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Tracer Diffusion in Concentrated Lattice Gas Models. Rectangular Lattices with Anisotropic Jump Rates

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An approximate theory is developed for tracer diffusion in rectangular lattice gas models with anisotropic jump rates to neighboring unoccupied sites in different directions. Comparison with Monte Carlo simulations on quadratic lattices with several ratios for the jump rates in orthogonal directions shows a satisfactory agreement in all cases investigated.

KEY WORDS: Tracer diffusion; Monte Carlo simulations; crossover behavior.

1. INTRODUCTION

In an earlier paper,[1] to be referred to as I, we derived a theory for the velocity autocorrelation function (or, equivalently, the mean-square displacement) and the correlation factor characterizing tracer diffusion by means of an isotropic nearest neighbor hopping process in lattice gas models. A more formal derivation leading to the same results has been given by Tahir-Kheli.[2] If the lattice is anisotropic or/and the jump rates for jumps in different directions are not all equal, the corresponding theory requires the solution of a set of coupled matrix equations.[3,4] In the case of simple rectangular lattices, however, this complication does not arise,

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because jumps in directions perpendicular to each other remain uncorrelated on average.

In this paper we extend the above theory to these lattices and compare its predictions for the time dependence of the mean-square displacements of a tracer particle and the corresponding correlation factors to the results of Monte Carlo simulations. We find a good agreement. Comparisons to other theories are also presented.

2. THEORY

Consider a simple d-dimensional rectangular lattice with one tracer particle occupying one of the lattice sites, while the remaining sites have probability c, independently of each other, of being occupied by a bulk particle. Tracer particle and bulk particles may jump to unoccupied neighboring sites in one of the principal directions, with jump rates Γ_κ for bulk particles and $\gamma_\kappa \Gamma_\kappa$ for tracer particles, for jumps in the $+\kappa$ or $-\kappa$ direction. Following closely the methods of *I*, we derive approximate expressions for the velocity autocorrelation functions

$$C_\kappa(t) = \langle v_\kappa(0)\, v_\kappa(t) \rangle \tag{1}$$

where $v_\kappa(t)$ is the κ component of the tracer particle velocity (see Ref. 5 for its proper definition) at time t and the brackets denote an equilibrium average. Nonvanishing contributions to (1) all result from realizations of the hopping process in which the tracer particle performs jumps in the $+\kappa$ or $-\kappa$ direction both at the initial time 0 and the final time t. As in I, the vacancy with which the tracer particle exchanges position at $t=0$ is called the *special vacancy*, the correlation between $v_\kappa(0)$ and $v_\kappa(t)$ is due to further interactions between the tracer particle and this special vacancy, and the actual dynamical process describing these interactions is approximated by a process in which the special vacancy performs a simple random walk with constant jump rates Γ_κ if not exchanging positions with the tracer particle, and the tracer particle likewise performs a simple random walk with effective jump rates $\beta_\kappa \gamma_\kappa \Gamma_\kappa$ if not exchanging positions with the special vacancy. The factors β_κ can be determined self-consistently, as we will show. The rate for exchange of positions between special vacancy and tracer particle when neighboring each other in the κ direction remains $\gamma_\kappa \Gamma_\kappa$. Finally some subtle symmetry arguments are needed, as explained in Ref. 6, for the situation that tracer particle and special vacancy are next to each other. Under the present approximation the relative position $\boldsymbol{\rho}$ of special vacancy with respect to the tracer particle describes a random walk, to be referred to as the *actual random walk* performed by $\boldsymbol{\rho}$, with jump rates

$\gamma_\kappa \Gamma_\kappa$ for jumps from $\pm a_\kappa \hat{\mathbf{e}}_\kappa$ to $\mp a_\kappa \hat{\mathbf{e}}_\kappa$, i.e., when the special vacancy jumps over the tracer particle (here a_κ is the lattice unit in the κ direction and $\hat{\mathbf{e}}_\kappa$ is the unit vector in this direction), and $(1+\beta_\kappa \gamma_\kappa)\,\Gamma_\kappa$ for jumps in the $+\kappa$ or $-\kappa$ direction to neighboring sites different from the origin.

