Effects of hydrogen-bond environment on single particle and pair dynamics in liquid water

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Abstract. We have performed molecular dynamics simulations of liquid water at 298 and 258 K to investigate the effects of hydrogen-bond environment on various single-particle and pair dynamical properties of water molecules at ambient and supercooled conditions. The water molecules are modelled by the extended simple point charge (SPC/E) model. We first calculate the distribution of hydrogen-bond environment in liquid water at both temperatures and then investigate how the self-diffusion and orientational relaxation of a single water molecule and also the relative diffusion and relaxation of the hydrogen-bond of a water pair depend on the nature of the hydrogen-bond environment of the tagged molecules. We find that the various dynamical quantities depend significantly on the hydrogen-bond environment, especially at the supercooled temperature. The present study provides a molecular-level insight into the dynamics of liquid water under ambient and supercooled conditions.

Keywords. Water; hydrogen-bonds; diffusion; orientational relaxation.

1. Introduction

The physical chemistry of water and aqueous solutions continues to attract a high level of interest because of the important role played by these systems as reaction media in numerous chemical and biological processes and also due to the fact that many of the equilibrium and dynamical properties of liquid water show anomalous behaviour with changes in temperature and pressure. Examples of such anomalous properties include enhancement of the rates of translational and rotational diffusion with application of pressure at low temperature, existence of a temperature of maximum density etc.[1–7]. It is generally believed that all this interesting and anomalous behaviour can be attributed to the presence of hydrogen-bonds in liquid water.

It is known now that liquid water is a totally connected random tetrahedral network of hydrogen-bonds[8,9]. However, this tetrahedral network with four hydrogen-bonds per molecule is not perfect. It contains structural defects or inhomogeneous regions at microscopic level. Previous studies have shown that, although the majority of the molecules participate in four hydrogen-bonds in liquid water, many of the molecules also participate in two, three or five hydrogen-bonds at a given time[10–14]. Statistically, the existence of this structural defect or microscopic inhomogeneity can be described by a distribution of the number of molecules with a given number of hydrogen-bonds. The number of hydrogen-bonds that a molecule has with its neighbours characterizes

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its hydrogen-bonding state, i.e., its hydrogen-bond environment and the above mentioned distribution describes the probability of finding a water molecule in a given hydrogen-bond environment. Both the equilibrium and dynamical properties of a water molecule depend on its hydrogen-bond environment although experimentally it has not been possible to resolve this dependence. Energetically, a molecule is in the most favourable configuration when it participates in four hydrogen-bonds. Dynamically, it has also been shown that a water molecule with five hydrogen-bonds diffuses at a faster rate than the one with four hydrogen-bonds and this enhanced diffusion of five-coordinated molecules plays a crucial role in the pressure and density dependence of the self-diffusion of water molecules at low temperature [10,15]. The dynamics of hydrogen-bond relaxation has also been shown to depend statistically on the nature of hydrogen-bond environment at molecular level [14].

Since there are different hydrogen-bond environments in which a water molecule can be found, the observed dynamical property of a water molecule is the weighted superposition of the dynamics of water molecules in different environments. For example, experimentally measured self-diffusion coefficient at temperature T can be written as

$$D(T) = \sum_{n=0}^{n_{max}} D_n(T) f_n(T),$$ (1)

where $D_n(T)$ and $f_n(T)$ are the temperature-dependent diffusion coefficient and the fraction of water molecules with n hydrogen-bonds and n_{max} is the maximum number of hydrogen-bonds that a water molecule can participate in. Clearly, a molecular-level understanding of the diffusive behaviour of water molecules would require knowledge of the distribution of the hydrogen-bond environment, the diffusion coefficients of water molecules in various environments and also the temperature dependence of the above quantities. Similar situations also appear for rotational motion and relative diffusion in liquid water.

