



Translational and Rotational Diffusion in Stretched Water

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We perform molecular dynamics simulations using the extended simple point charge SPC/E water model in order to investigate the dynamical behavior of supercooled-stretched water. We focus on the behavior of the translational diffusion coefficient, the orientational relaxation time, and the local hydrogen bond network. Decreasing density or pressure along an isothermal path, there is a minimum in the diffusion coefficient and a maximum in the orientational relaxation time, suggesting an initial enhancement and subsequent breakdown of the tetrahedral structure and of the hydrogen bond network as the density decreases. The analysis of the tetrahedral structure of the nearest neighbors help to clarify the relationship between the local structural changes and the system dynamics. We also find that the product of diffusion coefficient and relaxation time is nearly constant, indicating that the anomalous behavior observed in the rotational and translational diffusion arise from the same microscopic mechanism.

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1 Introduction

Water is one of the most intriguing subjects of research from the physical, chemical or biological point of view. Due to the ubiquity and anomalous thermodynamic behavior of water, it has been studied for centuries, and even now unexpected phenomena continue to be discovered [1].

Ordinary liquid water is highly locally ordered, with each molecule having almost exactly four tetrahedrally coordinated neighbors forming a connected random network of hydrogen bonds well above the percolation threshold. Despite possible expectations that water might behave like a stable network, the hydrogen bond network restructures itself in picosecond time scale. This indicates that the random tetrahedral network is not perfect, but contains some sort of structural defects, what it is supported by experiments. The local structure is sensitive to variable temperature or pressure, which can result in

modifications such as distortion of the hydrogen bond angles and distances, as well as increase (or decrease) in the number of neighbors. These changes in local order have been shown to be intimately connected with the thermodynamic anomalies [2]. This is the case of the existence of a maximum in the density at 4°C, unusually high melting, boiling and critical points, existence of a minimum in the constant pressure heat capacity, among several others.

These local network defects are also important for the mobility of water. In contrast to conventional wisdom, the increase of local density (and therefore the increase in pressure) leads to increased mobility in ambient water, a result of weakening and possible destructions of hydrogen bonds that favor an open structure, as shown by experimental observations [3, 4] and simulations [5, 6, 7]. At sufficiently large pressure, steric constraints become significant and mobility decreases on increasing density, as in common liquids. As a result, along each isotherm, there is a maximum of the diffusion coefficient as a function of density.

If the pressure is decreased it appears an opposite behavior, and if we analyze the diffusion coefficient along isotherms, a minimum of the diffusion coefficient can be found at a given low density [8, 9]. As a consequence, a minimum in the rotational correlation time is also expected.

The behavior of water over a wide range of pressures and temperatures can be summarized in a coherent picture [7]. The region in the phase diagram in which *thermodynamic anomalies* occur is entirely inside the region of *kinetic* or *dynamical anomalies* which in its turn is contained in the region of *structural anomalies*. This picture suggests that all the anomalous behavior of water can be explained on basis of its structure. In this case, within the region of structural anomalies the orientational and translational order should be inter-dependent [7]. In order to check this hypothesis, here we study the behavior of the orientational relaxation and diffusion coefficient of stretched supercooled water. By comparing these two quantities, as well as by studying the local structure of water [10], such as revealed by the angular distribution of neighbors and hydrogen bonds, we will be able to understand how the structure affects the mobility.

2 Methods

We performed molecular dynamics simulations using 216 water molecules described by the extended simple point charge (SPC/E) model [11], in the canonical ensemble (NVT), in a cubic simulation box using periodic boundary conditions. The Berendsen method for rescaling the velocities was applied [12], the electrostatic interactions were calculated using the reaction field method [13] with cutoff of 0.79 nm. The equations of motion were solved using the SHAKE algorithm [14, 15] with time steps of 1.0 fs for $T > 210$ K and 2.0 fs for $T = 210$ K.