By the arguments given in Ref. 6, the Laplace transform $\tilde{C}_\kappa(s)$ of $C_\kappa(t)$ can be expressed as

$$\tilde{C}_\kappa(s) = (1-c)\,\gamma_\kappa \Gamma_\kappa a_\kappa^2 \frac{1-\tilde{\psi}_\kappa(s)}{1+(2c-1)\,\tilde{\psi}_\kappa(s)} \tag{2}$$

where the inverse Laplace transform $\psi_\kappa(t)$ of $\tilde{\psi}_\kappa(s)$ is defined as the probability density for an actual random walk as defined above, but with an absorbing boundary at $\rho_\kappa = 0$ and with starting point $\boldsymbol{\rho} = a_\kappa \hat{\mathbf{e}}_\kappa$ at time 0, to first arrive at $\boldsymbol{\rho} = -a_\kappa \hat{\mathbf{e}}_\kappa$ at time t.[4] In analogy to (I.3), $\tilde{\psi}_\kappa$ can be expressed as

$$\psi_\kappa(s) = \frac{\gamma_\kappa \Gamma_\kappa}{s+q_\kappa \Gamma_\kappa} \left\{ \frac{1}{1-[(s+\nu)/(s+q_\kappa \Gamma_\kappa)]\,\tilde{R}_\kappa(s)} \right\} \tag{3}$$

with

$$\nu = 2 \sum_{\lambda=1}^{d} (1+\beta_\lambda \gamma_\lambda)\,\Gamma_\lambda \qquad \text{and} \qquad q_\kappa = \nu/\Gamma_\kappa - [1+(\beta_\kappa - 1)\,\gamma_\kappa]$$

The inverse Laplace transform $R_\kappa(t)$ of $\tilde{R}_\kappa(s)$ can be interpreted as the probability density for a first return to the site $a_\kappa \hat{\mathbf{e}}_\kappa$ in a *homogeneous random walk* $\boldsymbol{\rho}$ with jump rates $(1+\beta_\varepsilon \gamma_\varepsilon)\,\Gamma_\varepsilon$ for jumps to nearest neighbors in the $+\varepsilon$ or $-\varepsilon$ directions and an absorbing boundary at $\rho_\kappa = 0$. The expression in braces represents the Laplace transform of the probability density for an actual random walk with absorbing boundary at $\rho_\kappa = 0$, arriving at $\boldsymbol{\rho} = a_\kappa \hat{\mathbf{e}}_\kappa$ at $t = 0^+$, to arrive at this same position at time t without having crossed the plane $\rho_\kappa = 0$. Included is a δ-function contribution $\delta(t-0^+)$. The quantity R_κ is directly related to $P_\kappa(t)$, the probability for a homogeneous random walk as described above, with starting point $\boldsymbol{\rho}(0) = a_\kappa \hat{\mathbf{e}}_\kappa$, to be back at the same position at time t. In the Laplace domain this relation reads

$$\tilde{R}_\kappa(s) = [1-(s+\nu)\,\tilde{P}_\kappa(s)]^{-1} \tag{4}$$

[4] The definition of $\psi_\kappa(t)$ given in I could be used here, too. However, as soon as the random walk enters the plane $\rho_\kappa = 0$ the probabilities for subsequent exchanges between tracer particle and special vacancy in the $+\kappa$ and $-\kappa$ directions become strictly equal, and hence no net contributions in Eq. (I.2) arise and the definition of ψ_κ can be simplified to the one given here.

For a periodic lattice with periods N_ε in the principal directions, $\tilde{P}_\kappa$ can be expressed in terms of lattice sums[7] as

$$\tilde{P}_\kappa(s) = \prod_{\varepsilon=1}^{d} N_\varepsilon^{-1} \sum_{K_1} \cdots \sum_{K_d} \frac{2 \sin^2 K_\kappa}{s + 2 \sum_{\varepsilon=1}^{d} (1 + \beta_\varepsilon \gamma_\varepsilon) \Gamma_\varepsilon (1 - \cos K_\varepsilon)} \tag{5}$$

where $\sum_{K_\varepsilon}$ runs over the values $[0, 2\pi/N_\varepsilon, 4\pi/N_\varepsilon, \ldots, 2\pi(N_\varepsilon - 1)/N_\varepsilon]$.

Inserting (4) into (3) and then (3) into (2), one obtains for $\tilde{C}_\kappa(s)$ the expression

$$\tilde{C}_\kappa(s) = (1 - c) \gamma_\kappa \Gamma_\kappa a_\kappa^2 \frac{\nu(1 + \zeta) - (1 + \beta_\kappa \gamma_\kappa) \Gamma_\kappa \tilde{p}_\kappa(\zeta)}{\nu(1 + \zeta) - [1 + (\beta_\kappa - 2c)\gamma_\kappa] \Gamma_\kappa \tilde{p}_\kappa(\zeta)} \tag{6}$$

with $\zeta = s/\nu$ and $\tilde{p}_\kappa(\zeta) = \nu \tilde{P}_\kappa(s)$.

