DYNAMIC PROPERTIES OF STRETCHED WATER

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Abstract.

We investigate the dynamics of the extended simple point charge (SPC/E) model of water in the supercooled region. The dynamics at negative pressures show a minimum in the diffusion constant D when the density is decreased at constant temperature, complementary to the known maximum of D at higher pressures. A similar trend in the rotational diffusion is also observed.

1. Introduction

The thermodynamic description of supercooled water has been a major topic of research already for many years. Most of this scientific effort has been concentrated in understanding the static anomalies present in this complex fluid. 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]. These anomalies are linked with the microscopic structure of liquid water, which can be regarded as a transient gel—a highly associated liquid with strongly directional hydrogen bonds [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.

Several scenarios have been proposed to explain these anomalies. In the " stability limit conjecture " [4, 5], the liquid spinodal line for water is reentrant. It has a minimum at negative pressures and passes back to positive P as the temperature decreases. The increasingly anomalous thermodynamic behavior of liquid water as it is cooled at positive pressures can be interpreted in terms of approaching this spinodal. The " critical point hypothesis " proposes a second critical point as the terminus of a phase coexistence between a high density and a low density liquids. The increase in the response functions is then interpreted as a signature of being in the vicinity of this critical region. The " singularity-free hypothesis " suggests that there is no divergence in the response functions. They grow but stay finite [3, 6, 7].

Recently, dynamic properties of water have gained attention both experimentally [8, 9] and in computer simulations [10–16]. 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 and to a faster rotational diffusion [8, 9, 17]. These effects can be understood as follows. The increase of pressure leads to an increase in the number of defects and in the presence of interstitial water. This disrupts the tetrahedral local structure, weakening the hydrogen bonds, and thus increasing the diffusion constant [15, 16]. A further increase in the pressure leads to steric effects which works in the direction of lowering the mobility. The interplay of these factors leads to a maximum in the diffusion constant [15, 16] at some high density $\rho_{\max}$. As a result, for each isotherm a maximum of the diffusion coefficient and a minimum in the rotational correlation time are found. However, the behavior at very low ρ is less well understood.

In this manuscript, we present our recent studies of how the dynamics of low-temperature water are affected by the decrease of the density [18]. We perform molecular dynamics (MD) simulations of the SPC/E model of water in the range 210 K $< T <$ 280 K and 0.825 g/cm^3 $< \rho <$ 0.95 g/cm^3. We calculate the rotational and translational diffusion coefficients in this region. A relationship between the behavior of the two coefficients is suggested.

2. Results

We performed molecular dynamics simulations using 216 water molecules described by the extended simple point charge (SPC/E) model [19], in the canonical ensemble (NVT), in a cubic simulation box using periodic bound-

ary conditions. The diffusion coefficient D was calculated using the slope of the linear regression of the mean square displacement versus time using a range of time long enough to assure that the molecules have reached a diffusional behavior. We show D along isotherms in Figure 1. For $T \leq 260$ K, D has a minimum value at $\rho \approx 0.9$ g/cm^3, which becomes more pronounced at lower T (Figure 1). This behavior can be understood considering the structural changes that occur with decreasing density. At low T, the decreased density enhances the local tetrahedral ordering, which leads to a decrease in D. Further decreases in density reduces the stability of the tetrahedral structure and causes an increase of D. The location of the minimum is near the ice Ih density ≈ 0.915 g/cm^3, which is the density where the perfect tetrahedral order occurs. The orientational relaxation was analyzed using the rotational autocorrelation functions [20, 21]:

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

where $\mathbf{e}$ is a chosen unity vector describing the orientation of the molecules and P_i is the i-th order Legendre Polynomial (we restrict ourselves only to the study of the first two correlations):

$$P_1(x) = x$$

$$P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$$

We choose three vectors to describe the orientation. The first vector is the unit vector with the same orientation as the dipole moment. The second corresponds to the O-H bond direction and the third is a vector perpendicular to the plane of the molecule.
The correlation functions were fitted to a biexponential decay function [21], and two relaxation times were calculated, corresponding to a slower (I) and a faster (II) mode.

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

For each correlation using a given vector, two times were calculated, leading to a rather complicated symbology. For example, the slower relaxation time for the second-order correlation using the third vector would be $\tau_3^{I,(2)}$. With few exceptions, however, we have found only one relaxation time, for correlation in a given vector, that is $\tau_y^{I,(x)} = \tau_y^{II,(x)}$. We obtain therefore six correlation times for each simulated point, $\tau_1^{(1)}$ and $\tau_1^{(2)}$ for the first orientation vector and similarly $\tau_2^{(1)}$, $\tau_2^{(2)}$, $\tau_3^{(1)}$ and $\tau_3^{(2)}$. At T =

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240 K where a detailed analysis was carried out, we find a maximum in the orientational time as illustrated in Figure 2.

3. Conclusions

We analyze the dynamic properties of supercooled water. For high densities ($\rho > \rho_{max}$), water behaves as a normal liquid and the decrease of translational diffusion coefficient, D, with increasing pressure is governed by steric effects. For $\rho_{min} < \rho < \rho_{max}$, as the pressure is decreased, the presence of defects and interstitial water decrease, the tetrahedral structure dominates, with stronger hydrogen bonds. This process reaches its maximum at $\rho = \rho_{min} \approx \rho_{ice}$. Further stretching destabilizes the hydrogen bond network, leading to an increase in mobility. Preliminary studies of the rotational diffusion show a maximum in the orientational time at low density region in compass with the behavior of D.

4. Acknowledgments

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5. Caption Figures

Figure 1:(a) Dependence of the diffusion constant D on ρ along isotherms (for $\rho \leq 1.0$ g/cm^3). Open symbols are from ref. [18], and filled symbols are from ref. [15]. The dotted line separates liquid state points from phase separated state points, but is *not* an indication of the exact $\rho_{sp}(T)$, which varies slightly with T. (b) Full ρ dependence of D, also showing the maxima.

Figure 2: Dependence of the rotational relaxations times $\tau_1 - \tau_6$ along $T = 240K$ isotherm as a function of density.