



Research paper

Mechanism of translational jump of a hydrophobic solute in supercooled water: Importance of presolvation

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ABSTRACT

Despite long study of translational jump of solute in supercooled water, a detailed mechanism of this jump is still lacking. Through an analysis of several simulated cage-to-cage jumps of a dissolved hydrophobic solute we find support for a pathway very similar to the proton transport in aqueous solution. Presolvation of water molecules occurs such that the final solvent cage, where the solute arrives through jump, becomes structurally and energetically comparable to the initial cage where the solute was trapped. This mechanism therefore clearly emphasizes the role of solvent for determining the jump occurrence time of a solute in supercooled water.

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Supercooled liquids are often characterized by strong spatio-temporal heterogeneity. In such systems dynamics of a solute in one region of the medium can be orders of magnitude faster than that in another region, separated by only a few nanometer distance. This dynamical heterogeneity of the medium has created a center of attention for researchers for decades [1–5]. Solute's dynamics in supercooled liquids is remarkably intriguing. Breakdown of Stokes-Einstein (SE) relation for translational dynamics is evidenced near glass transition temperature while the Stokes-Einstein-Debye (SED) relation involving rotational diffusion is still valid [1–17]. This signifies that even when the rotational motion of solute molecule is coupled to the viscosity of the medium, the translation of the same molecule is decoupled from viscosity. Water, being a glass-former with the glass transition temperature ~ 136 K, is known to exhibit very similar behaviors including the decoupling of translational dynamics from viscosity, which even starts from room temperature [11,12].

The above translation-rotation decoupling of solute and solvent in supercooled liquids, supposedly, occurs due to the presence of spatio-temporal heterogeneity in the medium [1–17]. However, this decoupling can also stem from non-diffusive translation of molecules. The rationale behind this hypothesis is the following. The validity of the SE relation is based on the assumption that a solute molecule translates via Brownian motion with small amplitude displacements. Now, if the solute does not stringently follow the Brownian motion then the SE relation will be violated naturally. This hypothesis—first proposed by Goldstein—states that

while molecules in low temperature liquid move via crossing a potential energy barrier (activated transport or hopping), the liquid molecules diffuse freely without hopping at high temperature as the thermal energy is comparable to the barrier height [18]. Characteristics of this picture have been confirmed for more than one model liquids by theory and computer simulation [19–23]. However, a detailed molecular mechanism for this solute's jump from one solvent cage to another is still elusive. In this context it's worth mentioning that a recent paper shows that translation-rotation coupling can be a general mechanism of the breakdown of the SE relation in the case of polyatomic ions [24].

Attempts were made to explain this behavior, modifying the idealized mode coupling theory after incorporating the hopping, which is considered to be arising from vibrational fluctuations in the quasarrested state where particles are trapped inside solvent cage [25]. Regardless of the success of the theory for predicting the long time dynamics of the density fluctuation correlation, the origin of hopping from vibrational fluctuation of the solute in the solvent cage is still questionable. Similar to the Grotthuss mechanism for proton transport in aqueous solution, the water solvents must prearrange setting up the final cage before the solute actually jumps from the initial to the final cage. Otherwise, the free energy of the system will eventually increase and the jump process will be thermodynamically infeasible [26–30]. Therefore, the reaction coordinate for the solute's jump must be the collective solvent coordinate instead of the solute's rattling motion inside the cage. Interestingly, rotational jump of water molecules, at ambient condition, also shows similar behavior [31–33]. These motivate us to explore the pathway for the cage-to-cage jump of the solute in molecular detail.

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In this letter we present results focusing pathway of a hydrophobic solute's translational jump from one solvent cage to another in supercooled water using classical molecular dynamics (MD) simulations. Hydrophobic hydration has been a fascinating topic of debate for over decades (see eg., [34–39]). Both experiment and computer simulation studies evidenced that water solvent molecules around the hydrophobic solute form strongly hydrogen bonded clathrate like structure (“icebergs”) [34–39]. This clathrate like structure of solvent water strongly encapsulates the hydrophobic solute. The escaping of the solute from the well-defined solvent cage, with the help of presolvation, is therefore the key for the rattling-jump-rattling process in supercooled liquid. The mechanism of this rattling-jump-rattling process is the central focus of this letter.