We note that the existence of a distribution of hydrogen-bond environment has played a critical role in the development of phenomenological theories of water dynamics at microscopic level. For example, Lamanna *et al* [16] proposed a theoretical model where molecules could be found in five different hydrogen-bond environments depending on the number of linear hydrogen-bonds in which each molecule was involved. The distribution of water molecules among the various environments was found by solving an appropriate five-level master equation and the water self-diffusion was then evaluated by averaging over this distribution, (1). Similar approaches based on varying microscopic environments were also considered by Bertolini *et al* [17] in their phenomenological studies of the translational dynamics of liquid water.

The technique of molecular dynamics (MD) simulation [18] allows the calculation of the quantities of relevance to the phenomenological models such as the hydrogen-bond distribution and its effects on the dynamical properties of water molecules which are not directly accessible from experiments. MD calculations also offer additional insight into the translational and rotational dynamics of water molecules and help to verify the accuracy of the existing phenomenological models. In the present work, we have carried out such simulation studies and have calculated the distribution of hydrogen-bond environment and also the dependence of various dynamical properties on the

hydrogen-bond environment of a single molecule or a pair of water molecules. Our focus has been to examine how these environmental effects change as the liquid is cooled from the ambient to a supercooled temperature. In the simulations, the water molecules are modelled by the so-called SPC/E model[19] which is known to provide a good description of the structural, dielectric and dynamical properties of liquid water. We have carried out the simulations at two different temperatures: $T = 298$ and 258 K, and at a constant pressure of 0·1 MPa. It is found that the hydrogen-bond environmental effects can be significant for both single particle and pair dynamical properties, especially at the supercooled temperature.

The rest of the paper is organised as follows. In §2, we describe the model and the simulation details. The results of hydrogen-bond environmental effects on the single particle translational and rotational motions are presented in §§3 and 4, respectively. In §5, we discuss the results of relative diffusion and hydrogen-bond relaxation. Our conclusions are summarized in §6.

2. Model and simulation details

We have employed the SPC/E model of water where each water molecule is characterized by three interaction sites located on the oxygen and hydrogen atoms[19]. In this model, the O–H bond distances are constrained at 1·0 Å and the bond angle between two O–H bonds is fixed at 109·47°. Interaction between the atomic sites of two water molecules is expressed as

$$u(r_i, r_j) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{r_{ij}}, \tag{2}$$

where the first term is the Lennard–Jones interaction which is calculated only between the oxygen sites and the second term represents the electrostatic interaction. q_i is the charge of the ith atom. The values of the potential parameters σ, ε and q_i for SPC/E model are given in table 1.

The MD simulations were carried out at two different temperatures: $T = 298$ K and $T = 258$ K and at a pressure of $P = 0\cdot1$ MPa. A cubic box of 256 water molecules and periodic boundary conditions with minimum image convention were employed. We used a spherical truncation of the Lennard–Jones interaction potential at $0\cdot5\,L$, where L is the edge length of the simulation box. Long range electrostatic interactions were treated using the Ewald method with the dielectric constant of the surrounding medium $\varepsilon' = \infty$ and the convergence parameter $\alpha = 6\cdot4/L$ [18]. The real space portion of the Ewald

Table 1. Values of Lennard–Jones and electrostatic interaction potential parameters of the SPC/E model. *e* represents the magnitude of electronic charge.

Atom/ion	σ (Å)	ε (kJ/mol)	Charge (e)
O	3·169	0·6502	−0·8476
H	–	–	+0·4238

sum was evaluated by employing a spherical cut-off at $0.5\,L$. The temperature and pressure were monitored by using the weak coupling scheme of Berendsen *et al*[20] and, for integration over time, we adapted the leap-frog algorithm with a time step of 10^{-15} s (1 fs). In the starting configuration, the water molecules were located on a face-centred cubic lattice with random orientations. MD runs of 200–500 ps were used to equilibrate each system and each system was further run for 200–400 ps depending on the temperature for calculation of the various structural and dynamical quantities of interest.

