Diffusion dynamics of supercooled water modeled with the cage-jump motion and hydrogen-bond rearrangement

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The slow dynamics of glass-forming liquids is generally ascribed to the cage-jump motion. In the cage-jump picture, a molecule remains in a cage formed by neighboring molecules, and after a sufficiently long time, it jumps to escape from the original position by cage-breaking. The clarification of the cage-jump motion is therefore linked to unraveling the fundamental element of the slow dynamics. Here, we develop a cage-jump model for the dynamics of supercooled water. The caged and jumping states of a water molecule are introduced with respect to the hydrogen-bond (H-bond) rearrangement process, and describe the motion in supercooled states. It is then demonstrated from the molecular dynamics simulation of the TIP4P/2005 model that the characteristic length and time scales of cage-jump motions provide a good description of the self-diffusion constant that is determined in turn from the long-time behavior of the mean square displacement. Our cage-jump model thus enables to connect between H-bond dynamics and molecular diffusivity.

I. INTRODUCTION

The origin of slow dynamics observed in many supercooled liquids below their melting temperatures is frequently explained utilizing the cage-effect picture. This picture advocates that a molecule in supercooled liquids is trapped in the cage transiently formed by neighboring molecules and exhibits escape jump motions due to the cage-breaking after a sufficient long time. The cage-jump scenario also suggests intermittent molecular motions, which can be modeled by the continuous-time random walk using a random waiting time between cage-jumps. The cage-jump motion in glassy dynamics has been extensively addressed with molecular dynamics (MD) simulations and experiments using colloidal glasses.

As the temperature is decreased, the mean square displacement (MSD) exhibits a plateau in the intermediate time scales between ballistic and diffusive regimes, reflecting the localized motion inside the cage. This MSD plateau value is associated with the so-called Debye–Waller factor to characterize the degree of localization. However, it is often delicate to quantify the length and time scales of the cage effect from an MD trajectory, which is continuous in space and time and is generated through thermal fluctuations. The cage-jump model adopts a discretized view and introduces the caged and jumping states along the dynamics of a single molecule.

Pastore et al. have recently developed a cage-jump model to predict the long-time diffusivity from the short-time cage dynamics in supercooled liquids. In the study, a trajectory of a single particle is segmented into caged and jumping states. The segmentation criterion was given by the MSD plateau value. Remarkably, the evaluations of jumping length and duration time enabled to estimate the self-diffusion constant that is determined from the MSD long-time behavior at any temperature. This cage-jump modeling demonstrates that the underlying mechanism of the molecular diffusivity is essentially governed by the accumulation of successive cage-jump events.

The aim of this study is to develop a cage-jump model for supercooled water in strong connection to the dynamics of hydrogen-bond (H-bond) network. At normal liquid states, it has been widely accepted that a defect of 3- or 5-coordinated H-bond plays a crucial role for characterizing the H-bond breakage. By contrast, the number of defects decreases when liquid water is supercooled. Correspondingly, the tetrahedrality of H-bond network becomes significant, where the molecular motion is expected to be described by the cage-jump scenario. Indeed, there have been various MD results showing the plateau in MSD of supercooled water. The intermittent jump motions have also been illustrated in supercooled water by analyzing the trajectory of a single molecule. In particular, the connection of H-bond rearrangements with the jump motions has been examined.

We have recently revealed that the H-bond lifetime depends on the temperature in inverse proportion to the self-diffusion constant. This result was explained by the correlation between H-bond breakages and translational molecular jumps. Moreover, we have also examined the pathways of hydrogen-bond breakages on the profile of the two-dimensional potential of mean force. It has been clarified that H-bonds break due to translational, rather than rotational motions of the molecules, particularly at supercooled states. Although these studies suggest the strong relationship between the H-bond...
dynamics and molecular diffusivity in liquid water, the connection between the microscopic change of the H-bond network and molecular displacement remains elusive.

