Diffusion in liquids from a first-passage-time point of view

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(Received 11 January 1993)

A first-passage-time viewpoint is proposed and formulated as a tool to investigate diffusion in liquids. Application of our theory to a soft-core system shows that a continuous-diffusion model reproduces the observed first-passage-time distribution quite well for liquids in equilibrium and moderately supercooled states. Under a considerable degree of supercooling we find qualitatively different diffusion behavior reflected in the first-passage-time distribution, which cannot be explained by a continuous-diffusion model. Some models, which take into account effects of hopping, are discussed to reveal the diffusion mechanism in highly supercooled liquids.

PACS number(s): 66.10.−x, 61.20.Ja, 61.20.Lc, 05.40.+j

I. INTRODUCTION

Recently slow dynamics in liquids has gathered a lot of attention in connection with a glass and a freezing transition [1,2]. Since slow dynamics is mainly related to particle-diffusion processes, it is of considerable interest to study diffusion mechanisms in dense liquids.

In studies on self-diffusion in liquids molecular-dynamics simulations have been playing an important role [3,4]. They give the most detailed information on single-particle motion, such as the mean-square displacement $R^2(t)$, the velocity autocorrelation function $\phi(t)$, and the self part of the Van Hove correlation function $G_s(r,t)$ [5,6]. It is well known that the self-diffusion constant D is given by one of the following equations:

$$D=\lim_{t\to\infty} R^2(t)/(6t) , \tag{1}$$

$$D=\lim_{t\to\infty}\int_0^t dt\,\phi(t) , \tag{2}$$

$$D=\lim_{\omega\to 0}\lim_{q\to 0}\omega^2 S_s(q,\omega)/q^2 , \tag{3}$$

where $S_s(q,\omega)$, the self-part of the Van Hove dynamical structure factor, is the Fourier transform of the $G_s(r,t)$. We note that these relations involve the limiting procedure $t\to\infty$ or $\omega\to 0$. In practice, in order to obtain a reliable estimate of D we have to calculate $\phi(t)$ and $R^2(t)$ up to $t=t_{\rm cal}$, which satisfies $t_{\rm cal}>t_{\rm rel}$ with $t_{\rm rel}$ denoting the (longest) relaxation time in the system of interest. The diffusion constant D decreases as the temperature T (density n) of a liquid decreases (increases) and when D becomes as small as 10^{-7} cm^2/s, neither of the equations above could be used reliably to calculate D based on the molecular-dynamics data, since in this supercooled region $t_{\rm rel}$ exceeds the typical simulation time $t_{\rm cal}\simeq 10^{-10}$–$10^{-9}$ s [5]. In other words, the $\phi(t)$ does not relax to zero or the $R^2(t)$ does not take its asymptotic form linear in t for $t<t_{\rm cal}$.

Under these circumstances, we propose in this paper a first-passage-time (FPT) approach to diffusion in liquids, which is useful in extracting aspects of single-particle motion from molecular-dynamics-simulation data (Sec. II). From the FPT analysis of our molecular-dynamics simulations it turns out that a simple continuous-diffusion model gives an adequate description of single-particle motion for liquids in equilibrium and moderately supercooled states, occurring in the length scale $l\geq 2\sigma$ where σ denotes the characteristic interaction range [see Eq. (13)] (Sec. III). In a liquid which is mostly supercooled among the states attainable in our simulations, it turns out that the continuous-diffusion model is no longer capable of describing single-particle motion. From this fact and the snapshots of the particle configuration, we are led to consider some models that take the effects of particle hopping into consideration. Theoretical and numerical (simulation) results on the FPT distribution are used to discuss general features of the hopping diffusion models and their implications on diffusion in the highly supercooled liquids (Sec. IV). Concluding remarks are given in the final section (Sec. V).

II. THE FPT PROBLEM AND THE CONTINUOUS-DIFFUSION MODEL

We consider the following FPT problem in connection with particle diffusion in liquids [7,8]: In a liquid we pay attention to a particle, which is located at $\mathbf{r}_0$ at the time of observation t_0, and imagine a sphere $S(l;r_0)$ with radius l centered at $\mathbf{r}_0$. Then tracing the trajectory of the particle we record the time $t+t_0$ at which the trajectory crosses $S(l;r_0)$ for the first time. The time t is the FPT in our problem and after many repetitions of the experiment we have a histogram of t, which is called the FPT distribution, hereafter denoted by $P_{\rm MD}(t;l)$. This is normalized as

$$\int_0^\infty dt\,P_{\rm MD}(t;l)=1 . \tag{4}$$

The subscript "MD" indicates that this quantity is obtainable only via molecular-dynamics simulations.