The diffusion coefficient D was calculated from the asymptotic slope of the time dependence of the mean square displacement. The orientational relaxation was analyzed using the rotational autocorrelation functions [14]:

$$C^{(i)}(\mathbf{e}) = \langle P_i[\mathbf{e}(t) \cdot \mathbf{e}(0)] \rangle \quad (1)$$

where \mathbf{e} is a chosen unity vector describing the orientation of the molecule and P_i is the i -th order Legendre Polynomial. We restrict ourselves to the analysis of the first two Legendre Polynomials, using two choices of reference vectors: (1) the dipole vector and (2) a vector perpendicular to the plane of the molecule. The correlation functions were fitted to a biexponential decay function [16]:

$$C = a_0 \exp(-bt^2/2) + a_I \exp(-t/\tau^I) + a_{II} \exp(-t/\tau^{II}) \quad (2)$$

but in the most of the cases taking only one exponential yielded a reasonable result, and thus only one relaxation time was determined.

In order to understand the effect of the structure on the mobility we also carried out a detailed analysis of the local structure of water [10]: the distribution of the hydrogen bond angle (O-H \cdots O) and the distribution of the angle between water molecules linked to a central water molecule (that is, the angle O \cdots O \cdots O).

3 Results

Our results are summarized in Table 1. The presence of a second relaxation time (the faster one) is found mainly (but not only) at the higher densities, in agreement with the interpretation that these modes are linked to a disturbance of a tetrahedral local structure [16]. Since the contribution of this faster relaxation time is almost negligible, we show only the slow relaxation times in the Table 1.

Table 1: Results of the simulations. $\tau_x^{(y)}$ means the orientational relaxation time obtained by exponential fit of the y -th order Legendre Polynomial correlation using the x -th vector (1 = dipole, 2 = perpendicular)

T (K)	ρ ($g \times cm^{-3}$)	Diffusion coefficient ($\times 10^{-5} cm^2 s^{-1}$)	$\tau_1^{(1)}$ (ps)	$\tau_1^{(2)}$ (ps)	$\tau_2^{(1)}$ (ps)	$\tau_2^{(2)}$ (ps)
280	0.875	1.281	9.19	2.30	5.99	1.87
280	0.900	1.261	9.46	2.44	6.27	1.87
280	0.925	1.234	9.12	2.29	6.04	1.83
260	0.875	0.531	23.47	9.47	15.65	4.91
260	0.900	0.527	22.16	8.77	14.51	4.60
260	0.925	0.500	26.93	11.83	18.09	6.52
250	0.875	0.298	47.69	22.55	31.08	19.68
250	0.900	0.295	43.89	21.09	31.47	19.08
250	0.950	0.281	38.73	18.47	25.55	15.96
240	0.875	0.130	95.89	44.28	63.39	40.19
240	0.900	0.105	118.7	57.27	81.28	54.92
240	0.925	0.122	103.82	49.41	68.56	29.27
240	0.950	0.149	75.37	36.21	51.92	27.48
240	0.975	0.1783	66.06	31.83	46.33	28.61
240	1.000	0.2095	56.63	25.77	39.74	22.84
240	1.125	0.2913	28.85	13.14	19.32	2.06
230	0.875	0.0601	239.8	114.0	161.8	103.1
230	0.900	0.0435	314.3	163.3	210.8	159.1
230	0.925	0.048	238.8	119.6	161.8	112.2
220	0.900	0.0114	623.9	383.7	401.1	379.6
220	0.925	0.00612	1207.8	655.9	761.6	647.0
210	0.875	0.00373	3582	961	2736	2959
210	0.925	0.00303	3441	2393	2458	2412

The diffusion coefficient, as illustrated in Figure 1, has a minimum at low densities [8]. If we take into account the results at high pressures [5], a sigmoidal behavior is clear. The lines of minima and maxima of the diffusion coefficient are the borderlines of the region of kinetic or dynamic anomalies, and it can be shown that the thermodynamic anomalies occur inside the region of dynamic anomalies [7, 8].

The minimum in the diffusion coefficient is located at a density similar to ice I_h . It is interesting also to analyze, whether the orientational relaxation has a similar dependence on density.