The cage-jump model for supercooled water in the present work is established by analyzing the H-bond dynamics. In particular, the caged and jumping states are introduced from the rearrangement process of four-coordinated H-bonds. Thus, our cage-jump model does not rely on a dynamical criterion such as the MSD plateau value. We examine how the H-bond rearrangement process links to the long-time diffusivity.

II. MODEL AND SIMULATIONS

MD simulations were performed using the TIP4P/2005 water model\[12\]. All the simulations in this work were performed with the GROMACS2016.4 package\[33,34\]. The phase diagram of the TIP4P/2005 supercooled water was determined in Refs. \[35\] and \[36\]. The temperature crossing the Widom line in the $p$-$T$ phase diagram is $T_L \approx 210$ K at 1 g/cm$^3$. Furthermore, the mode-coupling glass transition is estimated as $T_C \approx 190$ K at 1 g/cm$^3$ in Refs. \[37\] and \[38\]. Recent MD simulations have reported that the divergence of the structural relaxation time occurs at $T_s \approx 136$ K under the constant 1 bar condition. As described next, we examined the systems close to $T_L$, while our simulation temperatures are above $T_C$ and $T_s$.

The mass density was fixed at 1 g/cm$^3$ and the simulation system contained $N = 8,000$ molecules in a cubic box with the periodic boundary conditions. The cell length was approximately $L = 6.2$ nm. The investigated temperatures were $T = 350, 320, 300, 280, 260, 240, 220, 210, 200$, and 190 K. At each temperature, the system was equilibrated for 10 ns in the NVT ensemble, followed by a production run in NVE for 20 ns. Other trajectories of 100 ns were generated for MSD and H-bond correlation function (see the definitions below) at temperatures 200 K and 190 K. A time step of 1 fs was used. As demonstrated below, this trajectory duration is larger than the H-bond lifetime $\tau_{HB}$ at all the temperatures examined. Furthermore, aging effects have not been detected in the course of MD simulations. The atomic coordinates were stored at 0.2 ps intervals, which were used for the analyses presented below. This interval was chosen as a time scale slightly larger than that of libration motions ($\sim 0.1$ ps).

The MSD, $\langle \delta r^2(t) \rangle = \sum_{i=1}^{N} | \Delta r_i(t) |^2 / N$, was calculated to quantify the self-diffusion constant $D$. Here, $\Delta r_i(t)$ represents the displacement vector of an O atom of the molecule $i$ between two times 0 and $t$. The results at various temperatures are shown in the inset of Fig. 1(b). At temperatures below 280 K, a plateau becomes noticeable during the intermediate times between ballistic and diffusive regimes, indicating the cage effect. The self-diffusion constant $D$ was determined from the long-time behavior of the MSD, $D = \lim_{t \to \infty} \langle \delta r^2(t) \rangle / 6t$.

The ratio of the Lennard–Jones diameter of TIP4P/2005 model and the unit cell is $\sigma/L \approx 0.05$, which is sufficiently small to eliminate the finite-size effect on the diffusion constant.