Two characteristics of $P_{\rm MD}(t;l)$ are worth mentioning. First, one can determine $P_{\rm MD}(t;l)$ in a time range $0<t<t_{\rm cal}$. If a sample trajectory does not cross the sphere within the observation time $t_{\rm cal}$, the sample con-

tributes to $p_{MD}(t;l)$ for $t > t_{cal}$. By increasing a particle number contained in a simulated system, we can achieve good statistics. Second, let us consider the role played by the radius l. If we set l to be small, P_{MD} would reflect small thermal vibrations of particles, which is not relevant to diffusion. On the other hand, if l is too large, we are sure to observe no crossing events within t_{cal}. Thus we have to choose l in such a way so that we could obtain information relevant to diffusion with high reliability (statistics). In this sense l plays the role of a filter to select useful information.

Once $P_{MD}(t;l)$ is obtained, it can be used as follows: Based on a theoretical model one can calculate, either analytically or numerically, the FPT distribution $P_{th}(t;l;M)$ with the subscript "th" meaning that it is based on a theoretical model and M denoting collectively all the parameters which characterize the model. By comparing P_{MD} with P_{th} we cannot only gain some insights on diffusion mechanisms but also, under favorable conditions, determine M which gives the best fit of P_{th} to P_{MD}.

We now turn to the mathematical aspects of the FPT problem [7,8]. Let the distribution function $P(\mathbf{r},t)$ express the probability density of finding a particle at a space-time point $(\mathbf{r},t)$. In a theoretical model it is assumed that $P(\mathbf{r},t)$ evolves in time according to

$$\frac{\partial P}{\partial t} = L(M)P \ , \tag{5}$$

where M in the operator $L(M)$ denotes parameters in the model. In order to calculate $P_{th}(t;l;M)$ one first solves Eq. (5) under the following initial and boundary conditions:

$$P(\mathbf{r},t=0)=\delta(\mathbf{r}) \ , \tag{6}$$

$$P(\mathbf{r},t)=0 \quad \text{for} |\mathbf{r}| \geq 1 \ . \tag{7}$$

Then the desired $P_{th}(t;l;m)$ is obtained from

$$P_{th}(t;l;M) = -\left[\frac{d}{dt}\right] \int d\mathbf{r}\, P(\mathbf{r},t) \ , \tag{8}$$

where the integral on the right-hand side (rhs) is performed within the sphere of radius l. We note that if only continuous trajectories are allowed (i.e., no hopping events) in the model we only need to impose $P(\mathbf{r},t)=0$ for $|\mathbf{r}|=l$ for the boundary condition.

In the remainder of this section we consider a continuous-diffusion model

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D\nabla^2 P(\mathbf{r},t) \ , \tag{9}$$

with D being the parameter in the model M. Since our problem is isotropic we express Eq. (9) in polar coordinates as

$$\frac{\partial P(r,t)}{\partial t} = D\left[\frac{\partial^2 P}{\partial r^2} + (2/r)\frac{\partial P}{\partial r}\right] \ , \tag{10}$$

and obtain, with use of the proper eigenvalue λ,

$$P(r,t) = \sum_{\lambda} (1/r)\{a(\lambda)\sin[r\sqrt{\lambda/D}\,] + b(\lambda)\cos[r\sqrt{\lambda/D}\,]\}\exp\{-\lambda t\} \ . \tag{11}$$

The cosine term should vanish $[b(\lambda)=0]$ in order to keep $P(r,t)$ finite at $r=0$. From the boundary condition (6) we see that $\sqrt{\lambda/D} = n\pi/l$ $(n=1,2,\ldots)$ and the initial condition (5) gives $a(\lambda)=n/(2l^2)$, leading with the aid of Eq. (8) to

$$P_{th}(t;l;D) = 2D(\pi/l)^2 \times \sum_{n=1}^{\infty} (-1)^{n+1} n^2 \exp\{-(n\pi/l)^2 Dt\} \ . \tag{12}$$

Usually the sum in Eq. (12) up to $n=100$ is enough to have a convergent value for P_{th}.

III. THE FPT DISTRIBUTION IN THE SOFT-CORE SYSTEM

We consider the FPT distribution in the soft-core system with the interparticle potential [5,9]

$$\phi(r) = \varepsilon(\sigma/r)^n \quad (n=12) \ . \tag{13}$$

Our system, containing $N=500$ particles in a fixed volume V, is simulated by a constant-energy molecular-dynamics method [4]. We note that the system is thermodynamically characterized by one parameter ρ^*, defined by

$$\rho^* = (N\sigma^3/V)(\varepsilon/k_B T)^{1/4} \ , \tag{14}$$

with k_B denoting the Boltzmann constant and the freezing and the glass transition points are reported to be $\rho_f^* = 1.15$ and $\rho_g^* = 1.56$, respectively [9].

