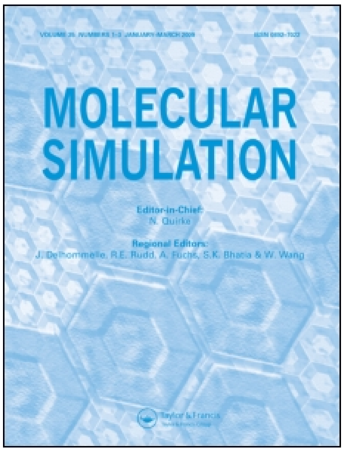

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Dynamics of Small Molecules in a Dense Polymer Matrix: Molecular Dynamics Studies

Hisao Takeuchi[a]; Keiji Okazaki[a]
[a] Yokohama Research Center, Mitsubishi Chemical Corporation, Yokohama, JAPAN

To cite this Article Takeuchi, Hisao and Okazaki, Keiji(1996) 'Dynamics of Small Molecules in a Dense Polymer Matrix: Molecular Dynamics Studies', Molecular Simulation, 16: 1, 59 — 74
To link to this Article: DOI: 10.1080/08927029608024061
URL: http://dx.doi.org/10.1080/08927029608024061

Molecular Simulation, 1996, Vol. 16, pp. 59–74
Reprints available directly from the publisher
Photocopying permitted by license only

DYNAMICS OF SMALL MOLECULES IN A DENSE POLYMER MATRIX: MOLECULAR DYNAMICS STUDIES

HISAO TAKEUCHI* and KEIJI OKAZAKI

Yokohama Research Center, Mitsubishi Chemical Corporation,
1000 Kamoshida-cho, Aoba-ku, Yokohama 227, JAPAN

(Received November 1994, accepted July 1995)

The anomalous diffusion regime appearing in the self-diffusion of small molecules in bulk amorphous polymers has been extensively studied by molecular dynamics simulations. A rather long simulation of duration $\sim 10^{-8}$ s is performed on a polyethylene-like simple polymer model containing either oxygen molecules or helium atoms as a diffusant. Dynamic properties evaluated for these diffusants are the mean-square displacement, the van Hove self correlation function, and the self part of the density autocorrelation. It is first confirmed that the anomalous diffusion regime appears in a few hundred picoseconds for oxygen molecule, while the Einstein relation adopted beyond this regime results in the self-diffusion coefficient of the order of $\sim 10^{-5}$ cm^2/s. This anomaly is still observed for helium that diffuses much faster than oxygen. In the anomalous diffusion regime, it is found that the correlation functions for the two diffusants show characteristic features and become essentially the same as time is scaled appropriately. These features allow the estimation of the two characteristic spatial scales which are probably dominated by the microstructure of the polymer matrix, namely, the cage size and the distance between adjacent cages. The time dependence of the mean-square displacements of the two diffusants can be well interpreted by these characteristic spatial scales as time is scaled with the self-diffusion coefficients. It is shown that the anomalous diffusion regime arises from the inhomogeneous microstructure of the polymer matrix.

KEY WORDS: Self-diffusion of small molecules in polymers, anomalous diffusion, relaxation process, polymer dynamics, density autocorrelation, molecular dynamics simulation.

1 INTRODUCTION

Diffusion of small molecules in bulk amorphous polymers is an important phenomenon for many technological applications. Molecular dynamics (MD) simulations on this subject have recently attracted considerable attention both from practical and theoretical view points [1], particularly for the diffusion of light gases such as H_2, O_2 and CH_4 [2–22]. Early MD works have mainly studied the diffusion mechanism, and revealed that small molecules diffuse in polymers through the hopping mechanism [2–10]. The influence of local structures and dynamics of polymers on the diffusion has also been clearly demonstrated by MD simulations [2, 5, 8, 18, 20]. Although most of these simulations were made for rather qualitative understanding, continuous efforts have been made towards quantitative simulations on real systems

---

* To whom correspondence should be addressed.

such as polyisobutylene/oxygen and poly(dimethylsiloxane)/ethanol [11–19, 22, 23]. Through these works, for example, it has been shown that a drawback of the united atom force field which tends to overestimate diffusion coefficients can be overcome either by introducing the anisotropic united atom model [17, 18] or by including hydrogen atoms explicitly [11]. It is now possible to perform such a quantitative simulation when careful choice is made on a model along with sufficient computational resources.

The self-diffusion coefficient D of a particle is generally obtained from its mean-square displacement $\langle r^2(t)\rangle$ with the Einstein relation [24]:

$$D = \lim_{t \to \infty} \langle r^2(t)\rangle / 6t. \tag{1}$$

In practice, Equation (1) is adopted after $\langle r^2(t)\rangle$ becomes linear in time t. For the self-diffusion of small molecules in polymers, early MD studies paid less attention on detailed time dependence of their $\langle r^2(t)\rangle$: the Einstein relation was adopted for $\langle r^2(t)\rangle$ obtained from simulations of several hundered picoseconds [2–10]. In most cases, $\langle r^2(t)\rangle$ were rather wobbly due to poor statistics caused by the short duration of simulations, but seemed to be approximately proportional to time. However, Müller-Plathe *et al.* [12] have performed longer MD simulations and found that $\langle r^2(t)\rangle$ is quite slow to become proportional to time even though the magnitude of D is comparable to that of a simple liquid, *i.e.*, $D \sim 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$. For example, $\langle r^2(t)\rangle$ of helium atom in polyisobutylene (PIB) becomes proportional to time after at least one hundred picoseconds, whereas D evaluated beyond this anomalous diffusion regime has the order of $10^{-5}\,\mathrm{cm}^2/\mathrm{s}$ [12]. For oxygen molecule in PIB, the anomalous diffusion regime is considerably prolonged, and lasts up to at least several nanoseconds [12]. Recent MD simulations on different polymer/small molecule systems have also confirmed the presence of the anomalous diffusion regime [21, 22]. Further, this anomaly has also been pointed out by a Monte Carlo simulation combined with the transition state theory [25, 26]. Since $\langle r^2(t)\rangle$ of a small molecule in polymers eventually becomes proportional to time, the corresponding self-diffusion is not the anomalous diffusion at a sufficiently long time scale. It is quite certain that the diffusion behavior depends on the scale of time and space. The anomalous diffusion regime observed at a particular time scale is thus considered to be a characteristic of the diffusion process of small molecules in dense polymer matrices, *i.e.*, ***complex fluids***. In other words, characteristics of a polymer matrix at a certain scale of time and space would be relevant to the anomalous diffusion behavior of small molecules. It is also expected that the anomalous diffusion regime is general for a similar system in which a particle diffuses through a *rigid* matrix like polymers. In view of the hopping mechanism that a small molecule hops from cage to cage, the spatial scales to be considered are, for example, the size of a cage and the distance between two cages. We have already studied the anomalous diffusion behavior by considering the residence time distribution of a small molecule in a cage [21], but this would be insufficient to understand the anomaly.

