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Relation between structural and dynamical anomalies in supercooled water

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Abstract

We step toward the elucidation of the relation between the structural and dynamic anomalies in supercooled water. We present the results of molecular dynamics simulations of the extended simple point charge (SPC/E) model of water for the translational and rotational diffusion and for the number of neighbors and hydrogen bonds. We find that the product of diffusion coefficient and relaxation time is nearly constant. The coupling between the two mobilities is explained in the framework of the structural anomalies.

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1. Introduction

Water is the most common liquid in nature and it is also important in technological applications. Despite the simple structure of water molecules, this system exhibits a very peculiar thermodynamical behavior. It expands on freezing and, at a pressure of 1 atm, the density has a maximum at 4°C. Additionally, there is a minimum of the isothermal compressibility at 46°C and a minimum of the isobaric heat capacity at 35°C [1]. Even

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in extreme conditions, the behavior of water has interesting applications. There is a number of transport phenomena in plants that occurs at low temperature and pressure. Moreover, since water yields strong solvent effects in reactions, it is commonly used as a solvent in chemistry.

The thermodynamic anomalies are explained by structural peculiarities of water. They are linked to the local structure: water has strong and directional hydrogen bonds in such a way that it behaves as a transient gel [2,3]. Each water molecule acts as both a donor and an acceptor of bonds, generating a structure that is locally ordered, similar to that of ice, but maintaining the long-range disorder typical of liquids.

Almost three decades of computer simulations on water have broadened our knowledge about this unusual liquid. It is now possible to reproduce in a molecular dynamics simulation a wide range of properties of water. Thus, besides the thermodynamic properties, the dynamics of water was also explored [4–12]. The surprising result of these works is that water also exhibits an anomalous dynamical behavior. The increase of the applied pressure leads to an increase in water translational diffusion coefficient [13–16] that has a maximum at $\rho_{D\max}$. 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 $\rho_{D\min}$ [12,17]. The rotational diffusion exhibits a complementary behavior to the translational diffusion [17,18].

Unlike the thermodynamic properties, the anomalous behavior of the mobility is still not well understood. Recently, it was proposed that the structural anomalous region is bounded at low densities by the maximum of the tetrahedrality and, at high densities by the minimum of the translational order [11]. Many experiments indicate that the random tetrahedral network cannot be perfect, but must contain some sort of structural defects associated with the region of maximum diffusivity [19]. The importance of such network defects for the mobility of water molecules has been supported by simulations [20], however the association between $\rho_{D\max}$ and the number of defects needs to be explored. Moreover, it is not also clear how the number of intact hydrogen bonds is related with $\rho_{D\min}$.

In this paper, we attempt to gain a quantitative understanding of the relationship between the anomalous behavior observed in the kinetics and the underlying structural properties. Our main hypothesis, based on experimental observations and simulations, is that the anomalies in the mobility have their origin in two structural properties: the distribution of the number of hydrogen bonds and the percentage of molecules with a certain number of neighbors. In order to check our assumption, using molecular dynamics we investigate how these quantities change with density and temperature in the region where the anomalies in the dynamics appear. Based on these result, we establish a relationship between the behavior of these distributions and the diffusivity. Moreover, within this framework we can explain the coupling between the rotational and translational diffusion, also observed in our simulations.

The remainder of this manuscript goes as follows. In Section 2 the method is explained in detail and in Section 3 we present our results and conclusions.

2. Methods

We performed an extensive set of molecular dynamics simulations using 216 SPC/E [21] water molecules, integrated using SHAKE [22,23], in the canonical ensemble (NVT). The rescaling of the velocities was made using the Berendsen thermostat [24], the electrostatic interactions were calculated using reaction field [25] with cut-off radius of 0.79 nm.

The orientational relaxation was analyzed using the rotational autocorrelation function [22]:

$$C(\mathbf{e}) = \langle \mathbf{e}(t) \cdot \mathbf{e}(0) \rangle \quad (1)$$

using an exponential decay fit function. The vector \mathbf{e} is a chosen unity vector describing the orientation of the dipole.

In order to understand the effect of the structure on the dynamics we also carried out a detailed analysis of the distribution of the number of H-bonds and distribution of the number of first neighbor molecules. Complementary to the analysis of the number distribution of neighbors and hydrogen bonds, the angle distribution of these quantities was also computed, and was discussed elsewhere [18]. The number of first neighbors is calculated by computing all molecules whose distance from a given molecule is less than 0.32 nm. This distance represents the first minimum in the oxygen–oxygen radial distribution function $g_{OO}(r)$ at moderate and low densities. In order to have a better comparison, the same O–O distance criterion is also applied for all state points, irrespective of the density.¹

The distribution of the number of hydrogen bonds is computed in a similar way. A hydrogen bond between two water molecules is counted if, besides the O–O, also a non-bonded H...O distance criterion is obeyed, i.e., the H...O distance should be less than 0.25 nm. This is similar to the geometrical definition of the hydrogen bonds [26] but modified in the sense that no restriction about hydrogen bond angle was applied.

