Molecular dynamics study of orientational cooperativity in water

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(Received 25 October 2005; published 10 April 2006)

Recent experiments on liquid water show collective dipole orientation fluctuations dramatically slower than expected (with relaxation time $>50$ ns) [D.P. Shelton, Phys. Rev. B 72, 020201(R) (2005)]. Molecular dynamics simulations of extended simple point charge (SPC/E) water show a large vortexlike structure of the dipole field at ambient conditions surviving over 300 ps [J. Higo et al., Proc. Natl. Acad. Sci. U.S.A. 98, 5961 (2001)]. Both results disagree with previous results on water dipoles in similar conditions, for which autocorrelation times are a few picoseconds. Motivated by these recent results, we study the water dipole reorientation using molecular dynamics simulations of the SPC/E model in bulk water for temperatures ranging from ambient 300 K down to the deep supercooled region of the phase diagram at 210 K. First, we calculate the dipole autocorrelation function and find that our simulations are well described by a stretched exponential decay, from which we calculate the orientational autocorrelation time $\tau_o$. Second, we define a second characteristic time, namely, the time required for the randomization of molecular dipole orientation, the self-dipole randomization time $\tau_r$, which is an upper limit on $\tau_o$; we find that $\tau_r \approx 5\tau_o$. Third, to check if there are correlated domains of dipoles in water which have large relaxation times compared to the individual dipoles, we calculate the randomization time $\tau_{box}$ of the site-dipole field, the net dipole moment formed by a set of molecules belonging to a box of edge $L_{box}$. We find that the site-dipole randomization time $\tau_{box} \approx 2.5\tau_r$ for $L_{box} \approx 3$ Å, i.e., it is shorter than the same quantity calculated for the self-dipole. Finally, we find that the orientational correlation length is short even at low $T$.

I. INTRODUCTION

Cooperative motion of water molecules [1] has been widely investigated in recent years, both by experiments [2–21] and using molecular dynamics (MD) simulations [22–35]. When water is cooled, the cooperativity of water molecules increases. Recent experiments on water show large correlated domains of dipoles at ambient conditions which have a relaxation time much larger than the autocorrelation time of individual dipoles [21]. MD studies of water models also show the possibility of formation of large correlated domains of dipoles in bulk as well as interfacial water [35] (where these correlated patterns of dipoles are pinned to solvated amino acids). These two studies are the principal motivation for the present investigation of the rotational cooperativity of water molecules.

A challenging problem is to develop methods of describing molecular motion in water that are better able to interpret experimental results, such as incoherent quasielastic neutron scattering, light scattering, dielectric, and nuclear magnetic resonance experiments [2,18]. Several approximation proposals have been made for various autocorrelation functions describing both rotational and translational motion [20,27]. These methods usually assume the Kohlrausch-Williams-Watts stretched exponential for the long-time relaxation behavior of autocorrelation functions $\phi(t)$, as predicted by mode coupling theory (MCT),

$$\phi(t) = A \exp \left[ -\frac{t}{\tau_a} \right].$$

The relaxation time $\tau_a$, the exponent $\beta$, and the nonergodicity factor $A$ are fitting parameters that depend on temperature $T$ and density $\rho$ [22–25,27–31].

Our interest here is to study the orientational dynamics of water by simulating water using the extended simple point charge (SPC/E) model. First we calculate the orientational autocorrelation function as the fitting parameter $\tau_o$ appearing in Eq. (1) [22,23]. Other definitions are possible, e.g., based on other fitting functions for the orientational autocorrelation function decay, such as the biexponential [26,36] or the von Schweidler law [33]. In all cases, the orientational autocorrelation times are the result of multiparameter fitting procedures [37] and roughly correspond to the characteristic time over which the orientational autocorrelation function decays by a factor of $e^{-1} = 2.7$.

