, for (a) the CsCl structure; (b) the NaCl structure; (c) the two-dimensional lattice. The data were taken from Tables I–III.

for lattices with large coordination number and for systems with the weakest correlations (i.e., when the background is not too slow compared to the tracer). When the correlations are not small, the predictions of the unembellished TKE noticeably deteriorate. Yet, when this occurs, it does so primarily in the limit of large particle displacements and long elapsed times. For short times[20,21] and for small particle displacements, correlations remain weak and are well described by TKE even without the embellishments included in the self-consistent evaluation of the repeated tracer–vacancy-pair scatterings. Thus, for finite k and ω [i.e., that is when $\mathbf{k}$ is at least $1/Z$th of the zone size and $\omega \geq (J^0Z)/Z$], the TKE predictions are not only qualitatively correct, they are also quantitatively accurate.[21]

It is therefore clear that the first order of business in verifying the usefulness of the theory presented in I is to test the accuracy of its predictions for the diffusive regime, where k and ω are small. The plausible assumption here is that in view of the established properties of TKE, if the results of I are found to be satisfactory for small k and ω, they can be expected to be reliable for finite k and ω.

II. MONTE CARLO SIMULATIONS

The well-established Monte Carlo regimen can be extended to treat the case of two interpenetrating[18,19] sublattices without any serious difficulty. Therefore to save space, we refer the reader to the earlier works for introductory details. The only additional points worth making are that, unlike in the previous works,[18,19] the Monte Carlo averages were taken over large samples (involving N_G different particle trajectories where N_G is in excess of one million for each of the cases studied). Equally important, the systems were monitored over long periods of time, τ_{max} [τ_{max} was 1000 Monte Carlo steps/period (MCS's/per) for the three-dimensional lattices and 2500 MCS's/per for the two-dimensional case]. After the long time limit sets in, i.e., for $\tau \geq \tau_0 \approx 500$ MCS's/per, the statistical fluctuations scale roughly as $[N_G(\tau_{max}-\tau_0)]^{-1/2}$. Moreover, the rounding off errors, which would be of order $1/\tau_0$, are further decreased by analyzing incremental displacements after τ_0 as, for instance, is described in Ref. 15.

III. COMPARISON WITH THEORY

We analyze four systems: Namely, (i) the CsCl structure with two interpenetrating sublattices with $Z=8$, (ii) the NaCl structure with two interpenetrating sublattices with $Z=6$, and (iii) their two-dimensional analogs.

For the purposes of tracer diffusion the two-dimensional analogs of these two structures are topologically equivalent, reducing to the quadratic lattice with $Z=4$. This equivalence provides a powerful check on the two sets of programs (i) and (ii). Even though the details of these programs are very different, their two-dimensional analogs are very simply achieved by eliminating the third dimension from all the three-dimensional do loops.

Of the three lattices being analyzed, the CsCl lattice has the largest value of Z and thus is the most mean field

TABLE I. CsCl—body-centered-cubic structure. Monte Carlo results for the tracer diffusion correlation factor f^{tr} are compared against those provided by the theory of paper I. The labeling in column 1 (e.g., *,†,§) is merely to assist the eye in locating results belonging to a particular class, e.g., for fixed C^B.

C^A	C^B	σ	f^{tr} Theory	f^{tr} Monte Carlo
0.500 00	0.500 00	1.000 00	0.8889	0.886±0.002
0.450 00	0.550 00	0.669 42	0.8864	0.883±0.002
0.400 00	0.600 00	0.444 44	0.8787	0.874±0.002
0.350 00	0.650 00	0.289 94	0.8653	0.859±0.002
0.300 00	0.700 00	0.183 68	0.8446	0.836±0.002
0.250 00	0.750 00	0.111 11	0.8145	0.800±0.002
0.200 00	0.800 00	0.062 50	0.7706	0.746±0.002
0.750 00*	0.750 00	1.000 00	0.8163	0.812±0.002
0.687 50*	0.81250	0.507 69	0.8125	0.809±0.002
0.625 00*	0.875 00	0.238 10	0.7964	0.791±0.002
0.593 75*	0.906 25	0.151 19	0.7843	0.776±0.002
0.562 50*	0.937 50	0.085 71	0.7684	0.759±0.002
0.8545†	0.8545	1.0000	0.7813	0.773±0.003
0.7324†	0.8545	0.4661	0.7973	0.790±0.003
0.6104†	0.8545	0.2667	0.8034	0.793±0.003
0.4883†	0.8545	0.1625	0.7994	0.788±0.003
0.3662†	0.8545	0.0984	0.7831	0.765±0.003