3. Results and conclusions

The behavior of the translational diffusion at the isotherm $T = 240$ K is illustrated in Fig. 1. For high densities ($\rho > \rho_{D_{\max}} \approx 1.1 \text{ g cm}^{-3}$), water behaves as a normal liquid and the decrease of translational diffusion coefficient, D , with increasing pressure is governed by steric effects. For $\rho < \rho_{D_{\max}}$, as the density is decreased, unlike other liquids, the mobility in water decreases. Further stretching, at $\rho < \rho_{D_{\min}}$, destabilizes the hydrogen bond network, leading to an increase in mobility. The interplay between these three different factors leads to a maximum in the diffusion constant D at $\rho_{D_{\max}}$ and a minimum at $\rho_{D_{\min}}$. In compass, the rotational diffusion time, also shown in Fig. 1, increases as the density is decreased and has a maximum at the ice-like

¹ Despite that for high density systems this O–O distance no longer corresponds to a minimum in the $g_{OO}(r)$. In this high densities the presence of non-tetrahedrally coordinated neighbors leads indeed to a deformation in the $g_{OO}(r)$, with the first minimum displaced to 0.40 nm.

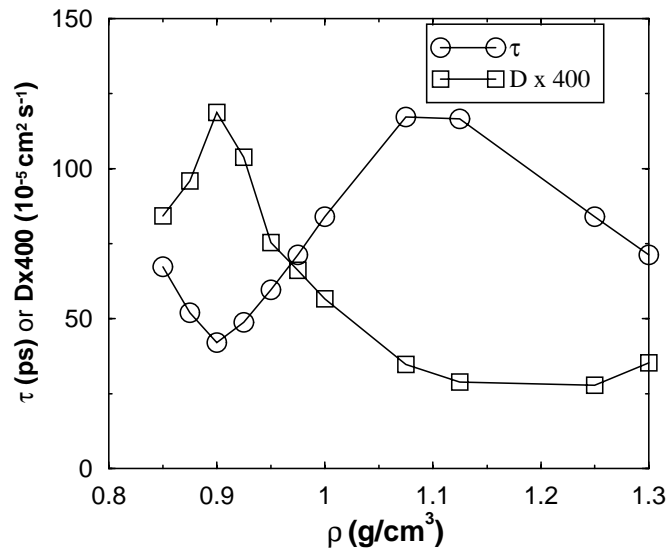


Fig. 1. Diffusion coefficient (circles) and rotational time (squares) versus density along the isotherm $T = 240$ K. In order to have the two graphs in the same plot, the diffusion coefficient was multiplied by a factor of 400.

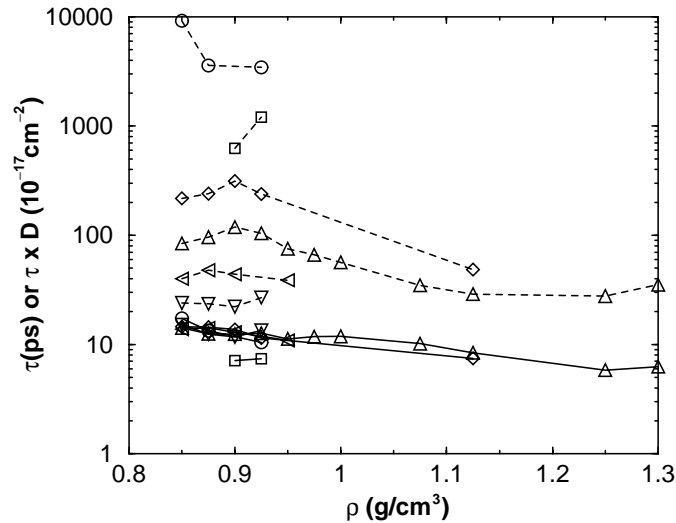


Fig. 2. The relaxation time for different temperatures (dashed lines) and the product of diffusion coefficient and relaxation time (solid lines). In this scale the product is nearly constant, independent of the temperature and density.

density, ρ_{Dmin} . Therefore, in the range of densities where the mobility is anomalous, $\rho_{Dmin} < \rho < \rho_{Dmax}$, the translational and rotational mobilities are not independent, but correlated. The product of $D \times \tau$, shown for various temperatures in Fig. 2, is nearly constant showing only a small decrease with increasing density, but no dependence on temperature, for the range $\rho_{Dmin} < \rho < \rho_{Dmax}$.