To find an upper limit of the orientational autocorrelation time $\tau_o$, we will introduce the dipole randomization time $\tau_r$ as the time after which the fluctuations of the dipoles resemble an uncorrelated random variable [38] (Sec. IV A). We find $\tau_r \sim \tau_o$, and that $\tau_r$ and $\tau_o$ are linearly related (Sec. IV B), which is consistent with the MCT predictions that (i) the autocorrelation times of all the autocorrelation functions of any fluctuation coupled to density fluctuations diverge at the same temperature $T_{MCT}$ with the same power law exponent; and (ii) all the characteristic times of a supercooled liquid are proportional to one another.
To characterize the increase of cooperativity and test for the presence of large correlated domains of dipoles, we also estimate the randomization time \( \tau_{\text{box}} \) for the site-dipole field (Sec. V), a quantity which measures the relaxation of the net dipole moment of all the molecules inside a box of edge \( L_{\text{box}} \). Our calculations show that \( \tau_{\text{box}} \) when \( L_{\text{box}} \approx 3 \) Å has a power law divergence at \( T_{\text{MCT}} \), but with \( \tau_{\text{box}} \ll \tau_r \). This result shows that the site-dipole field relaxes faster than the individual dipoles, resolving the apparent contradiction between Ref. [35] and previous results. Calculations of \( \tau_{\text{box}} \) for larger boxes show that \( \tau_{\text{box}} \) does not depend on the box size and hence do not support the experimental observation of long-lived large domains of correlated dipoles [21].

II. THE SPC/E MODEL

Our results are based on MD simulations of the extended simple point charge model [39]. The distance between the oxygen atom and each of the hydrogen atoms is 0.1 nm, and the HOH angle is the tetrahedral angle 109.47° [40]. Each hydrogen atom has a charge \( q_{\text{H}} = 0.432e \), where \( e \) is the electron charge, and the oxygen atom has a charge \( q_{\text{O}} = -2e \). In addition, to model the van der Waals interaction, pairs of oxygen atoms of different molecules interact with a Lennard-Jones potential,

\[
V_{ij}(r_{ij}) = 4 \epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right),
\]

where \( r_{ij} \) is the distance between molecules \( i \) and \( j \), \( \epsilon = 0.65 \text{ kJ/mol} \), and \( \sigma = 0.3166 \text{ nm} \). The SPC/E model has been used extensively to study various liquid properties of water [24]. It reproduces the density and diffusion anomalies qualitatively, and displays a power law behavior of dynamic quantities as observed in supercooled water at ambient pressure [41,42]. Compared with other water models, the SPC/E model describes the liquid-vapor coexistence better [43] (and the solid phase less well [44]).

We perform MD simulations for a system of \( N = 1728 \) molecules at density \( \rho = 1.0 \text{ g/cm}^3 \), 210 ≤ \( T \) ≤ 300 K, with periodic boundary conditions and a simulation time step of 1 fs. The temperature is controlled by the Berendsen method of rescaling the velocities [45]. The long-range Coulombic interactions [46] are treated with the reaction field technique with a cutoff of 0.79 nm. For each state point, we run two independent simulations to improve statistics.

III. THE ORIENTATIONAL AUTOCORRELATION FUNCTION \( C_1(t) \)

To estimate the orientational autocorrelation time of water molecules in the supercooled regime, we average the scalar product of the normalized dipole vectors \( \vec{\mu}_i \) of each water molecule \( i \) in the system,

\[
C_1(t) = \left\langle \sum_{i=1}^{N} \vec{\mu}_i(t) \cdot \vec{\mu}_i(0) \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \langle \cos \theta_i(t) \rangle ,
\]

where \( \theta_i(t) \) is the angle between \( \vec{\mu}_i(t) \) and \( \vec{\mu}_i(0) \). This function corresponds to the average of the Legendre polynomial

\[
P_i(\cos \theta_i(t))\] evaluated for each molecule and can be directly measured by dielectric experiments.

Figure 1(a) plots \( C_1(t) \) for 210 ≤ \( T \) ≤ 300 K, and displays the two-step decay of typical glass-forming systems. The long-time regime at low \( T \) can be fit well by Eq. (1) and the fitting parameters are shown in Table I. Both parameters in Eq. (1), \( A \) and \( \beta \), show weak dependences on \( T \). The resulting values of these parameters are consistent with previous simulations of a smaller system of SPC/E molecules [23].