It is sometimes convenient to choose an argon atom as the particle in our model and take $\varepsilon = 480$ K, $\sigma = 3.4$ Å, and $m = 6.63\times10^{-23}$ g as units of energy, length, and mass, respectively. This enables us to express D and T in units of cm^2/s and K, respectively, and the time mesh in our numerical integration scheme corresponds to 7.78×10^{-15} s.

Five runs [run (1) to run (5)] are performed with a quench rate $q = 6.27\times10^{11}$ K/s for runs (3) and (4) and $q = 1.25\times10^{11}$ K/s for run (5) (see Table I). Among these we show results of our simulations for runs (1), (4), and (5), with a remark that simulation results in run (2)

TABLE I. Five runs in our simulations.

Run	ρ^*	T [K]	D (cm^2/s)
(1)	1.023	95.1	2.75×10^{-5}
(2)	1.094	82.8	1.76×10^{-5}
(3)	1.19	51.5	8.97×10^{-6}
(4)	1.26	41.5	5.66×10^{-6}
(5)	1.35	31.7	1.04×10^{-7}

for a liquid near the freezing point and run (3) for a slightly supercooled liquid are excellently reproduced by the continuous-diffusion model, Eq. (9), for $l \geq 2\sigma$.

Figure 1 shows the FPT distribution $P_{\mathrm{MD}}(t;l)$ for $l=2\sigma$ (a), 2.5σ (b), and 3σ (c) together with the corresponding $P_{\mathrm{th}}(t;l;D)$ (dashed curves). We notice that in this relatively low-density system, we have to choose rather large l ($\geq 2.5\sigma$) to screen out diffusional behaviors. For runs (2) and (3) $l=2\sigma$ is large enough to yield the experimental results $P_{\mathrm{MD}}(t;l)$ and D_{MD}. The D values in $P_{\mathrm{th}}(t;l;D)$ are determined as follows: We first choose a value W ($0<W<1$) for the weight and define t_W by

$$W=\int_0^{t_W} dt\, P_{\mathrm{MD}}(t;l) . \tag{15}$$

In Fig. 1 W is chosen to be 0.6 as indicated. D is determined by demanding

$$W=\int_0^{t_W} dt\, P_{\mathrm{th}}(t;l;D) . \tag{16}$$

From Figs. 1(b) and 1(c) we note that single-particle dynamics occurring on the length scale $l \geq 2.5\sigma$ is adequately described by a diffusion equation (9). Results for run (4) are depicted in Fig. 2. Because of the smallness of both the diffusion constant and the total weight obtained by our simulations, we had to choose rather small W. In this moderately supercooled liquid the continuous-diffusion model is also seen to work well on the scale $l \geq 2\sigma$. Figure 3 shows results ($l=1.5\sigma$) for a highly supercooled liquid with $D_{\mathrm{MD}} \sim 10^{-7}$ cm^2/s. Although the calculated total weight W is small (0.013 for $t_W=t_{\mathrm{cal}}=2\times10^{-10}$ s), we notice qualitatively different features in $P_{\mathrm{MD}}(t;l)$ from those for runs (1)–(4). In this case we cannot reproduce the P_{MD} by any choice of D. If we take $D=6D_{\mathrm{MD}}$ for an illustration purpose, we have a