The purpose of the present work is to elucidate the dynamics of small molecules in a dense polymer matrix for a given scale of time and space. We here utilize a well-characterized polymer model [27, 28] which allows rather longer MD simulations. This model would be too simple to reproduce a real polymer, but quite appropriate for our purpose to gain physical understanding on the anomalous diffusion. MD simulations are performed on two systems each containing different small molecules. In order to characterize the dynamics of the small molecules, several dynamic properties, such as the van Hove correlation function and the density autocorrelation function, are evaluated from MD trajectories. These correlation functions are found to show characteristic behavior in the anomalous diffusion regime. Based on these observations, the mechanism of the anomalous diffusion is discussed.

2 SIMULATIONS

2.1 Model

We use the polymer model which mimics the amorphous phase of polyethylene. This model has been extensively studied by MD simulations and well characterized for the local relaxation and the glass transition [27,28]. We have utilized the same model to study the diffusion of small molecules in polymers as well [3–5,20,21], and already confirmed the presence of the anomalous diffusion regime [21]. As mentioned above, this model is appropriate to gain physical understanding on the diffusion process, although the isotropic united atom representation used in the model has been known to be rather poor in quantitative sense [11,17]. Details of the model have been already given previously [2–4], and only the outline is described here.

In the polymer model, a linear polymer chain is composed of spherically interacting particles each being a model of CH_2 unit (mass $m = 14$ amu) subjected to the bond stretching potential V_l, the bond-angle bending potential V_θ and the torsional potential V_ϕ:

$$V_l = k_l(l - l_0)^2/2, \tag{2}$$

$$V_\theta = k_\theta(\cos\theta - \cos\theta_0)^2/2, \tag{3}$$

$$V_\phi = k_\phi \sum_{n=0}^{5} a_n \cos^n\phi. \tag{4}$$

The cubic MD cell contains 600 such CH_2 units. The usual periodic boundary conditions produce replication of the basic cell in the three Cartesian directions. An additional periodic boundary condition [29] ties one end of a 600 units chain, spanning three MD cells, to the image of its other end. The length of the starting 600 units chain thus becomes effectively infinite, and all CH_2 units in the basic MD cell belong to this infinite length chain. The density of the polymer model is 0.86 g/cm^3 which approximately corresponds to the amorphous density of polyethylene [30]. This yields the cell edge length of 25.3 Å.

The model system mainly studied here contains $N = 10$ oxygen molecules ($m = 32$ amu) each being modeled by a spherically interacting particle. Also used for comparison contains $N = 10$ helium atoms ($m = 4$ amu) instead of oxygen molecules.

A truncated Lennard-Jones potential function V_{nb} is used for all the nonbonded interactions in the system:

$$V_{nb}=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}] \quad r<r_c, \tag{5}$$
$$V_{nb}=0 \quad r\geqslant r_c,$$

where an appropriate set of ε and σ is chosen for each particle species [31, 32]. For the interaction between different species, the Lorentz-Berthelot mixing rule is adopted. Note that the nonbonded interactions between CH_2 units, separated by three bonds or less along the chain, are omitted because of the presence of the internal potentials. All the potential parameters listed in Table 1 are the same as used in our previous works [3–5, 20, 21].

2.2 *Simulation*

The equations of motion for all the particles in the basic MD cell are solved numerically using Verlet's leapfrog algorithm [33] with the integration time step of 0.006 ps. This rather large time step is realized by a small value of k_l which is weakened by a factor of 7 from its realistic value [31]. An initial configuration is randomly generated, and well equilibrated by a run of $\sim 10^6$ steps. A production run of duration 10 ns ($\sim 1.7 \times 10^6$ steps) is then performed at 300 K which is well above the glass transition temperature T_g of the polymer model ($\sim$200 K) [28]. During this production run, the temperature is controlled by the *ad-hoc* scaling method [34]. The trajectory of the small molecules is recorded every 0.1 ps. The following dynamic properties of the diffusant (oxygen molecule or helium atom) are evaluated using the trajectory thus obtained. Note that another production run of duration 100 ps is also performed to examine the dynamics for $t < 0.1$ ps: the trajectory is recorded every time step for this short production run.

The mean-square displacement of the diffusant is computed by

$$\langle r^2(t)\rangle = N^{-1}\left\langle \sum_{j=1}^{N} |\mathbf{r}_j(t)-\mathbf{r}_j(0)|^2 \right\rangle. \tag{6}$$

The self-diffusion coefficient is then obtained by the Einstein relation, Equation (1).

Table 1 Parameters used in the simulations.

CH_2 unit in chain		oxygen molecule	
l_0	0.152 nm	ε	9.40×10^2 J mol^{-1}
$\cos\theta_0$	$-1/3$	σ	0.343 nm
k_l	3.46×10^7 J nm^{-2}mol^{-1}	helium atom	
k_θ	5.00×10^5 J mol^{-1}	ε	8.50×10^1 J mol^{-1}
k_ϕ	9.00×10^3 J mol^{-1}	σ	0.258 nm
ε	5.00×10^2 J mol^{-1}	cutoff distance	
σ	0.380 nm	r_c	0.570 nm

The self part of the density autocorrelation function $F_s(q,t)$ is defined by

$$F_s(q,t) = N^{-1}\left\langle \sum_{j=1}^{N} \exp[-i\mathbf{q}(\mathbf{r}_j(t) - \mathbf{r}_j(0))]\right\rangle \tag{7}$$

where the angular part is averaged over the wavevector $\mathbf{q}$, and $q = |\mathbf{q}|$. Within the gaussian approximation, this correlation function can be reduced to [24]:

$$F_s(q,t) = \exp(-q^2\langle r^2(t)\rangle/6), \tag{8}$$

and this gives a single exponential function at the hydrodynamic limit:

$$F_s(q,t) \sim \exp(-q^2Dt) = \exp(-t/\tau_D). \tag{9}$$

The correlation time thus has the q-dependence of $\tau_D \sim q^{-2}$. Another correlation function which relates to the self-diffusion is the van Hove self correlation function $G_s(r,t)$:

$$G_s(r,t) = N^{-1}\left\langle \sum_{j=1}^{N} \delta\,[|\mathbf{r}_j(t) - \mathbf{r}_j(0)| - r]\right\rangle. \tag{10}$$

