Mean Square Displacement of a Tracer Particle in a Hard-Core Lattice Gas

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A simple theory is developed for hopping diffusion in hard-core lattice gases. Its predictions for the mean square displacement of a tracer particle as a function of time are found to be in good agreement with the results of Monte Carlo simulations on a quadratic lattice. For long times a logarithmic term is found in accord with mode-coupling predictions. Our predictions for the tracer diffusion coefficient agree with those of Tahir-Kheli.

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In processes of hopping diffusion in systems of interacting particles the dynamics of tracer particles usually exhibit appreciable memory effects,[1] which are fairly complicated to describe. Here we develop a simple theory for tracer diffusion in lattice gases. To keep the analysis simple we restrict ourselves to isotropic lattices where the nearest neighbors on any lattice site form a regular polyhedron. One tracer particle is located randomly on the lattice, while all other lattice sites have probability c, independently of one another, to be occupied with a bulk particle. Both the bulk particles and the tracer particle may jump to unoccupied neighboring sites only, with direction-independent jump rates Γ and $\gamma\Gamma$ for bulk particles and tracer particles, respectively. Next observe[2] that the tracer particle velocity autocorrelation function $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$, with $\mathbf{v}(t)$ the tracer particle velocity at time t (see Ref. 2 for its proper definition) and the brackets denoting an equilibrium average, correlates jumps of the tracer particles at times 0 and t to each other. Restricting ourselves to realizations of the stochastic process where such jumps actually do occur, we find that nonvanishing contributions to the velocity autocorrelation function on average result entirely from dynamical correlations between the tracer particle and the so-called *special vacancy;* that is, the vacancy with which the tracer particle exchanges positions at the initial instant $t=0$. As in Kutner, van Beijeren, and Kehr,[3] we consider this special vacancy, when not neighboring the tracer particle, as performing a simple continuous-time random walk with constant jump rate Γ to each nearest-neighbor site, while the tracer particle, if not located next to the special vacancy, is assumed to perform a simple continuous-time random walk as well, with an effective jump rate $\beta\gamma\Gamma$, which has to be determined self-consistently. If the tracer particle and special vacancy are on adjacent sites, they may exchange positions at the unchanged rate $\gamma\Gamma$. Furthermore, some subtle symmetry arguments, explained in Ref. 3, are needed concerning the weighting factors for repeated returns of the special vacancy. Under the preceding assumptions the relative position $\boldsymbol{\rho}$ of the special vacancy with respect to the tracer particle performs a random walk, with jump rate $\gamma\Gamma$ for jumps from sites $\hat{\mathbf{n}}a$, where a is the nearest-neighbor distance, to $-\hat{\mathbf{n}}a$ and jump rate $(1+\beta\gamma)\Gamma$ for jumps to nearest-neighbor sites different from the origin. Following Ref. 3 we obtain an expression for the Laplace transform $\tilde{C}(s)$ of the tracer particle velocity autocorrelation function, in the form

$$\tilde{C}(s)=\frac{1}{2}Z(1-c)\gamma\Gamma a^2\frac{1-\tilde{\psi}(s)}{1+(2c-1)\tilde{\psi}(s)}, \tag{1}$$

where Z is the coordination number (number of nearest neighbors of a lattice site) of the lattice and $\tilde{\psi}(s)$ is the Laplace transform of $\psi(t)$, defined as

$$\psi(t)=\sum_{\hat{\mathbf{n}}}(\hat{\mathbf{m}}\cdot\hat{\mathbf{n}})p^{(1)}(\hat{\mathbf{n}},\hat{\mathbf{m}},t), \tag{2}$$