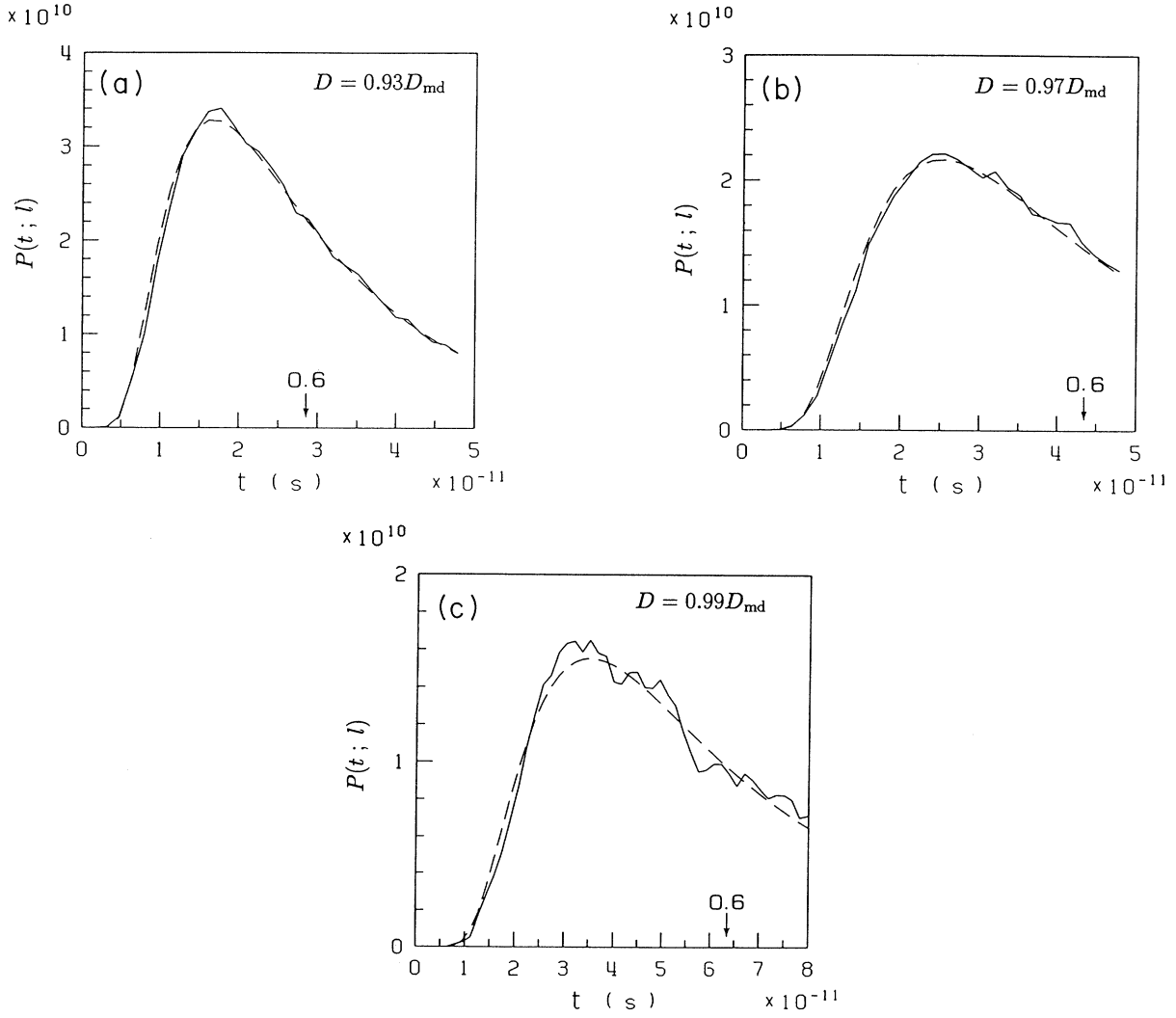

FIG. 1. The FPT distribution $P_{\mathrm{MD}}(t;l)$ for run (1). (a), (b), and (c) correspond to $l/\sigma=2$, 2.5, and 3, respectively. The full and dashed curves represent $P_{\mathrm{MD}}(t;l)$ and $P_{\mathrm{th}}(t;l;D)$, respectively. The diffusion constant D from the continuous-diffusion model is given as the ratio to the experimental result D_{MD}.

dashed curve quite different from the experimental one. From snapshots of the particle distribution in the system, we observe that particles are sitting on some sites, occasionally making hops to nearby (amorphous) sites. Thus we must consider a model which takes the effects of hopping into account as long as we are concerned with dynamical events occurring on a length scale of a few σ and a time of 10^{-10} or 10^{-9} s, which we can access by the molecular-dynamics method.

IV. HOPPING DIFFUSION MODELS AND THEIR PROPERTIES

In this section we consider some hopping models for which we obtain the FPT distribution by computer simulations. In passing it is remarked, however, that some models in this section can be treated analytically and these points will be discussed elsewhere [10]. The hopping model we consider is known as the continuous-time random-walk (CTRW) model [11] described by

$$\frac{\partial P(\mathbf{r},t)}{\partial t}=\int_0^t \phi(t-t')\int d\mathbf{r}'[W(\mathbf{r}|\mathbf{r}')P(\mathbf{r}',t) - W(\mathbf{r}'|\mathbf{r})P(\mathbf{r},t)] , \quad (17)$$

where the $\phi(t)$ is related to a waiting-time distribution $\psi(t)$ via

$$\phi(s)=s\psi(s)/[1-\psi(s)] , \quad (18)$$

where $\phi(s)$ and $\psi(s)$ denote the Laplace transforms of $\phi(t)$ and $\psi(t)$, respectively [11,12]. The transition probability from $\mathbf{r}'$ to $\mathbf{r}$, $W(\mathbf{r}|\mathbf{r}')$, is taken to be

$$W(\mathbf{r}|\mathbf{r}')=\delta(|\mathbf{r}-\mathbf{r}'|-a)/(4\pi a^2) , \quad (19)$$

which is seen to be normalized to 1. The a in Eq. (19) denotes the hopping length and l/a becomes an important parameter in our model. As is well known, if one takes the exponential waiting-time distribution $\psi(t)=\exp(-t/t_h)/t_h$, it holds that $\phi(t)=\delta(t)/t_h$ and Eq. (17) reduces to an ordinary Markovian master equation

