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Site Blocking Effect in Tracer Diffusion on a Lattice

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The self-diffusion constant of a tracer in the presence of other particles is calculated by assuming that not more than one particle can occupy the same lattice site. The formulation is exact at the two extrema of concentration $c=0$ and $c=1$ and it gives a good interpolation in between them.

Correlation effect in diffusion of particles on a lattice is one of the long standing problems.[1] Recent experiments on hydrogen diffusion[2] in metals and Monte Carlo simulations[3)~5)] of diffusion on lattices show that the interaction among particles influences the self-diffusion quite significantly at high concentrations. The self-diffusion coefficient is usually written as

$$D(c)=D_0(1-c)f(c), \tag{1}$$

where c is the concentration of diffusing particles. D_0 is the diffusion coefficient at the low concentration limit $c\to0$. $f(c)$ is the so-called correlation factor which represents the effect of interaction among particles. In this letter, we derive $f(c)$ for the diffusions of particles, which perform a random walk on a lattice with the constraint that more than one particle cannot occupy one lattice site at the same time.

To formulate the problem of self-diffusion, we consider a system of N_0 "white" particles and a "black" particle on a lattice of N lattice sites. We assign to a lattice site $\boldsymbol{n}$, one of three states; $|\boldsymbol{n}\alpha\rangle$ denotes the occupancy by a white particle, $|\boldsymbol{n}\beta\rangle$ by the black particle, and $|\boldsymbol{n}0\rangle$ no occupancy. We denote a configuration of N_0 white particles and the black particle by a set of vectors of occupied lattice sites $(\boldsymbol{i}_1, \boldsymbol{i}_2, \cdots, \boldsymbol{i}_{N_0}, \boldsymbol{m})$. Here, $\boldsymbol{i}_1, \cdots, \boldsymbol{i}_{N_0}$ are the lattice sites occupied by white particles and $\boldsymbol{m}$ is the site occupied by the black particle. The conditional probability of a configuration $(\boldsymbol{j}_1, \cdots, \boldsymbol{j}_{N_0}, \boldsymbol{n})$ at time t starting from an initial configuration $(\boldsymbol{i}_1, \cdots, \boldsymbol{i}_{N_0}, \boldsymbol{m})$ is written formally

$$\begin{aligned} P(\boldsymbol{j}_1, \cdots, \boldsymbol{j}_{N_0}, \boldsymbol{n}\leftarrow\boldsymbol{i}_1, \cdots, \boldsymbol{i}_{N_0}, \boldsymbol{m}; t) &= \Big(\prod_{l=N_0+1}^{N-1}\langle\boldsymbol{j}_l0|\Big)\Big(\prod_{l=1}^{N_0}\langle\boldsymbol{j}_l\alpha|\Big)\langle\boldsymbol{n}\beta|e^{Lt} \\ &\quad |\boldsymbol{m}\beta\rangle\Big(\prod_{l'=1}^{N_0}|\boldsymbol{i}_{l'}\alpha\rangle\Big)\Big(\prod_{l'=N_0+1}^{N-1}|\boldsymbol{i}_{l'}0\rangle\Big), \end{aligned} \tag{2}$$

where L describes the diffusion of particles,

$$\begin{aligned} L=\gamma_W\sum_{\langle n,m\rangle}&(|\boldsymbol{n}\alpha\rangle\langle\boldsymbol{n}0|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}\alpha|-|\boldsymbol{n}\alpha\rangle \\ &\times\langle\boldsymbol{n}\alpha|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}0|) \\ +\gamma_B\sum_{\langle n,m\rangle}&(|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}0|\cdot|\boldsymbol{m}0\rangle \\ &\times\langle\boldsymbol{m}\beta|-|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}\beta|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}0|). \end{aligned} \tag{3}$$

Here γ_W and γ_B are the jump frequencies of a white particle and a black particle respectively, to neighboring sites. The sums are taken over nearest neighbor sites. Assuming that white particles are randomly distributed initially, we obtain the conditional probability $P_{N_0}(\boldsymbol{n}\leftarrow\boldsymbol{m}; t)$