with $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ unit vectors in directions connecting nearest neighbors. The quantity $p^{(1)}(\hat{\mathbf{n}},\hat{\mathbf{m}},t)$ is the probability density that, given $\boldsymbol{\rho}=\hat{\mathbf{m}}a$ just after the initial jump of the tracer particle, the next exchange of positions between tracer particle and special vacancy occurs at a time t later and leads to the value $\boldsymbol{\rho}=-\hat{\mathbf{n}}a$. The inner product $\hat{\mathbf{m}}\cdot\hat{\mathbf{n}}$ in Eq. (2) results from the directional correlation between the initial and the final exchange. By comparing the *actual random walk* performed by $\boldsymbol{\rho}$ under the given approximation to a *homogeneous random walk* with jump rate $(1+\gamma\beta)\Gamma$ for all nearest-neighbor jumps and no jumps over larger distances allowed, one may express $\tilde{\psi}(s)$ as

$$\tilde{\psi}(s)=\frac{\gamma\Gamma}{s+q\Gamma}\left\{1-\frac{s+Z(1+\gamma\beta)\Gamma}{s+q\Gamma}\tilde{R}(s)\right\}^{-1}, \tag{3}$$

with $q=(Z-1)(1+\beta\gamma)+\gamma$. The quantity $\tilde{R}(s)$ is the Laplace transform of $R(t)$, defined for the homogeneous random walk as $R(t)=\sum_{\hat{\mathbf{n}}}(\hat{\mathbf{n}}\cdot\hat{\mathbf{m}})Q(\hat{\mathbf{n}},\hat{\mathbf{m}},t)$ with $Q(\hat{\mathbf{n}},\hat{\mathbf{m}},t)$ the probability density that a walk starting at $\boldsymbol{\rho}=\hat{\mathbf{m}}a$ arrives at $\hat{\mathbf{n}}a$ after a time interval t without having visited any neighbors of the origin during the intermediate time. If $\hat{\mathbf{n}}=\hat{\mathbf{m}}$, it is required that the walk has moved away from $\hat{\mathbf{m}}a$ before returning. Note that one need not exclude walks through the origin, since on symmetry grounds these do not contribute to $R(t)$. The expression between curly brackets in Eq. (3) is the Laplace transform of the probability density for an *actual* random walk arriving at $\boldsymbol{\rho}-\hat{\mathbf{m}}a$ at $t=0^+$ to arrive at a site $\hat{\mathbf{n}}a$ at time t, without having made a jump of length $2a$, multiplied by $\hat{\mathbf{m}}\cdot\hat{\mathbf{n}}$ and summed over $\hat{\mathbf{n}}$, including, if $\hat{\mathbf{m}}=\hat{\mathbf{n}}$, the initial arrival at $t=0^+$. The factor $[s+Z(1+\beta\gamma)\Gamma]/(s+q\Gamma)$ in the same equation results from the difference in waiting-time distributions at positions adjacent to the origin, between the homogeneous and the actual random walk. The quantity $\tilde{R}(s)$ can be expressed straightforwardly in terms of known lattice sums[4] through the relation

$$\tilde{P}(s)=\{s+Z(1+\beta\gamma)\Gamma\}^{-1}[1-\tilde{R}(s)]^{-1}, \tag{4}$$

with $\tilde{P}(s)$ the Laplace transform of $P(t)$, given as $P(t)=\sum_{\hat{\mathbf{n}}}(\hat{\mathbf{n}}\cdot\hat{\mathbf{m}})P(\hat{\mathbf{n}}a,\hat{\mathbf{m}}a,t)$ where $P(\hat{\mathbf{n}}a,\hat{\mathbf{m}},t)$ is the probability for a homogeneous random walk with jump rate $(1+\beta\gamma)\Gamma$ for jumps to neighboring sites, starting at $\hat{\mathbf{m}}a$ at time 0, to be at $\hat{\mathbf{n}}a$ at time t. Solving for $\tilde{R}(s)$ in Eq. (4), substituting the results into Eq. (3), and inserting Eq. (3) into Eq. (1), one obtains for $\tilde{C}(s)$ the expression