![Figure 1](image)

**TABLE I.** Parameters of the fit of \( C_1(t) \) in Fig. 1 with Eq. (1). The error on each parameter is ±10%.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( A )</th>
<th>( \tau_a ) (ps)</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.93</td>
<td>4.9 × 10^3</td>
<td>0.88</td>
</tr>
<tr>
<td>260</td>
<td>0.94</td>
<td>1.7 × 10^1</td>
<td>0.85</td>
</tr>
<tr>
<td>250</td>
<td>0.94</td>
<td>2.8 × 10^1</td>
<td>0.85</td>
</tr>
<tr>
<td>240</td>
<td>0.94</td>
<td>4.9 × 10^1</td>
<td>0.84</td>
</tr>
<tr>
<td>230</td>
<td>0.94</td>
<td>1.1 × 10^2</td>
<td>0.84</td>
</tr>
<tr>
<td>220</td>
<td>0.94</td>
<td>2.7 × 10^2</td>
<td>0.83</td>
</tr>
<tr>
<td>210</td>
<td>0.94</td>
<td>1.1 × 10^3</td>
<td>0.82</td>
</tr>
</tbody>
</table>
corresponding to the maximum or minimum of these quantities, two consecutive samples of the maximum and minimum values we found for 188 choices of \( T \) over a time interval \( \Delta t \). Based on the results in (b), our estimate of \( T \) is \( 194 \pm 4 \) K and \( \gamma_0 = 2.9 \pm 0.3 \).

The estimated autocorrelation times \( \tau_0 \) agree (Fig. 2) with the power law behavior predicted by the MCT,

\[
\tau_0 \sim (T - T_{\text{MCT}})^{-\gamma_0}. \tag{4}
\]

We estimate \( T_{\text{MCT}} = 194 \pm 4 \) K and \( \gamma_0 = 2.9 \pm 0.3 \), in agreement with previous results for similar densities and temperatures [24].

The estimated values of \( \tau_0 \) verify well the von Schweidler law (see the Appendix) and the time-temperature superposition principle predicted by MCT, i.e., that the autocorrelation functions in the \( \alpha \)-relaxation regime at different temperatures follow the same master curve if the time is rescaled by the autocorrelation time [Fig. 1(b)] [29].

IV. THE SELF-DIPOLE RANDOMIZATION TIME \( \tau_r \)

A. Definition and methods

Here we define the randomization time \( \tau_r \), a quantity that we propose to characterize the orientational autocorrelation time. We consider the normalized dipole \( \vec{\mu}_i \) of molecule \( i \) over a time interval \( \Delta t = N\Delta \delta t \),

\[
\vec{\mu}_i = \frac{1}{N} \sum_{k=1}^{N} \vec{\mu}_i(t_k), \tag{5}
\]

where \( \vec{\mu}_i \) is a function of \( \delta t \) and \( \Delta t \), \( t_k = k\delta t \), and \( \delta t \) is the time interval between two consecutive samples of \( \vec{\mu}_i \).

If \( \delta t \) is greater than the autocorrelation time of \( \vec{\mu}_i \), then two consecutive samples \( \vec{\mu}_i(t) \) and \( \vec{\mu}_i(t + \delta t) \) are independent; hence \( \langle \vec{\mu}_i(t_j) \cdot \vec{\mu}_i(t_k) \rangle = 0 \) if \( j \neq k \), where \( \langle \cdots \rangle \) denotes the average over all the molecules \( N \) in the system. Hence

\[
\langle \vec{\mu}_i^2 \rangle = \langle \vec{\mu}_i \cdot \vec{\mu}_i \rangle = \frac{1}{N} \left( \sum_{j,k} \vec{\mu}_i(t_j) \cdot \vec{\mu}_i(t_k) \right) = \frac{1}{N}, \tag{6}
\]

because \( \langle \vec{\mu}_i^2 \rangle = 1 \) for any \( \tau_0 \), and

\[
\mu_{\text{rms}} = \sqrt{\langle \vec{\mu}_i^2 \rangle} = \sqrt{\frac{\Delta \delta t}{\Delta t}}. \tag{7}
\]