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for the black particle by summing up the above expression (2) over all possible initial and final configurations of white particles. This summation can be performed by noting that $P_{N_0}(\boldsymbol{n}\leftarrow\boldsymbol{m};t)$ is in fact the coefficient of x^{N_0} of the expansion of a generating function defined by

$$\begin{aligned}
G(\boldsymbol{n}\leftarrow\boldsymbol{m};t;x)
&\equiv C(1+x)^{N-1}g(\boldsymbol{n}\leftarrow\boldsymbol{m};t;x)\\
&\equiv C\langle\{0\}|\prod_{l=1}^{N}(1+\sqrt{x}\,|\boldsymbol{j}_l0\rangle\langle\boldsymbol{j}_l\alpha|)\\
&\quad\times|\boldsymbol{n}0\rangle\langle\boldsymbol{n}\beta|e^{Lt}|\boldsymbol{m}\beta\rangle\langle\boldsymbol{m}0|\\
&\quad\times\prod_{l'=1}^{N}(1+\sqrt{x}\,|\boldsymbol{j}_{l'}\alpha\rangle\langle\boldsymbol{j}_{l'}0|)|\{0\}\rangle,
\end{aligned}\tag{4}$$

where $|\{0\}\rangle$ denotes the state of no occupancy at all sites. The factor $(1+x)^{N-1}$ is taken out in order that $g(\boldsymbol{n}\leftarrow\boldsymbol{m};0;x)=\delta_{\boldsymbol{nm}}$ holds at $t=0$. The generating function is related to the conditional probability by

$$P_{N_0}(\boldsymbol{n}\leftarrow\boldsymbol{m};t)=\frac{C}{2\pi i}\int dx\frac{(1+x)^{N-1}}{x^{N_0+1}}g(\boldsymbol{n}\leftarrow\boldsymbol{m};t;x).\tag{5}$$

If we take the thermodynamic limit $N\to\infty$, $N_0\to\infty$ such $c=N_0/N$ (finite), we may apply the saddle point method to the integration in (5), which results in

$$P_{N_0}(\boldsymbol{n}\leftarrow\boldsymbol{m};t)\approx g\left(\boldsymbol{n}\leftarrow\boldsymbol{m};t;\frac{c}{1-c}\right).\tag{6}$$

The expression of the generating function is further simplified by introducing an operator

$$S=\sum_{l=1}^{N}(|\boldsymbol{i}_l\alpha\rangle\langle\boldsymbol{i}_l0|-|\boldsymbol{i}_l0\rangle\langle\boldsymbol{i}_l\alpha|).\tag{7}$$

We thus obtain

$$g(\boldsymbol{n}\leftarrow\boldsymbol{m};t;x)=\langle\{0\}',\boldsymbol{m}\beta|e^{\tilde{L}t}|\boldsymbol{n}\beta,\{0\}'\rangle.\tag{8}$$

Here $|\boldsymbol{n}\beta,\{0\}'\rangle$ denotes the states of no occupancy at all sites except at the site $\boldsymbol{n}$ occupied by the black particle. The transformed Liouvillian $\tilde{L}=e^{-\theta S}Le^{\theta S}$, with $\tan\theta=\sqrt{x}=\sqrt{c/(1-c)}$, consists of two parts, $\tilde{L}=L_0+L'$, where

$$\begin{aligned}
L_0=\gamma_W&\sum_{\langle n,m\rangle}(|\boldsymbol{n}\alpha\rangle\langle\boldsymbol{n}0|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}\alpha|\\
&-|\boldsymbol{n}\alpha\rangle\langle\boldsymbol{n}\alpha|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}0|)\\
&+\gamma_B(1-c)\sum_{\langle n,m\rangle}(|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}0|\cdot|\boldsymbol{m}0\rangle\\
&\times\langle\boldsymbol{m}\beta|-|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}\beta|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}0|)\\
&+\gamma_Bc\sum_{\langle n,m\rangle}(|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}\alpha|\cdot|\boldsymbol{m}\alpha\rangle\\
&\times\langle\boldsymbol{m}\beta|-|\boldsymbol{n}\alpha\rangle\langle\boldsymbol{n}\alpha|\cdot|\boldsymbol{m}\beta\rangle\langle\boldsymbol{m}\beta|)
\end{aligned}\tag{9}$$