3. Hydrogen-bond structure

Following previous work[12–14], we have used a geometric criterion where two water molecules are taken to be hydrogen-bonded if their interoxygen distance is less than $3.5\,\text{Å}$ and simultaneously the hydrogen–oxygen distance is less than $2.45\,\text{Å}$ and the oxygen–oxygen–hydrogen angle is less than $30°$. We note that the critical distances of $3.5\,\text{Å}$ and $2.45\,\text{Å}$ are essentially the positions of the first minimum in the oxygen–oxygen and oxygen–hydrogen radial distribution functions respectively. The angular criterion reflects the directional character of the hydrogen-bonds. The quantities of interest are the percentages f_n of water molecules that engage in n hydrogen-bonds and the average number of hydrogen-bonds per water molecule n_{HB}. The values of f_n ($n = 1,...,5$) and n_{HB} are included in table 2 for both the temperatures. Pure water is dominated by molecules that form four hydrogen-bonds. However, the fractions of molecules having two, three or five hydrogen-bonds are also significant, especially at the ambient temperature. At the supercooled temperature, the hydrogen-bond structure is found to be more perfect with about 65% of the water molecules participating in four hydrogen-bonds. Nevertheless, it is clear that there is a distribution of hydrogen-bond environment in liquid water and this varying environment can affect the dynamics of water molecules at microscopic level as shown in the next two sections. Of course, experimentally we observe quantities which are averaged over all possible hydrogen-bond environments.

4. Single particle dynamics: Self-diffusion and orientational relaxation

The translational motion of water molecules is usually analysed in terms of the velocity–velocity autocorrelation function, $C_v(t)$, defined by

$$C_v(t) = \frac{\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle}{\langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle},$$

(3)

Table 2. The percentage of water molecules having n number of hydrogen-bonds and the average number of hydrogen-bonds per water molecule at $T = 298$ K and $T = 258$ K.

T (K)	f_1	f_2	f_3	f_4	f_5	n_{HB}
298	1·2	9·6	33·2	49·5	6·2	3·50
258	0·5	5·0	24·8	63·0	6·7	3·70

where $\mathbf{v}_i(t)$ is the velocity of a molecule at time t and the average is carried out over all the molecules in the system and over the initial time. The translational self-diffusion coefficient D is related to the time integral of the velocity–velocity autocorrelation function (VAF) by

$$D = \frac{k_B T}{m} \int_0^\infty C_v(t)\,\mathrm{d}t, \tag{4}$$

where k_B is Boltzmann constant and m is the mass of a water molecule. In order to investigate the dependence of the translational motion on hydrogen-bond environment, we have calculated the quantity $C_v^{(n)}(t)$ which is the velocity–velocity autocorrelation function averaged over only those molecules which had n hydrogen-bonds at time $t = 0$. The corresponding diffusion coefficient $D^{(n)}$ is obtained by integrating $C_v^{(n)}(t)$. As discussed before, the index n characterizes the hydrogen-bonding state of a tagged molecule. We have calculated $C_v^{(n)}(t)$ and $D^{(n)}$ for $n = 1, 5$.

The effects of hydrogen-bond environment on the single particle orientational motion of water molecules is analysed by calculating the orientational time correlation function, $C_l^{(n)}(t)$, defined by

$$C_{l;\boldsymbol{a}}^{(n)}(t) = \frac{\langle P_l(e^{\boldsymbol{a}}(t) \cdot e^{\boldsymbol{a}}(0)) \rangle_n}{\langle P_l(e^{\boldsymbol{a}}(0) \cdot e^{\boldsymbol{a}}(0)) \rangle_n}, \tag{5}$$