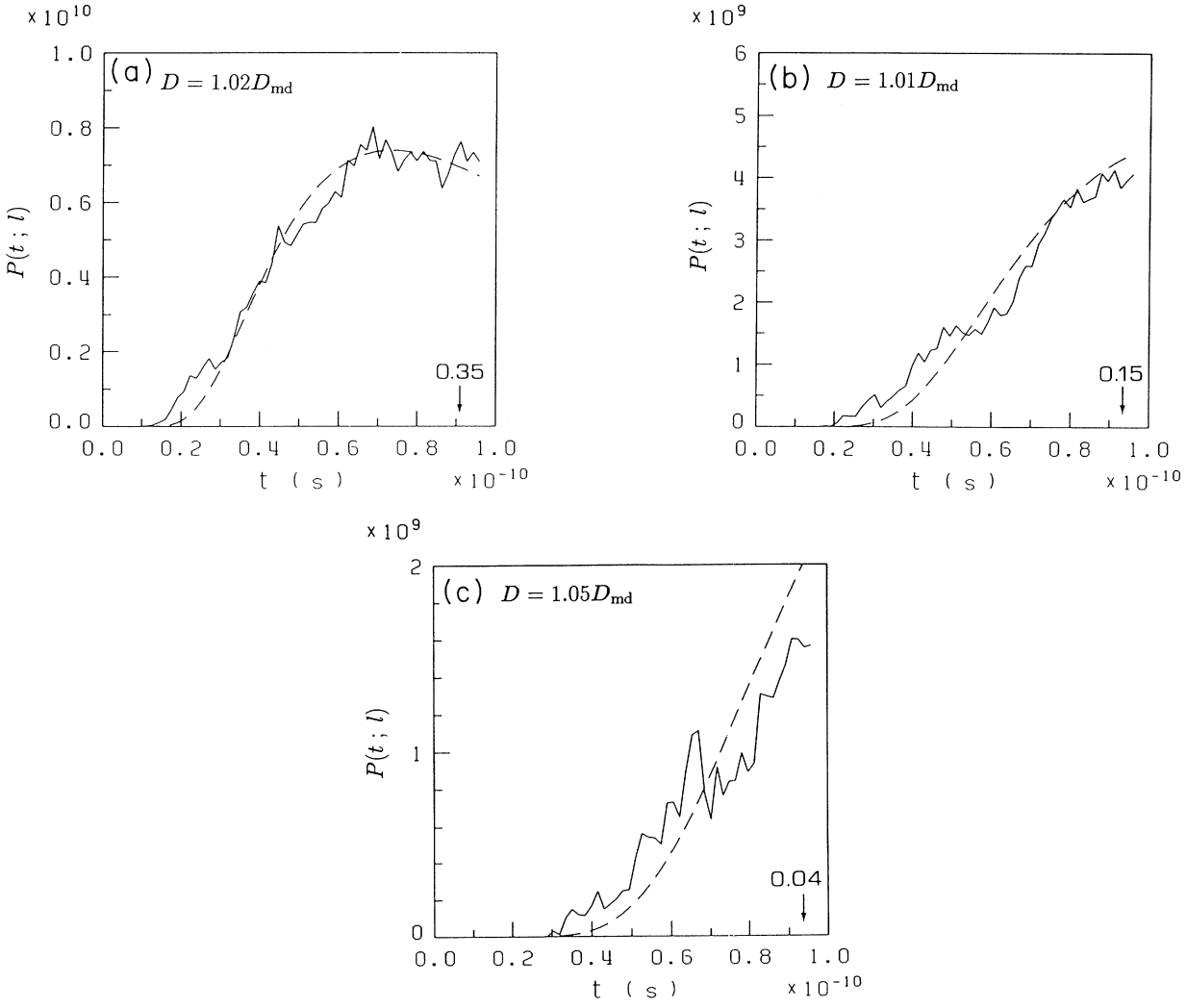

FIG. 2. The FPT distribution $P_{\mathrm{MD}}(t;l)$ for run (4). The meaning of the figures is the same as in Fig. 1.