and

$$\begin{aligned}
L'=\gamma_B\sqrt{c(1-c)}&\sum_{\langle n,m\rangle}(|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}\beta|\cdot|\boldsymbol{m}0\rangle\\
&\times\langle\boldsymbol{m}\alpha|+|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}\beta|\cdot|\boldsymbol{m}\alpha\rangle\langle\boldsymbol{m}0|\\
&-|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}0|\cdot|\boldsymbol{m}\alpha\rangle\langle\boldsymbol{m}\beta|\\
&-|\boldsymbol{n}\beta\rangle\langle\boldsymbol{n}\alpha|\cdot|\boldsymbol{m}0\rangle\langle\boldsymbol{m}\beta|).
\end{aligned}\tag{10}$$

The first term of L_0 is the simple diffusion of white particles. The second term is the diffusion of the black particle in an effective medium in which the black particle finds a vacant site among the neighboring sites with probability $1-c$. The third term is effective when $c\to1$. It represents a diffusion mechanism due to the exchange of the black and a white particle at the neighboring sites. We take L' to be the perturbation; since L' does not conserve the particle number, the perturbation expansion is actually the expansion in the power of $c(1-c)$, which is small in the two extrema $c\to0$ and $c\to1$. Hence we may expect that the perturbation expansion would result in a good interpolation between the two extrema.

The incoherent response function $S(\boldsymbol{k},z)$ is obtained by the projection operator technique.[6] The diffusion constant $D_{\mu\nu}(z)$, defined by

$$S(\boldsymbol{k},z)^{-1}=z+\sum_{\mu\nu}D_{\mu\nu}(z)k_\mu k_\nu+\cdots,\tag{11}$$

has the following form,

$$D_{\mu\nu}(z)=\frac{1}{2}\gamma_B(1-c)\sum_r(\boldsymbol{a}_r)_\mu(\boldsymbol{a}_r)_\nu$$
$$-\gamma_B{}^2c(1-c)$$
$$\times\sum_{r,r'}(\boldsymbol{a}_r)_\mu(\boldsymbol{a}_{r'})_\nu G_{\boldsymbol{a}_r\boldsymbol{a}_{r'}}(z),\quad(12)$$

where $\boldsymbol{a}_r$ is the vector from one site to a nearest neighbor site and $(\boldsymbol{a}_r)_\mu$ is its component. The summations are taken over all nearest neighbor sites. The function $G_{\boldsymbol{a}_r\boldsymbol{a}_{r'}}(z)$ is defined by

$$G_{\boldsymbol{a}_r\boldsymbol{a}_{r'}}(z)=\frac{1}{N}\sum_{\boldsymbol{n},\boldsymbol{m}}\langle\{0\}'',\boldsymbol{n}\beta,\boldsymbol{n}+\boldsymbol{a}_r\alpha|$$
$$\frac{1}{z-\tilde{L}}|\boldsymbol{m}+\boldsymbol{a}_{r'}\alpha,\boldsymbol{m}\beta,\{0\}''\rangle,\quad(13)$$

where $|\boldsymbol{n}\alpha,\boldsymbol{m}\beta,\{0\}''\rangle$ denotes the state of no occupancy at all sites except at the site $\boldsymbol{n}$ occupied by a white particle, and at the site $\boldsymbol{m}$ by the black particle. In order to obtain an expression for $D_{\mu\nu}(z)$, we approximate $\tilde{L}$ in Eq. (13) by L_0. Then for the simple cubic lattice of d dimensions, we obtain $D_{\mu\nu}(z)=D(z)\delta^{Kr}_{\mu\nu}$, where

$$D(z)=\gamma_B a^2(1-c)f(c,\gamma,z),\quad(14)$$

$$f(c,\gamma,z)=\frac{[\gamma(1-c)+1][1-\alpha(z)]}{\gamma(1-c)+1-\alpha(z)[1+\gamma(1-3c)]}.\quad(15)$$

