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Relative diffusion and memory effects in supercooled water

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The relative motion of tagged pairs of water molecules, which are in a given state of the pair configuration space at the initial time, is followed along simulated trajectories in the supercooled liquid. The initial state selects particles of the first coordination shell with specific relative orientations. This allows one to study the effects produced by the local orientational order on the translational dynamics. The states of the first coordination shell, indicated as transition states (TS) in the structural study, show higher mobility than the hydrogen bonded (HB) ones. The memory of the initial state results completely last only after 20 ps. In the first 10 ps the memory effects produce an increasing difference between the mean square displacements of pairs originally tagged as TS and HB pairs. Between 10 and 20 ps, the relative motions relax toward the normal diffusion regime along trajectories with a fractal dimension higher and lower than 2 for TS and HB pairs, respectively. This fact and the evaluation of the average lifetime of H bonds suggest that the time length of the anomalous diffusion regime and the memory time are determined by the dynamics of the hydrogen bond network rearrangements. Our approach can be relevant to understand the interplay between structure and dynamics in orientationally disordered media and, particularly, to interpret the results of recent studies on protein hydration water and confined water. [S1063-651X(98)50105-5]

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Recently, we have performed the division of the angular space of the water dimer by considering the set of eulerian angles $\omega=\{\theta,\Psi,\Phi\}$ in the local reference frame [1,2] [see Fig. 1(a)]. The total angular space $\Omega=\{\omega_1,\omega_2\}$ of a pair is divided in subspaces Ω^Γ which collect a set of distorted dimer geometries; each set is referred to as a configuration state Γ (or simply configuration or state). Such states are particularly suitable for describing the structural properties. From the study of the water structure, some dynamical implications were inferred. Here, we consider two configurations which should represent the extreme cases of dynamical behavior if the interpretation of the structural data was correct. They are the hydrogen-bond (HB) states and the transition states (TS) sketched in Fig. 1. In recent years, several studies have focused on the relation between structure and dynamics. It is established [3–5] that specific groups of particles, which include network defects, move faster than other ones. Further, the self-diffusions along the three principal axes of a local reference frame, defined by the molecular orientation at the initial time, are different [6–8]. Relative motions of selected pairs have been carefully investigated in monatomic liquids [9–11]. In molecular liquids, the investigations are complicated by the orientational correlations and the knowledge of the orientational pair distribution function, $g(\mathbf{r},\omega_1,\omega_2)$, is necessary to link structure and dynamics. By exploiting the partition in subspaces of the total angular space of a pair, we can write the main physical quantities concerning the translational motion as follows:

$$D_r^\Gamma(r_0,t)=R^2(r_0,\Omega^\Gamma;t)/12t=(\langle|\mathbf{r}_{12}(t)|^2\rangle_{0,\Gamma}-\langle|\mathbf{r}_{12}(0)|^2\rangle_{0,\Gamma})/12t, \tag{1}$$

$$\mathcal{D}_r^\Gamma(r_0,t)=\mathcal{R}^2(r_0,\Omega^\Gamma;t)/12t=\langle|\mathbf{r}_{12}(t)-\mathbf{r}_{12}(0)|^2\rangle_{0,\Gamma}/12t, \tag{2}$$

$$\begin{aligned}D_s^\Gamma(r_0,t)&=\langle|\mathbf{r}_1(t)-\mathbf{r}_1(0)|^2\rangle_{0\Gamma}/6t\\&=\mathcal{D}_r^\Gamma(r_0,t)+\langle[\mathbf{r}_2(t)-\mathbf{r}_1(0)]\\&\quad\times[\mathbf{r}_1(t)-\mathbf{r}_2(0)]\rangle_{0\Gamma}/6t,\end{aligned} \tag{3}$$

where $\mathbf{r}_{12}$ is the intermolecular center of mass separation vector and $\langle\rangle_{0,\Gamma}$ stands for averages over tagged pairs of molecules which at the time 0 are in a given portion of the configuration space characterized by the distance $\mathbf{r}_0=\mathbf{r}_{12}(0)$ and by orientations belonging to the subspace Ω^Γ. These expressions can be compared with the self-diffusion function $D_s(t)=\langle|\mathbf{r}_1(t)-\mathbf{r}_1(0)|^2\rangle/6t$, which asymptotically yields the self-diffusion coefficient D_s.