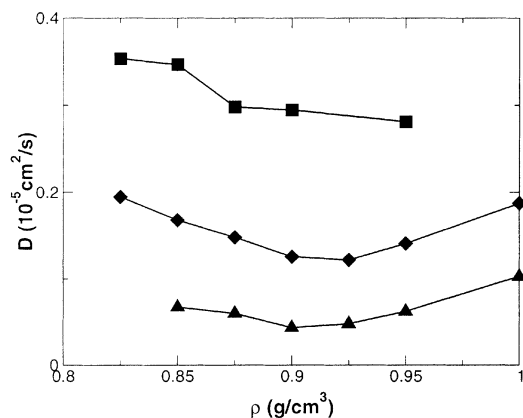


Fig 1. Diffusion Coefficient versus Density along isotherms: Detail of the minimum, from top to bottom $T = 250 \text{ K}$, 240 K and $T = 230 \text{ K}$

The analysis of the reorientational correlation times show peculiar aspects. First, we can look (see Table 1) at the values of the relaxation times for each chosen vector in order to see some trends. At high temperatures, the relaxation times using the first order Legendre polynomial has nearly three times the value of the corresponding second order Legendre polynomial. This ratio decays to about two or even less at lower temperatures. This, however, can be attributed to enhancement of the fluctuations at the supercooled region. According to the Debye rotational diffusion model, this ratio should be indeed three [17]. The agreement between our results and the theory is quite striking since that for the diffusion of the molecules in supercooled liquids, it is known that the rotational and translational diffusion can become uncorrelated if the probe molecules are of similar size as the solvent molecules [18].

The behavior of the relaxation times with the density, as can be seen in Table 1, was also analyzed for the several vectors using either first or second order Legendre polynomials. At high temperatures, $T = 280 \text{ K}$ and $T = 260 \text{ K}$, the relaxations times show no specific trend with the density. There is a small decrease at low densities, but this

decrease can be attributed to statistical fluctuations. At lower temperatures a maximum is observed at about the same density as the translational diffusion coefficients display their minima [8, 9]. This result shows that the enhancement of the water structure has both influence in the translational as well as in the rotational diffusion, as expected.

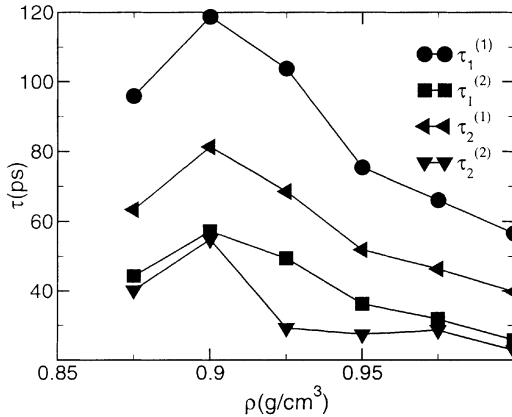


Fig 2. Relaxation times obtained from orientational correlation as discussed in the text, for simulations at $T = 240$ K and several densities

For studying the mobility of large molecules in a solvent made of small particles, hydrodynamic arguments are valid. In that case, the product of diffusion coefficient and orientational relaxation time is a constant, independent of density, viscosity and temperature [17]. For studying the mobility of water in its own solution, neither the continuous description of the solvent nor modeling the water molecule as compact object are appropriated, so the hydrodynamic description is expected not to be valid. Nevertheless, the similarity between the results for diffusion coefficient and relaxation times seems to indicate that these two quantities are related. Therefore we computed the product of $D \times \tau$. For all simulations (see Figure 3) this product remains almost constant.

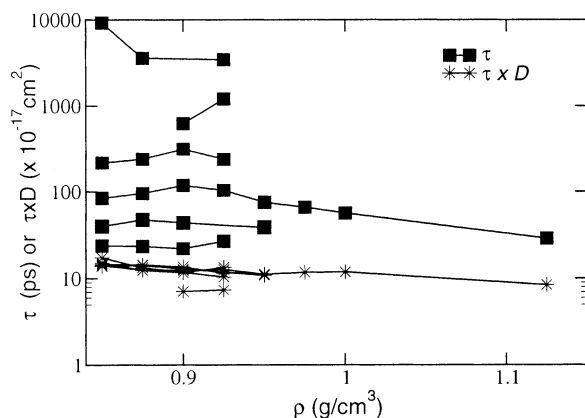


Fig. 3 The product of diffusion coefficient and relaxation time is nearly constant, independent of the temperature and density

If the diffusing molecules were bigger than the solvent molecules, the hydrodynamic description would be valid. In this case, D and τ scale as T/η and η/T respectively and, therefore, the product $D \times \tau$ is constant. This is not the case for supercooled water where, even though the product is still a constant, there is a breakdown of the hydrodynamic description in the individual terms. We can explain, however, the relation between the translational and the rotational diffusion assuming that both motions are correlated by a common mechanism. Both anomalies in the translational and rotational diffusion are located inside the region of structural anomalies what seems to indicate that the structure controls the mobility. Even though we have no definitive proof of this statement, we have some clues. A detailed analysis of the local structure of water reveals the enhancement of the tetrahedrality at low temperatures and ice-like densities. This can be detected from the distribution of the hydrogen bond angle and the distribution of the angle between neighbors $O \cdots O \cdots O$ illustrated as a function of density for $T = 240$ K in Figures 4a,4b and as a function of temperature for density 0.925 g cm⁻³ in Figures 5a,5b.

