

## Optical Kerr Effect in Supercooled Water

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We present molecular dynamics simulations of the optical Kerr effect in liquid and supercooled water and compare with recent time-resolved Kerr spectroscopy measurements [R. Torre *et al.*, *Nature (London)* **428**, 296 (2004)]. The short time features of the Kerr response, characterized by peaks near 15, 60, and 160 fs, are weakly temperature dependent. The long-time decay is well described by a stretched exponential with a nearly constant stretch parameter and relaxation times that follow a power law  $\sim (T - T_S)^{-\gamma}$ , with  $T_S = 198.3$  K and  $\gamma = 2.35$ . Our findings are discussed in the light of the spectroscopy data and previous simulation analyzes of the structural relaxation in supercooled water.

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There is a large body of experimental measurements showing that supercooled water exhibits critical behavior typical of fragile glass forming liquids [1]. The temperature dependence of several properties diverges as a power law  $\sim (T - T_S)^{-x}$  for  $T$  not too close to  $T_S$ . A variety of experimental estimates places the singularity temperature in the range  $T_S \approx 220$ – $230$  K, slightly below the homogeneous nucleation temperature (235 K), and exponents that depend on whether the measurement refers to a thermodynamic ( $x \sim 0.02$ – $0.35$ ) or a transport property ( $x \sim 1.5$ – $2.5$ ) [2–4]. The nature of this critical behavior, the aqueous glass transition, and the putative relationship between structural, thermodynamic, and dynamic supercooled anomalies are subjects of intense research activity currently [5–11].

Molecular dynamics (MD) simulations and experimental works have been reported in recent years which successfully interpret the dynamics of weakly supercooled water ( $T \geq 250$  K) within the framework of the mode coupling theory (MCT) of ordinary glass forming liquids [12–14]. The underlying physical picture of the MCT is that the slowing down of the dynamics of supercooled states arises from density fluctuation modes over length scales comparable to the distance between nearest neighbors (transient caging effects). In short, the main predictions of the MCT are: (1) The long-time decay ( $\alpha$  relaxation) of dynamical correlations follows a stretched exponential form,

$$F(t) = A \exp[-(t/\tau)^\beta], \quad (1)$$

with a temperature independent stretch exponent  $\beta$ ; (2) The characteristic relaxation time exhibits a power law temperature dependence of the type,

$$\tau(T) = \tau_0 \left( \frac{T}{T_S} - 1 \right)^{-\gamma}, \quad (2)$$

divergent at some temperature related to the liquid's structural arrest.

Through extensive MD simulations on the extended simple point charge (SPC/E) potential, Sciortino, Stanley, and co-workers investigated the time-dependent structural correlations of supercooled water over a wide range of temperatures [15], the diffusivity along different isobars [16], and the spatially heterogeneous dynamics [17] in connection to the Adam-Gibbs theory of supercooled dynamics [3]. The structural relaxation in supercooled states shows two time separated processes [15], the slowest of which is identified with the  $\alpha$  relaxation. In this regime, the relaxation is well described by Eq. (1) in which the wave vector dependence of the parameters  $A$ ,  $\beta$ , and  $\tau$  are nicely correlated with the oscillations in the static structure factor, in agreement with the MCT predictions. The first experimental confirmation of these MD predictions were obtained by Bellissent-Funel and co-workers through time-domain neutron spin-echo spectroscopy, although only two supercooled temperatures were studied [18]. Other experimental measurements based on time-resolved ultrafast laser techniques, such as time-domain terahertz (THz) and Raman induced optical Kerr effect (OKE) spectroscopies, have been reported in recent years for various temperatures in the range 270–370 K. The analysis and interpretation of the observed dynamics differ: The THz dynamics [19] has been characterized as an intermolecular structural relaxation with a singular point estimated at 228 K, whereas the OKE relaxation was interpreted as single particle diffusive reorientational motions [20].

In contrast, Torre *et al.* [21] have very recently reported new state-of-the-art OKE measurements, which fully support the scenario predicted by the MCT. The observed OKE relaxation rates are notably consistent with the MCT structural relaxation behavior: Stretched exponential decay with  $\beta \approx 0.6$ , independently of temperature, and a power law dependence for the relaxation time with  $T_S = 221 \pm 5$  K and  $\gamma = 2.2 \pm 0.3$ .

