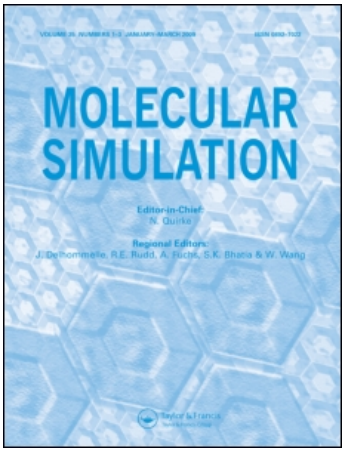

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A FIRST-PASSAGE TIME APPROACH TO DIFFUSION IN LIQUIDS AND SUPERIONIC CONDUCTORS

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As a new tool to investigate single-particle motion in condensed matter, a first-passage time (FPT) approach to diffusion is developed and applied to the molecular dynamics simulations of simple liquids and superionic conductor CaF_2. It is shown that a continuous diffusion model reproduces the observed FPT distribution quite well for both liquids and CaF_2, which enables us to evaluate diffusion constants with good accuracy by our method. On a length scale as small as a lattice constant, however, the effect of hopping appears in the FPT distribution of F^- ions, which can not be described by a continuous diffusion model. A simple hopping diffusion model is proposed and examined from the FPT viewpoint.

KEY WORDS: First-passage time, molecular dynamics, diffusion, liquids, superionic conductor.

1 INTRODUCTION

Self-diffusion of atoms and molecules in condensed media is a fundamental transport process in physics and chemistry. It has been well recognized that a molecular dynamics (MD) simulation is a powerful tool to investigate microscopic processes of atomic transport in solids, liquids, plasmas, and so on. [1] The self-diffusion constant D in liquids is of the order of $10^{-5}\,cm^2/s$, which is evaluated reliably from the mean square displacement (MSD) or the velocity autocorrelation function (VAF) via the following formulae;

$$D = \lim_{n\to\infty} \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle \tag{1}$$

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(t)\cdot\mathbf{v}(0) \rangle \, dt. \tag{2}$$

In strongly supercooled and glassy states, however, D becomes as small as $10^{-7}\,cm^2/s$, which is difficult to evaluate since the MSD does not take the t-linear form and the VAF does not converge to zero within the time scale of computations. [2] Recently we have developed a first-passage time (FPT) viewpoint as a new tool to evaluate diffusion constants in MD simulations in connection with the analysis of slow dynamics in supercooled liquids. [3] As discussed in our previous paper [3]

(referred to as I), the FPT approach is useful for extracting new aspects of single-particle motion from the MD data.

In the present work we apply the approach proposed in I to diffusion in simple liquids and superionic conductor CaF_2 to investigate the diffusion mechanism from the FPT viewpoint. Superionic conductors are the solid state systems characterized by the ionic conductivity as high as that found in liquids. [4, 5] Well below a melting point carrier ions diffuse through the sublattice formed by other ion species, and the diffusion constant becomes as large as $10^{-5}\,cm^2/s$. Among various kinds of superionic materials, CaF_2 is known as a typical example of those which exhibit hopping-type diffusion. According to the experiments [6] and the MD simulations [7], diffusion of F^- ions occurs by discrete hops among the well-defined sites in Ca^{2+}-sublattice, which is quite different from the liquid-like diffusion in AgI-type superionic conductors. Thus the characteristics of the FPT distribution in CaF_2 are expected to be different from those found in liquids, and it is of interest to compare the diffusion mechanisms in liquids and CaF_2 from the FPT viewpoint.

The outline of this paper is as follows. In the next section we describe our theory following I. The results of the simulations are given in Section 3. We investigate the FPT distributions in a soft-sphere liquid and CaF_2 based on the continuous diffusion model. A simple hopping diffusion model is also analyzed to interpret the FPT distribution of F^- ions. Summary and some remarks are given in Section 4.

2 THE FPT PROBLEM

In this section we briefly describe our FPT problem and a continuous diffusion model following I. Let us assume that a particle is located at $\mathbf{r}_0$ at time 0 in a liquid, and imagine a sphere with radius l_0 centered at $\mathbf{r}_0$. We pay attention to the time t at which the particle crosses the sphere for the first time. This time t is defined as the FPT in our problem. By tracing the trajectories of particles in MD simulations, the distribution function of FPT is obtained as a histogram of t. We denote the FPT distribution obtained from MD data as $P_{MD}(t; l_0)$, and normalize it as

$$\int_{-\infty}^{\infty} P_{MD}(t; l_0)\,dt = 1, \tag{3}$$

so as to compare with theoretical results.