where P_l is the Legendre polynomial of rank l and $e^{\boldsymbol{a}}$ is the unit vector which points along the $\boldsymbol{a}$-axis in the molecular frame and $\langle ... \rangle_n$ denotes an average over of those molecules which had n hydrogen-bonds at time $t = 0$. We have calculated the time dependence of $C_{l;\boldsymbol{a}}^{(n)}(t)$ for $l = 1, 2$, $n = 1, 5$ and for three different $e^{\boldsymbol{a}}$, the molecular dipole vector $\boldsymbol{m}$ the H–H vector and the O–H vector. Experimentally, the orientational relaxation of the H–H and O–H vectors averaged over all possible hydrogen-bond environments can be measured by ^{1}H–^{1}H and ^{1}H–^{17}O dipolar relaxation NMR experiments, respectively, which yield the Fourier transform of a correlation function[21–25]. Theoretically, it has been shown that, at short times, the decay of $C_{l;\boldsymbol{a}}^{(n)}(t)$ is generally non-exponential because of inertial and non-Markovian effects[26,27]. At long times, when these effects are not important and the relaxation is diffusional, $C_{l;\boldsymbol{a}}^{(n)}(t)$ decays exponentially. The orientational correlation time, $\boldsymbol{t}_{l;\boldsymbol{a}}^{(n)}$, is defined as the time integral of the orientational correlation function

$$\boldsymbol{t}_{l;\boldsymbol{a}}^{(n)} = \int_0^\infty \mathrm{d}t\, C_{l;\boldsymbol{a}}^{(n)}(t). \tag{6}$$

In the present study we have calculated $\boldsymbol{t}_{l;\boldsymbol{a}}^{(n)}$ by explicit integration of the data of $C_{l;\boldsymbol{a}}^{(n)}(t)$ obtained from simulations and by calculating the integral for the tail from the fitted exponential functions.

In figure 1, we have shown the time dependence of $C_v^{(n)}(t)$ and $C_{1;\boldsymbol{m}}^{(n)}(t)$ for $n = 2, 5$ and for $T = 298$ and 258 K. It is found that, up to $n = 4$, the caging effect in the velocity relaxation increases with increase of the number of hydrogen-bonds. The extent of
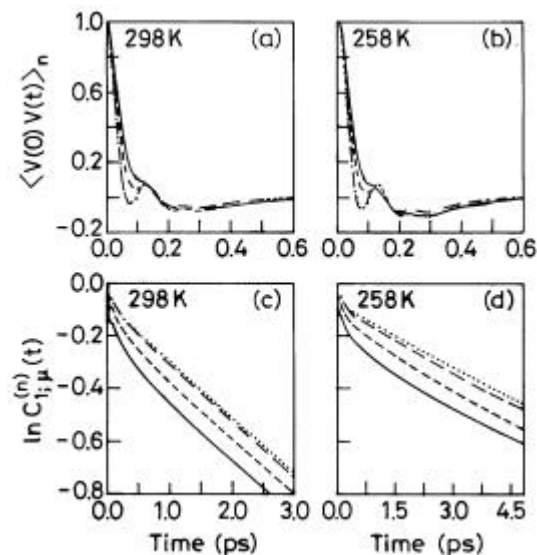
Figure 1. Time dependence of single-particle velocity autocorrelation and dipole orientational correlation functions. The solid, short-dashed, dotted and long-dashed curves correspond to the hydrogen-bonding states, $n = 2, 3, 4$ and 5 respectively.

caging is found to be maximum for $n = 4$. The decay profiles of $C_{1;\boldsymbol{m}}^{(n)}(t)$ show that the orientational relaxation occurs at the slowest rate for $n = 4$. The other orientational correlation functions also show similar behaviour with respect to variations of temperature and hydrogen-bond environment and, therefore, are not shown in the figure. However, for the rotation of O–H and H–H vectors, the rates of relaxation for $n = 4$ and $n = 5$ are found to essentially the same. The differences between the rates of both translational and rotational relaxation for different hydrogen-bond environments are found to be more prominent at the supercooled temperature. The values of the diffusion coefficients and orientational relaxation times are included in table 3. The rotational relaxation times of O–H and H–H vectors are also included in this table. It is interesting to note that a water molecule with five hydrogen-bonds moves at a faster rate than one with four hydrogen-bonds. We note that at least one hydrogen-bond has to be broken for a hydrogen-bonded water molecule to translate or rotate. A water molecule with four hydrogen-bonds is in the most stable configuration. Whereas, five-hydrogen-bonded water molecule participates in two bifurcated hydrogen-bonds through one of its hydrogen atoms [10]. These bifurcated hydrogen-bonds, being of higher energy than the regular hydrogen-bonds, are easier to break. The presence of these bifurcated hydrogen-bonds leads to an enhanced diffusional and rotational mobility of five-hydrogen-bonded water molecules compared to those with four hydrogen-bonds.