We use GROMACS package [40] in order to obtain trajectory of the molecules, placed in a cubic simulation box. The box contains 500 water molecules and 1 solute molecule. While the water molecules are modeled as rigid SPC/E, the solute is considered as a single Lennard-Jones (LJ) atom having LJ parameters similar to those of argon. (We have also checked the validity of our results using TIP4P/2005 model [41] of water, presented in [Supplementary Material \(SM\)](#).) The simulation is first run for 10 ns, during which the temperature is kept constant at 250 K using Nosé-Hoover thermostat and the pressure at 1 atmosphere using Berendsen barostat with a coupling constant of 0.5 ps. The above NPT simulation is run in order to obtain appropriate density of the system at the given temperature and pressure. The equations of motions are solved by Leapfrog-Verlet algorithm with time step of 1 fs. Starting from the final configuration we initiate simulation using NVT ensemble for another 40 ns using Nosé-Hoover thermostat with the same coupling constant as before. Equations of motions are solved by Leapfrog-Verlet algorithm again with time step of 1 fs. The trajectory is saved once in 50 fs. A cut-off of 1.2 nm (around the half of the box length) is applied for LJ and Coulomb interactions. Particle Mesh Ewald summation technique and SHAKE algorithm are used to handle long-range Coulomb interactions and constrain O–H bonds of water molecule respectively. This 40 ns long trajectory is used for analyses, which we discuss now.

The simulation results are organized as follows. First, we show that the solute is momentarily trapped inside the solvent cage. Next, we detail the spatial and orientational structure of the cage water molecules in order to check whether it is hydrophobic hydration structure or not. The escaping of the solute from one solvent cage and then trapping again in another cage are then examined by following over time the solute coordinate, which is actually the position of the solute. Lastly, we focus on the solvent's role in facilitating the jump process.

In order to get indication for caged dynamics of the solute we have calculated here time dependent mean square displacement (MSD) of the solute. MSD is calculated using the equation, $\langle |\Delta \mathbf{r}(t)|^2 \rangle = \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$, where $\mathbf{r}(t)$ is the time dependent position vector of the solute. Fig. 1 exhibits MSD as a function of time. Clearly, the plateau region of MSD with fractional time dependence ($\langle |\Delta \mathbf{r}(t)|^2 \rangle \propto t^\alpha$; $\alpha \sim 0.2$)—in between the short time ballistic ($\langle |\Delta \mathbf{r}(t)|^2 \rangle \propto t^2$) and the long time diffusion regime ($\langle |\Delta \mathbf{r}(t)|^2 \rangle \propto t$)—implies rattling of the solute inside the solvent cage [3].

The present solute, being nonpolar in nature, is expected to have hydrophobic hydration structure of solvent water molecules [34–39]. This hydrophobic hydration structure evidenced from spatial and orientational structure of the solvent water molecules around the solute. We have presented in Fig. 2a, the radial distribution function (RDF) between the solute and the water oxygen atom and two-dimensional probability density distribution with the angle (between water O–H bond and the solute-water O atom vec-

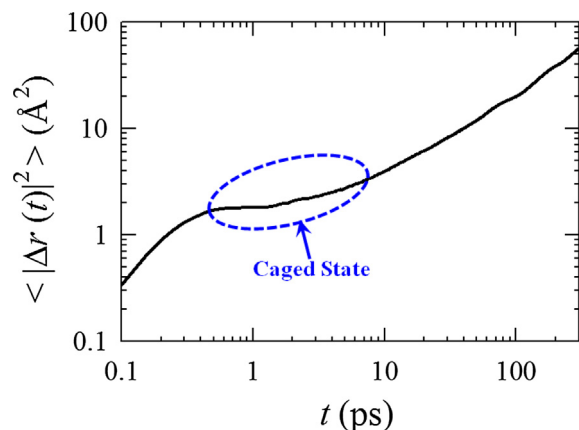


Fig. 1. MSD of the solute as a function of time. The highlighted region signifies the rattling motion of the solute in solvent water cage.