In monatomic fluids $R^2\ (r_0;t)$ depends on the radial part of the generalized time-dependent pair distribution function $G_2(\mathbf{r}_0,\mathbf{r}_t;t)$. This function is proportional to the joint probability of finding two particles separated by $\mathbf{r}_t$ at the time t if their separation was $\mathbf{r}_0$ at $t=0$. For molecular fluids, the role of $G_2(\mathbf{r}_0,\mathbf{r}_t;t)$ is played by $G_2(\mathbf{r}_0,\Omega^\Gamma,\mathbf{r}_t;t)$, which adds to the pair of molecules the constraint to belong to the configuration state Γ at $t=0$. By definition

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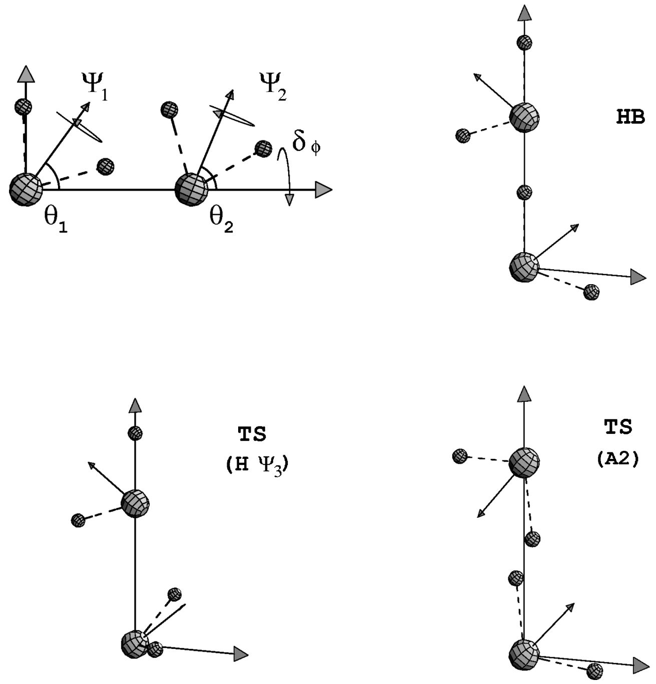

FIG. 1. (a) The eulerian angles $\omega=\{\theta,\Psi,\phi\}$ used to describe hydrogen and nonhydrogen-bonded pairs; $\delta_\phi=\phi_2-\phi_1$ stands for the dihedral angle between the plains of the two molecules. The other figures show sketches of the geometries HB and TS. The HB state is defined by $20°<\theta_1<80°$, $0°<\Psi_1<30°$, $0°<\theta_2<90°$, $0°<\Psi_2<180°$ and the transition states correspond to the configurations $H\Psi_3$ and A2 of Ref. [1] given by $20°<\theta_1<90°$, $60°<\Psi_1<90°$, $0°<\theta_2<90°$, $0°<\Psi_2<180°$ and by $0°<\theta_1<90°$, $65°<\Psi_1<90°$, $90°<\theta_2<180°$, $25°<\Psi_2<90°$, respectively. The dihedral angle δ_ϕ varies between 0° and 360° for all the configurations.

$$G_2(\mathbf{r}_0,\Omega^\Gamma,\mathbf{r}_t;t=0)=\rho g^\Gamma(r)\delta(\mathbf{r}_t-\mathbf{r}_0), \tag{4}$$

where ρ is the number density and $g^\Gamma(r)$ is the restricted average of $g(\mathbf{r},\omega_1,\omega_2)$ over the angular values of the configuration Γ. Therefore, Eqs. (1) and (2) give the required detailed description of the way in which the local structure influences the translational dynamics in molecular liquids.