$$\tilde{C}(s)=\tfrac{1}{2}Z(1-c)\gamma\Gamma a^2\frac{(1+\beta\gamma)\{1-\tilde{p}(\zeta)\}}{1+\beta\gamma-[1+(\beta-2c)\gamma]\tilde{p}(\zeta)}, \tag{5}$$

with $\zeta=s/[(1+\beta\gamma)Z\Gamma]$ and $\tilde{p}(\zeta)=(1+\beta\gamma)\Gamma\tilde{P}(s)$. The factor β is related to Bardeen and Herring's correlation factor f[1] as

$$\beta=(1-c)f. \tag{6}$$

Setting β equal to $(1-c)$ in Eq. (5) we recover the expression for $\tilde{C}(s)$ obtained by Nakazato and Kitahara.[5]

We can do better, however, by solving for β self-consistently in Eq. (5). In the limit $s\to 0$ the quantity $\tilde{C}(s)/d$, with d the dimensionality of the lattice, according to the Green-Kubo formula reduces to the tracer diffusion coefficient D^t. On the other hand, for the effective random walk with jump rate $\beta\gamma\Gamma$, assumed to be performed by the tracer particle, the diffusion coefficient is given as $D^t=\frac{1}{2}Z\beta\gamma\Gamma a^2/d$. Equating these two expression for D^t, solving for β and dividing with $(1-c)$, one finds the correlation factor as

$$f=[2\gamma(1-c)f_0]^{-1}(\{[(1-\gamma)(1-c)f_0+c]^2+4\gamma(1-c)f_0^2\}^{1/2}-[(1-\gamma)(1-c)f_0+c]), \tag{7}$$

with $f_0=f(c=1)=[1-\tilde{p}(0)]/[1+(2\gamma-1)\tilde{p}(0)]$. This is identical to the result Tahir-Kheli obtained[6] by similar but not obviously equivalent approximations.

The long-time behavior of the velocity autocorrelation function follows from the small-ζ behavior of $\tilde{p}(\zeta)$. The latter can be expressed in terms of lattice sums [Eq. (4)] and, setting $\tilde{p}(\zeta)=\tilde{p}(0)+\Delta\tilde{p}(\zeta)$, one finds that $\Delta\tilde{p}(\zeta)$ in the thermodynamic limit exhibits a nonanalyticity proportional to $\zeta^{d/2}$ or $\zeta^{d/2}\ln\zeta$ for odd and even dimensionality, respectively. In the time regime this leads to a long-time tail in the velocity autocorrelation function of the form

$$C(t)\approx -2dc(1-c)\{\gamma\Gamma af/[1-\tilde{p}(0)]\}(4\pi)^{-d/2}\{(1+\beta\gamma)\Gamma t\}^{-(d+2)/2} \tag{8}$$

for large t. Mode-coupling theory[7] predicts the same type of power-law behavior. The coefficient so far has been worked out in detail for the case $\gamma=1$ only. In our specific model the result can be represented as

$$C^{\mathrm{MC}}(t)\approx -\tfrac{1}{2}dc(1-c)(\Gamma a)^2(4\pi)^{-d/2}\{(1-\beta)/c-(\partial\beta/\partial c)\}^2\{(1+\beta)\Gamma t\}^{-(d+2)/2}. \tag{9}$$

If Eqs. (6) and (7) are inserted for β, the expressions (8) and (9) become asymptotically equal as a function of c in the two limits, $c\to 0$ and $c\to 1$, where indeed our theory becomes exact[5] and identical to the theory of Nakazato and Kitahara. However, this equality does not hold for general c which underlines the approximative character of our theory.

The theory of Nakazato and Kitahara[5] leads to an expression similar to Eq. (8), with f replaced by

$$f_{\mathrm{NK}}=\frac{1-2c\gamma\tilde{p}(0)}{1+(1-c)\gamma-\{1+(1-3c)\gamma\}\tilde{p}(0)}$$

and likewise β by $\beta_{\mathrm{NK}}=(1-c)f_{\mathrm{NK}}$; in addition one has to multiply the right-hand side by a factor $(1+\beta_{\mathrm{NK}}\gamma)/\{1+(1-c)\gamma\}$.

