

Dielectric Relaxation in Liquid Water: Two Fractions or Two Dynamics?

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Dielectric relaxation in liquid water is studied using molecular dynamics (MD) simulations in the temperature range of 240 to 340 K at atmospheric pressure. The main dielectric and fast relaxation mode are identified in the spectra of dipole moment autocorrelation functions. The microscopic origin of the fast dielectric relaxation process, which takes place on a time scale of subpicoseconds at room temperature, is discussed. A new hypothesis for the fast dielectric mode is presented. It is based on the assumption of the *intrawell* rotational relaxation taking place during the waiting period between thermally activated large angle jumps occurring in the course of changing H-bond partners.

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A two-state description of the structure and dynamics in liquid water has a long and rich history. Evidence of such a description can be found on the fringes of numerous theoretical and heuristic efforts undertaken to understand its unusual properties from very beginning. Wilhelm Röntgen was probably the first to suggest a two-state structural model for liquid water [1]. Later, a number of two-state models emerged and several were outlined in the famous book by Eisenberg and Kauzmann [2]. Two types of solid amorphous water with a featured molecular packing were discovered at lower temperatures [3,4]. Two sounds and two dielectric modes in liquid water were detected and discussed in [5–7]. Tanaka put forward an elegant model to describe the thermodynamic properties of water via the two-state “locally favored structures” formalism [8]. Recent analyses of high resolution x-ray observations again prompted to introduce a combination of two species: tetrahedral and strongly distorted hydrogen-bonded domains [9]. This short list of examples is, of course, far from complete.

In the present Letter, we focus on *two* spectral modes in dielectric relaxation, in particular, on the second *fast* relaxation observed in the high frequency wing of the microwave spectrum, and their possible connection to *two* different types of dynamics or dynamic environments in liquid water. For the first time, the possibility of fast relaxation mode in the dielectric spectrum of water was suggested in the works [6,7]. The strength of this fast mode was found to be low (about 3%–4% that of the main peak). The characteristic time of fast relaxation was estimated to be ~ 1 ps, about 1 order of magnitude faster than the main relaxation process. Temperature effects on the fast relaxation process were examined in [10], and no evidence of any steady trend of its characteristic time with temperature was found. Later, the value of fast relaxation time was corrected to become ~ 0.4 ps at room temperature based on combined dielectric, terahertz, and Raman experimental studies [11].

Experimental data concerning the absorption coefficient in the far-infrared region are also controversial. Using a far-infrared Fourier transform spectrometer with synchrotron radiation as a source, a relatively weak excitation mode at 40 cm^{-1} was identified and reported to be temperature independent in the temperature range of 283 to 343 K [12]. In contrast, the absorption spectra recorded using an intense source of radiation in the range of 10 to 100 cm^{-1} reveal a noticeable temperature effect [13].

Several simulation works have dealt with the absorption spectra in the far-infrared region. A low-frequency mode near 60 cm^{-1} in the spectra of rototranslational cross correlation functions is discussed in [14]. The band was found to be temperature independent and explained as “arising from low-frequency translational modes”. In subsequent work [15], the fast mode with characteristic times of ~ 1 ps was also attributed to the rototranslational coupling in the disordered domains. More detailed simulation results have been reported on the kinetics of hydrogen bonds. For example, Luzar and Chandler [16] have shown that the H-bond kinetics is governed by interplay between diffusion and H-bond dynamics and has the rate constant within the time scale of 0.1 to 1 ps. The H-bond life time distribution with *four* characteristic times has been recently reported by Voloshin and Naberukhin [17], two of which (0.13 and 0.4 ps) can possibly be attributed to the fast dielectric relaxation (*vide infra*).

In general, however, the current state of experimental and theoretical tools accessible for characterization of relaxation processes on a time scale of subpicoseconds cannot as yet be defined as good. Available experimental data in the wave number range of 1 to 100 cm^{-1} are limited, the accuracy of these data is insufficient for an accurate characterization of fast processes (because of their weak intensity), and computer simulation studies of the processes on a time scale of picoseconds over a wide range of temperatures are scarce. As a result, the physical nature of fast relaxation in water is still poorly understood, and we

have undertaken a MD simulations study to examine more closely the microscopic origin of the fast relaxation mode.

We carried out molecular dynamics simulations for a system consisting of 2048 water molecules on NVIDIA Tesla multi core processors for high-performance computing using our own MD code [18] and the TIP4P/2005 potential function [19]. The equations of motion were solved with the quaternion velocity explicit Verlet algorithm [18] subject to the rectangular periodic boundary conditions and a time step of 2 fs. We performed MD simulations in the *NVT* ensemble using the density values reported in [19] with temperature controlled by the Nose–Hoover thermostat.