From (6) one obtains a set of self-consistency relations for the constants β_κ by observing that the diagonal elements $D^t_{\kappa\kappa}$ of the tracer diffusion tensor are given on one hand through the Green–Kubo formulas as

$$D^t_{\kappa\kappa} = \lim_{s \to 0^+} \tilde{C}_\kappa(s) \tag{7}$$

on the other hand through the assumption of an effective random walk with jump rates $\beta_\varepsilon \gamma_\varepsilon \Gamma_\varepsilon$, as

$$D^t_{\kappa\kappa} = \beta_\kappa \gamma_\kappa \Gamma_\kappa a_\kappa^2 \tag{8}$$

Equating (7) and (8), one explicitly obtains the self-consistency equations as

$$\beta_\kappa = (1 - c) \frac{\sum_{\varepsilon=1}^{d} 2(1 + \beta_\varepsilon \gamma_\varepsilon) \Gamma_\varepsilon - (1 + \beta_\kappa \gamma_\kappa) \Gamma_\kappa \tilde{p}_\kappa(0)}{\sum_{\varepsilon=1}^{d} 2(1 + \beta_\varepsilon \gamma_\varepsilon) \Gamma_\varepsilon - [1 + (\beta_\kappa - 2c) \gamma_\kappa] \Gamma_\kappa \tilde{p}_\kappa(0)} \tag{9}$$

In general these equations must be solved numerically, as $\tilde{p}_\kappa(0)$ is a transcendental function of the variables β_ε. For the quadratic lattice these equations can be made more explicit by evaluating the $\tilde{p}_\kappa(0)$ from (5) in the thermodynamic limit, with the result

$$\tilde{p}_x(0) = \frac{2}{\pi} (1 + r)[(1 + r) \operatorname{arccotg}(\sqrt{r}) - \sqrt{r}] \tag{10}$$

where $r = (1 + \beta_y \gamma_y)\Gamma_y / [(1 + \beta_x \gamma_x)\Gamma_x]$, and a similar expression holds for $\tilde{p}_y(0)$.

3. MONTE CARLO SIMULATIONS IN TWO DIMENSIONS

In order to investigate the merits of the theory explained above, we have performed numerical simulations on quadratic lattices for two fixed concentrations, $c = 0.501$ and 0.920, setting $\gamma_x = \gamma_y = 1$ and varying $\alpha = \Gamma_y/\Gamma_x$ between 0.001 and 1.0. The numerical simulations of the hopping process were performed by Monte Carlo techniques comprehensively described in Ref. 6; here we mention some special features and characteristic modifications used for the present model. Lattices with $N = 600 \times 600$ and (for the longest runs) 200×200 sites were introduced with periodic boundary conditions. For $c = 0.920$, in order to achieve good enough statistics we directly simulate the hopping of the vacancies, as was done by Murch. In order to compare our numerical results to the theory of the preceding section, we solved numerically in (10) for the anisotropic correlation factors

$$f_\kappa = \beta_\kappa/(1-c) \tag{11}$$

The results for different values of α and c are shown in the third and sixth columns of Table I, respectively. For comparison we also give the values f_κ^{TK} resulting from a theory by Tahir-Kheli.[9],[5] We can reproduce these by replacing all parameters β_ε on the right-hand side of (9) by $(1-c)$.

Employing our numerical results for f_κ in (6) and determining $\tilde{p}_\kappa(\zeta)$ from (5) by doing one integration analytically and the next one numerically, we performed a numerical inverse Laplace transform of

[5] In the isotropic case this coincides with the theory of Ref. 10.

Table I. Comparison of the Theoretical and Experimental Correlation Factors in the *x* and *y* Directions for Two Concentrations and for Different Values of the Jump Rate Ratio α