5. Pair dynamics: Relative diffusion and hydrogen-bond relaxation

We define $C_{v;12}^{(m,n)}(t)$ as the time correlation function of relative velocity of two initially hydrogen-bonded water molecules with one molecule having m and the other having n hydrogen-bonds with their nearest neighbours,

Table 3. Self-diffusion coefficient and orientational relaxation times of water molecules with n hydrogen-bonds. Diffusion coefficient and relaxation times are expressed in units of 10^{-5} cm^2 s^{-1} and ps respectively.

T (K)	n	$D^{(n)}$	$t_{1;m}^{(n)}$	$m_{2;m}^{(n)}$	$t_{1;OH}^{(n)}$	$t_{2;OH}^{(n)}$	$t_{1;HH}^{(n)}$	$t_{2;HH}^{(n)}$
298	1	5·05	2·90	0·85	2·10	0·70	1·75	0·70
	2	4·20	3·10	0·95	2·70	1·00	2·50	1·00
	3	3·05	3·48	1·20	3·40	1·35	3·35	1·45
	4	2·10	4·00	1·45	4·15	1·72	4·25	1·90
	5	2·25	3·88	1·40	4·14	1·70	4·23	1·90
	Average	2·65	3·70	1·30	3·72	1·50	3·74	1·64
258	1	2·40	8·12	2·52	5·64	2·00	4·70	1·90
	2	1·85	8·40	2·80	7·35	2·80	6·80	2·54
	3	1·20	9·30	3·30	9·30	3·80	9·20	3·85
	4	0·64	11·30	4·30	11·95	5·00	12·20	5·30
	5	0·82	10·80	4·00	11·85	4·80	12·18	5·30
	Average	0·86	10·60	3·95	11·00	4·55	11·15	4·78

$$C_{v;12}^{(m,n)}(t) = \langle v_{12}(t)v_{12}(0)\rangle_{m,n} / \langle v_{12}(0)^2\rangle_{m,n}, \tag{7}$$

where $v_{12}(t)$ is the relative velocity of two water molecules at time t which were hydrogen-bonded at time $t = 0$ and $\langle ...\rangle_{m,n}$ means the average is carried out over those pairs where one molecule participated in m hydrogen-bonds and the other participated in n hydrogen-bonds with their neighbours at time $t = 0$. The indices m and n characterize the hydrogen-bonding state of the tagged pair. It may be noted that, for a given hydrogen-bond environment, the correlation function of the relative velocity can be decomposed into two parts: The autocorrelation of single particle velocity and the cross correlation of velocities of two particles. The cross part determines the momentum transfer between neighbouring molecules[28–32]. The relative diffusion coefficient of two initially hydrogen-bonded water molecules with a given hydrogen-bond environment is defined as the time integral of the corresponding relative velocity correlation function,

$$D_{12}^{(m,n)} = \frac{k_B T}{M} \int_0^\infty C_{v;12}^{(m,n)}(t), \tag{8}$$

where M is the reduced mass of the water pair. We note that, in the absence of any cross velocity correlation, $D_{12}^{(m,n)} = D^{(m)} + D^{(n)}$, where $D^{(m)}$ is the self-diffusion coefficient of water molecules with m hydrogen-bonds as defined before. In figure 2, we have shown the time dependence of $C_{v;12}^{(m,n)}(t)$ at both temperatures for different hydrogen-bond environments. The values of the relative diffusion coefficients are included in table 4. Here again it is found that the caging effect in the relaxation of relative velocity increases with increase in the number of hydrogen-bonds till $m, n = 4$. The relative diffusion coefficient shows a minimum for $m, n = 4$ indicating the presence of a large cross correlation between the velocities of two hydrogen-bonded

molecules when both have four hydrogen-bonds. The relative diffusion coefficient increases when one or both the molecules have five hydrogen-bonds which can again be attributed to the presence of higher energy bifurcated hydrogen-bonds in such environments.