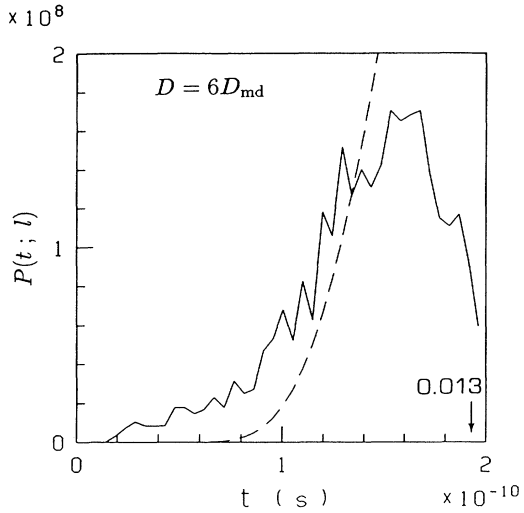

FIG. 3. The FPT distribution $P_{MD}(t;l)$ for run (5) and $l/\sigma=1.5$. The dashed curve is the result of the continuous-diffusion model for $D=6D_{MD}$.

[7,13]. Instead of the exponential $\psi(t)$, we consider the following $\psi(t)$:

$$\psi(t)=\begin{cases}0 & \text{for } t<t_d \\ \exp[-(t-t_d)/t_h]/t_h & \text{for } t\geq t_d\end{cases} . \tag{20}$$

The delay time t_d denotes the time necessary for the surrounding particles to adjust themselves to allow for the next hopping and t_h is the average waiting time after the adjustment. Putting $t_d=0$ we recover the Markovian model. We note that the ratio t_d/t_h is an important parameter, in addition to l/a, in this model. One can also introduce a probability distribution for t_d as will be commented on later in this section. The model above will be collectively refered to as a hopping model without Brownian motion (HMWOB) and the diffusion constant of which is given by

$$D_H=a^2/[6(t_d+t_h)] . \tag{21}$$

Now we explain a hopping model with Brownian motion (HMWB). We consider that a particle hops, as described by Eqs. (17)–(20), at time $\{t_i\}$ $(i=1,2,\ldots)$ and during the time $t_i<t<t_{i+1}$ $(i=1,2,\ldots)$ the particle undergoes bounded Brownian movement [7,14] with the center of attraction at $\mathbf{R}_i$, where the particle arrived at time t_i. With the origin of the coordinate set at $\mathbf{R}_i$, the Langevin equation is given by

$$m\ddot{\mathbf{r}}=-k\mathbf{r}-m\zeta\dot{\mathbf{r}}+\mathbf{F}(t) , \tag{22a}$$