The theoretical expression for the FPT distribution is derived as follows. Here we start from a continuous diffusion model, and assume that the probability density $f(\mathbf{r}, t)$ of finding a particle at $\mathbf{r}$ at time t evolves in time according to the diffusion equation

$$\frac{\partial f(\mathbf{r}, t)}{\partial t} = D\nabla^2 f(\mathbf{r}, t). \tag{4}$$

The solution of Equation (4) under the initial and boundary conditions

$$f(\mathbf{r}, 0) = \delta(\mathbf{r}), \quad f(|\mathbf{r}| = l_0, t) = 0 \tag{5}$$

is given by

$$f(\mathbf{r},t) = \sum_{n=1}^{\infty} \frac{n}{2l_0^2} \exp\left[-D\left(\frac{n\pi}{l_0}\right)^2 t\right] \frac{\sin(n\pi r/l_0)}{r}. \tag{6}$$

The FPT distribution function of this model, which we denote as $P_{\mathrm{TH}}(t; l_0, D)$, is related to $f(\mathbf{r}, t)$ via the following formula

$$P_{\mathrm{TH}}(t; l_0, D) = -\frac{\mathrm{d}}{\mathrm{d}t}\int f(\mathbf{r}, t)\,\mathrm{d}\mathbf{r}, \tag{7}$$

where the integral in Equation (7) is performed within the sphere of radius l_0. Inserting (6) into (7), we obtain

$$P_{\mathrm{TH}}(t; l_0, D) = 2\sum_{n=1}^{\infty} (-1)^{n+1} D\left(\frac{n\pi}{l_0}\right)^2 \exp\left[-D\left(\frac{n\pi}{l_0}\right)^2 t\right]. \tag{8}$$

In our test calculations we obtained a convergent value of P_{TH} by taking the summation in Equation (8) up to 100.

Once $P_{\mathrm{MD}}(t; l_0)$ is obtained for a given l_0, we compare it with $P_{\mathrm{TH}}(t; l_0, D)$ and determine D which gives the best fit of $P_{\mathrm{TH}}(t; l_0, D)$ to $P_{\mathrm{MD}}(t; l_0)$. Hereafter the diffusion constant determined by the fitting is denoted as D_{FPT}. Through this procedure, we can not only evaluate D, but also extract some information on the diffusion mechanism. The advantage of our method is that we focus our attention only on the trajectories relevant to diffusion by taking l_0 moderately large so that the influence of small vibrations is not reflected in the FPT distribution. In this sense our approach is different from the analyses based on the quantities such as MSD and VAF which are averaged over all particles in the system.

3 RESULTS

Simple Liquids

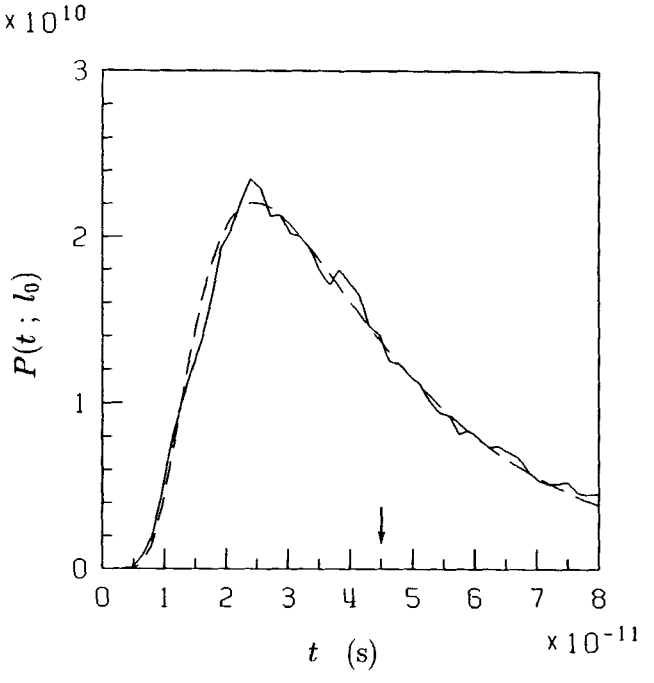
We consider the FPT distribution in a one-component soft-core system. [8] The interatomic potential is given by

$$\phi(r) = \varepsilon\left(\frac{\sigma}{r}\right)^n, \tag{9}$$

where σ is an effective core radius. The parameters are taken as $\varepsilon/k_B = 480\,\mathrm{K}$, $\sigma = 3.4$ Å and $n = 12$, which correspond to the repulsive part of the Lennard-Jones potential for liquid argon. [9] The system with the potential (9) has an interesting scaling property [8] and the thermodynamic state is specified by the reduced density

$$\rho^* = \frac{N\sigma^3}{V}\left(\frac{\varepsilon}{k_B T}\right)^{3/n}. \tag{10}$$