like. For this lattice, we therefore expect the TKE decoupling to give accurate results for the self-diffusion case (with $J^0=J$, see paper I for notational details) as long as σ is not much less than about $\frac{1}{6}$. (Without any loss of generality we consider only the cases for which $\sigma \leq 1$.) This is borne out by the contents of Table I [see also Fig. 1(a)] which refers to the CsCl lattice.

Results for the $V=\frac{1}{2}$ cases are listed first in Table I. For $\sigma=1$, the theoretical estimate $f^{tr}=0.8889$ is barely resolvable from the Monte Carlo one, $f^{tr}=0.886\pm0.002$. The situation is only slightly worse when σ falls to about $\frac{2}{3}$ (see the second entry of the first column in Table I). Now, for $\sigma=0.6694$, $f^{tr}=0.8864$, according to the theory, whereas the Monte Carlo result is 0.883 ± 0.002.

Looking at other entries down the list, we observe that for $\sigma\sim0.1837$, f^{tr} (Monte Carlo)$=0.836\pm0.002$ now lies a full percentage point lower than the corresponding theoretical estimate, $f^{tr}=0.8446$. This trend is continued and by the time $\sigma\sim\frac{1}{16}$, the Monte Carlo estimates are fully 2% lower than those given by the theory. [See Fig. 1(a) for a rough but easier comparison of these results.]

Despite the noticeable discrepancy between the Monte Carlo and the theory when σ falls below $<1/(Z-2)$, the qualitative behavior of the results as a function of σ is, nevertheless, accurately predicted by the theory. Even the quantitative error is within "acceptable" limits.

To test as to whether the pronounced dip in f^{tr} for small σ, that is observed (see Table I) to occur for $V\sim\frac{1}{2}$,

TABLE II. NaCl—simple-cubic structure. Comparisons and notations are the same as described in the caption of Table I.

C^A	C^B	σ	f^{tr} Theory	f^{tr} Monte Carlo
5.000 00	0.500 00	1.000 00	0.8494	0.846±0.002
0.455 20	0.54480	0.697 93	0.8471	0.842±0.002
0.398 30	0.601 70	0.438 08	0.8363	0.830±0.002
0.341 40	0.658 60	0.268 65	0.8159	0.806±0.002
0.284 50	0.715 50	0.158 07	0.7838	0.767±0.002
0.250 00	0.750 00	0.111 11	0.7569	0.733±0.002
0.227 60	0.772 40	0.086 81	0.7354	0.707±0.002
0.7500*	0.7500	1.0000	0.7584	0.751±0.002
0.5000*	0.7500	0.3333	0.7841	0.774±0.002
0.4750*	0.7500	0.3016	0.7841	0.774±0.002
0.875 00†	0.875 00	1.000 00	0.7077	0.703±0.002
0.750 00†	0.875 00	0.428 57	0.7253	0.719±0.002
0.625 00†	0.875 00	0.238 10	0.7345	0.724±0.002
0.500 00†	0.875 00	0.142 86	0.7289	0.712±0.002
0.375 00†	0.875 00	0.085 71	0.7075	0.682±0.002

TABLE III. Two sublattice square lattice. Comparisons and notations are the same as described in the caption of Table I.