At the hydrodynamic limit, this can be expressed by the gaussian function [24]:

$$G_s(r,t) = (1/4\pi Dt)^{3/2}\exp(-r^2/4Dt). \tag{11}$$

3 RESULTS AND DISCUSSION

3.1 Mean-Square Displacement

Figure 1 shows that $\langle r^2(t)\rangle$ of oxygen molecule becomes proportional to t after a few hundred picoseconds, while the Einstein relation adopted for $t > 500$ ps results in $D = 1.47 \times 10^{-5}$ cm^2/s. One can thus find a striking difference in the time dependence of $\langle r^2(t)\rangle$ between the present system and a simple liquid, such Ar liquid, in which $\langle r^2(t)\rangle$ more quickly becomes proportional to t [34]. As $\langle r^2(t)\rangle$ is expressed by $\langle r^2(t)\rangle \sim t^\alpha, \alpha$ seems to have a value close to 2, which reflects the free particle motion, for $t < 1$ ps. Then the anomalous diffusion regime giving $\alpha < 1$ follows this towards the Einstein diffusion. The discrepancy from the Einstein diffusion is particularly significant for $t < 100$ ps. This feature can also be clearly shown in Figure 2 where $\langle r^2(t)\rangle/6Dt$ is plotted against t: $\langle r^2(t)\rangle/6Dt$ of oxygen molecule considerably overshoots, and approaches the unity quite slowly. For helium atom, $\langle r^2(t)\rangle$ is about one order of magnitude larger than that of oxygen molecule, and the Einstein relation adopted in the same way gives $D = 1.48 \times 10^{-4}$ cm^2/s. Although the diffusion of helium is much faster than that of oxygen, the anomalous diffusion behavior can still be observed.

In the time domain shown in Figure 1, $\langle r^2(t)\rangle$ of CH_2 unit of the polymer chain is always smaller than that of oxygen molecule or helium atom. Another interesting

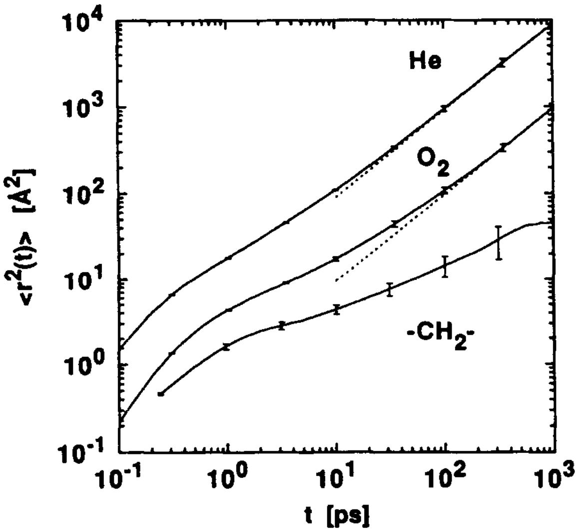

Figure 1 Mean-square displacements $\langle r^2(t)\rangle$ of oxygen molecule, helium atom and CH_2 unit in the polymer model: the broken lines denote $\langle r^2(t)\rangle \propto t$. The trajectories of ~ 10 ns were thoroughly used for oxygen molecule and helium atom, whereas a part (~ 2 ns) for CH_2 unit.

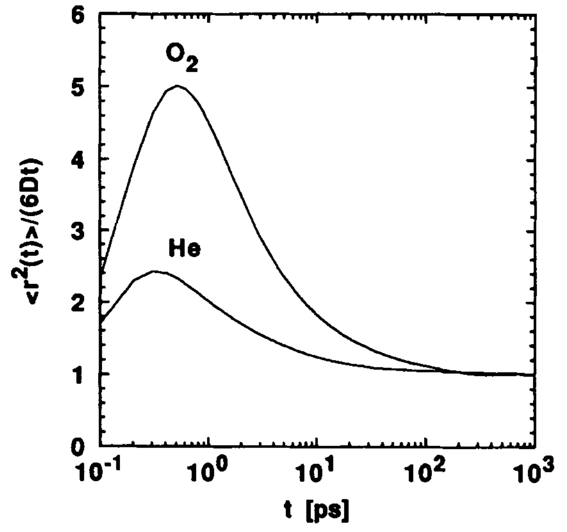

Figure 2 Time dependence of $\langle r^2(t)\rangle/6Dt$ of oxygen molecule and helium atom. The self-diffusion coefficients used here are 1.47×10^{-5} and 1.48×10^{-4} cm^2/s for oxygen and helium, respectively.

feature is that $\langle r^2(t)\rangle$ of CH_2 unit also shows the anomalous diffusion behavior of $\langle r^2(t)\rangle \sim t^{0.5}$. This time dependence has been experimentally deduced from the incoherent quasielastic neutron scattering of several polymers at $T > T_g$ [35]. In addition, a recent MD study on polyethylene-like system has also shown the same result with a somewhat different power [36]. It is then expected that the anomalous diffusion behavior of the small molecules arises from the fact that the constituent of the polymer matrix (*i.e.*, CH_2 unit) itself undergoes the anomalous diffusion. This will be discussed in Sec. 3.4 along with detailed analyses of the dynamics of the small molecules.