Molecular dynamics runs were performed by exploiting the transferrable intermolecular potential with four points (TIP4P) potential [12] at constant number of particles, volume, and total energy (NVE) conditions and using a time step of 1 fs. The particle configurations were stored every 5 time steps in runs of 90 ps length. To avoid errors due to the periodic boundary conditions, the tagged pairs have been controlled to never escape from the box. The number of particles of the system has been varied from 256 to 500 and to 864; correspondingly, the half-box length varies from 9.88 to 12.4 and 14.8 Å. Each of them was chosen as the interaction cut-off length in the corresponding particle system. The conclusions we draw are the same when 500 and 864 particles are used. For the 256 particle system serious drift in the temperature of the system arose and the use of a thermal bath [13] was necessary. In this work only the 500 and 864 particle systems are considered. The temperature of the corresponding runs fluctuated within 251±6 K and 245±5 K, respectively.

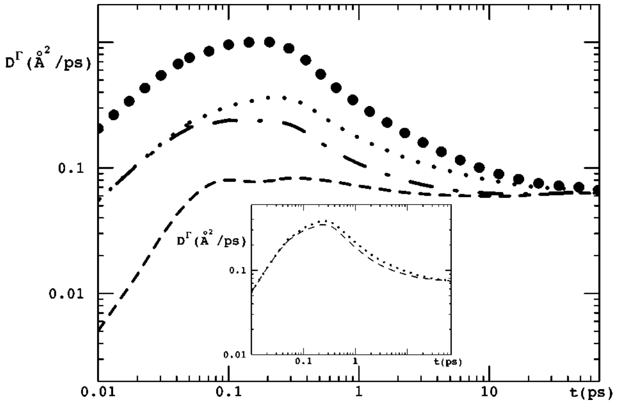

FIG. 2. Time dependent functions $D^\Gamma(r_0,t)$ of relative motions for TS and HB pairs: $D_r^{TS}(r_0,t)$ (large dots), $\mathcal{D}_r^{HB}(r_0,t)$ (small dots), $\mathcal{D}_r^{TS}(r_0,t)$ (-·-·-), and $D_r^{HB}(r_0,t)$ (— — —). The inset shows $D_s^{TS}(r_0,t)$ (· · · ·) and $D_s^{HB}(r_0,t)$ (— — —). The function $D_s(t)$ of the usual self-diffusion motion is not shown since it practically coincides with the $D_s^{HB}(r_0,t)$ one. All the curves refer to the 864 particle system at 245 K.