The H-bond was defined using geometric variables between two water molecules. We adopted O-O distance $R$ and OH-O angle $\beta$\[22\]. Two water molecules are considered H-bonded if the distance-angle relationship meets the condition, $(R, \beta) \leq (0.34$ nm, $30^\circ)$. The H-bond correlation function $c(t) = \langle h(0) h(t) \rangle / \langle h(0) \rangle$ was calculated with the H-bond indicator $h(t)$ at a time $t$\[31,34\]. It analyzes ‘history-independent’ H-bond correlations, in the sense that $h(t)$ is evaluated only from the configuration at time $t$ without taking into account the reformation of the H-bond in the interval between times 0 and $t$. The H-bond lifetime $\tau_{HB}$ was then determined from $c(t)$ by fitting it to the stretched-exponential function $\exp[-(t/\tau_{HB})^\beta]$. We classify the time course of each water molecule into two states. One is called caged (C) state, where the tagged water molecule is initially H-bonded to other four water molecules. The schematic illustration of the J and C states is given in Fig. 1. Since an H-bond is of finite lifetime, the four H-bonds with the tagged molecule are all broken at a certain time. This time is set to the start of the jumping (J) state. The next C state then begins at the formation of four H-bonds with water molecules that are totally different from those in the previous C state. The complete changes of the H-bond partners is the con-
diction of transition from one C state to the next. The end time of a C state is when the four H-bonds are first broken, and the start time is when new, four bonds are formed. The adjacent C states are bridged by a J state, and by definition, a C state may be of 1, 2, 3 or 4 H-bonds and a J state may experience the reformation of an H-bond that was present in the previous C state. When an H-bond in the previous C state reforms after all the four bonds are once broken, the tagged molecule is still in the J state. The duration times of the C and J states are denoted as $\tau_C$ and $\tau_J$, respectively. We also quantified the displacement vectors of the O atom of the molecule $i$ during the J state, which is represented as $\Delta r_i^j(\theta)$. Here, $\theta$ is the counter for molecule $i$ to stay at J states from the initial time of the trajectory. Furthermore, many $\tau_C$ and $\tau_J$ were obtained for the single-molecule trajectory of each water molecule. The averages of $\tau_C$ and $\tau_J$ over all the single-molecule trajectories are denoted as $\langle \tau_C \rangle$ and $\langle \tau_J \rangle$, respectively. On the other hand, the sum of $\tau_J$ along a single trajectory was obtained and its ratio to the total length of that trajectory was also determined. The average of this ratio over all the single-molecule trajectories is then called $\rho_J$. Due to the difference in the order of averaging, $\rho_J$ is in principle different from $\langle \tau_J \rangle/(\langle \tau_C \rangle + \langle \tau_J \rangle)$; this point will be examined at the end of Sec. III. These quantities provide time coarse-grained information filtering out the thermal fluctuations within the J states as well as the libration motions.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the distribution of the duration time of the C state, $P(\tau_C)$, at the temperatures examined. The peak of $P(\tau_C)$ appears at around 10 ps at 300 K, which shifts to time scale of 50 ps at 190 K. In addition, the distribution is gradually extended to slower time scales with decreasing the temperature. The temperature dependence of the average duration time $\langle \tau_C \rangle$ is plotted in Fig. 2(b). In comparison, the temperature
dependence of $\tau_{\text{HB}}$ and $D^{-1}$ is also plotted in Fig. 2(b). It is demonstrated that the time scales of $\langle \tau_C \rangle$ is akin to $\tau_{\text{HB}}$, although the temperature dependence is slightly different. Note that the mean value of H-bond number depends on the temperature ranging from 3.62 at 300 K to 3.97 at 190 K, presumably resulting in the difference between $\langle \tau_C \rangle$ and $\tau_{\text{HB}}$. Furthermore, the intimate connection between self-diffusion constant $D$ and H-bond lifetime $\tau_{\text{HB}}$ is clarified in Fig. 2(b), which is equivalent to the previous demonstration, $D \propto \tau_{\text{HB}}^{-1}$, in TIP4P/2005 supercooled water. The roles of $\langle \tau_C \rangle$ and $\tau_{\text{HB}}$ for the cage-jump model will be discussed later.

Figure 3(a) shows the distribution of the duration time $\langle \tau_J \rangle$ of $\langle \tau_J \rangle$ obtained from $P(\tau_J)$ and $P(\tau_C)$. The black line represents $D_J = \langle \tau_J^2 \rangle / \langle \tau_J \rangle$. Inset: Ratio of jumping state $\rho_J$ vs. the ratio of average jumping time $\langle \tau_J \rangle / (\langle \tau_C \rangle + \langle \tau_J \rangle)$. The black line represents $\rho_J = \langle \tau_J \rangle / (\langle \tau_C \rangle + \langle \tau_J \rangle)$. These distributions in the JMSD, particularly for larger $\Theta_J$, is akin to $\tau_{\text{HB}}$, at each temperature. However, we observed some deviations in the JMSD, particularly for larger $\Theta_J$ at lower temperatures (see the inset of Fig. 3(a)). These deviations in the JMSD, particularly for larger $\Theta_J$, are clarified in Fig. 2(b), which is equivalent to $\rho_J$, at each temperature. However, we observed some deviations in the JMSD, particularly for larger $\Theta_J$ at lower temperatures (see the inset of Fig. 3(a)). These deviations in the JMSD, particularly for larger $\Theta_J$ at lower temperatures (see the inset of Fig. 3(a)).