3.2 van Hove Self Correlation Function

The anomalous diffusion regime described above is then analyzed in consideration of the correlation functions relevant to the self-diffusion. Figure 3 compares $G_s(r,t)$ of oxygen molecule directly obtained from the MD trajectory with that evaluated by Equation (11) with $D = 1.47 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$. Characteristic differences between these two results can be easily noticed for the anomalous diffusion regime, *i.e.*, $t = 10$, 50 and 100 ps. The MD result of $4\pi r^2 G_S(r,t)$ shows a tail reaching $r \sim 10$ Å at $t = 10$ ps. This indicates that an oxygen molecule can gain larger displacement than what is expected from the hydrodynamic result. As time elapses in the anomalous diffusion regime, the MD result shows a fairly wider distribution than the hydrodynamic result, and seems to have two peaks. Interestingly the first peak around $r \sim 3$ Å, appearing as a shoulder for a larger t, keeps its position as time elapses over 100 ps, while the second has almost the same peak position as the hydrodynamic result. Even at $t = 200$ ps where $\langle r^2(t)\rangle$ almost approaches $\langle r^2(t)\rangle \sim t$, the shoulder around $r \sim 3$ Å is still visible. These results suggest that CH_2 units of the polymer chain form stable cages which capture oxygen molecules. Our previous study on the residence time distribution of oxygen molecules has also shown the possibility that an oxygen molecule is trapped by a cage over 100 ps.

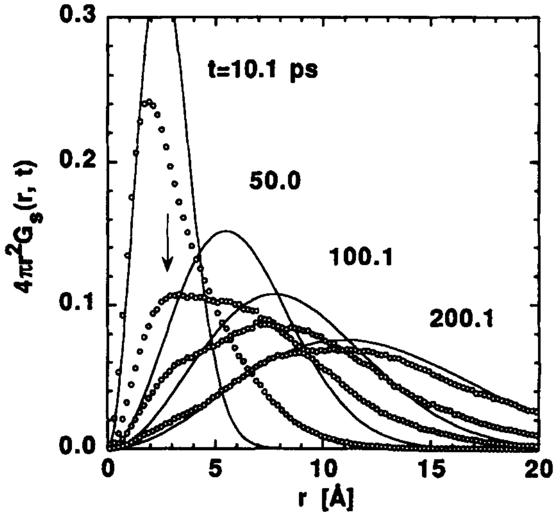

Figure 3 The van Hove self correlation function $G_S(r,t)$ of oxygen molecule directly obtained from the MD trajectory (open circles), and calculated by Equation (11) with $D = 1.47 \times 10^{-5}$ cm^2/s (solid lines). The arrow shows a peak (or shoulder) around $r \sim 3$ Å.

Although helium diffuses much faster than oxygen, no significant difference of $G_S(r,t)$ can be found between these two diffusants as time is scaled by D^{-1}: the peak (or shoulder) around $r \sim 3$ Å appears also in $4\pi r^2 G_S(r,t)$ of helium atom (see Figure 4). The characteristic features of $G_S(r,t)$ found for the anomalous diffusion regime are thus considered to arise from the presence of stable cages formed by the polymer chain. The average size of cages ξ_c could be estimated by the position of the first peak, namely, $\xi_c \sim 3$ Å. Further the result shown in Figure 4 suggests that the spatial scale relevant to the anomalous diffusion behavior reflects the microstructure of the polymer matrix, while the corresponding time scale depends on the diffusants.

3.3 Density Autocorrelation Function

Since $\langle r^2(t)\rangle$ eventually becomes proportional to t, $F_S(q,t)$ must approach Equation (9) as q decreases. Figure 5 actually shows this trend for oxygen molecule: $F_S(q,t)$ obtained from the simulation significantly deviates from Equation (9) for $q = 1.24$ Å^{-1}, but approaches it for $q = 0.25$ Å^{-1}. However, the relaxation behavior becomes complicated as q increases: a fast relaxation process seems to be followed by a slow one appearing as a tail of $F_S(q,t)$. In view of the hopping mechanism, we here consider two distinct processes for the dynamics of oxygen molecule, namely, the relaxation in a cage and the escape motion from it. When the wavelength is shorter than the cage size and time is sufficiently short, $F_S(q,t)$ may correspond to the free particle motion:

$$F_S(q,t) = \exp[-(t/\tau_f)^2], \qquad \tau_f = q^{-1}(2m/k_bT)^{1/2}, \tag{12}$$

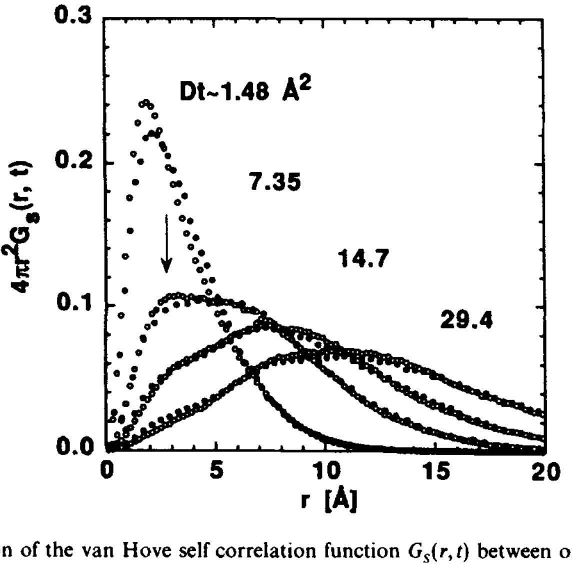

Figure 4 Comparison of the van Hove self correlation function $G_S(r,t)$ between oxygen molecule (open circles) and helium atom (filled circles) at various time given by Dt. The arrow shows a peak (or shoulder) around $r \sim 3$ Å.

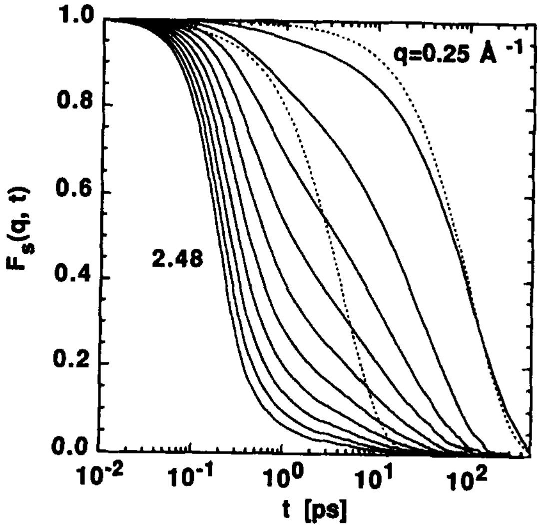

Figure 5 Self part of the density autocorrelation function $F_S(q,t)$ of oxygen molecule at various q (solid lines). The value of q increases from 0.25 to 2.48 Å^{-1} by an increment of ~0.25 (from right to left). The broken lines denote $F_S(q,t)$ calculated by Equation (9) with $D = 1.47 \times 10^{-5}$ cm^2/s for $q = 0.25$ Å^{-1} (right) and 1.24 Å^{-1} (left), respectively.

where k_b denotes the Boltzmann constant. Figure 6 clearly shows that the free particle motion mainly dominates over the relaxation behavior at $q = 2.48$ Å^{-1} for both helium atom and oxygen molecule (note that $\xi_c \sim 3$ Å).