In this Letter, we report MD simulations for the OKE response of liquid and weakly supercooled water and compare the results directly to the most recent experimental Kerr study [21]. We find that the short time features of

the Kerr response have a limited temperature dependence, whereas the behavior of the long-time relaxation is well described by Eqs. (1) and (2), with a nearly constant stretch parameter  $\beta \sim 0.6$ ,  $T_S = 198.3$  K, and  $\gamma = 2.35$ , in very good agreement with experiments. Our simulations were performed in the  $NVE$  ensemble on systems containing  $N = 500$  SPC/E [22] water molecules at a fixed density of  $1 \text{ g/cm}^3$  and several (average) temperatures in the range 215–323 K. We use a cutoff at half the box length for Lennard-Jones forces and Ewald sums for Coulomb interactions.

The dynamics of interest here is the relaxation of the polarizability anisotropy expressed by the time correlation function (tcf) of the off-diagonal elements of the collective polarizability tensor [23]:

$$\Psi(t) = \langle \Pi_{xz}(t) \Pi_{xz}(0) \rangle / (N\delta^2/15), \quad (3)$$

with  $\delta^2 = 1/2[(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_2 - \alpha_3)^2]$  being the square of the ideal polarizability anisotropy and  $\alpha_j$  the principal polarizability components. The collective polarizability tensor,  $\Pi = \Pi^M + \Pi^I$ , is comprised by the sum of gas phase molecular polarizabilities and induced polarizability contributions computed according to [24]:

$$\Pi^I = \sum_i^N \sum_{j \neq i} (\alpha_i^M \cdot T_{ij} \cdot \alpha_j + \beta_i^M \cdot T_{ij} \cdot \mu_j). \quad (4)$$

The enhanced polarizability tensor and dipole vectors are obtained by iteratively solving the equations:

$$\alpha_i = \alpha_i^M + \sum_{j \neq i} \alpha_i^M \cdot T_{ij} \cdot \alpha_j, \quad (5)$$

$$\mu_i = \mu_i^M + \sum_{j \neq i} \alpha_i^M \cdot T_{ij} \cdot \mu_j, \quad (6)$$

where  $\mu_i^M$ ,  $\alpha_i^M$ , and  $\beta_i^M$  are the gas phase dipole, polarizability, and hyperpolarizability of molecule  $i$ , respectively.  $T_{ij} = \nabla_i \nabla_j |r_i - r_j|^{-1}$  is the dipole tensor between molecules  $i$  and  $j$ . The molecular  $\alpha^M$  and  $\beta^M$  tensors needed in this scheme were computed from *ab initio* quantum chemical calculations [25] and are shown in Table I. The hyperpolarizability contributions are very small in

TABLE I. Molecular polarizability and first hyperpolarizability tensors obtained from restricted Hartree-Fock electronic structure calculations at the MP2/6-311++G(d,p) level. The  $z$  and  $y$  directions are along the main symmetry axis and normal to the molecular plane, respectively.  $\beta_{y33}$  is smaller than  $0.05 \text{ \AA}^5/e$  and the remainders are zero.

$[\text{\AA}^3]$	$\alpha_{11}^M$	$\alpha_{12}^M$	$\alpha_{22}^M$	$\alpha_{33}^M$	
	1.04	...	1.00	1.17	
$[\text{\AA}^5/e]$	$\beta_{x11}^M$	$\beta_{x13}^M$	$\beta_{x22}^M$	$\beta_{y23}^M$	$\beta_{z33}^M$
	0.80	-0.19	0.06	0.05	0.86

liquid water, but some degree of nonlinear electronic response is incorporated through the “ $\beta T\mu$ ” term. The optically heterodyne-detected OKE signal obtained from the time-resolved spectroscopy provides the intermolecular dynamics through the nuclear response function, given by the time derivative of the polarizability anisotropy tcf [26,27]:

$$R^{\text{nuc}}(t) = -\frac{\Theta(t)}{k_B T} \frac{\partial \Psi(t)}{\partial t}, \quad (7)$$

where  $\Theta(t)$  is the Heaviside step function.