Here $\gamma=\gamma_B/\gamma_W$ is the ratio of jump rates of the two species. $\alpha(z)$ is defined by

$$\alpha(z)=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi}dk_1\cdots\int_{-\pi}^{\pi}dk_d$$
$$\times\frac{(\sin k_1)^2}{\frac{z}{2[\gamma_W+\gamma_B(1-c)]}+\sum_{i=1}^{d}(1-\cos k_i)}.\quad(16)$$

The limit $\alpha(z\to0)$ is evaluated; $\alpha(0)=1$ for $d=1$, $\alpha(0)=0.363$ for $d=2$ and $\alpha(0)=0.209$ for $d=3$. The diffusion constant in Eq. (1) is obtained by $D=\lim_{z\to0}D(z)$. In Fig. 1 we show the correlation factor $f(c)$ for the case of self-diffusion (i.e., $\gamma=1$). For $d=3$, a comparison is made with the Monte Carlo calculation of Murch and Thorn[4)] and the agreement is considered good. We obtain $f(c)=0$ for $d=1$. This is suggestive of the non-diffusion character of one-dimensional systems. The case $\gamma\neq1$ corresponds to tracer diffusion on the lattice in the presence of another species. When the jump rate γ_W of a white particle is smaller than the jump rate of γ_B of the black particle, white particles block the motion of the black particle. This effect is seen in Fig. 2 by plotting the ratio of the diffusion constants of a black particle and a white particle D_B/D_W versus the ratio of the jump rates of the two species $\gamma=\gamma_B/\gamma_W$. It is noted that at the high concentration limit $c=1$, D_B/D_W is bounded even if the jump rate of the black particle is very large, i.e., $\gamma\to\infty$.

Finally, we mention that the above procedure of summing over configurations of white particles can be applied to other

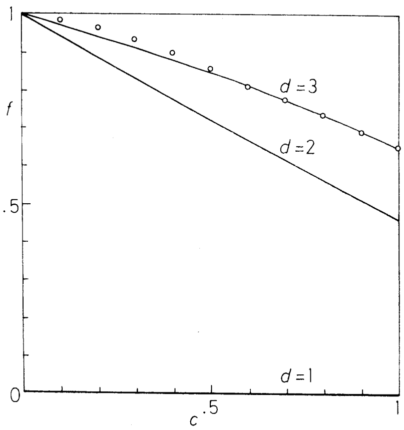

Fig. 1. Correlation factor f as a function of the concentration c for simple cubic lattice of dimensionality d. The circles are the result of Monte Carlo simulations by Murch and Thorn (Ref. 4)).

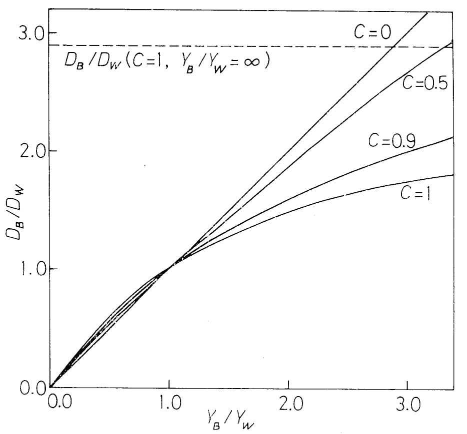

Fig. 2. The ratio of diffusion constants D_B/D_W versus the ratio of jump rates γ_B/γ_W. γ_B and γ_W are the jump rates of a "black" particle and a "white" particle, respectively. D_W and D_B are the diffusion constants of a white tracer particle and of the black tracer particle in the presence of a given concentration c of white particles. The dashed line shows the value of D_B/D_W in the limit $c=1$ and $\gamma_B/\gamma_W=\infty$.

problems of disordered systems since up to the formula (8) we did not use the specific properties of L. We may also generalize the calculation to self-diffusion in a mixture, for example, in hydrogen-deuterium systems.[7]

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