It is known that the freezing and glass transition points of this model are $\rho_f^* \sim 1.15$ and $\rho_g^* \sim 1.56$, respectively. [10] The MD simulations are performed under constant-volume and constant-energy condition for a 500-atom system. The equations of motion are integrated up to 20000 steps with the time mesh $\Delta t = 7.98 \times 10^{-15}\,\mathrm{s}$.



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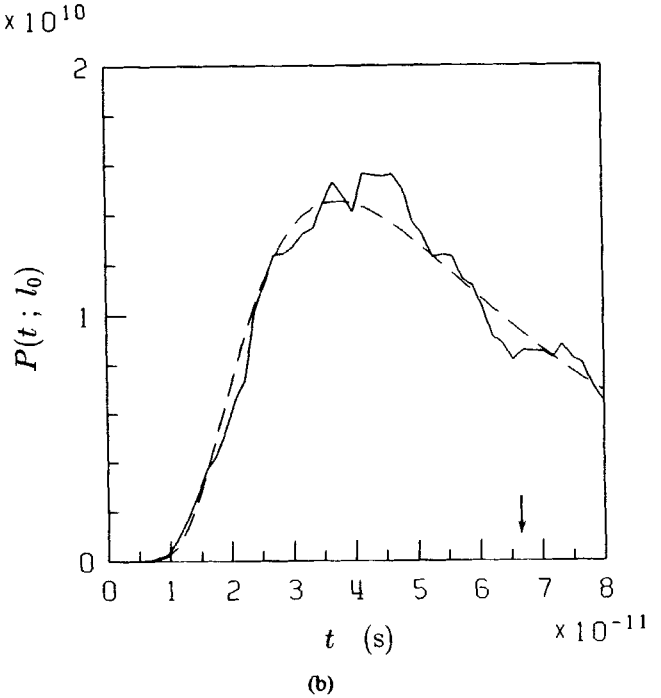

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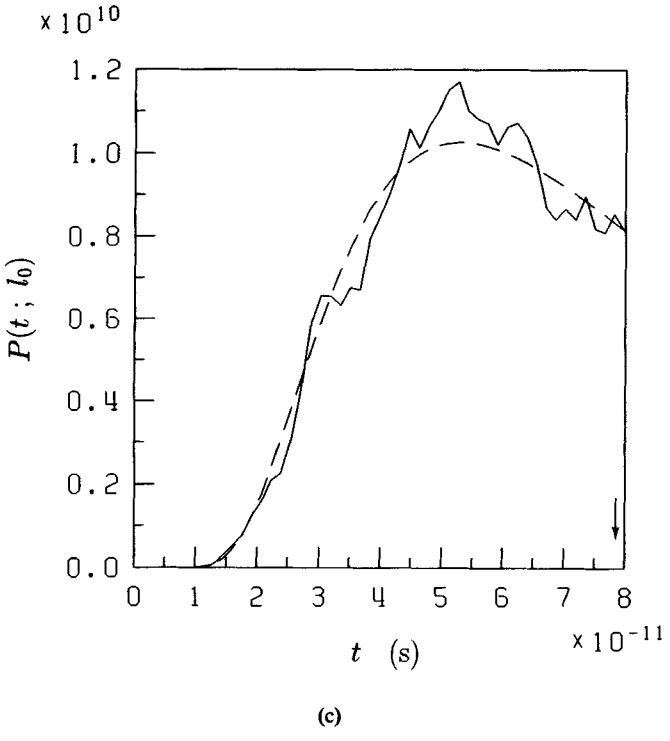


Figure 1 The FPT distribution functions $P_{MD}(t; l_0)$ (solid line) and $P_{TH}(t; l_0, D)$ (dashed line) for a soft-core system at $\rho^* = 1.094$. (a), (b) and (c) correspond to $l_0 = 2\sigma$, 2.5σ and 3σ, respectively.