In order to test the validity of mode-coupling theory and the accuracy of the theory described above, we performed Monte Carlo simulations on a quadratic lattice, with $\gamma=1$, computing the mean square displacement $\langle\Delta r^2(t)\rangle$ of a tagged particle. This quantity is directly related to the tagged-particle velocity autocorrelation function, through the relation[8] $d^2\langle r^2(t)\rangle/dt^2=2C(t)$. In two-dimensional systems the long-time tail in the velocity autocorrelation function gives rise to a logarithmic term in the mean square displacement as a function of time. Specifically, for the quadratic lattice with isotropic jump rates, $\tilde{p}(\zeta)$ for small ζ assumes the form[9]

$$\tilde{p}(\zeta)=1-\frac{2}{\pi}-\frac{1}{\pi}[\ln(8/\zeta)-\pi+1]\zeta+O(\zeta). \quad (10)$$

Hence one finds a mean square displacement behaving for long times as

$$\langle\Delta r^2(t)\rangle=2(1-c)a^2f\left[2\Gamma t+\frac{\pi fc(\ln\{32\Gamma t[1+(1-c)f]\}-\pi+1-C)}{4\{1+(1-c)f\}^2}+O(1)\right] \quad (11)$$

where C is Euler's constant, $C=0.5772\ldots$, and the correlation factor explicitly reads

$$f=\frac{\{(\pi-1)^2c^2+4(1-c)\}^{1/2}-(\pi-1)c}{2(1-c)}.$$

Our Monte Carlo simulations were performed on lattices with 600×600 sites at the two concentrations $c=0.50077$ and $c=0.92325$. For the details of the numerical procedure we refer to Kehr, Kutner, and Binder.[10] The runs were performed over a total of 1000 Monte Carlo steps per particle (MCS/p) at density $c=0.50077$. The mean square displacements were computed by averaging over all particles and over about ten different runs at both densities. The logarithm of the mean square displacement was fitted by a curve of the form

$$\ln[\langle\Delta^2r(t)\rangle_{\mathrm{MCS}}/a^2]=\ln[(1-c)4C_0\Gamma t+C_1\ln(4\Gamma t)+C_2] \quad (12)$$

by application of a least-mean-square fitting procedure in the range $2\leq4\Gamma t\leq150$ at concentration $c=0.50077$ and in the range $6\leq4\Gamma t\leq1000$ at concentration $c=0.92325$. As explained in Ref. 3, the reason for fitting the logarithm of Δ^2r instead of this quantity itself is that the *relative* errors in the simulation data are roughly independent of t. In Table I we have listed our best fitting values of the constants $C_0(=f_{\mathrm{MCS}})$, $(C_1)_{\mathrm{MCS}}$, and $(C_2)_{\mathrm{MCS}}$ together with the theoretical predictions f, C_1, and C_2 from Eq. (11), and f_{NK} and $(C_1)_{\mathrm{NK}}$ as obtained from the theory of Nakazato and Kitahara. Furthermore, we have listed the mode-coupling results for C_1 using in Eq. (9) the Monte Carlo value of β, but, since we could not determine $\partial\beta/\partial c$ from our Monte Carlo results, we approximated this quantity using the theoretical expressions given above for f and f_{NK}, together with $\beta=(1-c)f$. The two resulting values for C_1 are listed under $(C_1)_{\mathrm{MC}}$ and $(C_1)_{\mathrm{MC}}^{\mathrm{NK}}$, respectively. They differ only slightly from each other.

