Slow Dynamics of Water under Pressure

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Abstract: We perform lengthy molecular dynamics simulations to investigate the dynamics of water under pressure at many temperatures and compare with experimental measurements. We calculate the isochrones of the diffusion constant $D$ and find, as observed experimentally, power-law behavior of $D$ as temperature approaches $T_c(P)$. We find that the dynamics are consistent with slowing down due to the transient caging of molecules, as described by the mode-coupling theory (MCT). This supports the hypothesis that the apparent divergences of dynamic quantities along the line $T_c(P)$ in water may be associated with "slowing down" as predicted by MCT.

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On supercooling water at atmospheric pressure, many thermodynamic and dynamic quantities show power-law growth [1]. This power-law behavior also appears under pressure, which allows measurement of the locus of apparent power-law singularities in water [Fig. 1(a)]. The possible explanations of this behavior have generated a great deal of interest. In particular, three scenarios have been considered: (i) the existence of a spinodal bounding the stability of the liquid in the superheated, stretched, and supercooled states [4]; (ii) the existence of a liquid-liquid transition line between two liquid phases differing in density [5–7]; (iii) a singularity-free scenario in which the thermodynamic anomalies are related to the presence of low-density and low-entropy structural heterogeneities [8]. Based on both experiments [3,9,10] and recent simulations [11], several authors have suggested that the power-law behavior of dynamic quantities might be explained by the transient caging of molecules by neighboring molecules, as described by the mode-coupling theory (MCT) [12]. This hypothesis implies that the dynamics of water are explainable in the same framework developed for other fragile liquids [13], at least for temperatures above the homogeneous nucleation temperature $T_H$. Moreover, this explanation of dynamic behavior on supercooling may be independent of the above scenarios suggested for thermodynamic behavior [Fig. 1(a)].

Here we focus on the behavior of the diffusion constant $D$ under pressure, which has been studied experimentally [3]. We perform molecular dynamics simulations in the temperature range 210–350 K for densities ranging from 0.95–1.40 g/cm$^3$ [14] using the extended simple point charge potential (SPC/E) [15]. We select the SPC/E potential because it has been previously shown to display power-law behavior of dynamic quantities, as observed in supercooled water at ambient pressure [11,19].

In Fig. 2, we compare the behavior of $D$ under pressure at several temperatures for our simulations and for the experiments of Ref. [3]. The anomalous increase in $D$ is qualitatively reproduced by SPC/E, but the quantitative increase of $D$ is significantly larger than that observed experimentally. This discrepancy may arise from the fact that the SPC/E potential is understructured relative to water [20], so applying pressure allows for more bond breaking and thus greater diffusivity than observed experimentally. That SPC/E is understructured relative to water is further supported by the fact that the anomalous $P$ dependence of $D$ persists to higher $T$ in water. We also find that the pressure where $D$ begins to decrease with pressure—normal behavior for a liquid—is larger than that observed experimentally. This simple comparison of $D$ leads us to expect that the qualitative dynamic features we observe in the SPC/E potential will aid in the understanding of the dynamics of water under pressure, but will likely not be quantitatively accurate.

We next determine the approximate form of the lines of constant $D$ (iscochrones) by interpolating our data over the region of the phase diagram studied [Fig. 1(b)] [21]. At each density studied, we fit $D$ to a power law $D \sim (T/T_c - 1) \gamma$. The shape of the locus of $T_c$ values compares well with experimental data [3] [Figs. 1(a) and 1(b)]. We find the striking feature that $\gamma$ decreases under pressure for the SPC/E model, while $\gamma$ increases experimentally (Fig. 3). This disagreement underscores the need to improve the dynamic properties of water models, most of which already provide an adequate account of static properties [22]. We next consider interpretation of our results using the idealized MCT, which has been used to quantitatively describe the weak supercooling regime [23]—i.e., the temperature range where the characteristic times become 3 or 4 orders of magnitude larger than those of the normal liquid [24]. The region where experimental data are available in supercooled water is exactly the region where MCT holds. MCT provides a theoretical framework in which the slowing down of the dynamics arises from caging effects, related to the coupling between density
modes, mainly over length scales on the order of the nearest-neighbor distance. In this respect, MCT does not require the presence of a thermodynamic instability to explain the power-law behavior of the characteristic times.