This is the result of a freely jointed chain of \( N \) bonds of the same length, for which the mean square end-to-end distance is \( N^{\frac{1}{2}} \langle \vec{\mu}_i^2 \rangle = \frac{N}{2} [47] \). Therefore, if \( \delta \) \( \Delta \delta t \) is larger than the orientational autocorrelation time for \( \vec{\mu}_i \), the \( \mu_{\text{rms}} \) decreases as \( 1/\sqrt{\Delta t} \).

If, instead, \( \delta \) \( \delta \Delta t \) is shorter than the orientational autocorrelation time, consecutive elements in the sum in Eq. (6) are correlated \( \langle \vec{\mu}_i(t) \cdot \vec{\mu}_i(t + \delta t) \rangle = \frac{1}{2} \), resulting in a smaller fluctuation. This can be formally understood by considering the freely rotating chain model [47], where consecutive bonds in the chain are free to rotate, each around the axis of the previous bond, at an angle \( \theta \), such that \( \cos(\theta) = \rho \). With this assumption, the resulting mean square end-to-end distance for \( n \) bonds of unit length is

\[
\langle \vec{r}_n^2 \rangle = n \left( 1 - \rho \right) - 2 \left( 1 - \rho^2 \right), \tag{8}
\]

In the case of small \( \theta \), we have \( \rho = 1 - \epsilon + O(\epsilon^2) \), with \( \epsilon = \theta^2/2 \ll 1 \) and \( z = \exp(-z \epsilon) \). Then, from Eq. (8), we obtain

\[
\left( \frac{1}{n} \sqrt{\vec{r}_n^2} \right) = \frac{1}{n \epsilon} \left[ 2(n \epsilon - 1 + e^{-n \epsilon}) \right]^{1/2}. \tag{9}
\]

In our problem, the bonds are dipole vectors sampled at time intervals \( \Delta \delta t \), and \( n = \Delta t/\Delta \delta t = N \). Therefore Eq. (9) becomes

\[
\mu_{\text{rms}} \sim \frac{1}{N \epsilon} \left[ 2(N \epsilon - 1 + e^{-N \epsilon}) \right]^{1/2}. \tag{10}
\]

The right-hand side of this equation behaves as \( 1/\sqrt{\Delta t} \) for \( N \to \infty \), i.e., the random case behavior is recovered for large \( \Delta t/\Delta \delta t \).

Therefore, if we define \( \tau_\rho \) as the time at which the correlation goes to zero as \( 1/\sqrt{\Delta t} \), it is possible to see that

\[
\mu_{\text{rms}} \sim \frac{1}{1/\Delta t} \begin{cases} \text{for any } \Delta t & \text{if } \delta \gg \tau_\rho, \\ \text{for } \Delta t \gg \tau_\rho & \text{if } \delta \ll \tau_\rho. \end{cases} \tag{11}
\]

If we consider the fluctuation of any observable, the relation (11) defines the randomization time \( \tau_r \) for that observable [38] and \( \tau_r \) is equal to the smallest \( \delta t \) such that \( \mu_{\text{rms}} \sim 1/\sqrt{\Delta t} \) for any \( \Delta t \).

B. Calculation of \( \tau_r \)

In Fig. 3, we show \( \mu_{\text{rms}} \) for \( T = 220 \) K calculated for different values of \( \delta t \). For small \( \delta t \) and small \( \Delta t \), \( \mu_{\text{rms}} \) deviates greatly from the asymptotic law. However, for increasing \( \delta t \),
the deviation decreases. For $\delta t=1280$ ps the asymptotic behavior, within the error of our calculations, is reached.