To investigate the validity of the long-time approximation [Eq. (12)] over the time range investigated we made the following checks: First, we applied the same mean-square fitting procedure for $c=0.50077$ over the restricted time range $6\leq4\Gamma t\leq150$, and for $c=0.92325$ over the restricted time range $10\leq4\Gamma t\leq1000$. This caused no significant change in the values of the coefficients C_i $(i=0,1,2)$. Secondly, in Fig. 1 we plotted $\langle\Delta^2r(t)\rangle_{\mathrm{MCS}}a^{-2}-4(1-c)f_{\mathrm{MCS}}\Gamma t$, where f_{MCS} is determined from the fitting procedure, as a function of $\ln4\Gamma t$. The filled circles show the Monte Carlo results and the dashed lines represent the least-mean-squares approximation. One sees that the latter is justified over the time ranges where it was applied.

Also shown in Fig. 1 (solid lines) are the values $\langle\Delta r^2(t)\rangle a^{-2}-4(1-c)f\Gamma t$ obtained by a numerical inverse Laplace transform[11] of $2\tilde{C}(s)/s^2$ with $\tilde{C}(s)$ given by Eq. (5), as well as the corresponding quantity resulting from the theory of Nakazato-Kitahara (dot-dashed lines). One sees that the agreement between Monte Carlo results and theory is quite good at all times, although small systematic differences clearly are present. In conclusion, we note that our Monte Carlo

TABLE I. Comparison of the characteristic coefficients correlation factor, slope, and shift obtained by the Monte Carlo simulations with the ones predicted by the present theory, the theory of Nakazato and Kitahara, and mode-coupling theory.

c	0.9233	0.5008
f_{MCS}	0.4989	0.7089
f	0.4962	0.7026
f_{NK}	0.5052	0.7240
$(C_1)_{\mathrm{MCS}}$	0.0566	0.2774
C_1	0.0556	0.2447
$(C_1)_{\mathrm{NK}}$	0.0540	0.2110
$(C_1)_{\mathrm{MC}}$	0.0593	0.2592
$(C_1)_{\mathrm{MC}}^{\mathrm{NK}}$	0.0628	0.3073
$(C_2)_{\mathrm{MCS}}$	0.0194	0.0650
C_2	0.0197	0.0867
$(C_2)_{\mathrm{NK}}$	0.0197	0.0814

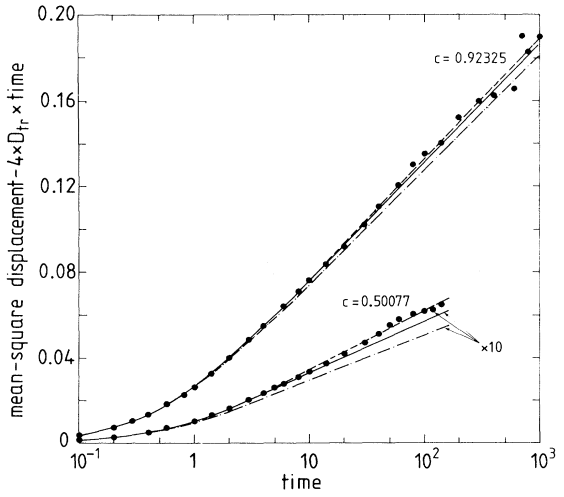

FIG. 1. Mean square displacement minus linear term for a tagged particle on a square lattice at concentrations $c = 0.9233$ and $c = 0.5008$. For the latter concentration the vertical scale should be multiplied by a factor of 10. Dashed lines, phenomenological fit by (12); solid lines, present theory; dot-dashed lines, theory of Nakazato and Kitahara; filled circles, results of the numerical simulations.

results confirm the existence of a logarithmic term in the mean square displacement of a tracer particle as a function of time, in agreement with mode-coupling theory. Notice that this situation compares favorably with that of the Lorentz gas, a model in which point particles move among randomly placed scatterers. For this model mode-coupling theory in two dimensions also predicts a logarithmic term in the mean square displacement,[12] but its predicted coefficient depends on spatial fluctuations in the local diffusion tensor, for which no explicit theoretical results nor simulation values are available, except in the limit of vanishing scatterer density.

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