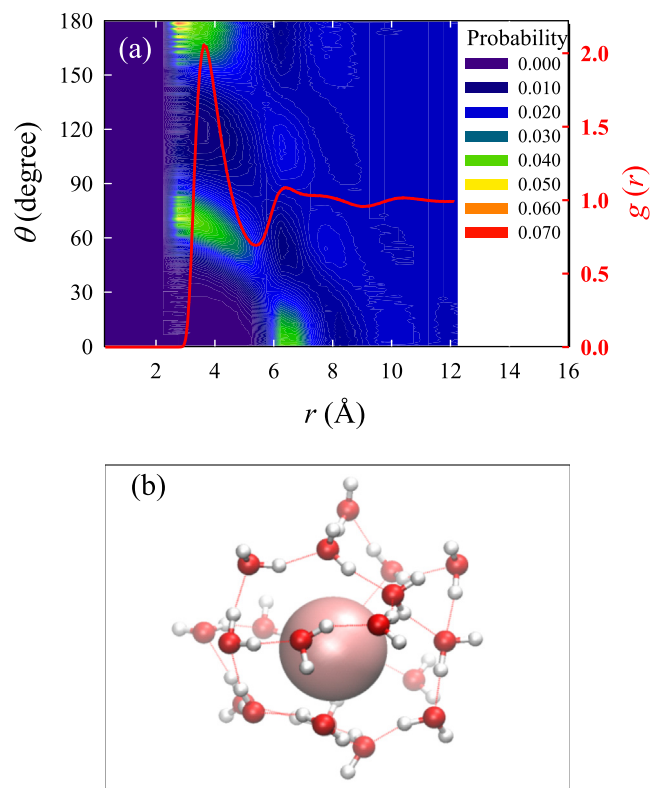


Fig. 2. Spatial and orientational structures of water molecules around the hydrophobic solute: (a) radial distribution function between solute and water O atom (red solid line; values given by the right-hand ordinate axis) and two-dimensional probability density distribution of the angle between water O–H bond and the solute-water O atom vectors in y-axis (values given by the left-hand ordinate axis) and the distance (between the solute and water O) in x-axis, (b) snapshot of the cage water molecules and the spherical solute at some time point along trajectory. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tors) in y-axis and the distance (between the solute and water O atoms) in x-axis. The positions of the first peak and the first minima at $\sim 3.6 \text{\AA}$ and $\sim 5.35 \text{\AA}$ respectively show that the first hydration shell is centered around 3.6\AA and extends up to $\sim 5.35 \text{\AA}$ from the solute. The majority of O–H bonds in the first hydration shell water molecules are either tangentially aligned around the solute or towards the bulk water molecules. In the second hydration shell, on the other hand, majority of the O–H bonds are direc-

ted towards the hydrophobic solute. These water molecules basically donate H-bonds to the tangentially aligned first hydration shell water molecules. The above picture is further visualized in Fig. 2b, where the first hydration shell O–H bonds are mainly either tangentially aligned or directed towards the bulk water molecules. This picture is in close agreement with other simulation studies, focused on hydrophobic hydration [34–39]. These tangential H-bonds are much stronger than bulk H-bonds and therefore determine the lifetime of the solvent cage [34].

We now focus on the solute's jump mechanism from one solvent cage to another. In Fig. S1 of SM we have shown a portion of the displacement of the solute where two jumps are clearly visible. Here, we divide the complete process into three steps: rattling of the solute inside its initial cage, jump from one cage to another, and rattling of the solute again inside the final cage. The whole process is exhibited in Fig. 3a. Note that this rattling-jump-rattling process of small solute is also seen in room temperature ionic liquids using MD simulation [23]. Here we examine 30 large amplitude jumps, the occurrence times of which are listed in Table S1 of SM. The average amplitude of these 30 jumps is ~ 3.25 Å and is centered around ~ 3.45 Å (see Fig. S2 of SM). Analysis of all these jump trajectories is useful to obtain the average picture, which is essential for predicting a precise mechanism. We follow all the jump processes over 20 ps duration with 10 ps each side of the jump occurrence time.