The evaluation of $\tau_r$ from a plot such as in Fig. 3 could be problematic, since it depends critically on the data errors. Therefore, to define in a clear way $\tau_r$, we fit the first eight points ($\Delta t = \delta t, 2 \delta t, \ldots, 8 \delta t$) using

$$\mu_{\text{rms}} \sim (\Delta t)^{\lambda},$$

where $\lambda=\lambda(\delta t)$. In this way we study how the deviation from the asymptotic regime decreases by increasing $\delta t$. We find that the exponent $\lambda$ increases toward the asymptotic value 1/2 for increasing $\delta t$, and $\lambda=1/2$ for any $\delta t \gg \tau_r$ (Fig. 4). We therefore define $\tau_r$ as the extrapolated value of $\delta t$ at which $\lambda=1/2$. We find that $\lambda$ approaches 1/2 as $1/\delta t$, to the leading order, for low temperatures (Fig. 4).

The resulting values of $\tau_r$ are presented in Fig. 5(a) as functions of $T-T_{\text{MCT}}$, showing that the power law behavior $\tau_r \propto (T-T_{\text{MCT}})^{\gamma_r}$ is well satisfied by $\tau_r$. In this case our estimates are $T_{\text{MCT}}=191.5\pm2.5$ K and $\gamma_r=3.3\pm0.2$, both consistent within the errors with the estimates based on $\tau_\theta$ (Fig. 2). Therefore, the prediction (i) of MCT is verified.

By plotting $\tau_r$ against $\tau_\theta$, we verify the MCT prediction (ii). We find (Fig. 6) that $\tau_r$ and $\tau_\theta$ are linearly related and that $\tau_r$ is approximately five times larger than $\tau_\theta$.

The large value of $\tau_r$ with respect to $\tau_\theta$ is consistent with the fact that the latter measures the decay of the self-dipole
correlation to a finite value, while the former measures the time needed for the self-dipole autocorrelation to decay to zero. This result is also reminiscent of the recent MD analysis in bulk water for the site-dipole field, a measure of the average orientation of the molecules passing through each spatial position, introduced in Ref. [35]. Higo et al. [35] find coherent patterns for the site-dipole field, at ambient pressure and $T=298$ and $300$ K, that persist for more than 100 ps, a time much larger than the single molecule orientational relaxation time $\tau_a$ of approximately 5 ps (Table I). A similar analysis for water dipoles at the interface with nanometer-size hydrophobic solutes has confirmed these results [48]. It is, therefore, interesting to calculate the randomization time $\tau_{\text{box}}$ and to find its relation with the autocorrelation time $\tau_a$ for $T \rightarrow T_{\text{MCT}}$.

V. THE SITE-DIPOLE FIELD

To check if there are large correlated domains of dipoles in water which have large relaxation times compared to the individual dipole correlation time, we next study site-dipole field introduced by Higo et al. [35]. We define the instantaneous coarse-grained site-dipole field

$$d_{\text{rms}}^r = \bar{d}(r_i, t) = \frac{1}{n_i(t)_{\text{box}}} \sum \bar{\mu}_i$$

as the average of dipoles $\bar{\mu}_i$ of all the molecules $n_i(t)$ at time $t$ belonging to box $i$ of edge $L_{\text{box}}$, volume $v=L_{\text{box}}^3$, and centered at $r_i$. If $n_i(t)=0$, then $d_{\text{rms}}^r=0$ by definition [48,49]. We chose vectors $r_i$ in such a way that the corresponding boxes do not overlap [51]. The time average $\bar{d}_{\text{rms}}^r$ over an interval $\Delta t$ is defined analogously to Eq. (5). The rms average $d_{\text{rms}}^r$ is defined in analogy to Eqs. (6) and (7), but instead of summation over all molecules we perform a summation over all boxes.