It is then tempting to assume that the appearance of the tail in $F_S(q,t)$ arises from a random walk in a cage and/or the escape motion. This slower process is expected to become clear at a wavelength longer than ξ_c. In order to investigate this slower process in more detail, a log-log plot of $F_S(q,t)$ is shown in Figure 7 for $q = 1.49$ and 0.25 Å^{-1}. It is evident from the plot for $q = 1.49$ Å^{-1} that the faster process given by Equation (12) is in fact followed by two slower processes: one is the slowest process appearing as the tail of $F_S(q,t)$ and this should correspond to the escape motion from a cage as described below. The other is the intermediate process which can be seen between the initial decay expressed by Equation (12) and the tail of $F_S(q$, t). This crossover regime presumably reflects the relaxation in a cage.

The slowest process can be apparently fitted well by a stretched exponential function

$$F_S(q,t) = A \exp[-(t/\tau)^{\beta}] \quad (\beta < 1) \tag{13}$$

as shown in Figure 7. The tail of $F_S(q,t)$ is fitted fairly well for $q = 1.49$ Å^{-1}, and the overall shape is also well reproduced for $q = 0.25$ Å^{-1}. In particular, the dependence of the fitting-parameters on the wavelength is important to investigate how the dynamics of the diffusants changes by the spatial scale. For the slowest process of oxygen molecule, the fitting-parameters A, τ and β are plotted in Figure 8 as a function of q. Interestingly the contribution of this process estimated by the value

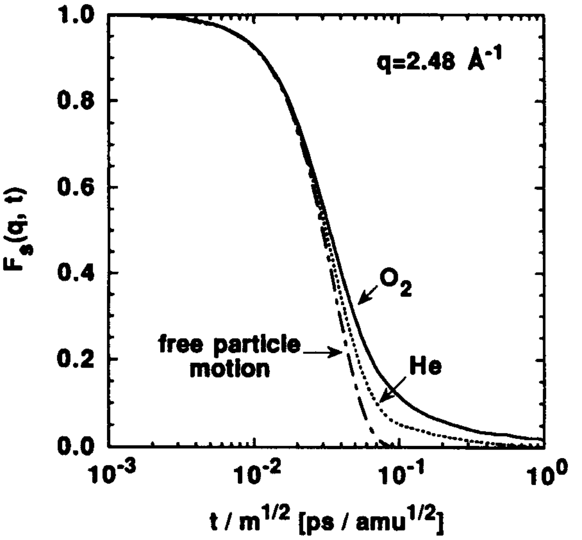

Figure 6 Comparison of the self part of the density autocorrelation function $F_S(q,t)$ between oxygen molecule and helium atom at $q = 2.48$ Å^{-1} in the scaled time $tm^{-1/2}$: $F_S(q,t)$ for the free particle motion is calculated by Equation (12).

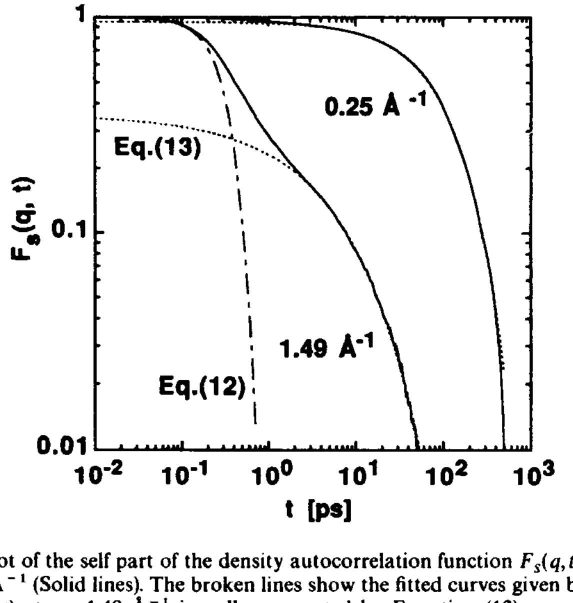

Figure 7 Log-log plot of the self part of the density autocorrelation function $F_S(q,t)$ of oxygen molecule at $q = 0.25$ and 1.49 Å^{-1} (Solid lines). The broken lines show the fitted curves given by Equation (13). The initial decay of $F_S(q,t)$ at $q = 1.49$ Å^{-1} is well represented by Equation (12) corresponding to the free particle motion.

of A abruptly changes at $q \sim 1$ Å^{-1}. In relation to this, β is almost the same at $q > 1$ Å^{-1} ($\beta \sim 0.5$), while it increases towards the unity as q becomes smaller. Further, τ shows the q-dependence of $\tau \sim q^{-2}$ at $q < 1$ Å^{-1}. These results could be