In order to follow the solute's coordinate quantitatively we calculate jump coordinate Q_j —normalized version of the solute coordinate—using the following equation:

$$Q_j = \frac{|\mathbf{r}(t) - \langle \mathbf{r}_i \rangle| + |\mathbf{r}(t) - \langle \mathbf{r}_f \rangle|}{|\mathbf{r}(t) - \langle \mathbf{r}_i \rangle| - |\mathbf{r}(t) - \langle \mathbf{r}_f \rangle|}, \quad (1)$$

where $\mathbf{r}(t)$ is the time dependent position of the solute. $\langle \mathbf{r}_i \rangle$ and $\langle \mathbf{r}_f \rangle$ are the initial and final reference positions of the solute respectively. These are calculated by averaging over unnormalized solute's positions for 7 ps before and after the jump, as shown in Fig. 3a. Therefore, $\langle \mathbf{r}_i \rangle$ and $\langle \mathbf{r}_f \rangle$ are the average positions during the solute's rattling motion inside the initial (state I in Fig. 3a) and the final cages (state III in Fig. 3a) respectively. Evidently, Q_j is an 'order parameter' indicating the solute's position. Note that Q_j is -1 when the solute is in its initial cage and is close to 1 when that is in the final cage. This prompts our definition of the jump occurrence time when Q_j first crosses "0", which is the midpoint between the initial and the final cage positions. Note that the form of Eq. (1) is actually motivated from the equation for normalized proton transfer coordinate, where the proton shifts its position from acid to base side [42]. 30 trajectory-averaged Q_j is displayed in Fig. 3b as a function of time. The conspicuous fluctuations of Q_j before and after the jump are due to the rattling in the initial and the final cage respectively. The swift transition of Q_j value from ~ -1 to ~ 1 in ~ 1 ps duration characterizes the solute's jump motion. Similar picture emerges on using TIP4P/2005 model of water, as shown in Fig. S3a of SM.

However, the sudden jump of the solute from the initial cage to final one would cause higher energy unless solvent water molecules, which are in close proximity to the solute's final cage position, do not rearrange to accommodate the arriving solute. Because of the slower structural relaxation compared to ultrafast solute-jump, the solvent water molecules must prearrange before the jump occurs such that the final cage is almost built-up at the jump occurrence time. This is along the same line of Marcus theory [43] for electron transfer and Ando-Hynes theory [26,28] for proton transfer reaction in solution phase, where the thermally induced restructuring of the surrounding solvent molecules is the key rate determining process. The role of water solvent for the jump of the solute is now discussed.

Fig. 3b also displays the coordination number, N_h , of the first hydration shell (up to 5.35 Å distance from the solute) of the solute as a function of time. N_h quickly decreases to ~ 18.4 from the equilibrium value ($N_h \sim 20$) at the jump occurrence time ($t = 0$ ps) and then immediately regains its value. This subtle change of N_h value occurs within ~ 1 ps time, while the solute is on the fly between the initial and the final cage. Note, this timescale is much smaller than structural relaxation timescale in supercooled water at 250 K [1,44–47]. Therefore the slight decrease of N_h value at $t = 0$ cannot be due to the solvent water's rearrangement. Instead, the above decrease can be due to the fact that the first hydration shell of the solute is slightly less crowded at the jump occurrence time when the solute is halfway to the final cage. The similar picture emerges for TIP4P/2005 model of water (see Fig. S3b of SM).