Since the argument presented for $\mu_{\text{rms}}$ is also valid for $d_{\text{rms}}^r$, the relation (11) also holds for $d_{\text{rms}}^r$ and allows us to estimate the randomization time $\tau_{\text{box}}$ for $d_{\text{rms}}^r$. We find that

$$\tau_{\text{box}}, \text{ calculated for } L_{\text{box}}=3.33 \ \text{Å}, \text{ diverges at } T_{\text{box}}=194 \pm 2 \ \text{K} \text{ with a power law with exponent } \gamma_{\text{box}}=3.2 \pm 0.2, \text{ consistent with our estimates of } \gamma_a \text{ and } T_{\text{MCT}}, \text{ respectively (Fig. 7).}$$

If we compare $\tau_{\text{box}}$ with $\tau_a$ (Fig. 8), we again find a linear relation, as in Fig. 6 for $\tau_a$, consistent with the MCT statement (ii). The proportionality factor is approximately 2.5 [52], smaller than the factor $=5$ found for $\tau_a$ in Fig. 6. Therefore, we conclude that in bulk water the coarse-grained site-dipole randomization time $\tau_{\text{box}}$ is larger than the self-dipole autocorrelation time $\tau_a$, but smaller than $\tau_a$. Thus we do not find a significant increase in the box dipole autocorrelation time compared to the autocorrelation time $\tau_a$.

FIG. 8. Analog of Fig. 6; a parametric plot of the site-dipole randomization time $\tau_{\text{box}}$ (a) We find a power law behavior in $T−T_{\text{box}}$, calculated for $L_{\text{box}}=3.33$ Å. The line is a fit with $T_{\text{MCT}}=194$ K and exponent $\gamma_{\text{box}}=3.2$. (b) Optimization analysis for $T_{\text{box}}$: correlation coefficient $R$ (solid line) and $\chi^2$ (dashed line), both rescaled to the maximum and minimum values found for $188 \leq T_{\text{box}} \leq 202$ K. (c) The exponent $\gamma_{\text{box}}$ corresponding to different choices of $T_{\text{box}}$ decreases linearly with increasing choice of $T_{\text{box}}$. We estimate $T_{\text{box}}=194\pm 2$ K and $\gamma_{\text{box}}=3.2\pm 0.2$.\n
FIG. 7. Analog of Figs. 2 and 6 for the site-dipole randomization time $\tau_{\text{box}}$. (a) We find a power law behavior in $T−T_{\text{box}}$, calculated for $L_{\text{box}}=3.33$ Å. The line is a fit with $T_{\text{MCT}}=194$ K and exponent $\gamma_{\text{box}}=3.2$. (b) Optimization analysis for $T_{\text{box}}$: correlation coefficient $R$ (solid line) and $\chi^2$ (dashed line), both rescaled to the maximum and minimum values found for $188 \leq T_{\text{box}} \leq 202$ K. (c) The exponent $\gamma_{\text{box}}$ corresponding to different choices of $T_{\text{box}}$ decreases linearly with increasing choice of $T_{\text{box}}$. We estimate $T_{\text{box}}=194\pm 2$ K and $\gamma_{\text{box}}=3.2\pm 0.2$.\n
FIG. 6. Parametric plot of the times $\tau_a(T)$ and $\tau_a(T)$, within the range $220 \leq T \leq 300$ K, with the lowest time corresponding to the highest $T$. The line reflects the linear one-parameter fit $\tau_a=(5.1 \pm 0.2)\tau_a$.\n
FIG. 7. Analog of Figs. 2 and 6 for the site-dipole randomization time $\tau_{\text{box}}$. (a) We find a power law behavior in $T−T_{\text{box}}$, calculated for $L_{\text{box}}=3.33$ Å. The line is a fit with $T_{\text{MCT}}=194$ K and exponent $\gamma_{\text{box}}=3.2$. (b) Optimization analysis for $T_{\text{box}}$: correlation coefficient $R$ (solid line) and $\chi^2$ (dashed line), both rescaled to the maximum and minimum values found for $188 \leq T_{\text{box}} \leq 202$ K. (c) The exponent $\gamma_{\text{box}}$ corresponding to different choices of $T_{\text{box}}$ decreases linearly with increasing choice of $T_{\text{box}}$. We estimate $T_{\text{box}}=194\pm 2$ K and $\gamma_{\text{box}}=3.2\pm 0.2$.
inversely proportional to
in the box are independent random variables,

exists of only short-range orientational autocorrelation in
3.33 and 6 Å, comparable to the dipole-dipole correlation
dependence of
d for two different temperatures