The FPT distribution functions at $\rho^* = 1.094$ are shown in Figures 1 (a), (b) and (c) for $l_0 = 2.0\sigma$, 2.5σ and 3.0σ, respectively. We notice that fluctuations appear in $P_{MD}(t; l_0)$ in Figures 1 (b) and (c) since the number of trajectories which cross the sphere becomes small as l_0 increases. The procedure to evaluate D from $P_{MD}(t; l_0)$ is the following. We pay attention to the weight W and define t_w by

$$W = \int_0^{tw} P_{MD}(t; l_0)\, dt. \tag{11}$$

D_{FPT} is defined as the value which satisfy the relation

$$W = \int_0^{tw} P_{TH}(t; l_0, D_{FPT})\, dt. \tag{12}$$

In Figure 1 W is taken as (a) 0.6, (b) 0.6 and (c) 0.46, and t_w is indicated by arrows. It is observed that $P_{TH}(t; l_0, D)$ fits well with corresponding $P_{MD}(t; l_0)$ for $l_0 \geq 2\sigma$. The diffusion constants determined by the fitting are (a) 1.74×10^{-5}, (b) 1.79×10^{-5} and (c) $1.81 \times 10^{-5}\,cm/s^2$, which are in good agreement with $D_{MSD} = 1.76 \times 10^{-5}\,cm/s^2$ evaluated from Equation (1). This tells us that the continuous diffusion model is appropriate for diffusion in simple liquids on the length

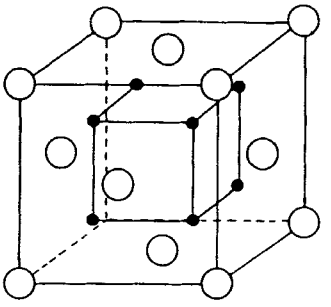


Figure 2 The structure of CaF_2. Open circles denote Ca^{2+} ions and solid circles F^- ions.

scale $l_0 \geq 2.0\sigma$, which enables us to evaluate D with good accuracy by the FPT approach.

Superionic Conductor CaF_2

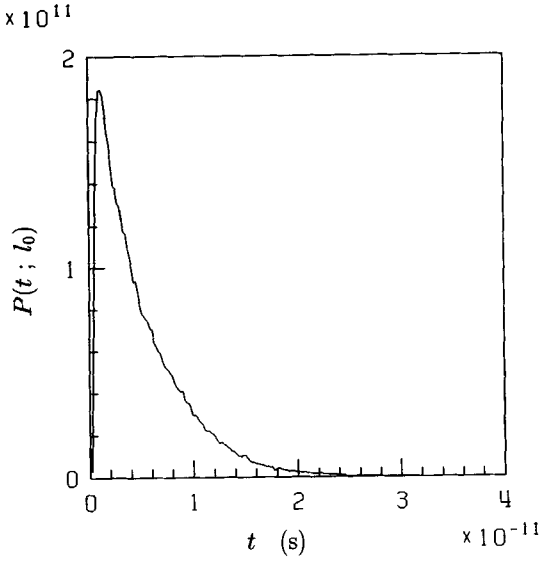
In this section we investigate the FPT distribution in superionic conductor CaF_2 to see how the FPT approach works for diffusion in solids. The structure of CaF_2 is shown in Figure 2. Fluorine ions occupy tetrahedral sites in the fcc arrangement of Ca^{2+} ions. That is, F^- ions form a simple cubic lattice with Ca^{2+} on every other body centered position. In the superionic phase ($T \geq 1423$ K [11]) F^- ions diffuse with a high mobility among tetrahedral sites.

The MD simulations are carried out for a 768-ion system with the interionic potential of the form

$$\phi_{ij}(r) = \varepsilon\left(\frac{\sigma_i + \sigma_j}{r}\right)^n + \frac{Z_i Z_j (fe)^2}{r}, \tag{13}$$

where σ_i and Z_i are the ionic radius and the valence of ion i, respectively, and f is the ionicity. The potential parameters are chosen as $n = 7$, $\varepsilon = 0.28$ eV, $\sigma_{Ca} = 1.28$ Å, $\sigma_F = 1.28$ Å and $f = 1.0$. [7, 12] As reported in Reference [7], these parameters realize the experimentally-observed transition temperature and diffusion constants. The nearest neighbor distance between tetrahedral sites is taken as $a = 2.95$ Å, which is the jump distance of F^- ions. The MD simulation is performed up to $38000\Delta t$ with $\Delta t = 1.95 \times 10^{-15}$ s. The average temperature is $T = 1874$ K, and the diffusion constant of F^- evaluated from Equation (1) is $D_{MSD} = 3.68 \times 10^{-5}$ cm/s^2.