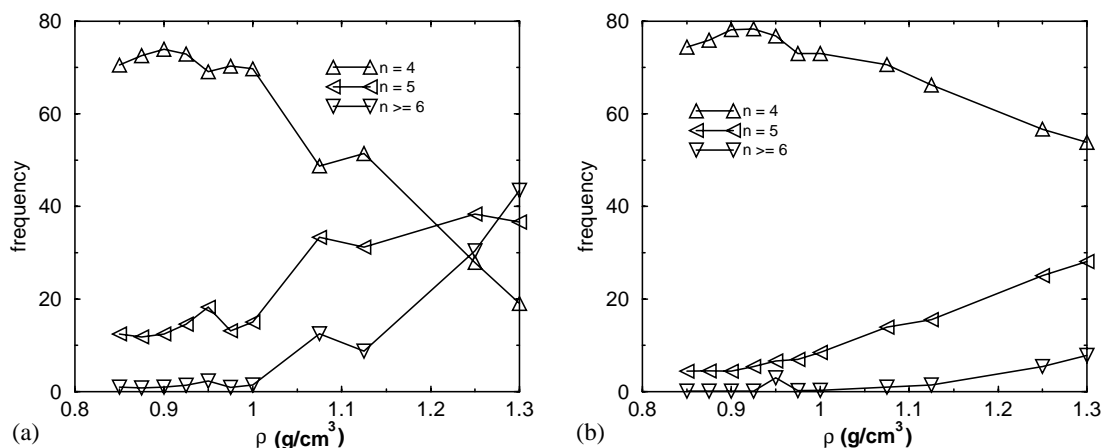


Fig. 3. (a) Fraction of molecules with n neighbors and (b) fraction of molecules with n hydrogen bonds, both calculated within a distance r_{\min} versus density for $T = 240$ K.

The diffusivity of a large particle in a solvent made of small particles can be described in the framework of hydrodynamic arguments. In that case, the product of diffusion coefficient and orientational relaxation time is a constant, independent of density, viscosity and temperature [27]. 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.

We propose that the anomalous behavior in the mobility and the correlation between the translational and rotational diffusion can be rationalized on the basis of two structural properties: the distribution of the number of hydrogen bonds and of the number of neighbors. In order to check our hypothesis, we calculate these two quantities for wide range of temperatures and densities. We show in Table 1 the fraction of molecules with n neighbors within the same distance $r=r_{\min}$ for different temperatures and densities. In Fig. 3 we show the behavior of the isotherm $T=240$ K for the neighbors and hydrogen bond distributions. All the temperatures exhibit almost the same trend. The number of molecules with four neighbors has a maximum at $\rho_{D\min} \approx 0.9 \text{ g cm}^{-3}$ and decreases as the density is increased. On its expenses, the higher coordinated molecules, particularly with five and six neighbors, increase their number. At $\rho_{D\max} \approx 1.1 \text{ g cm}^{-3}$, the sum of molecules with five and six neighbors overcomes the number with four. Fig. 3 shows the number of intact hydrogen bonds is not strongly affected by the change in density.

How are these structural properties related to the dynamic anomalies? The increase of the number of molecules with higher coordination number indicates that imperfections in the tetrahedral network are formed in the density range from $\rho_{D\min}$ to $\rho_{D\max}$. The number of hydrogen bonds do not alter significantly, therefore these imperfections arise from inclusion of extra molecules that will share an hydrogen bond with another one and not from the formation of an extra hydrogen bond. As a result, the bond is weakened. The molecule is then free to move. The shared bond breaks and the molecule by means of a small rotation connects to another molecule enabling the translational

Table 1
Results of the simulations. Distribution of the number of H bonds and neighbors