MCT predicts power-law behavior of $D$, and also that the Fourier transform of the density-density correlation function $F(q, t)$, typically referred to as the intermediate scattering function, decays via a two-step process. $F(q, t)$ can be measured by neutron scattering experiments and is calculated via

$$F(q, t) = \frac{1}{S(q)} \left( \sum_{j,k=1}^N e^{-i(q \cdot r_j(t) - q \cdot r_k(0))} \right), \tag{1}$$

where $S(q)$ is the structure factor [25]. In the first relaxation step, $F(q, t)$ approaches a plateau value $F_{\text{plateau}}(q)$; the decay from the plateau has the form $F_{\text{plateau}}(q) - F(q, t) \sim t^b$, where $b$ is known as the von Schweidler exponent. According to MCT, the value $b$ is completely determined by the value of $\gamma$ [26], so independent calculation of these exponents for SPC/E determines if MCT is consistent with our results.
The range of validity of the power law $t^b$ is strongly $q$ dependent [27], making unambiguous calculation of $b$ difficult. Fortunately, the same exponent $b$ controls the long-time behavior of $F(q,t)$ at large $q$. Indeed, MCT predicts that at long time, $F(q,t)$ decays according to a Kohlrausch-Williams-Watts stretched exponential

$$F(q,t) = A(q) \exp \left( -\frac{t}{\tau(q)}^{\beta(q)} \right),$$  

with $\lim_{q \to \infty} \beta(q) = b$ [28]. We show the $q$ dependence of $\beta$ for each density studied at $T = 210$ K [Fig. 4]. We also calculate $\beta$ for the “self-part” of $F(q,t)$, denoted $F_{\text{self}}(q,t)$ [29]. In addition, we show the expected value of $b$ according to MCT, using the values of $\gamma$ extrapolated from Fig. 3. The large-$q$ limit of $\beta$ appears to approach the value predicted by MCT [30]. Hence we conclude that the dynamic behavior of the SPC/E potential in the pressure range we study is consistent with slowing down as described by MCT [Fig. 5]. For comparison, we quote the values of the exponents for hard-sphere ($\gamma = 2.58$ and $b = 0.545$) and Lennard-Jones ($\gamma = 2.37$ and $b = 0.617$) systems [31]. It is interesting to note that in the case of SPC/E potential, a single system displays a large variation of $b$ (and $\gamma$) as a function of pressure. Such a large variation of exponent values is consistent with the significant changes in the local structure of the liquid—as evidenced by the pressure dependence of $S(q)$ [32].

A significant result of our analysis is the demonstration that MCT is able to rationalize the dynamic behavior of the SPC/E model of water at all pressures. In doing so, MCT encompasses the behavior both at low pressures, where the mobility is essentially controlled by the presence of strong energetic cages of hydrogen bonds, and at high pressures, where the dynamics are dominated by excluded volume effects and where the local structure of the liquid is very different from the four-coordinated tetrahedral network.

We believe that the analysis presented here for $D(P,T)$ should be repeated for other commonly used water potentials to clarify the origin of the difference in $P$ dependence of $\gamma$ observed for the SPC/E potential comparison with experiments. Also, new experiments on the $T$ dependence of $D$ of real water under pressure would be quite valuable.

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We simulate 216 water molecules interacting via the SHAKE algorithm [18] with a time step of 1 fs. The equations of motion evolve using a cutoff of 0.79 nm accounts for the long-range Coulomb interactions. We equilibrate all simulated state points to a constant correlation time makes time averaging more difficult. For hard spheres, see J. L. Barrat, W. Götze, and F. Sciortino, Mol. Phys. 81, 2409 (1997).

Additional details can be found in Ref. [11]. We confirm that the values of $\alpha$ and $\epsilon$ are consistent with the von Schweidler power law.

We noth that the locus of points where $-q_H dP/d\rho$ attains a maximum value.

In addition, the oxygen atoms of separate molecules which have an OH distance of 1.0 Å and HOH angle located at the atomic centers of the oxygen and hydrogen water as a rigid molecule consisting of three point charges located at the atomic centers of the oxygen and hydrogen which have an OH distance of 1.0 Å and HOH angle of 109.47°, the tetrahedral angle. Each hydrogen has a charge $q_H = 0.4238e$, where $e$ is the magnitude of the electron charge, and the oxygen has a charge $q_O = -2q_H$.