While the above discussion precludes the possibility of solvent rearrangement during the ultrafast jump occurrence, we now show the actual presolvation near the two reference positions of the solute ($\langle \mathbf{r}_i \rangle$ and $\langle \mathbf{r}_f \rangle$ in Eq. (1)). We have plotted in Fig. 4 (Fig. S4 in SM for TIP4P/2005 model of water) the time dependent average distance of the water molecules ($\langle r_{sw} \rangle$), present inside the distance 5.35 Å (first minima of solute-water RDF in Fig. 2a) distance from the two reference positions of the solute. Therefore, $\langle r_{sw} \rangle$ provides time dependent structural information of the solvent water forming the cage. This analysis is based on a simple anticipation that $\langle r_{sw} \rangle$ has lower value when the solvent water molecules fill the entire spherical space in the absence of hydrophobic solute than when they are organized to form solvent cage around the hydrophobic solute. Therefore, time dependent $\langle r_{sw} \rangle$ will reveal candidly the presolvation of water molecules, if any, near the initial

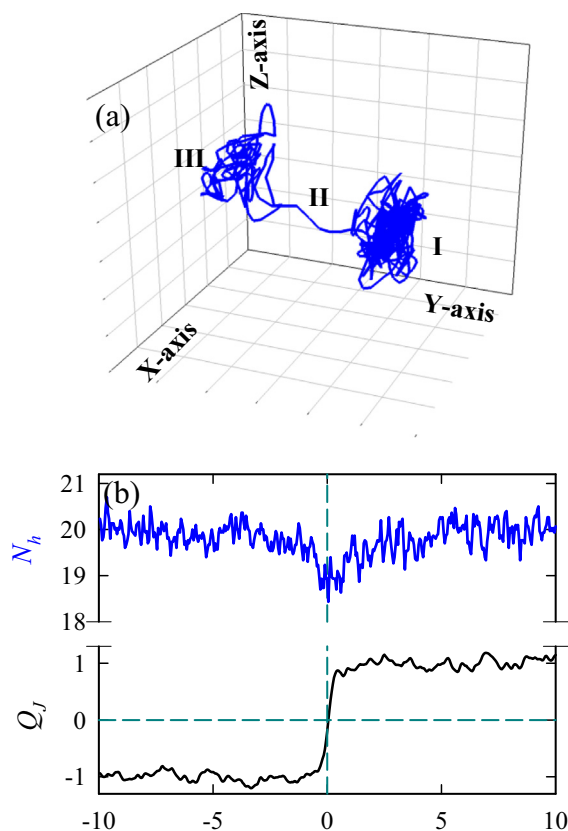


Fig. 3. (a) A portion of the solute's trajectory in XYZ plane showing (I) the rattling motion of the solute inside the initial cage, (II) the jump motion from the initial to the final cage, and (III) the rattling motion of the solute inside the final cage; (b) Time evolution of the 30 trajectory-averaged jump coordinate Q_j (black solid line) and the coordination number N_h of the solute with $t = 0$ fixed at the jump occurrence time. While the vertical dashed line represents the jump occurrence time ($t = 0$ ps), $Q_j = 0$ is indicated by horizontal dashed line.

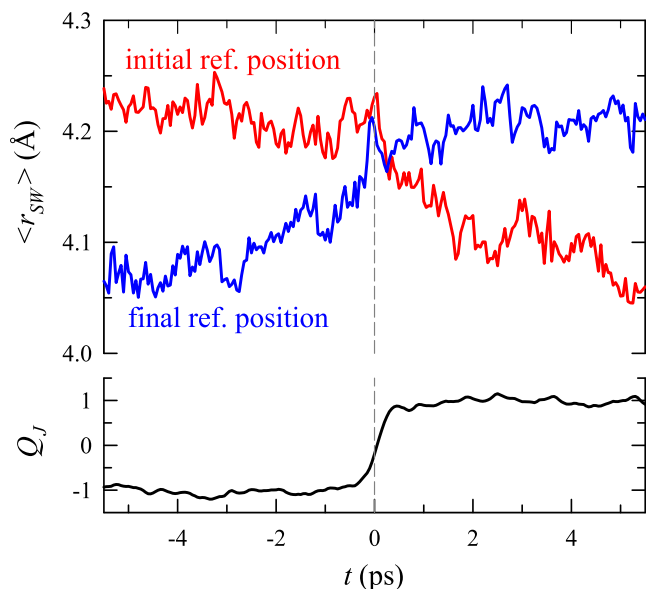


Fig. 4. Time evolution, centered on jump occurrence time, of average distance of water molecules (r_{SW}) present inside the sphere of 5.35 Å radius from the two reference positions. Q_j is re-plotted (black solid line) for further elucidation. The vertical dashed line represents the jump occurrence time ($t = 0$ ps).