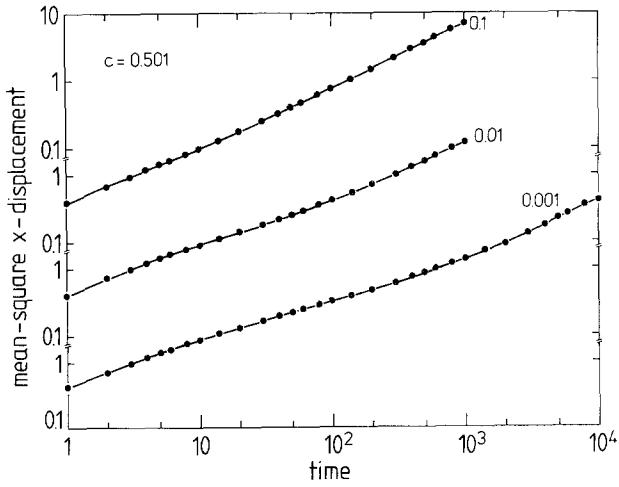
c	α	f_x^{exp}	f_x	f_x^{TK}	f_y^{exp}	f_y	f_y^{TK}
0.501	1.0	0.704 ± 0.001	0.703	0.724	0.704 ± 0.001	0.703	0.724
	0.1	0.387 ± 0.002	0.380	0.410	0.903 ± 0.002	0.895	0.909
	0.01	0.150 ± 0.0003	0.145	0.167	0.969 ± 0.002	0.966	0.972
	0.001	0.052 ± 0.0004	0.048	0.058	0.985 ± 0.004	0.989	0.991
0.920	1.0	0.500 ± 0.0003	0.496	0.507	0.500 ± 0.0003	0.496	0.507
	0.1	0.210 ± 0.0002	0.206	0.214	0.791 ± 0.0003	0.787	0.795
	0.01	0.072 ± 0.0002	0.070	0.073	0.934 ± 0.001	0.927	0.930
	0.001	0.023 ± 0.0001	0.023	0.023	0.996 ± 0.002	0.976	0.977

$2\tilde{C}_\kappa(s)/s^2$ by means of the procedure of Honig and Hirdes[11] to obtain a prediction for the mean square displacements of the tracer particle in the x direction and y direction as a function of time.

The same quantities were computed in our Monte Carlo simulations in the time range $0 \lesssim 2(\Gamma_x + \Gamma_y)t \leqslant 10^4$ for $\alpha = 0.001$ and in the time range $0 \lesssim 2(\Gamma_x + \Gamma_y)t \lesssim 10^3$ for $\alpha = 1.0$, 0.1, and 0.01. {The time unit $[2(\Gamma_x + \Gamma_y)]^{-1}$ is the usual Monte Carlo step per particle, MCS/p.}

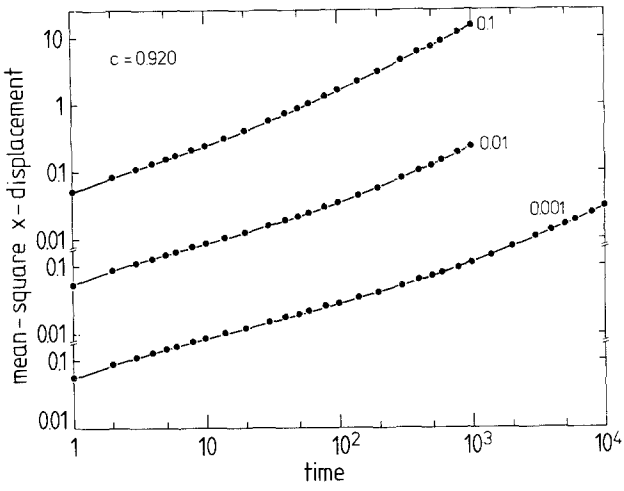
In Fig. 1 we compare theory and simulation results for two different concentrations ($c = 0.501$ and 0.920) and three different jump rate ratios ($\alpha = 0.1$, 0.01, and 0.001). The agreement is seen to be quite satisfactory in all cases investigated. The plots in the figures were made on a doubly logarithmic scale, but the agreement also looks quite good on a linear scale; the relative difference between theory and simulation results never exceeds a few percent. (The statistical errors in the data points are in all cases smaller than the plotting symbols.) Small systematic differences are present, however, especially at $c = 0.501$ and large jump rate ratios. These are not visible in Fig. 1 and would hardly be so in a linear plot.

Finally, we determined the "experimental" correlation factors $f_\kappa^{\exp}$ from the average slope of the mean square displacements in the time range $10^3 \lesssim 2(\Gamma_x + \Gamma_y)t \lesssim 10^4$ for $\alpha = 0.001$ and the time range $10^2 \lesssim 2(\Gamma_x + \Gamma_y)t \lesssim 10^3$ for $\alpha = 0.1$, 0.01. The results are shown in Table I. Note that for small