C^A	C^B	σ	f^{tr} Theory	f^{tr} Monte Carlo
0.500 00	0.500 00	1.000 00	0.7244	0.710±0.001
0.450 00	0.550 00	0.669 42	0.7203	0.705±0.003
0.400 00	0.600 00	0.444 44	0.7081	0.690±0.003
0.350 00	0.650 00	0.289 94	0.6870	0.662±0.003
0.300 00	0.700 00	0.183 67	0.6560	0.623±0.003
0.250 00	0.750 00	0.111 11	0.6130	0.563±0.003
0.5556§	0.5556	1.000 00	0.6949	0.679±0.002
0.4889§	0.6222	0.5808	0.6879	0.670±0.003
0.4444§	0.6667	0.4000	0.6751	0.654±0.003
0.4000§	0.7111	0.2708	0.6553	0.629±0.003
0.3556§	0.7556	0.1785	0.6276	0.592±0.003
0.3111§	0.8000	0.1129	0.5907	0.544±0.003
0.2667§	0.8444	0.0670	0.5424	0.483±0.003
0.750 00†	0.750 00	1.000 00	0.5935	0.5795±0.0005
0.718 80†	0.750 00	0.851 59	0.6011	0.587±0.002
0.625 00†	0.750 00	0.555 56	0.6196	0.602±0.002
0.500 00†	0.750 00	0.333 33	0.6334	0.610±0.002
0.375 00†	0.750 00	0.200 00	0.6327	0.600±0.002

becomes less pronounced for other values of V, we also examine the case of $V=\frac{1}{4}$. [See entries (8 thru 12), labeled with an * in the first column.] Again, the qualitative behavior of the theoretical results accurately mirrors those given by the Monte Carlo. Furthermore, we notice that while $f^{tr}(\sigma\sim\frac{1}{9})/f^{tr}(\sigma=1)$ is ~ 0.90 when $V=\frac{1}{2}$, for the $V=\frac{1}{4}$ case even when $\sigma\sim\frac{1}{12}$, $f^{tr}(\sigma\sim\frac{1}{12})$ is only about ~ 0.93 of $f^{tr}(\sigma=1)$. Thus for a given value of σ, the dip is noticeably deeper for the $V\sim\frac{1}{2}$ case.

An interesting check on the theory is provided when the concentration C^B on the favored sublattice is kept fixed and σ is varied (i.e., decreased) by a gradual decrease in the particle concentration, C^A, on the unfavored sublattice. In this case, the theory predicts an initial increase in f^{tr} followed by a decrease (see Table I).

As a perusal of the last five entries in Table I (where a † appears in the first column) demonstrates, the Monte Carlo data reproduces the general behavior of f^{tr} as a function of C^A for fixed C^B.

Let us examine next the NaCl-like case which is analyzed in Table II. Here the coordination number $Z=6$ and the correlations are stronger than for the CsCl lattice. Nevertheless, the qualitative feature of the results—both theoretical and Monte Carlo—are similar.

For instance, for the half-filled case with $V=0.5$ [see the first seven entries in the first column of Table II and Fig. 1(b)], both the theory and the Monte Carlo results indicate the development of a dip in the value of f^{tr} as σ becomes small compared to unity. The only difference between the NaCl-like and the CsCl-like cases is the increase in the discrepancy between the theoretical and the Monte Carlo estimates.

Looking at the first entry in Table II, it is observed that even for the uniform lattice case with $\sigma=1$, the Monte Carlo estimate for f^{tr}, i.e., 0.846±0.001, lies significantly below that of the theory $f^{tr}=0.8494$. Moreover, for $\sigma=\frac{1}{9}$, both the relative size of the depression in f^{tr}, indicated by the ratio,

$$f^{tr}(\sigma=\tfrac{1}{9})/f^{tr}(\sigma=1)\sim 0.733/0.846\sim 0.866$$

as well as the relative discrepancy between the theory and the Monte Carlo, namely

$$(0.7569-0.733)/0.733\sim 3\%$$

are larger than for the CsCl case.