and final cage positions of the solute. Fig. 4 clearly shows that $\langle r_{SW} \rangle$ from initial (final) reference position of the solute decreases (increases) from a value of ~ 4.22 Å (~ 4.05 Å) to ~ 4.05 Å (~ 4.22 Å) after the jump occurrence. Interestingly, $\langle r_{SW} \rangle$ values, at initial and final reference positions, become equal at the jump occurrence time. In other words, the solute jumps from initial to final solvent cage only when the hydration structures around the two reference positions of the solute are equivalent to each other. A closer inspection of Fig. 4 further reveals that the increase of $\langle r_{SW} \rangle$ for final reference position starts increasing well before (~ 3 ps) the solute actually jumps and almost levels off immediately after the jump. This provides absolutely clear picture that water solvents' prearrangement starts when the solute stays in the initial cage and continues till the final cage is almost built, immediately after that the solute jumps to the final cage. This picture resembles to the presolvation of water molecules facilitating proton transport in aqueous solution following the Grothuss mechanism [26–30].

Now we focus on the effect of the above prearrangement on the hydration structure around the two reference positions of the solute. Fig. 5 displays the average number distribution of the solvent water molecules (N_W) at various distances (up to 5.35 Å distance) from the reference positions at three different time slabs:

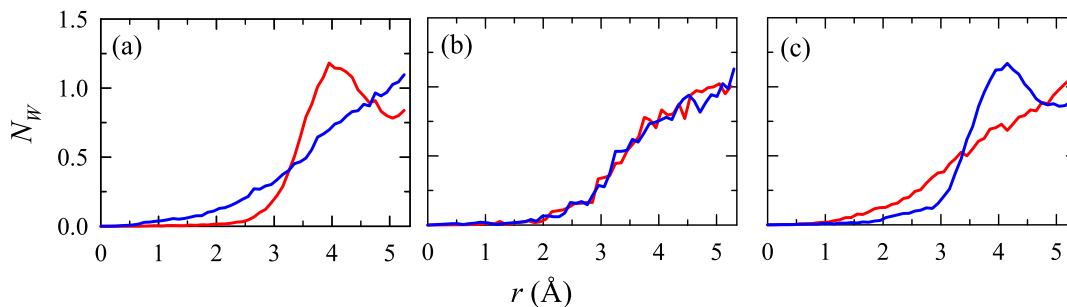


Fig. 5. Water molecule number distribution, N_W , as a function of distance from the initial (red line) and the final reference positions (blue) of the solute at three time points—(a) before jump, (b) during jump, and (c) after jump—along the trajectory of Fig. 3b. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

before (-10 ps to -3 ps), during (-0.5 to 0.5 ps), and after (3 – 10 ps) the jump occurrence time. The initial and the final reference positions of the solute mimic H-bonded proton donor acid and acceptor base complex in acid-base PT reaction in aqueous solution [42]. Clearly, the two distinctly different distributions in Fig. 5a before the jump indicate different hydration structures around the two reference positions. While the one around the initial reference position corresponds to the hydrophobic hydration, the other around the final reference position corresponds to the neat liquid water in a sphere. These two distributions become almost identical at the jump occurrence time of the solute (see Fig. 5b). This indicates that the hydration structures around the initial and final reference positions of the solute become equivalent with each other right at the jump occurrence time. This symmetrization of hydration structures at the jump occurrence time clearly stems from the presolvation of water molecules around the final reference position, as shown in Fig. 4. Now, when the solute jump is over and the solute is trapped inside the final cage, the switching between the hydration structures takes place, as evidenced from Fig. 5c. This signifies stabilization of the solute in its final solvent cage. We find similar results, presented in Fig. S5 of SM, from the simulation considering TIP4P/2005 model of water.