Figure 2 shows the time dependence of $\mathcal{D}_r^\Gamma(r_0,t)$ and $D_r^\Gamma(r_0,t)$ and the inset that of $D_s^\Gamma(r_0,t)$ for the 864 particle system. At the initial time, pairs of the first coordination shell ($r<3.5$ Å) with orientations belonging to the configurations HB and TS have been selected. As for local motions in simple molecular liquids [14], one can observe three main time domains: a dynamical domain at very short times ($t<0.03$ ps), an anomalous regime of diffusion (well evident at least up to 10 ps), and the constant trend of classical diffusion ($t>20$ ps). The inset shows that the self-diffusion motions coincide in the asymptotic trends ($t>20$ ps) and yield a self-diffusion coefficient $D_s=(0.71\pm0.01)10^{-5}$ cm^2/s, while $D_s=(1.02\pm0.02)10^{-5}$ cm^2/s was obtained for the 500 particle system at 251 K. These results are in fair agreement with previous simulations of TIP4P water [7]. In the anomalous region the molecules that are in the TS state at the initial time have higher mobility than those in the HB one. The difference increases when relative motions are considered and is very strong for $D_r^{HB}(r_0,t)$ and $D_r^{TS}(r_0,t)$. It is worth noting that all the relative motions tend to the asymptotic value of $D_r=(0.64\pm0.01)10^{-5}$ cm^2/s, about 20% smaller than D_s. This effect has been observed in dense monatomic liquids beyond a time of 1 ps [11] and is due to the distinct velocity correlation function which produces the momentum spread over more distant particles. In supercooled TIP4P water, the same mechanism is established beyond 20 ps and is due to the cross diffusion term of Eq. (3). As discussed later, this long delay is attributable to the average life time of the tetrahedral network. At short times, the mean square displacement is usually proportional to t^2, indicating a free flight motion over a small free space volume. Figure 2 shows that this is the case for all the diffusive curves with the exception of the radial motions of the HB pairs. This fact depends on the way in which the HB and TS molecules leave the first coordination shell and can be understood by analyzing the correlation function of the relative displacement. We plan to discuss the short time behavior elsewhere. Beyond 0.5 ps the anomalous region of diffusion is established. This region is characterized by a t^α dependence of the mean square displacement with $\alpha\neq(1$ or $2)$. The α exponent is related to the fractal

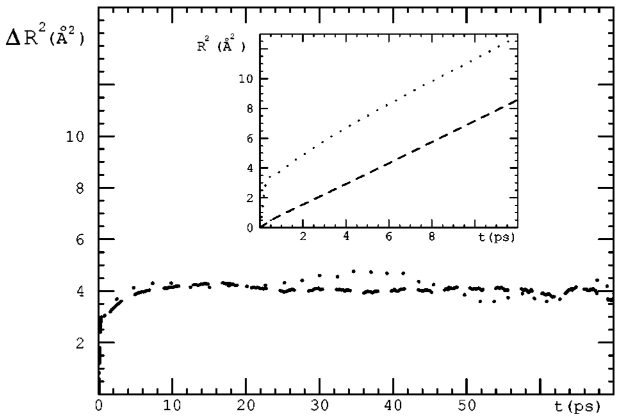

FIG. 3. Difference ΔR^2 between the mean square displacements $R^2\ (r_0,\Omega^{\Gamma};t)$ of pairs belonging to TS and HB states at the initial time: (···) refers to the 500 particle system at 251 K, (— — —) to the 864 particle system at 245 K. For this last one, the inset shows $R^2\ (r_0,\Omega^{\Gamma};t)$ for TS (···) and HB (— — —) pairs.