![FIG. 4](image)

**FIG. 4.** (a) Jumping mean square displacement (JMSD), $\langle \delta r_J^2(t) \rangle$, as a function of the number of jumps $\Theta_J$ at the temperatures examined. Inset: $\langle \delta r_J^2(t) \rangle / \Theta_J$ as a function of $\Theta_J$ at temperatures below $T = 200$ K. The straight lines indicate the diffusion behavior, of which slope gives a jumping self-diffusion constant $D_J$. (b) Jumping self-diffusion constant $D_J$ vs. $\langle \tau_J^2 \rangle / \langle \tau_J \rangle$ obtained from $P(\tau_J)$ and $P(\tau_C)$. The black line represents $D_J = \langle \tau_J^2 \rangle / \langle \tau_J \rangle$. Inset: Mean square displacement (MSD), $\langle \delta r^2(t) \rangle$, at the temperatures examined. Dashed line represents the long-time asymptote $6Dt$ at $T = 190$ K. Points indicate values of the average jump length $\langle \tau_J \rangle$ at each temperature.

![FIG. 5](image)

**FIG. 5.** Self-diffusion constant $D$ vs. the estimate from the cage-jump model $\rho_J(\langle \tau_J^2 \rangle / \langle \tau_J \rangle)$. The black line represents $D = \rho_J(\langle \tau_J^2 \rangle / \langle \tau_J \rangle)$. Inset: Ratio of jumping state $\rho_J$ vs. the ratio of average jumping time $\langle \tau_J \rangle / (\langle \tau_C \rangle + \langle \tau_J \rangle)$. The black line represents $\rho_J = \langle \tau_J \rangle / (\langle \tau_C \rangle + \langle \tau_J \rangle)$.
viations from the linearity at large $\Theta_J$ are due to the fact that $N_J$ becomes much smaller than $N$, leading to the insufficient ensemble average over the molecules. At $190\,\text{K}$, for example, $N_J$ becomes smaller than $N$ at $\Theta_J \gtrsim 10$. The average self-diffusion constant $D_J$ of successive jumping events is determined from the relation, $D_J = \lim_{\delta r_J \to \infty} \langle \delta r_J^2 \rangle / \langle \Theta_J \langle \tau_J \rangle \rangle$, where the linear fit was done by excluding the $N_J < N$ regions. Figure 4(b) demonstrates that the second-order moment $\langle \delta r_J^2 \rangle$ of the distribution $P(\tau_J)$ provides the good description of $D_J$ at each temperature. As discussed in Ref. 26, these features of the JMSD and $D_J$ indicate that the diffusion process of a single molecule can be described by the random walk with independent jumps, which is characterized by $\langle \delta r_J^2 \rangle$.

Furthermore, the decrease in $D_J$ with the temperature reduction is attributed to the corresponding decrease in the jumping length scale $\langle \delta r_J^2 \rangle$. The inset of Fig. 4(b) illustrates the location of $\langle \delta r_J^2 \rangle$ in the MSD. At each temperature, the value of $\langle \delta r_J^2 \rangle$ slightly exceeds beyond the MSD plateau. This observation indicates the validity of our modeling for cage-jump motions.