We start by discussing the short time behavior of the OKE relaxation, shown in Fig. 1(a) for several temperatures. The response functions show a fast rise to a maximum at  $\sim 15$  fs, followed by a satellite peak near 60 fs and a third, broader, local maximum at 160 fs. The remaining decay is comprised by slowly relaxing components. The short time features are in agreement with previous simulation results for near ambient conditions [28,29] and experimental OKE signals [30,31], which report peaks near 20, 60, and 200 fs. The first peak is mainly due to inertial and librational motions of the Hydrogen atoms, while the peaks at 60 and 200 fs have been ascribed to a

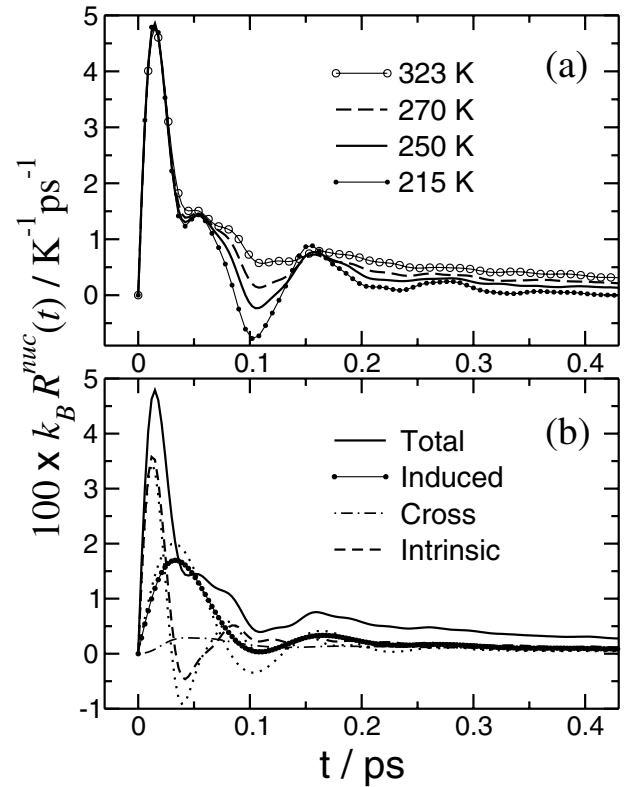


FIG. 1. (a) Simulated Kerr nuclear responses for different temperatures. The effect of  $T$  on the short time features is restricted to a sharpening of the peaks without affecting their positions. (b) Total and separate contributions to the Kerr response at ambient conditions. For comparison, the intrinsic and induced contributions at 250 K are also shown (dotted lines).

superposition of librational and hindered translational modes within the cage of neighbors [31]. This picture is supported by the behavior of the separate contributions to  $R^{\text{nuc}}$  depicted in Fig. 1(b). The intrinsic part is mainly responsible for the rapid rise of the response, whereas the collision induced contribution accounts for most of the librational and hindered translation peaks. In frequency domain, such translational motions appear at  $\sim 60$  and  $\sim 180 \text{ cm}^{-1}$  [31,32]. The temperature dependence of the short time oscillations in  $R^{\text{nuc}}(t)$  [Fig. 1(a)] is limited to an enhancement in the definition of the translational peaks, which are sharper at lower temperatures. Essentially no changes in the peak positions are observed, indicating that the underlying “intracage” motions are not affected by  $T$ . This trend is very consistent with the experimental Kerr signals obtained by Vöhringer and co-workers [20] and the earlier light scattering spectra by Sokolov *et al.* [33].

The slow relaxation of the response is best seen from the polarizability anisotropy tcf itself. The normalized tcfs were computed for times up to 12 ps at several different temperatures and are shown in Fig. 2 (symbols). The  $\Psi(t)$  tcfs are very well described by stretched exponentials (lines) and our best fit parameters are listed for each temperature, accordingly. The stretch parameter  $\beta \approx 0.6$ , independent of  $T$  within the range of temperatures considered, is in very good agreement with the OKE experiments [21]. Other studies, theoretical and experimental, of the structural relaxation of supercooled water based on the framework of MCT report very similar values of  $\beta$  [15,18]. The time scale of the simulated OKE relaxation corresponds to the early part of the structural  $\alpha$  relaxation and is roughly 2 orders of magnitude smaller than the time scales involved in previous studies of the intermediate scattering functions and diffusion constants. This is an

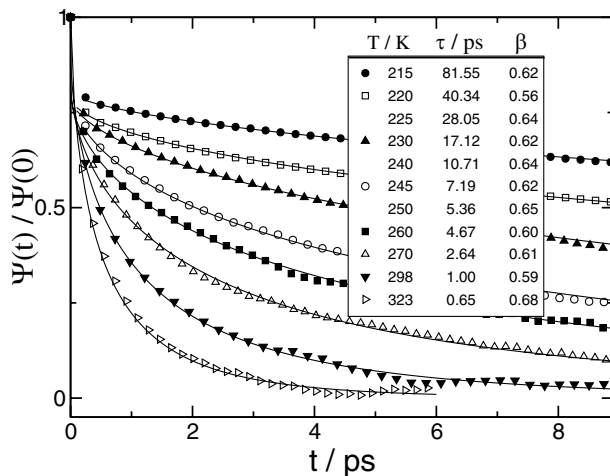


FIG. 2. Collective polarizability anisotropy relaxation for SPC/E water at  $\rho = 1.0 \text{ g/cm}^3$  and different temperatures (symbols). The lines are  $\exp[-(t/\tau)^\beta]$  fits to the data ( $t > 0.2 \text{ ps}$ ) and the best-fitting parameters are tabulated.