0.49±0.01. For each
b = 220 and 300 K. The collapse of all the
curves confirms the hypothesis of very weak autocorrelations

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T suggesting that at this
existence of only short-range orientational autocorrelation in

MCT predic-
tions apply to orientational dynamics of water, despite the

fact that MCT has been developed for particles interacting
through spherically symmetric potentials [53]. However, re-
cent extensions of MCT to liquids of linear molecules
[54,55], and single solute molecules in a simple solvent li-

Our study of supercooled water confirms the validity of
MCT predictions for the orientational autocorrelation time

τa, estimated through a stretched exponential of the dipole
autocorrelation function, for the temperature range 210 ≤ T
≤ 300 K at density ρ = 1 g/cm³. Our results agree with the
time-temperature superposition principle and the power law
Eq. (4), with

T_{MCT} = 194±4 K and
γ_a = 2.9±0.3.

By evaluating the randomization time τr, defined as the
time needed to randomize the molecular dipoles, we verify
the MCT prediction that all the characteristic times of quan-
tities coupled to density fluctuations of a supercooled liquid
are proportional to each other and follow the same power law
Eq. (4). We find τr = 5 τa, with

T_{MCT} = 191.5±2.5 K and
γ_r = 3.3±0.2, consistent with the estimates based on the calcu-
lation of τa.

We also calculate the randomization time τbox for the box
dipole field, a quantity introduced in Ref. [35] to measure
the local orientational memory of molecules passing through a
given spatial position. Our results for

L_{box} = 3.33 Å show that

τbox diverges at

T_{box} = T_{MCT}, following a power law with ex-
ponent

γ_{box} = γ_a, and that

τ_{box} = τ_a/2. As a consequence, the
local memory is lost faster than the self-dipole orientational

memory.

Our results also show the existence of domains of corre-
lated dipoles of short spatial range, with a correlation length
comparable to the dipole-dipole correlation length at ambient
T [50], raising the possibility of using the calculations on
confined water to study the interesting case when the corre-
lation length is comparable to the system size [57–59].
Whether this conclusion is specific to the SPC/E model with
reaction field is an open question, and requires further inves-

tigation using other models of water, e.g., polarizable mod-

els.

ACKNOWLEDGMENTS

We thank M. Sasai for motivating our interest in this
project and his hospitality during a visit to Nagoya Univer-
sity, and N. Giovambattista for his helpful collaboration on
initial phases of this work. We thank NSF grant No. CHE-
0096892 and Spanish Ministerio de Educació

VI. DISCUSSION

Considerable numerical evidence shows that MCT predic-
tions apply to orientational dynamics of water, despite the

FIG. 9. Size dependence of site-dipole autocorrelation function
d^{(v)}_m as a function of t for

L_{box} = 3.33 ( ), 6 ( ), and 10 Å ( ) and for
two different temperatures

T = (a) 300 and (b) 220 K. In (a) the

line is a fit of data for

L_{box} = 3.33 Å with

d^{(v)}_m = a/t, with

a = 0.08±0.01. In (b) the same fit is for the data at

L_{box} = 6 Å and

t > 10³, with

a = 0.49±0.01. For each T all the values of

d^{(v)}_m overlaps, suggesting that the orientational autocorrelation is short range.

To test the existence of cooperative domains in the SPC/E
model, we perform coarse-graining of the dipole field for
boxes of sizes

3.33 ≤ L_{box} ≤ 10 Å. If the dipoles of molecules
in the box are independent random variables,

d^{(v)}_m must be inversely proportional to

\sqrt{\langle n \rangle} \sim \sqrt{v}, since the average num-
ber of molecules in the box is proportional to its volume.
The dependence of

d^{(v)}_m on time t must be the same for the

boxes of different volumes v. We show in Fig. 9 the behavior
of

d^{(v)}_m for

T = 220 and 300 K. The collapse of all the
curves confirms the hypothesis of very weak autocorrelations
among neighboring dipoles. Only for

T = 220 K do we ob-
serve a weak size dependence of

d^{(v)}_m for the smallest size,
suggesting that at this T the correlation length is between
3.33 and 6 Å, comparable to the dipole-dipole correlation
length at ambient

T [50]. Thus our simulations support the
existence of only short-range orientational autocorrelation in
SPC/E water even at low

T.