T	ρ	n_{HB}						n_{neighb}					
		≤ 1	2	3	4	5	≥ 6	≤ 1	2	3	4	5	≥ 6
280	0.850	0.43	6.15	28.06	58.17	6.66	0.46	0.15	3.78	22.38	56.55	15.05	2.55
280	0.875	0.46	5.84	27.26	58.26	7.69	0.49	0.17	3.47	21.20	56.20	16.68	2.28
280	0.900	0.51	4.62	24.64	62.21	7.68	0.34	0.14	2.60	17.84	58.03	19.14	2.25
280	0.925	0.36	4.76	24.20	61.28	8.86	0.53	0.13	2.46	17.31	56.42	20.35	0.31
280	1.125	0.22	3.13	19.59	56.35	18.01	2.69	0.03	1.31	10.53	44.10	32.41	11.62
260	0.850	0.33	4.48	23.97	65.14	5.87	0.21	0.10	3.05	18.93	62.39	14.21	1.32
260	0.875	0.34	3.49	22.55	67.23	6.18	0.21	0.14	1.98	17.74	63.76	14.85	1.54
260	0.900	0.26	3.65	20.41	68.87	6.62	0.20	0.10	2.03	15.35	63.95	16.60	1.97
260	0.925	0.18	2.89	18.89	70.16	7.52	3.62	0.04	1.38	13.54	64.66	18.21	2.16
260	1.125	0.19	2.30	17.61	60.33	17.20	2.37	0.02	0.88	9.45	47.40	31.28	10.98
250	0.850	0.20	3.33	21.47	69.86	4.94	0.21	0.08	1.95	17.25	66.51	13.13	1.08
250	0.875	0.22	2.86	19.65	72.24	4.86	1.76	0.08	1.72	15.23	68.42	13.42	1.14
250	0.900	0.21	2.58	18.20	72.80	6.09	0.21	0.06	1.45	13.53	68.44	15.23	1.21
250	0.950	0.14	2.28	17.26	72.06	7.93	0.31	0.01	1.06	11.84	64.51	19.90	2.68
240	0.850	0.11	2.81	18.14	74.41	4.40	0.13	0.07	1.56	14.41	70.49	12.49	0.98
240	0.875	0.14	2.27	17.18	75.84	4.46	0.11	0.02	1.26	13.53	72.53	11.84	0.81
240	0.900	0.11	1.96	15.22	78.16	4.43	0.13	0.02	1.09	11.50	73.93	12.46	1.00
240	0.925	0.09	1.67	14.31	78.35	5.42	0.16	0.02	0.73	10.40	72.88	14.58	1.39
240	0.950	0.08	1.86	14.34	76.79	6.63	3.00	0.02	0.65	9.73	69.05	18.25	2.29
240	0.975	0.17	2.37	17.24	73.00	6.99	0.22	0.06	1.45	14.07	70.29	13.17	0.95
240	1.000	0.10	2.18	15.91	73.00	8.50	0.31	0.02	1.27	12.50	69.71	15.06	1.42
240	1.075	0.06	1.43	12.93	70.60	13.98	1.00	0.00	0.26	5.16	48.75	33.30	12.53
240	1.125	0.09	1.74	14.77	66.24	15.58	1.47	0.02	0.48	8.09	51.44	31.21	8.76
240	1.250	0.05	1.11	11.68	56.69	25.04	5.43	0.0	0.11	3.23	27.91	38.34	30.40
240	1.300	0.05	0.80	9.31	53.84	28.11	7.85	0.00	0.05	1.76	19.05	35.64	43.47
230	0.850	0.10	2.19	15.27	78.76	3.61	0.07	0.02	1.28	12.43	74.85	10.76	0.66
230	0.875	0.08	1.70	14.35	80.09	3.69	0.09	0.01	0.91	11.17	77.05	10.24	0.63
230	0.900	0.06	1.33	12.72	82.34	3.51	0.04	0.01	0.60	9.79	78.48	10.55	0.57
230	0.925	0.06	1.31	11.70	82.09	4.72	0.11	0.01	0.53	8.47	77.03	12.95	1.00
230	1.125	0.07	1.49	13.60	68.99	14.55	1.30	0.00	4.74	7.38	54.67	29.83	7.63
220	0.900	0.04	1.04	9.55	86.30	3.01	0.05	0.00	0.40	7.30	82.58	9.22	5.00
220	0.925	0.02	0.84	7.88	88.15	3.05	0.05	0.00	0.26	5.66	83.61	9.92	0.56
210	0.850	0.02	1.04	8.51	88.95	1.48	0.02	0.00	0.45	6.90	87.19	5.25	0.20
210	875	0.04	0.91	9.08	88.12	1.83	0.03	0.00	0.34	7.27	85.52	6.62	0.24
210	0.925	0.00	0.57	4.44	92.61	2.35	0.03	0.00	0.02	1.50	73.67	21.52	3.25

diffusion. Since the number of hydrogen bonds do not alter, the molecule has to rotate to keep all the bonds. The net motion of water structure consists of slow non-oscillatory or quasioscillatory translational and rotational displacements [28]. This slow dynamics couples the translation to the rotation of the molecule.

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