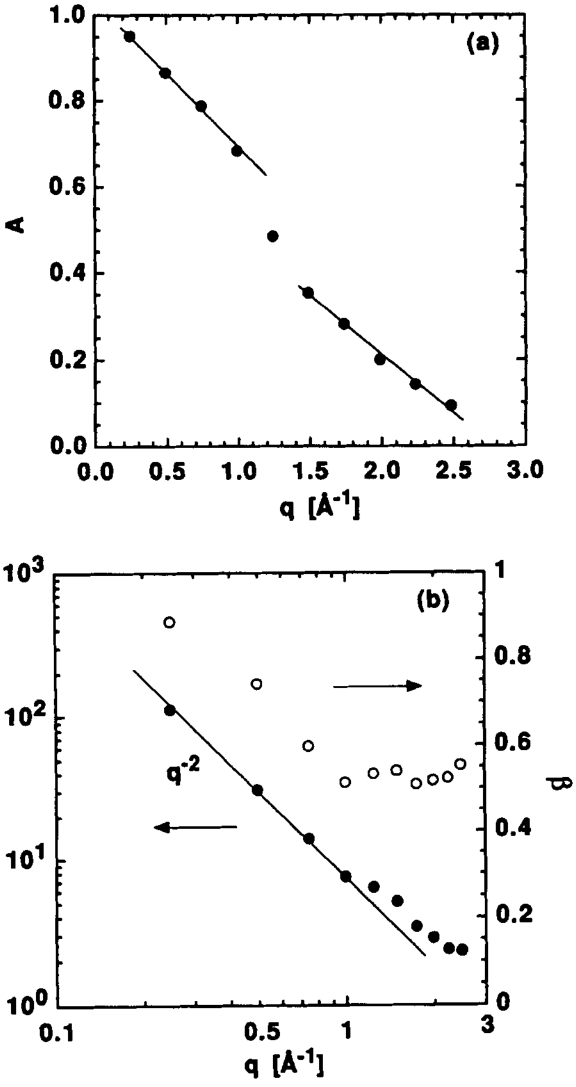

Figure 8 q-dependence of the fitting parameters of A(a), τ and β(b) in Equation (13) for the slowest relaxation process of oxygen molecule.

interpreted as follows. At $q > 1$ Å^{-1}, the wavelength is shorter than the average distance between two adjacent cages ξ_h, and the relaxation behavior is mostly dominated by a hopping event. As the wavelength becomes longer than ξ_h, the contribution of successive hopping events which result in the diffusion mode gradually increases. The diffusion mode expressed by Equation (9) finally appears at a sufficiently longer wavelength. This explanation allows the estimation of the average distance between two adjacent cages, ξ_h. The q-dependence of the fitting parameters suggests $\xi_h \sim 6$ Å corresponding to $q \sim 1$ Å^{-1}.

Although $F_S(q, t)$ approaches Equation (9) as q becomes smaller, the value of β is somewhat smaller than the unity at $q = 0.25$ Å^{-1} (see Figure 8). According to the above estimation of ξ_h, the size of the MD cell (edge length of 25.3 Å) would be inadequate to realize the self-diffusion due to hopping motions traveling through a number of uncorrelated cages. This may affect the upper limit of the anomalous diffusion regime. However, we consider that the qualitative discussion made here remains the same as the system size becomes larger.

For helium atom, the relaxation behavior observed by $F_S(q, t)$ is somewhat different at $q \sim 1.5$ Å^{-1} as shown in Figure 9. Although $F_S(q, t)$ of helium atom also suggests two or more relaxation processes, it is difficult to extract the slowest one which can be fitted well by equation (13), as in the case of oxygen molecule. In fact, no meaningful values of the fitting-parameters are obtained except for $q = 0.25$ and 0.50 Å^{-1} when equation (13) is adopted to fit $F_S(q, t)$ of helium atom. This difference of $F_S(q, t)$ between oxygen molecule and helium atom should arise from the fact that the motion of a helium atom is more continuous than that of an oxygen molecule: the discrete hopping motion becomes less well defined for a small diffusant like helium atom [10, 14]. However, it is noted that $G_S(r, t)$ of helium atom indicates the presence of cages. These results suggest that both the continuous and discrete motions contribute to the diffusion process, and the discrete motion prevails as the diffusant size becomes larger.

3.4 Anomalous Diffusion Regime

We finally discuss the anomalous diffusion regime in view of the polymer dynamics. As described in Sec. 3.1, the constituent of the polymer matrix (*i.e.*, CH_2 unit) shows

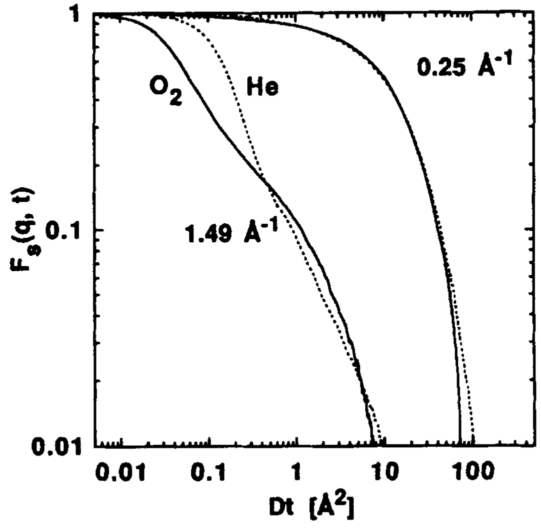

Figure 9 Comparison of the self part of the density autocorrelation function $F_S(q, t)$ between oxygen molecule (solid lines) and helium atom (broken lines) at $q = 0.25$ and 1.49 Å^{-1} in the scaled time Dt. The large discrepancy found in the initial decay at $q = 1.49$ Å^{-1} is due to the contribution of the free particle motion.

the anomalous diffusion behavior as $\langle r^2(t)\rangle \sim t^{0.5}$. This would originate in the connectivity of CH_2 units along the chain. According to this time dependence of $\langle r^2(t)\rangle$, $F_S(q, t)$ of CH_2 unit may be given by

$$F_S(q, t) \sim \exp[-q^2\langle r^2(t)\rangle] = \exp[-(t/q^{-4})^{1/2}] \tag{14}$$

where the gaussian approximation is employed and constants are neglected. The relaxation time, τ_p, of CH_2 unit is thus expected to have the q-dependence of $\tau_p \sim q^{-4}$. We have actually confirmed this relation by a MD simulation separately conducted on the same polymer model containing no small molecule [37]. The strong q-dependence of τ_p makes the relaxation of CH_2 unit become much slower than that of oxygen molecule or helium atom particularly at a long wavelength ($q < 1\,\text{Å}^{-1}$). This suggests that the polymer matrix provides a rather "static" medium at a spatial scale giving the diffusion mode of the diffusants.