Our primary focus is on the (normalized) single molecule dipole moment autocorrelation function (ACF) $c(t) = \langle \boldsymbol{\mu}(t)\boldsymbol{\mu}(0) \rangle / \mu^2$, where $\boldsymbol{\mu}$ is the permanent dipole moment of water molecule, with μ being its absolute value. Then, the dielectric permittivity $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ can be computed as

$$\varepsilon(\omega) - n_\infty^2 \approx \frac{N\mu^2 g}{2kTV} \left[1 - \int_0^\infty dt e^{-i\omega t} \frac{\delta c(t)}{\delta t} \right], \quad (1)$$

under the assumption that the reaction field correction factor is $\sim 3/2$. In Eq. (1), g is the Kirkwood factor, n_∞ is the refractive index at very high frequencies, T is the temperature, N is the number of molecules, V is the volume of simulation cell, and k is the Boltzmann constant, and assuming that To minimize numerical errors, the averaging is carried out over initial values of $\boldsymbol{\mu}(0)$ and the reported properties are calculated by averaging over trajectories of 50 ns long. While massive averaging is required at shorter times (< 1 ps) to ensure an accurate characterization of fast modes, lengthy trajectories are needed to ensure accurate calculations of ACFs at longer times.

An example of the single dipole moment ACF for water at room temperature is shown in Fig. 1. It is clearly seen that the relaxation is exponential at longer times (> 1 ps). There is virtually no deviation from a single exponential with the time constant of 5.5 ps up to 16 ps. At shorter times, however, the decay of $c(t)$ is more complex. In addition to fast damped oscillations, shown in the inset of Fig. 1, there is a clear indication of the second relaxation process, which is denoted by the second asymptote (dashed line), with the time constant of about 1 order of magnitude shorter.

A formal approximation of calculated ACFs by a set of single exponentials (using the procedure described in [18], see Eq. 14 wherein) gives relaxation time distributions with three modes (see Fig. 2). The slowest and strongest mode has a relaxation time of the order of several picoseconds and is related to the main dielectric process. The peak position of the main dielectric mode shifts rapidly toward shorter times (from 41 ps at 240 K to 3 ps at 330 K) with increasing temperature, thus indicating the relaxational

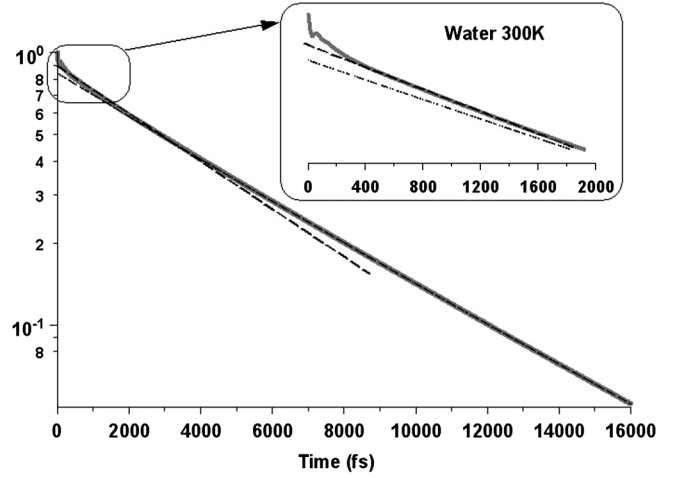


FIG. 1. Single molecule dipole moment ACF for water at 300 K. Two relaxation processes are indicated by the dashed lines (asymptotes).

nature of this mode. The fastest mode is indicated by the peak centered at about 0.1–0.3 ps. It should be noted that deriving an exact position of this mode from the distribution functions with the technique described in [18] is not viable, as an exponential is not a good approximation of damped oscillations such as shown in the inset of Fig. 1, and we will use a more rigorous approach later. Nevertheless, the mode is clearly resolved and centered near 0.1 ps (50 cm^{-1}) at 240 K and near 0.25 ps (20 cm^{-1}) at 330 K. The intermediate mode appears as a weak peak centered at 2.5 ps in supercooled water at 240 K. Its amplitude increases slightly with increasing temperature and shifts toward shorter times reaching the value of 0.8 ps at 330 K.