Figure 3 shows the FPT distribution of F^- ions for $l_0 = a$ (a), $1.5a$ (b) and $3.5a$ (c). When l_0 is as small as a, F^- can escape from the sphere by only one jump. Therefore $P_{MD}(t; l_0 = a)$ is considered as the distribution function of the residence time of F^- at a tetrahedral site, which shows fast decay as observed in Figure 3(a). In Figure 3(b) $P_{MD}(t; l_0)$ and $P_{TH}(t; l_0, D)$ are compared for $l_0 = 1.5a$, where P_{TH} is drawn with $D = 3.23 \times 10^{-5}$ cm/s^2 determined by the relation (12) ($W = 0.9$). In this length scale $P_{TH}(t; l_0, D)$ exhibits departures from $P_{MD}(t; l_0)$ at t less than 1.5×10^{-11} s, which means that the continuous model is not appropriate to explain the FPT distribution of F^- ions. When l_0 becomes as large as $3.5a$,



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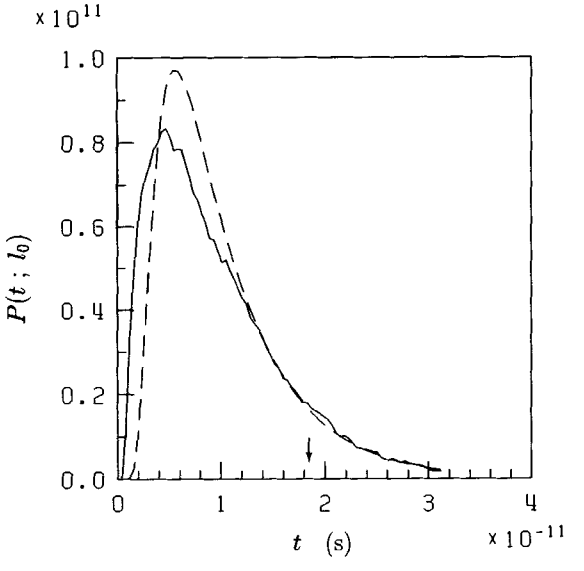
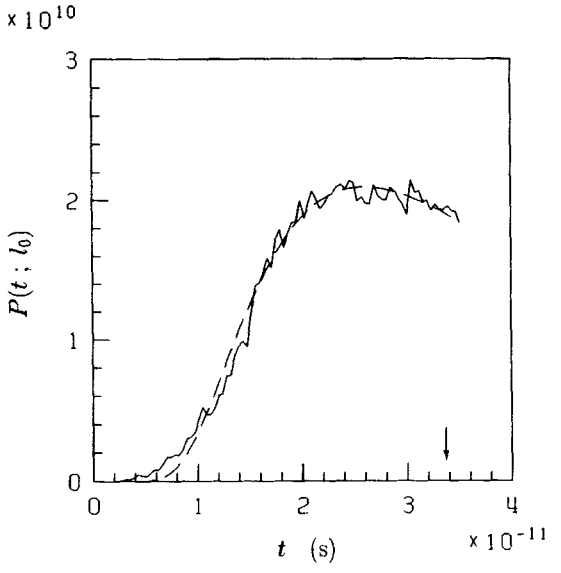


(b)

Figure 3 The FPT distribution functions $P_{MD}(t; l_0)$ (solid line) and $P_{TH}(t; l_0, D)$ (dashed line) for F^- ions. (a), (b) and (c) correspond to $l_0 = a$, $1.5a$ and $3.5a$, respectively. In the fitting procedure W is taken as (b) 0.9 and (c) 0.46.



(c)

Figure 3 cont.

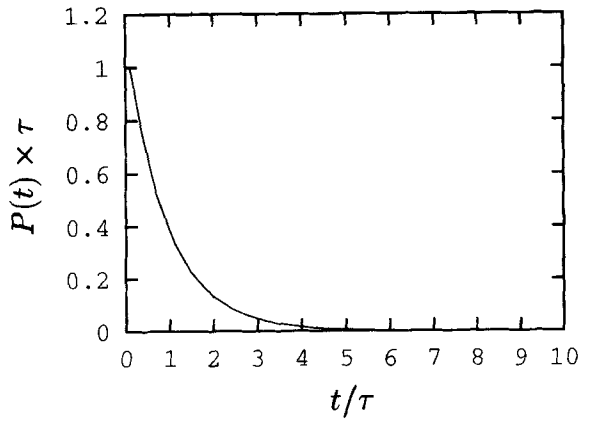
however, $P_{TH}(t; l_0, D)$ agrees well with $P_{MD}(t; l_0)$ as shown in Figure 3(c). The diffusion constant obtained from the fitting is $D_{FPT} = 3.77 \times 10^{-5}\,cm/s^2$, which is in good agreement with D_{MSD}. Therefore the continuous diffusion model works well for describing the behavior of F^- ions on the length scale larger than ~ 3a, and D is determined reliably by our method.