In order to put this into perspective we have plotted in Fig. 6, one-dimensional potential energy (PE) as a function of distance of the solute from the initial reference position at three different time points along 20 ps duration. These three time points are representative of before the jump (at -10 ps), at the jump (at 0 ps), and after the jump (at 10 ps) occurrences. PEs are evaluated by calculating the total interaction energy of the system (summation of solute-solvent and solvent-solvent interaction energy) at various positions of the solute along the solute's jump trajectory. Fig. 6 clearly reveals that while the solute is much more stable at the initial reference position before the jump occurrence, after the jump occurrence the solute becomes more stable in the final reference position. This is evidenced by comparing the minima of the PE wells. Before the jump occurrence the minimum of the PE well shows up at $r = 0$ Å (center of the initial cage). After the jump occurrence, on the other hand, the minimum of the PE well is centered at $r \sim 6$ Å (center of the final cage). Now, at the jump occurrence time the PE minima are almost the same for the solute at the two reference positions and in-between the barrier almost vanishes. The symmetrization of PE clearly occurs by the prearrangement of water molecules, as seen in Fig. 4. Interestingly, the similar symmetrization is also observed during rotational motion of water and some other dipolar liquids during H-bond partner exchange [31–33,48–50], electron transfer reaction in aqueous solution [43], acid-base proton transfer reaction in aqueous solution [42], and hopping of proton/hydroxide ion from one water to another in liquid water following Grothuss mechanism of proton transport [26–30].

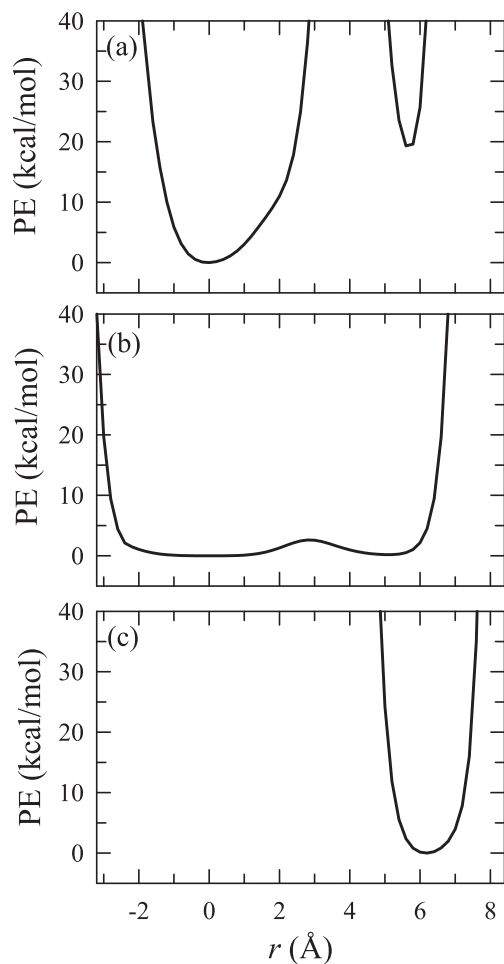


Fig. 6. Potential energies (solute-solvent plus solvent-solvent interaction potential) at several positions of the solute along the line joining the initial and final reference positions of the solute at three reference time points: (a) –10 ps, (b) 0 ps, and (c) 10 ps. See text for details. The potential energy minima around $r = 0$ in panel (c) is too high to fit in the y-axis scale.

In conclusion, we have investigated the jump mechanism of a solute from one water solvent cage to another in supercooled water using molecular dynamics simulation. We have found support for a pathway, very similar to the proton transport in aqueous solution, where presolvation of solvent water molecules is the key rate determining step. Presolvation of water molecules starts when the solute is still in the initial cage. The jump occurs only when the final cage becomes structurally and energetically comparable with the initial cage. This mechanism, therefore, clearly emphasizes that the solvent coordinate is the reaction coordinate. We have also checked the validity of the results using two different models of water, SPC/E and TIP4P/2005 model, and found that the results are almost model independent.

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Appendix A. Supplementary material

Supplementary material contains (i) a small portion of the solute's displacement in order to show representative jumps, (ii) a table listing the jump occurrence times of the individual jumps, examined for analysis, (iii) figure showing the distribution of 30

jump amplitudes, and (iv) the results for TIP4P/2005 model of water. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2017.07.084>.

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