We note that the relative diffusion coefficient as defined by the integral of (8) is different from the so-called mutual diffusion coefficient[33]. In the literature, the mutual diffusion coefficient is traditionally defined only for multi-component systems through an integral of the collective velocity variables[34–37]. Its definition also includes a thermodynamic factor and it describes the mutual diffusion of molecules of one species against those of another species in the mixture. The mutual diffusion coefficient, as defined earlier[34–37], vanishes for a one-component liquid. In the present work, the integral of (8) is a microscopic quantity which describes how fast a pair of initially hydrogen-bonded water molecules diffuse away from each other and hence we call it the relative diffusion coefficient. A similar definition of the relative diffusion in a one-component Lennard–Jones fluid was used earlier[32].
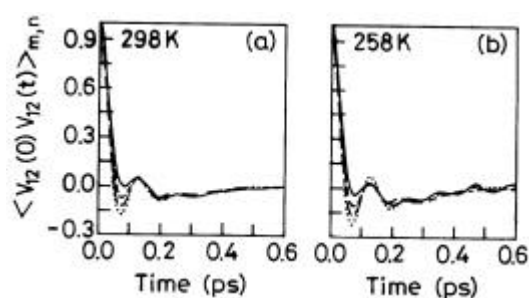

Figure 2. Time dependence of the correlation function of relative velocity of two water molecules which were hydrogen-bonded at time $t = 0$. The solid, short-dashed, dotted and long-dashed curves correspond to the hydrogen-bonding states of the water pair $(m, n) = (2,2)$, $(3,3)$, $(4,4)$ and $(5,5)$ respectively.

Table 4. Relative diffusion coefficient of a hydrogen-bonded water pair and structural relaxation time of a hydrogen-bond between two water molecules with one having m and the other having n hydrogen-bonds. The diffusion coefficient and the relaxation time are expressed in units of 10^{-5} cm^2 s^{-1} and ps respectively.

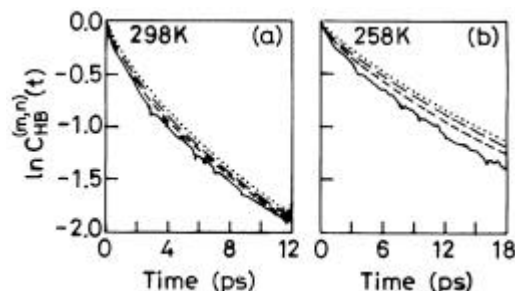| m	n	$D_{12}^{(m,n)}$ (298 K)	$D_{12}^{(m,n)}$ (258 K)	$t_{HB}^{(m,n)}$ (298 K)	$t_{HB}^{(m,n)}$ (258 K)
2	2	5·60	3·92	6·10	13·15
2	3	4·65	2·75	6·20	14·45
3	3	3·85	1·80	6·30	15·70
3	4	2·82	1·10	6·48	16·30
4	4	2·00	0·55	6·60	17·00
4	5	2·58	0·95	6·56	16·90
5	5	2·85	1·24	6·56	16·75
Average		3·00	1·08	6·55	16·70

Figure 3. Time dependence of hydrogen-bond correlation function. The different curves are as in figure 2.