The correlation functions shown in Secs. 3.2 and 3.3 reveal two distinct spatial scales: one is the average cage size ξ_c, and the other the average distance between two adjacent cages ξ_h which is rather obscure for helium atom at the moment. These characteristic spatial scales are considered to reflect the rather "static" nature of the polymer matrix. Now we discuss how these characteristic spatial scales affect $\langle r^2(t)\rangle$ of the diffusants. As pointed out in Sec. 3.2, both helium atom and oxygen molecule give almost the same $G_S(r, t)$ as t is scaled by D^{-1}. It is then expected that a master curve of $\langle r^2(t)\rangle$ is obtained as t is scaled in the same manner. Figure 10 shows $\langle r^2(t)\rangle$ of the two diffusants as a function of Dt. Because the initial increase in $\langle r^2(t)\rangle$ is dominated by the free particle motion which depends on the mass of the diffusants as shown in Sec. 3.3, the scaled time Dt does not result in a master

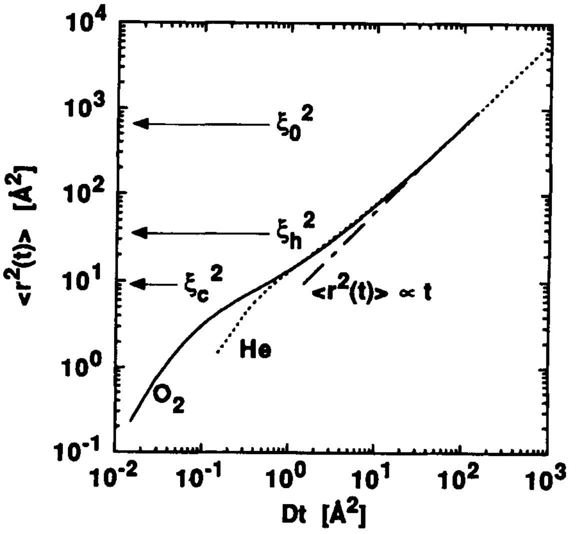

Figure 10 Mean-square displacements $\langle r^2(t)\rangle$ of oxygen molecule (solid line) and helium atom (broken line) as a function of the scaled time Dt. Two characteristic spatial scales are shown by arrows: ξ_c stands for the average cage size, while ξ_h for the average distance between two adjacent cages. ξ_0 represents the edge length of the MD cell.

curve of $\langle r^2(t)\rangle$ in the beginning. However, this initial increase is damped as $\langle r^2(t)\rangle$ becomes comparable to $\xi_c{}^2$ for both helium atom and oxygen molecule as shown in Figure 10. The presence of cages in the polymer matrix is again confirmed. As Dt becomes larger, $\langle r^2(t)\rangle$ of oxygen molecule, including the anomalous diffusion regime, fairly coincides with that of helium atom. It is evident that the anomalous diffusion regime clearly appears for $\langle r^2(t)\rangle \leqslant \xi_h{}^2$ regardless of the diffusants. The characteristic spatial scales of the polymer matrix, given by ξ_c and ξ_h, thus relate to these features found for $\langle r^2(t)\rangle$. This suggests that the mass of the diffusant gives minor influence on the appearance of the anomalous diffusion regime.

Consequently we conclude that the anomalous diffusion regime is caused by the inhomogeneous microstructure of the polymer matrix. The characteristic spatial scales of this inhomogeneity, namely the average cage size ξ_c and the average distance between two adjacent cages ξ_h, could be in turn estimated by the anomalous diffusion regime.

4 SUMMARY

The anomalous diffusion regime found for the self-diffusion of small molecules in polymers [12] has been extensively studied by rather long MD simulations with the well-characterized polymer model. Two diffusants having different sizes are used: one is oxygen molecule and the other helium atom. The dynamic properties relevant to the self-diffusion clearly show the characteristic behavior for the anomalous diffusion regime. These findings are summarized as follows.

First it is noted that the self-diffusion of the diffusants takes place in the medium of which constituent itself undergoes the anomalous diffusion for the time scale studied here. The relaxation of CH_2 unit of the polymer chain is strongly damped as the wavelength becomes longer such that the dynamics of the small molecules approaches the hydrodynamic limit behavior. The polymer matrix thus provides a rather "static" medium. Secondly the van Hove self correlation function $G_S(r,t)$ clearly shows the presence of cages. This provides a characteristic spatial scale, *i.e.*, the average cage size ξ_c, which depends on the microstructure of the polymer matrix. Thirdly the self part of the density autocorrelation function $F_S(q,t)$ reveals several relaxation processes depending on the wavelength. For the wavelength shorter than the average cage size, the free particle motion is dominant. As the wave length becomes longer, the contribution of the slower relaxation process, appearing as the tail of $F_S(q,t)$, gradually increases. This process then turns into the diffusion mode at a sufficiently long wavelength. In view of the hopping mechanism, the wavelength at which $F_S(q,t)$ shows the characteristic change should correspond to the average distance between two adjacent cages ξ_h. This is another characteristic spatial scale which is successfully estimated for oxygen molecule, although it is rather obscure for helium atom possibly due to the contribution of continuous motions rather than discrete hops.

These two characteristic spatial scales well interpret the time dependence of $\langle r^2(t)\rangle$ as time is scaled by D^{-1}. The initial increase in $\langle r^2(t)\rangle$ is damped at

$\langle r^2(t)\rangle \sim \xi_c^2$, and then the anomalous diffusion regime clearly appears for $\langle r^2(t)\rangle \leqslant \xi_h^2$. Finally $\langle r^2(t)\rangle$ becomes proportional to time for $\langle r^2(t)\rangle \gg \xi_h^2$. It is thus concluded that the anomalous diffusion regime arises from the inhomogeneous microstructure of the polymer matrix. The characteristic spatial scales of this inhomogeneity could be in turn estimated by the anomalous diffusion regime. The upper limit of the anomalous diffusion regime, however, should be carefully studied by a larger system which provides a number of uncorrelated cages.

References

[1] F. Müller-Plathe, "Permeation of polymers – A computational approach", *Acta Polymer.*, **45**, 259 (1994). This reviews the progress of MD simulations on the diffusion of small molecules in polymers.

[2] H. Takeuchi and K. Okazaki, "Molecular dynamics simulation of diffusion of simple gas molecules in a short chain polymer", *J. Chem. Phys.*, **92**, 5643 (1990).

[3] H. Takeuchi, "A jump motion of small molecules in glassy polymers: A molecular dynamics study", *J. Chem. Phys.*, **93**, 2062 (1990).

[4] H. Takeuchi, "Molecular dynamics simulation of diffusion of small molecules in polymers: Effects of chain length", *J. Chem. Phys.*, **93**, 4490 (1990).

[5] H. Takeuchi, R.-J. Roe and J. E. Mark, "Molecular dynamics simulation of diffusion of small molecules in polymers II. Effect of free volume distribution", *J. Chem. Phys.*, **93**, 9042 (1990).