$$\langle\mathbf{F}(t)\mathbf{F}\rangle=2m\zeta k_B T\delta(t)I , \tag{22b}$$

where k and ζ denote the spring constant and the fric-

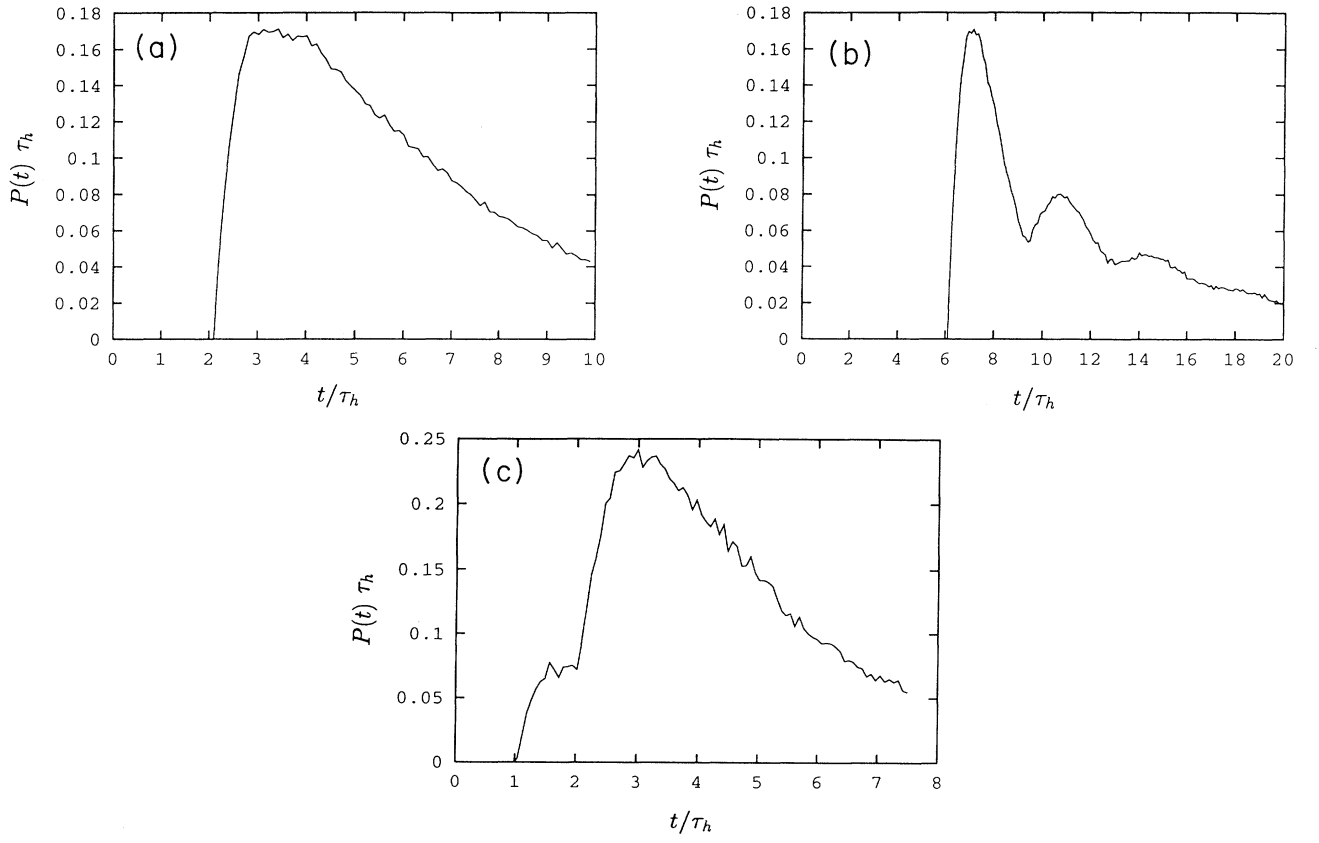

FIG. 4. The FPT distribution based on the HMWOB [(a) $t_d/t_h=1$ and (b) $t_d/t_h=3$] and HMWB [(c) $t_d/t_h=1$, $\alpha_L=0.2$, and $D_H/D_B=0.1$] obtained from computer simulations of hopping and Brownian processes.

tion, respectively, and I is the 3×3 unit matrix. Since heavy damping is assumed, Eq. (22a) is reduced to

$$\dot{\mathbf{r}}=-(\omega^2/\zeta)\mathbf{r}+\mathbf{F}(t)/(m\zeta)\ , \tag{22a'}$$

with $\omega^2=(k/m)$. The Fokker-Planck equation, which corresponds to Eq. (22a'), is

$$\frac{\partial P(\mathbf{r},t)}{\partial t}=\nabla\cdot[(\omega^2/\zeta)\mathbf{r}P]+D_B\nabla^2P\ , \tag{23}$$

with

$$D_B=k_BT/(m\zeta)\ . \tag{24}$$

From Eq. (23) we readily see that the mean-square deviation $\langle r^2\rangle$ for large t is given by $3k_BT/(m\omega^2)$. The Lindemann constant

$$\alpha_L=[\langle r^2\rangle]^{1/2}/a \tag{25}$$

characterizes the range of excursion of the Brownian particle around the center $\mathbf{R}_i$.

Hereafter we consider the case $l/a=1.5$ where at least two hops are necessary for the FPT event to occur if Brownian motion is not allowed. First we show $P(t;l)$ for the HMWOB when t_d and t_h are comparable to each other ($t_d/t_h=1$ [Fig. 4(a)] and $t_d/t_h=3$ [Fig. 4(b)]). When t_d is larger than t_h we see some peaks in $P(t;l)$ with the first (second) one coming from the two- (three-) hop events. Since the distribution of t_d is not allowed here, it is clear that $P(t;l)$ becomes nonzero only after $2t_d$. The effects of Brownian motion are shown in Fig. 4(c) where Brownian motion with $\alpha_L=0.2$ and $D_H/D_B=0.1$ [see Eqs. (21) and (24)] are superimposed on the system shown in Fig. 4(a). The bump in the region $t_h<t<2t_h$ represents the contribution of the Brownian motion which enables a particle to cross the sphere by one hop.

Some general observations from our numerical simulations of $P(t;l=1.5a)$ are noted in order: When t_h is by an order of magnitude larger than t_d, e.g., $t_d/t_h\simeq30-50$, $P(t;l)$ becomes very small in the range of a few t_d, reminiscent of the small-time behavior depicted in Fig. 3. The Lindemann constant, Eq. (25), is an important factor to control effects of the Brownian motion. For example, if we reduce α_L from 0.2 to 0.1 we could see no clear contribution to $P(t;l)$ from the Brownian motion in the small-time region [see Fig. 4(c)]. Finally the effects of distribution in t_d were investigated by giving an exponential probability $P(t_d)=\exp(-t_d/\langle t_d\rangle)/\langle t_d\rangle$ to t_d, with $\langle t_d\rangle$ playing the role of t_d in a previous fixed-t_d model. As expected, the steep slope near $t=2t_d$ in Figs. 4(a) and 4(b) becomes smooth and a sharp structure in Fig. 4(b) becomes smeared.