We now turn to the FPT distribution for l_0 as small as the jump distance. In order to interpret the results in Figures 3(a) and (b) we examine a simple hopping diffusion model by computer simulations. This model is characterized by two parameters, that is, the hopping rate $1/\tau$ and the jump length a_0. A particle is put at the origin and is allowed to undergo hopping with the probability $\Delta t/\tau$, where Δt is a sufficiently small time increment in the simulation. We trace the trajectory of the particle and monitor the time at which the trajectory crosses the sphere of radius l_0 centered at the origin. After many repetitions of the experiment, we obtain the FPT distribution of this model.

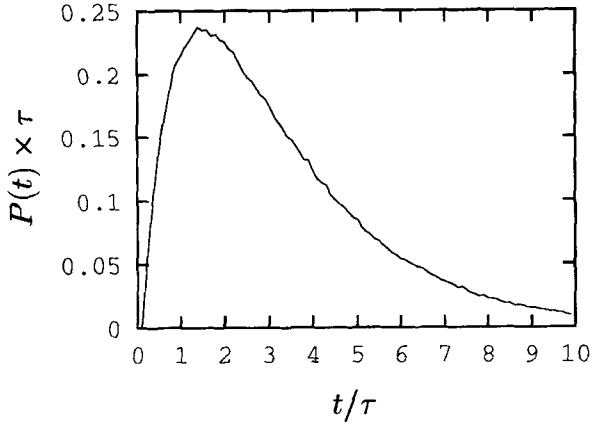
The FPT distribution functions $P(t)$ of this model are given in Figure 4 for $l_0 = 0.5a_0$ (a) and $1.5a_0$ (b). If we take l_0 less than a_0, $P(t)$ reduces to the residence time distribution which is known to decay exponentially as

$$\psi(t) = \frac{1}{\tau}\exp(-t/\tau). \tag{14}$$

This feature corresponds to the $l_0 = a$ case of $P_{MD}(t; l_0)$ of F^- ions. In Figure 4(b) we observe a rapid increase in $P(t)$ in the short time ($t \lesssim 1.5\tau$) regime. The overall feature of the distribution in Figure 4(b) is quite similar to $P_{MD}(t; l_0)$ of F^- with $l_0 = 1.5a$. Thus the behavior of $P_{MD}(t; l_0)$ observed in Figure 3(b) is considered as



(a)



(b)

Figure 4 The FPT distribution functions of the hopping model for (a) $l_0 = 0.5a_0$ and (b) $l_0 = 1.5a_0$.

the typical feature of the hopping diffusion, which is not reproduced by the continuous diffusion model.

4 SUMMARY

In this paper we have developed the FPT approach to diffusion in condensed media, which is useful not only for the evaluation of diffusion constants but also for the investigation of the diffusion mechanism. Our method is applied to the MD simulations of simple liquids and superionic conductor CaF_2 with the following results.

(1) The FPT distribution in a simple liquid is reproduced by the continuous model quite well and the diffusion constants are evaluated with good accuracy.
(2) The continuous diffusion model also reproduces the FPT distribution of CaF_2 if we take l_0 as large as $3a \sim 4a$. In the length scale as small as the jump distance, however, $P_{MD}(t; l_0)$ shows a rapid increase in the short time regime, which can not be fitted by the continuous diffusion model. This short time behavior is described by the simple hopping diffusion model.

Finally let us give a remark on the diffusion in strongly supercooled liquids. As reported in I, the continuous diffusion model works well for the supercooled state up to $\rho^* \sim 1.26$. Under considerable degree of supercooling, however, we found a qualitative change in the FPT distribution, which can be explained neither by the continuous diffusion model nor by the simple hopping diffusion model. In connection with this problem, we are performing the simulation of the glassy as well as supercooled state of a two component soft-core system. The theoretical analysis of more refined hopping models is also in progress.

Acknowledgement

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