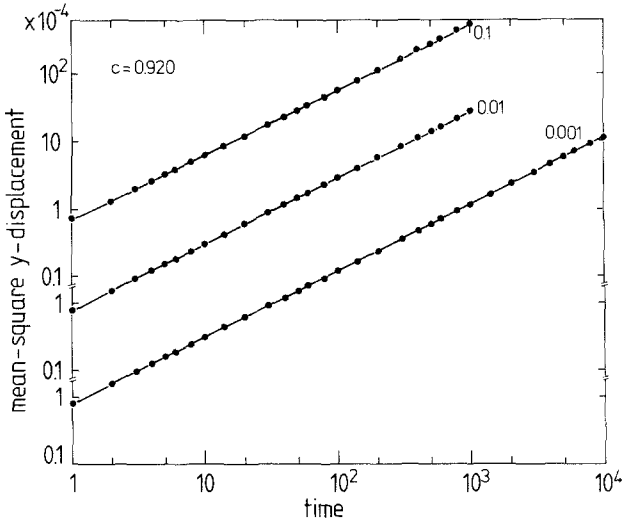


(a)

Fig. 1. Mean square x and y displacements of the tagged particles on an anisotropic square lattices. (—) Theory; (●) results of the Monte Carlo simulations. (The ratio α of the perpendicular to the horizontal jump rate is indicated to the right; the concentrations are also indicated.)



(b)



(c)

Fig. 1 (*continued*)

values of α, diffusion in the x direction shows a crossover from quasi-one-dimensional behavior for short and intermediate times (i.e., the mean square displacement in the x direction grows proportionally to t for very short times and to $t^{1/2}$ for intermediate times[5]) to normal diffusive behavior for long times. In the crossover region it may be described by an intermediate power law behavior, just as in the case of diffusion on two coupled lines.[6]

Tahir-Kheli's theory is seen to be quite satisfactory. However, for concentration 0.5 the present theory appears to be slightly better. The error estimates in Table I correspond to one standard deviation. They were obtained by a least mean squares fit, giving equal weight to each of the data points and ignoring possible correlations between statistical deviations. Due to this neglect of correlations our error estimates may be somewhat too low, but, since in almost all cases the errors are extremely small, this should be without consequences regarding our conclusions.

Note, however, that our fitting procedure introduces small systematic errors: first, the mean square displacement as a function of time for two-dimensional diffusive systems exhibits a logarithmically growing term[1,2,12] beyond the leading linear one, which enhances the average slope over a finite time interval. Second, for large jump rate ratio the system behaves quasi-one-dimensionally for intermediate times, implying the occurrence of a $t^{1/2}$ term in the mean square displacement in the x direction as a function of time, which also increases the average slope over finite time intervals.

4. PERCOLATION TRANSITION

Finally we remark on the percolation transition, manifesting itself through the vanishing of the correlation factors f_κ at concentrations beyond a percolation vacancy concentration c_{pv}, in the limit that γ_κ tends to infinity.[1,2] In the anisotropic case it is not *a priori* obvious, although physically reasonable, that all correlation factors vanish at the same percolation density. However, from (6) and (5) one readily sees that this must be the case; the assumption that one or some of the β variables vanishes while the others remain finite immediately gives rise to contradictions. Moreover, in the two-dimensional case it is easy to show that, as c approaches the percolation density, the tracer diffusion, at least under our approximations, becomes isotropic, which means that the ratio $\beta_x\gamma_x/\beta_y\gamma_y$ tends to unity. As a consequence, the percolation density c_{pv} is independent of the values of the parameters Γ_κ.

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REFERENCES

1. H. van Beijeren and R. Kutner, *Phys. Rev. Lett.* **55**:238 (1985).
2. R. A. Tahir-Kheli, *Phys. Rev. B* **28**:3049 (1983).
3. R. Howard, *Phys. Rev.* **144**:650 (1966).
4. H. van Beijeren and K. W. Kehr, *J. Phys. C* **19**:1319 (1986).
5. H. van Beijeren, K. W. Kehr, and R. Kutner, *Phys. Rev. B* **28**:5711 (1983).
6. R. Kutner, H. van Beijeren, and K. W. Kehr, *Phys. Rev. B* **30**:4382 (1984).
7. E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**:167 (1965); D. Bedeaux, K. Lakatos-Lindenberg, and K. E. Shuler, *J. Math. Phys.* **12**:2116 (1971).
8. G. E. Murch, *Phil. Mag.* **49**:21 (1984).
9. R. A. Tahir-Kheli, *Phys. Rev. B* **27**:6072 (1983).
10. K. Nakazato and K. Kitahara, *Progr. Theor. Phys.* **64**:122 (1980).
11. G. Honig and U. Hirdes, *J. Comput. Appl. Math.* **10**:113 (1984).
12. H. van Beijeren, *J. Stat. Phys.* **35**:399 (1984).