[6] J. Sonnenburg, J. Gao and J. H. Weiner, "Molecular dynamics simulations of gas diffusion through polymer networks", *Macromolecules*, **23**, 4653 (1990).

[7] S. Trohalaki, D. Rigby, A. Kloczkowski, J. E. Mark and R. J. Roe, "Estimation of diffusion coefficients for small molecular penetration in amorphous polyethylene", in *Computer Simulation of Polymers*, R. J. Roe, ed, Prentice Hall, Englewood Cliffs, N. J., 1991, pp. 220.

[8] R. H. Boyd and P. V. K. Pant, "Molecular packing and diffusion in polyisobutylene", *Macromolecules*, **24**, 6325 (1991).

[9] F. Müller-Plathe, "Diffusion of penetrants in amorphous polymers: A molecular dynamics study", *J. Chem. Phys.*, **94**, 3192 (1991).

[10] F. Müller-Plathe, "Molecular dynamics simulation of gas transport in amorphous polypropylene", *J. Chem. Phys.*, **96**, 3200 (1992).

[11] F. Müller-Plathe, S. C. Rogers and W. F. van Gunsteren, "Diffusion coefficients of penetrant gases in polyisobutylene can be calculated correctly by molecular dynamics simulations", *Macromolecules*, **25**, 6722 (1992).

[12] F. Müller-Plathe, S. C. Rogers and W. F. van Gunsteren, "Computational evidence for anomalous diffusion of small molecules in amorphous polymers", *Chem. Phys. Lett.*, **199**, 237 (1992).

[13] S. Trohalaki, A. Kloczkowski, J. E. Mark, R. J. Roe and D. Rigby, "Molecular-dynamics simulations of small-molecule diffusion in polyethylene", *Comp. Polym. Sci.*, **2**, 147 (1992).

[14] R. M. Sok, H. J. C. Berendsen and W. F. van Gunsteren, "Molecular dynamics simulation of the transport of small molecules across a polymer membrane", *J. Chem. Phys.*, **96**, 4699 (1992).

[15] S. Kashihara, T. Aoyagi, S. Yamanaka and T. Komatsu, "Molecular dynamic simulation of the gas diffusion in polyethylene and poly (vinylalchohol-co-ethylene)", *Chem. Express*, **7**, 537 (1992).

[16] E. Smit, M. H. V. Mulder, C. A. Smolders, H. Karrenbeld, J. van Eerden and D. Feil, "Modelling of the diffusion of carbon dioxide in polyimide matrices by computer simulation", *J. Membrane Sci.*, **73**, 247 (1992).

[17] P. V. K. Pant and R. H. Boyd, "Simulation of diffusion of small-molecule penetrants in polymers", *Macromolecules*, **25**, 494 (1992).

[18] P. V. K. Pant and R. H. Boyd, "Molecular dynamics simulation of diffusion of small penetrants in polymers", *Macromolecules*, **26**, 679 (1993).

[19] F. Müller-Plathe, S. C. Rogers and W. F. van Gunsteren, "Gas sorption and transport in polyisobutylene: Equilibrium and nonequilibrium molecular dynamics simulations", *J. Chem. Phys.*, **98**, 9895 (1993).

[20] H. Takeuchi and K. Okazaki, "Relation between amorphous structure of polymers and penetrant diffusion: A molecular dynamics study", *Makromol. Chem., Macromol. Symp.*, **65**, 81 (1993).

[21] H. Takeuchi and K. Okazaki, "On the anomaly of penetrant diffusion in polymers: A molecular dynamics simulation", *Jpn. J. Polym. Sci. Tech. (Kobunshi Ronbunshu)*, **51**, 387 (1994).

[22] Y. Tamai, H. Tanaka and K. Nakanishi, "Molecular simulation of permeation of small penetrants through membranes. 1. Diffusion coefficients", *Macromolecules*, **27**, 4498, (1994).

[23] J. Han and R. H. Boyd, "Small-molecule penetrant diffusion in hydrocarbon polymers as studied by molecular dynamics simulation", *Macromolecules*, **27**, 5365 (1994).

[24] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, New York, 1986.

[25] A. A. Gusev, S. Arizzi and U. W. Suter, "Dynamics of light gases in rigid matrices of dense polymers", *J. Chem. Phys.*, **99**, 2221 (1993).

[26] A. A. Gusev and U. W. Suter, "Dynamics of small molecules in dense polymers subjected to thermal motion", *J. Chem. Phys.*, **99**, 2228 (1993).

[27] H. Takeuchi and R.-J. Roe, "Molecular dynamics simulation of local chain motion in bulk amorphous polymers I. Dynamics above the glass transition", *J. Chem. Phys.*, **94**, 7446 (1991).

[28] H. Takeuchi and R.-J. Roe, "Molecular dynamics simulation of local chain motion in bulk amorphous polymers, II. Dynamics at glass transition", *J. Chem. Phys.*, **94**, 7458 (1991).

[29] T. A. Weber and E. Helfand, "Molecular dynamics simulation of polymers I. Structure", *J. Chem. Phys.*, **71**, 4760 (1979).

[30] A. S. Michaels and H. J. Bixler, "Flow of gases through polyethylene", *J. Polym. Sci.*, **50**, 413 (1961).

[31] D. Rigby and R.-J. Roe, "Molecular dynamics simulation of polymer liquid and glass I. Glass transition", *J. Chem. Phys.*, **87**, 7285 (1987).

[32] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.

[33] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, Oxford, 1987.

[34] D. Brown and J. H. R. Clarke, "A comparison of constant energy, constant temperature and constant pressure ensembles in molecular dynamics simulations of atomic liquids", *Mol. Phys.*, **51**, 1243 (1984).

[35] J. Colmenero, A. Alegria and A. Arbe, "Correlation between non-Debye behavior and Q behavior of the α relaxation in glass-forming polymeric systems", *Phys. Rev. Lett.*, **69**, 478 (1992).

[36] R. J. Roe, "Short time dynamics of polymer liquid and glass studied by molecular dynamics simulation", *J. Chem. Phys.*, **100**, 1610 (1994).

[37] H. Takeuchi and K. Okazaki, "Molecular dynamics simulation on low energy excitation of glassy polymers", *Polym. Prep. Jpn.* (Soc. Polym. Sci. Jpn.), **43(4)**, 1289 (1994): this contains only preliminary data. Ref.[36] reports essentially the same results on a similar model polymer.