V. CONCLUDING REMARKS

In this paper we proposed a FPT viewpoint to study diffusion in liquids and applied it to a soft-core system. Except for a highly supercooled liquid the continuous-diffusion model works well to describe diffusion on the scale $l\geq2\sigma$.

In concluding this paper we give two remarks concerning diffusion in highly supercooled liquids. The first one is related to $P_{\rm MD}(t;l)$ when l is a little smaller than a hopping length. In this case $P_{\rm MD}(t;l)$ is expected to represent a waiting-time distribution (WTD) since one hop is enough to cross a sphere. In Fig. 5 we show $P_{\rm MD}(t;l=\sigma)$ obtained for run (5). We notice that the WTD has a long plateau, which reminds us of the assumption of the algebraically slow decay (t^{-a}) of the WTD employed to describe particle (exciton) diffusion in supercooled or amorphous materials [15,11]. The second remark is concerned with the recent work by Roux, Barrat, and Hansen [16] on diffusion in supercooled liquids. They showed through molecular-dynamics simulations that there exists some (critical) density below (above) which particle movement is dominated by a continuous-(hopping) diffusion mechanism. Their conclusion is based on a detailed analysis of the function $r^2G_s(r,t)$ which de-

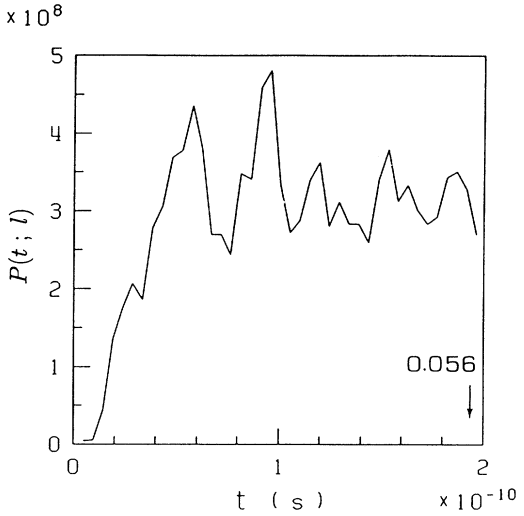

FIG. 5. The FPT distribution $P_{\rm MD}(t;l)$ for run (5) and $l/\sigma=1.0$.

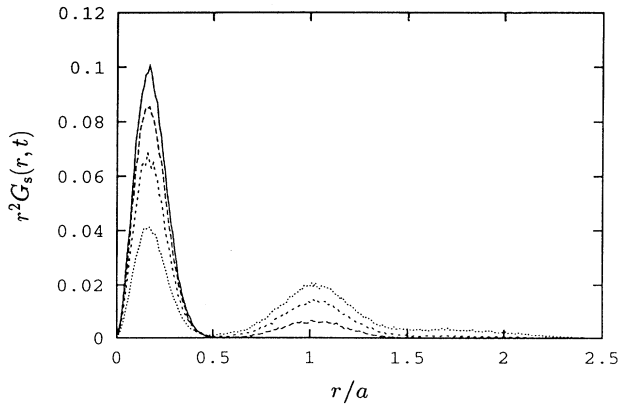

FIG. 6. $r^2G_s(r,t)$ of the HMWB with $\alpha_L=0.2$, $t_d/t_h=\frac{1}{50}$, and $D_H/D_B=0.1$ for $t/t_d=0.94$ (full line), 8.0 (long-dashed line), 20.0 (short-dashed line), and 44.0 (dotted line).

scribes how a particle put at the origin moves away in the course of time. Based on the HMWB with $\alpha_L = 0.2$, $t_d/t_h = \frac{1}{50}$, and $D/D_B = 0.1$ we also calculated $r^2 G_s(r,t)$, which is shown in Fig. 6. A particle put at the origin is seen to first equilibrate and then undergo hopping, giving weight around $r/a = 1$ and so on, and these behaviors are precisely what were observed by Roux, Barrat, and Hansen. At the moment we are performing molecular-dynamics simulations of a two-component system, whose data are to be analyzed based on the FPT viewpoint.

ACKNOWLEDGMENTS

The authors express their gratitude to Mr. R. Noziri of Kawasaki Steel Corporation for useful discussions and his assistance in numerical calculations at an early stage of this work.

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