dimension d of the particle trajectories ($\alpha = d/2$). The results of Fig. 2 show that the relative mean square displacement has a fractal dimension very different for the trajectories of TS and HB pairs. In particular, the TS particles reaches the asymptotic classical diffusion ($\alpha = 1$) with a fractal dimension $d<2$ ($\alpha = 0.78 \pm 0.01$ in the 10–30 ps interval), while the HB ones with $d>2$ ($\alpha = 1.05 \pm 0.02$ in the same time interval). This is well visible in the negative and positive slopes of $D_r^{TS}(r_0,t)$ and $D_r^{HB}(r_0,t)$, respectively (Fig. 2). A similar behavior is found for mean square displacement of simple monatomic fluids at constant density versus temperature [15]. High temperature thermodynamic states produce particle trajectories that reach the asymptotic fractal dimension $d=2$ from above ($d>2$), the low temperature ones from below ($d<2$). This suggests that the TS pairs behave as structural ‘‘defects’’ of the tetrahedral network: they explore the free space between the network chains with high mobility and relax toward the bulk mobility when the network breaks and allows defects to be included in the network chains. In other words, the time necessary to experience the different types of bonding (such as the A, B, and C types of Ref. [16]) must elapse before a molecule assumes the usual Brownian motion. As shown by Ohmine and co-workers [16–18], the order of magnitude of this time interval is of tens of picoseconds. To further support this view, Fig. 3 shows the difference between Eq. (2) for the HB and TS pairs. As is seen, the TS pairs move faster than the HB ones in the first 10 ps, while beyond 20 ps the two species HB and TS show the same diffusion coefficient. This means that the memory of the initial configuration state is of about 20 ps; this time should relate to the time of the network rearrangements. Calculations of the lifetime gel, defined as the average time interval over which a spanning cluster restructures itself, have been performed for other models of water [19]. τ_{gel} results slightly smaller than the H-bond lifetime τ_H (about 7 and 9 ps, respectively, at 240 K). The calculation of the average HB lifetime for TIP4P water performed from the distribution $P(\tau)$ as in [19], but for our HB definition, yield the values of 10 and 12 ps at 251 and 245 K, respectively. Figure 2 shows that these results agree very well with the time at which the difference between $R^2(r_0,\Omega^{TS};t)$ and $R^2\ (r_0,\Omega^{HB};t)$ ceases to increase and the motions start the approach to the classical diffusion regime. Figures 2 and 3 lead one to conclude that the memory time τ_m, defined as the time at which the memory of any initial condition ceases, is about twice the time τ_{gel} (or τ_H) of the network rearrangement; that is, $\tau_m \simeq 20$ ps for supercooled TIP4P water around 245 K. This value agrees with the decay time of the heterogeneity topological index [20]; this decay is determined by the dynamics of the H-bond network rearrangements. In summary, we have shown that the relative motions of tagged pairs of molecules result in a useful tool to describe the relation between local structure and dynamics in supercooled water. The role of transition states, played by specific configurations and suggested by static structural studies [1,2], is confirmed by the dynamical behavior. Preliminary data show that the same results hold for other states that populate the first coordination shell (the $H\Theta^{(0)}$ states of Refs. [1,2]). Other configurations, which play the role of ‘‘bridge’’ states, have a dynamical behavior different from both HB and TS states. The memory of the initial state of water molecules persists for a very long time (about 20 ps). In simple liquids, a similar behavior was found in the self-diffusion of liquid CS_2 near the triple point [21,22] and is explained in terms of cage formation controlled by packing constraints [21–23]. Liquid water forms locally more and more open structures as the temperature decreases. The open network of H bonds, as opposed to the packing constraints of simple liquids, controls the diffusion process in water. The time length of the memory effects (τ_m) is about two times that of the HB network rearrangement (τ_{gel} or τ_H). Recent works [24,25] indicate that similar relaxation processes control the slow dynamics in water and in simple liquids, notwithstanding the very different physical constraints giving rise to the cage formation in the two systems.

Figure 2 shows that self- and relative mean square displacements of water molecules are both affected by memory effects. Memory effects in the self-diffusion of water have been observed by Lie and Clementi [26] in the Matsuoka Clementi, Yoshimine, and Lie room temperature water. They noted that differences in the self-diffusions of oxygens and hydrogens persist at the maximum observed time length (2 ps). For room temperature water, if $\tau_H = 4$ ps is assumed [19], a memory time $\tau_m \simeq 8$ ps is expected. Very recently, the translational dynamics in room temperature water has been investigated in the special system of protein hydration water [27]. It is found that the time length of the anomalous diffusion (i.e., the memory time) is of about 10 ps and seems to increase as both the distance from the protein surface and the hydration level decrease. Correspondingly, the exponent α of the time dependence t^{α} decreases. Our studies can explain the α decrease via an increase of the concentration of TS (non-H-bonded) configurations [28]; the increase of τ_m, by the fact that the dynamics of the HB network rearrangement is replaced by that of the protein as the molecules move nearer to the protein surface. This qualitative argumentation indicates that the study of the relative diffusion of tagged oriented pairs can help one to understand the interplay between local structure and dynamics in the hydration water as well as the role played by the protein surface in restructuring the bulk water. Similar conclusions can be drawn for systems of confined water, which was recently investigated [29].

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