Next in Table II we examine the behavior of f^{tr} for a fixed value of $C^B=0.75$ as a function of σ (or equivalently, of C^A). Again, the characteristic initial increase in f^{tr}, which reaches a maximum before falling off, as a function of decreasing σ is accurately mirrored by both the theory and the Monte Carlo. Once again, however, the increase in the relative size of the discrepancy between the theory and the Monte Carlo, over the case of the CsCl-like system, is observed.

Finally, Table II displays similar results for an even larger fixed value of C^B (see the last five entries). Once again, the qualitative correctness of the results, coupled with a somewhat larger quantitative discrepancy (which for $\sigma\sim\frac{1}{12}$ reaches the order of 4%) is observed.

We have also analyzed the quadratic lattice. For the $V=\frac{1}{2}$ case, Table III and Fig. 1(c) reveal a large increase in the quantitative discrepancy between the theoretical results for f^{tr} and the corresponding estimates. Nevertheless, even here the qualitative behavior of the two sets of results, as a function of σ, is correctly represented by the theory.

In addition to the $V=0.5$ case, the case of $V=\frac{4}{9}$ (see entries 7 thru 13, labeled with a § in Table III) has also been studied. This offered itself as an interesting choice since the theory of paper I indicates a deeper dip in the curve for f^{tr} as a function of V (for fixed small σ) when

$V=\frac{4}{9}$ as compared to its value for $V=0.5$. Despite their closeness in the V space, the f^{tr} results for these cases are predicted to be substantially different, it is therefore worth checking this point against an accurate Monte Carlo analysis.

As shown in Table III, entries 7 thru 13, marked with a §, the Monte Carlo estimates accurately track those supplied by the theory. Accordingly, while for $\sigma=0.111$, $f^{tr}\simeq 0.563\pm 0.003$ for the case of $V=\frac{1}{2}$, for $V=\frac{4}{9}$, f^{tr} has fallen as low as 0.544 ± 0.003 even when σ is still somewhat larger, i.e., $\sigma\simeq 0.113$, than was the case for $V=\frac{1}{2}$. The corresponding theoretical results for these two cases are 0.6130 and 0.5907, respectively.

Finally, in Table III we display the results for fixed C^B $(=0.75)$ as a function of σ (or equivalently, that of C^A). Once again, both the theory and the Monte Carlo lead to an identical qualitative picture.

IV. CONCLUSION

The theory of I is tested against precision Monte Carlo simulations involving large, megasamples, whose dynamics is observed power over extended periods of time. This tests the theory at its weakest point: Namely, its predictions regarding the diffusive behavior of the labeled tracer atoms.

Qualitative features of the theoretical results are accurately verified [see Figs. 1(a)–1(c); also compare Ref. 19]. Quantitatively, the theory is less satisfactory (see Tables I–III). Nevertheless, it is found to do reasonably well for the large coordination number systems, i.e., $(Z-2)\gg 1$. For the quadratic lattice, where $(Z-2)$ is not a large number compared to unity, the range of validity, i.e., $(Z-2)>\sigma>1/(Z-2)$, is rather narrow. And, at the edge of this range, i.e., $\sigma\sim 1/(Z-2)$, theoretical results appear to incorporate errors of the order $\gtrsim 3\%$ or so. From Tables I–III, the size of these errors is seen to be a strong function of Z.

To improve the theory for application to the strongly correlated systems, where either σ lies well outside the range $(Z-2)>\sigma>1/(Z-2)$ or where $(J/J^0)<1/(Z-2)$, or both, the TKE decoupling used in I will have to be re-examined along the lines suggested by Tahir-Kheli[22] and more recently by Holdsworth and Elliott.[23]

ACKNOWLEDGMENTS

One of us (P.C.W.H.) is indebted to the United Kingdom Science and Engineering Research Council for financial support. R.A.T.-K. acknowledges financial support from the National Science Foundation as well as the Temple University Research and Study Leaves Fund.

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