The hydrogen-bond environmental effects on the pair dynamics of two hydrogen-bonded water molecules is also investigated by calculating the following hydrogen-bond correlation function

$$C_{HB}^{(m,n)}(t) = \langle h_{HB}(0) h_{HB}(t) \rangle_{m,n} / \langle h_{HB} \rangle_{m,n},$$ (9)

where $h_{HB}(t)$ is a time-dependent hydrogen-bond variable which is equal to 1 if a pair of water molecules is hydrogen-bonded at time t and zero otherwise and, as before, m and n describe the hydrogen-bonding state of the tagged water pair. The correlation function $C_{HB}^{(m,n)}(t)$ describes the probability that a hydrogen-bond is intact at time t, given it was intact at time zero with the bonding state (m, n). Thus, the dynamics of $C_{HB}^{(m,n)}(t)$ describes the structural relaxation of hydrogen-bonds[14,38–40] and the associated relaxation time $t_R^{(m,n)}$ can be interpreted as the time scale of reorganization of hydrogen-bonds in a particular hydrogen-bond environment in an aqueous medium. The time dependence of $C_{HB}^{(m,n)}(t)$ for the ambient and supercooled water is shown in figure 3 for varying hydrogen-bond environment and the values of the corresponding relaxation times $t_R^{(m,n)}$ are included in table 4. It is found that the rates of hydrogen-bond structural relaxation can depend significantly on the hydrogen-bond environment, especially in supercooled water. Again, the relaxation is found to occur at the slowest rate when each molecule of the tagged pair participates in four hydrogen-bonds. However, at room temperature, the rates of relaxation of $C_{HB}^{(m,n)}(t)$ for $(m, n) = (4,4)$, (4,5) and (5,5) are found to be essentially the same. At the supercooled temperature, however, noticeable difference is found in the rates of relaxation of these quantities with $C_{HB}^{(4,4)}(t)$ relaxing at the slowest rate. Overall, the effects of hydrogen-bond environment on the decay of $C_{HB}^{(m,n)}(t)$ is found to be weaker than that on single particle and relative diffusion coefficients.

6. Conclusion

We have presented molecular dynamics simulation results of the effects of hydrogen-bond environment on various single particle and pair dynamical quantities of liquid water. The water molecules are modelled by the so-called SPC/E model which is known to provide a good description of the structural, dielectric and dynamical properties of liquid water. The present simulations are carried out at two different

temperatures of 298 and 258 K and at a constant pressure of 0·1 MPa. The main goal of the present work has been to investigate how the hydrogen-bond environmental effects change as the liquid is cooled from room temperature to supercooled temperature. The present study reveals that hydrogen-bond environmental effects can be rather significant for various dynamical properties and these effects are enhanced in the supercooled state.

We have studied the environmental effects on single-particle dynamics by calculating the velocity–velocity autocorrelation function, self-diffusion coefficient and the orientational correlation functions for varying hydrogen-bonding state of tagged molecules. It is found that both translational and orientational relaxation occur at the slowest rate when tagged molecule participates in four hydrogen-bonds. The mobility of a water molecule is rather large when it participates in one or two hydrogen-bonds. A five-coordinated water molecule is also found to move at a faster rate than one with four hydrogen-bonds which can be attributed to the presence of higher energy bifurcated hydrogen-bonds in the former case.

The pair dynamical behaviour of water molecules is investigated by calculating the relaxation of the time correlation function of relative velocity of two hydrogen-bonded molecules and also by calculating the relaxation of a hydrogen-bond of the tagged pair in varying environments. The relative diffusion coefficient of a hydrogen-bonded pair, which is defined as the integral of the relative velocity correlation function, shows a minimum when each molecule of the tagged pair participates in four hydrogen-bonds. Significant cross correlation of molecular velocities is also found for this environment. Again, the relative diffusion coefficient is found to increase when one or both molecules of the tagged pair are involved in five hydrogen-bonds. The rate of hydrogen-bond relaxation also shows a similar trend on variation of the hydrogen-bond environment of the tagged pair, although the effect is found to be weaker than that on single particle and relative diffusion coefficients.

The relative differences between the rates of both single particle and pair relaxation for different hydrogen-bond environments are found to be more prominent at the super-cooled temperature. This is, at least partially, a statistical effect which arises due to the narrower distribution of hydrogen-bond environment at supercooled temperatures.

Acknowledgement

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