The relevance of the cage-jump modeling is examined in Fig. 5 by plotting the relationship between the self-diffusion constant $D$ and $\rho_1 D_J = \rho_3 \langle \delta r_J^2 \rangle / \langle \tau_J \rangle$. Note that the inset of Fig. 5 demonstrates the ratio of the J state $\rho_3$ is essentially equal to the ratio of the average jumping time $\langle \tau_J \rangle / (\langle \tau_C \rangle + \langle \tau_J \rangle)$. A similar result was also reported in Ref. 26. It should be noted that $\rho_3$ is obtained by first analyzing each single-molecule trajectory and then taking an average over all the single-molecule trajectories, while $\langle \tau_J \rangle$ and $\langle \tau_C \rangle$ are computed without distinguishing the trajectories of distinct water molecules. $\rho_3 = \langle \tau_J \rangle / (\langle \tau_C \rangle + \langle \tau_J \rangle)$ thus implies the validity of a mean-field-type view in that the average over the single-molecule trajectories can be determined without taking into account the differences among the trajectories. Figure 5 shows that $\rho_1 D_J$ from our cage-jump model is a good indicator for the self-diffusion constant $D$, although slight deviations are apparent at $190\,\text{K}$ and higher temperatures above $300\,\text{K}$. As shown in Fig. 2(b), the inverse of the self-diffusion constant $D^{-1}$ is strongly coupled with $\tau_{\text{HB}}$, which becomes slightly larger than $\langle \tau_C \rangle$. When $\langle \tau_J \rangle \ll \langle \tau_C \rangle$, $\rho_1 D_J$ is approximated by $\langle \delta r_J^2 \rangle / \langle \tau_C \rangle$, which holds particularly at lower temperatures. Thus, the difference between $\langle \tau_C \rangle$ and $\tau_{\text{HB}}$ results in the small difference between $D$ and $\rho_1 D_J$ at $190\,\text{K}$. The deviations at high temperatures are attributed to the observation that the MSD plateau was not well developed, as shown in the inset of Fig. 1(b). In fact, at higher temperatures, the cage structures are weakened and water molecules immediately diffuse without exhibiting intermittent cage-jump motions.

IV. CONCLUSIONS

In this paper, we have developed a cage-jump model for the diffusion in supercooled water. Unlike the scheme proposed by Pastore et al.\cite{29,31} we classify the trajectory of a single water molecule into the caged and jumping states from the analysis of H-bond rearrangements. The quantification of the average length and time scales of the jumping state enabled to predict the self-diffusion constant $D$ that is determined in principle from the long-time MSD behavior. We have thus succeeded in connecting the H-bond dynamics and the molecular diffusivity through the cage-jump events. This cage-jump event can be regarded as an element of the collective motions, which are often visualized by string-like motions. In fact, the time scale is $\langle \tau_J \rangle \approx 1\,\text{ps}$, whereas that of collective motions is typically characterized by the time of the last stage in the MSD plateau.

Our cage-jump model gives an estimate of $D$ when the caged and jumping states are identified from an MD trajectory, without extensive MSD evaluation to the diffusive regime. In fact, the diffusion asymptote $6Dt$ is observed at times much larger than $\tau_{\text{HB}}$, as shown in the inset of Fig. 1(b). However, particularly at lower temperatures, the duration time of the C state $\langle \tau_C \rangle$ becomes slightly smaller than the H-bond lifetime $\tau_{\text{HB}}$. This causes the small difference between $D$ and $\rho_1 D_J$, particularly at $190\,\text{K}$, as observed in Fig. 5. The local structure changes from high-density liquid to low-density liquid with decreasing the temperature below the so-called Widom line ($T_L \approx 210\,\text{K}$). The tetrahedral order becomes higher and the number of the defect correspondingly decreases in the low-density liquid state, where the hydrogen-bond break needs more activation energy, and correspondingly the H-bond network rearranges over a wider range in space. In contrast, our cage-jump model is constructed based on the information on the first nearest neighbor shell only. This leads to the underestimation of $\langle \tau_C \rangle$ compared with $\tau_{\text{HB}}$. A possible refinement is thus to incorporate order parameters for H-bond network such as the local structure index, which focuses on the second nearest neighbor. In this respect, further study is currently undertaken toward the appropriate inference of the self-diffusion constant $D$, particularly at much deeper supercooled states inside the so-called no man’s land region.\cite{39,40,41,42} It is also worthy to apply our cage-jump model to various water models to give deeper insight into the role of the H-bond breakage on the molecular diffusivity in supercooled water.

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