APPENDIX: THE VON SCHWEIDLER LAW

The MCT predicts that the autocorrelation function de-
parts from the plateau A as a power law with exponent

b, known as the von Schweidler law,

C_1(t) = A \sim (t/\tau_a)^b, \quad (A1)

where the von Schweidler exponent

b does not depend on
T. We verify that at lower temperatures Eq. (A1) holds for

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roughly two decades in time (Fig. 10) and we find a clear deviation only for $T \geq 260$ K at short times, possibly due to the fact that for $T \geq 260$ K it is more difficult to estimate the plateau A. The estimated value of $b$ is $0.6 \pm 0.1$, consistent with previous results [29] and with the MCT prediction that $\gamma_\alpha$, $a$, and $b$ are related by the equation

$$\gamma_\alpha = \frac{1}{2a} + \frac{1}{2b}. \quad (A2)$$

Here $a$ is the exponent of the power law that describes the short-time approach to the plateau $C_1 - A \sim t^{-\gamma_\alpha}$, and $a$ is related to $b$ by the transcendental equation

$$\frac{[\Gamma(1-a)]^2}{\Gamma(1-a)\Gamma(1+2a)} = \frac{[\Gamma(1+b)]^2}{\Gamma(1+b)\Gamma(1+2b)}, \quad (A3)$$

where $\Gamma(x)$ is the Euler gamma function. Our estimates of $b$ and $\gamma_\alpha$ are consistent with both Eqs. (A2) and (A3) with $a = 0.25 \pm 0.05$.

The values of the exponents $a$, $b$, and $\gamma_\alpha$ are not universal, but depend on density. However, the rescaling of the autocorrelation functions for different $T$ on the same master curve, shows that the orientational correlation function depends on $T$ and $\rho$ only through the dependence on $\tau_\alpha$, as predicted by the MCT.
[40] Microwave spectroscopy and infrared spectroscopy on H2O at equilibrium in the gas phase give 0.9575 Å for the O-H distance and 104.51° for the HOH angle [CRC Handbook of Chemistry and Physics, 84th ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 2003)].
[49] In Eq. (13) we normalize the average with the time-dependent number of molecules \( n(t) \), instead of the total number of cells inside the box as in Ref. [35]. Our choice has the advantage of giving rise to a value of the average dipole in a box \( \delta_{ij} \) inde-
pendent of the system density (see for example [50]). However, as a consequence, the distribution of \( \delta_{ij} \) is not Gaussian, as would be expected by normalizing by a constant factor. We have verified that by using a constant normalization factor we recover a Gaussian distribution. Moreover, we have verified that our final results are not affected by the choice of the normalization factor in Eq. (13).
[51] The definition in Eq. (13) differs from the one introduced in Ref. [35], where the coarse-grained site-dipole field is averaged over spheres with radius \( R \) and centered at a distance shorter than \( 2R \). The definition in Ref. [35] emphasizes the spatial patterns of coarse-grained site dipoles, because each molecular dipole contributes to the coarse-grained site dipole for all the (overlapping) spheres that contain the same molecule. We therefore expect to find patterns that survive for a time shorter than that measured in Ref. [35]. Indeed, we do not find strong evidence of surviving patterns in bulk water within our time resolution.
[52] At \( T=300 \) K we find a autocorrelation time \( \tau \), approximately ten times smaller than the persistence time found in Ref. [35] for the site-dipole patterns. This is due to the difference in the definition in Eq. (13). We verify that, by adopting the same definition of Ref. [35], we can reproduce the bulk-water results of Higo et al. See also [50].