The first clue comes from the $O \cdots O \cdots O$ angle distribution. At low densities, it is centered around the tetrahedral angle, (109.5°) confirming the enhancement of the ice-like structure. However, a small peak at angle 60° is found. This peak increases slightly with increasing densities until the density ($\rho_M = 1.125$ g/cm³) and it is related to the presence of a fifth neighbor molecule in the first coordination shell. At higher densities, a shoulder also appears around 90° , that may be related to the appearance of a 6th neighbor. Therefore, at very high densities, the $O \cdots O \cdots O$ distribution looks very different with strong distortions in the structure.

The second clue, comes from the hydrogen bond angle distribution. The effect of the density is negligible: at low densities all curves almost collapse in a single curve with only one peak at low angles, indicating a rigid structure. Only at high densities the distortions become strong.

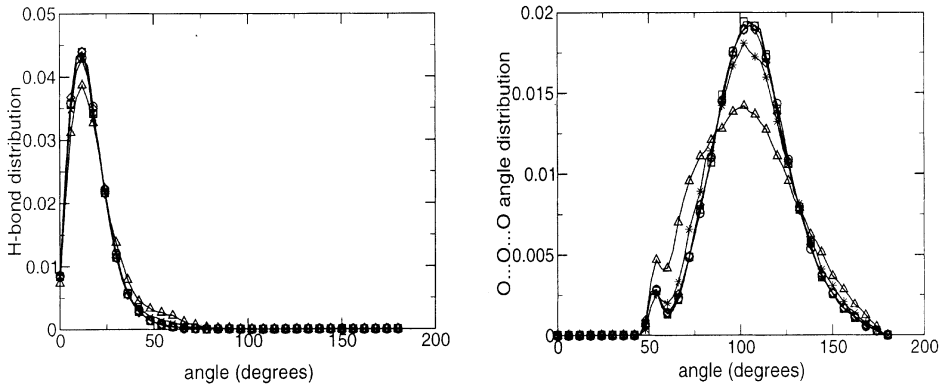


Fig. 4 (a) Hydrogen bond angle distribution and (b) neighbors $O \cdots O \cdots O$ angle distribution for several densities at the temperature $T = 240$ K. Shown are the results for $\rho = 0.875$ g cm⁻³ (O), 0.900 (□), 0.925 (◇), 1.000 (★) and 1.125 g cm⁻³ (△)

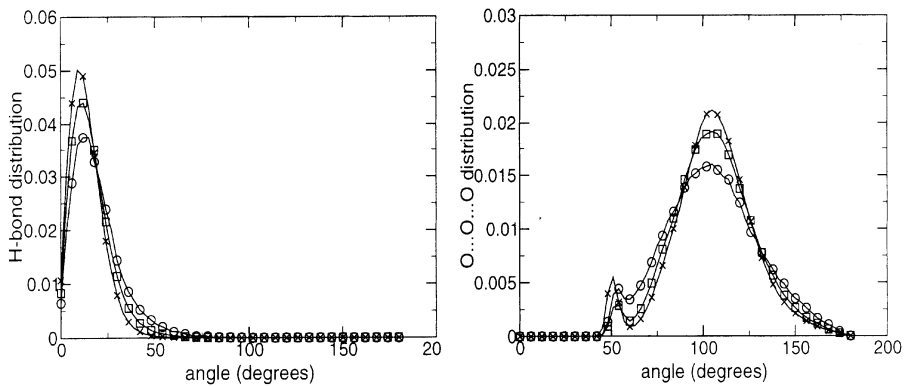


Fig. 5 The same as Fig. 4, but for several temperatures at fixed $\rho = 0.925$ g cm⁻³. Shown are the results for $T = 280$ K (O), $T = 240$ K (□) and $T = 210$ K (★)

As shown in Figure 5a, the increase of temperature leads to a broader hydrogen bond distribution, but peaked in the same value, indicating almost no distortion, apart from the

thermal fluctuation. Figure 5b illustrates the $O \cdots O \cdots O$ angle distribution. One can observe that the presence of interstitial water is not strongly affected by the temperature. The increase of temperature has, as only effect, a thermal broadening of the distribution.