important feature, not only because of the shorter MD runs that are required here, but mainly because it has enabled experimental observation [21] of the structural relaxation through a technique that works best for times shorter than a few tens of picoseconds due to the nearly isotropic polarizability of the water molecule, which renders OKE signals of very low intensity.

The relaxation time  $\tau$  is strongly temperature dependent and spans a range substantially larger than the corresponding experimental range, which goes from 0.22 ps at 314 K to 2.20 ps at 254 K [21]. Nevertheless, the temperature dependence of  $\tau$  is very well reproduced by the power law of Eq. (2), with  $\tau_0 = 0.242 \text{ ps}$ ,  $T_S = 198.3 \text{ K}$ , and  $\gamma = 2.35$ , as shown in Fig. 3. These results are in good agreement with the time-resolved Kerr experiments ( $T_S^{\text{exp.}} = 221 \pm 5 \text{ K}$  and  $\gamma^{\text{exp.}} = 2.2 \pm 0.3$ ). The experimental characteristic time is  $\tau_0^{\text{exp.}} = 0.03 \text{ ps}$ . The  $T_S$  obtained from the simulations is  $\sim 22 \text{ K}$  lower than the experimental estimate. This shift is comparable to the maximum density temperature difference ( $\approx 35 \text{ K}$ ) between experiments and MD simulations using the SPC/E model under similar conditions ( $P = 0 \text{ MPa}$ ). Our results for  $T_S$  and  $\gamma$  agree remarkably well with the MD results (199 K,  $\gamma = 2.73$ ) reported by Sciortino *et al.* [15] from the temperature dependence of the incoherent scattering function and mean square displacement. Our findings therefore provide unambiguous support to the interpretation of the Kerr experiments in terms of an underlying dynamics that is closely tied to the liquid’s structural relaxation.

In summary, we have reported for the first time an MD simulation analysis of the optical Kerr effect relaxation for weakly supercooled water and compared directly to very recent time-resolved Kerr spectroscopy measurements. The short time dynamics is quite insensitive to cooling, whereas the long-time relaxation follows the behavior predicted by the MCT in the temperature range considered,

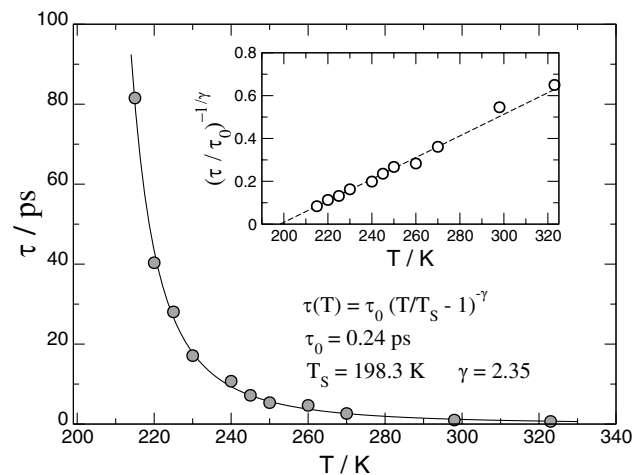


FIG. 3. Temperature dependence of the Kerr relaxation time (symbols). The lines correspond to the power law fit to  $\tau(T)$  with  $T_S = 198.3 \text{ K}$  and  $\gamma = 2.35$ .

in a remarkable agreement with the experimental observation. The characteristic parameters  $\beta$ ,  $T_S$ , and  $\gamma$  we obtain agree well with the parameters obtained from other descriptors of the structural relaxation in supercooled water, thus demonstrating that MCT is a useful framework to analyze the temperature dependence of the post-librational relaxation as probed by time-domain ultrafast spectroscopies. The close relationship between the liquid's responses obtained from the optically heterodyne-detected OKE signal and the solvation responses extracted from the well-known time-resolved fluorescence spectroscopy technique, opens the interesting possibility of investigating the structural relaxation of supercooled water and other liquids by means of fluorescence up-conversion experiments using soluble dyes as spectroscopic probes.

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