4 Conclusions

We have studied the mobility of SPC/E water. In contrast with the behavior of a normal fluid, the diffusion coefficient of liquid water increases with the density in a broad range of thermodynamic conditions, and exhibits a minimum at the ice-like density and a maximum at ρ_M . In compass, the rotational diffusion times increase as the density is decreased and has a maximum at the ice-like density. Therefore, in this supercooled stretched region, the translational and rotational mobilities are not independent, but correlated. The product of $D \times \tau$ is a constant in the region of supercooled stretched water.

Since the hydrodynamic arguments are not valid for describing the mobility of water in its own medium, we look for another mechanism for this correlation between D and τ . The analysis of the $O \cdots O \cdots O$ and hydrogen bond angle distributions in the stretched region indicates that the increase in pressure disturbs the structure by inclusion of interstitial molecules but does not cause significative distortions in the H-bonds. This shows that the increase of the number of water molecules found in the first coordination shell and the fraction of water molecules with more than four intact H-bonds correlates with the increase of the mobility. This suggests that the structural defects are directly associated with the anomalous behavior of translational and rotational diffusion.

References

- [1] P. G. Debenedetti, *Metastable Liquids*, (Princeton University Press, Princeton NJ, 1996); O. Mishima and H. E. Stanley, *Nature* 396(1998)329; *Supercooled Liquids: Advances and Novel Applications*, ed. by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. A. Nelson (ACS Books, Washington DC, 1997)
- [2] M. Chaplin, *Water Structure and Behavior*, <http://www.sbu.ac.uk/water/>
- [3] J. Jonas, T. DeFrieas and D. J. Wilbur *J. Chem. Phys.* 65(1976)582.
- [4] F. X. Prielmeier, E. W. Lang, R. J. Speedy and H. -D. Lüdemann *Phys. Rev. Lett.* 59(1987)1128.
- [5] F. W. Starr, F. Sciortino, and H. E. Stanley, *Phys. Rev. E* 60(1999)6757; F. W. Starr, S. T. Harrington, F. Sciortino, and H. E. Stanley, *Phys. Rev. Lett.* 82(1999)3629; A. Scala, F. W. Starr, E. La Nave, F. Sciortino, and H. E. Stanley, *Nature* 406(2000)166.
- [6] K. Bagchi, S. Balasubramanian and M. L. Klein *J. Chem. Phys.* 107(1997)8561.

- [7] J. R. Errington and P. G. Debenedetti *Nature* 409(2001)318.
- [8] P. A. Netz, F. W. Starr, H. E. Stanley, and M. C. Barbosa, *J. Chem. Phys.* 115(2001)344.
- [9] P. A. Netz, F. W. Starr, H. E. Stanley, and M. C. Barbosa, *Dynamic Properties of Stretched Water*, *NATO Advanced Research Series of books (Kluwer)*.
- [10] T. Head-Gordon and F.H. Stillinger *J. Chem. Phys.* 98(1993)3313.
- [11] H.J.C. Berendsen, J.R. Grigera, and T.P. Straatsma. *J. Phys. Chem.* 91(1987)6269.
- [12] H.J.C. Berendsen, J.P.M. Postma, W.F.van Gunsteren, A. DiNola, and J.R. Haak. *J. Chem. Phys.* 81(1984)3684.
- [13] O. Steinhauser, *Mol. Phys.* 45(1982)335.
- [14] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids*, (Clarendon Press, Oxford, 1987).
- [15] J.P. Ryckaert, G. Ciccotti, and H.J.C. Berendsen. *J. Comp. Phys.* 23(1977)327.
- [16] Y-ling Yeh and C-Y. Mou, *J. Phys. Chem. B* 103(1999)3699.
- [17] S. Ravichandran, A. Perera, M. Moreau and B. Bagchi *J. Chem. Phys.* 107(1997)8469.
- [18] M. T. Cicerone and M.D. Ediger *J. Chem. Phys.* 104(1996)7210.