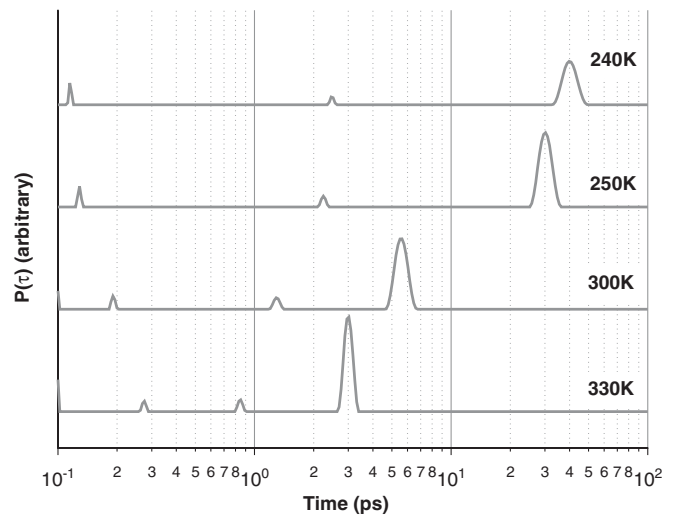


FIG. 2. Temperature effects on relaxation time distributions derived by the inversion of single dipole moment ACFs for liquid water.

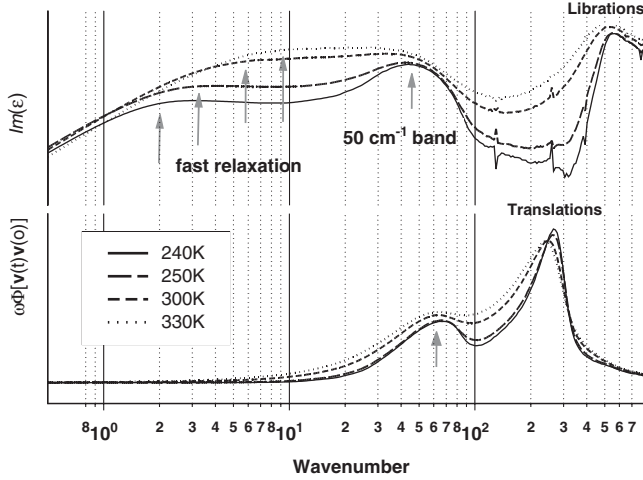


FIG. 3. Spectra of the imaginary part of dielectric permittivity (top plot) and spectral density of states for center-of-mass translations (bottom plot).

Further analysis was performed using Eq. (1). For illustration purposes, the main dielectric relaxation (shown by the dashed line at longer times in Fig. 1) was subtracted from the total ACFs before calculations. The imaginary part of dielectric permittivity calculated with Eq. (1) is shown in the top plot of Fig. 3. All computed parameters are also given in Table I. The strong librational band is seen at higher frequencies ($\sim 600 \text{ cm}^{-1}$). At lower frequencies, the spectra of dielectric permittivity indicate two overlapped modes: (1) a vibrational band centered at $\sim 50 \text{ cm}^{-1}$ and a mode that undergoes temperature transition from 2 cm^{-1} at 240 K to 9 cm^{-1} at 330 K. The peak positions of this mode are indicated by arrows in the top plot of Fig. 3. It is this spectral mode that is referred to as the *fast relaxation* and is the central topic of the discussions that follows.

The parameters of dielectric relaxation in liquid water derived from MD simulations are summarized in Table I. The main (single molecule) relaxation time decreases with increasing temperature from 41 ps at 240 K to 2.6 ps at

340 K. The characteristic time of the second fast relaxation also decreases from 2.5 to 0.5 ps, while the mode at 50 cm^{-1} appears to be temperature independent. In order to examine its connection to the translational motion in water, we computed the spectral density of states for velocity of center-of-mass (COM) ACFs, $c_V(t) = \langle \mathbf{v}(t)\mathbf{v}(0) \rangle$, as follows $c_V(\omega) = \int dt e^{-i\omega t} \delta c_V(t) / \delta t$, and $\mathbf{v}(t)$ is the COM velocity. Calculated translational densities of states are shown in the bottom plot of Fig. 3. A similar temperature independent spectral feature near $50\text{--}60 \text{ cm}^{-1}$ is well-resolved, indicating that the mode at 50 cm^{-1} is indeed linked to strong rototranslational interactions [14,15]. At the same time, no indication of slower ($< 50 \text{ cm}^{-1}$) relaxation can be seen in the translational spectra, and the fast relaxation mode observed in the dielectric spectra between 2 and 10 cm^{-1} (see the top plot of Fig. 3) appears to be purely rotational in nature. Two scenarios are considered here to account for the fast relaxation process in liquid water.

Scenario 1 is familiar *structural* interpretation and is based on a two-fraction description. Namely, a small fraction of weakly bound molecules is responsible for the fast relaxation mode, while remaining vast majority of the molecules are responsible for the main slow dielectric relaxation. The fraction value follows from the decomposition of experimental data into two Debye terms and is about 4% or less [6,7,10,11]. Buchner *et al.* [10] related the fast relaxation mode to large angle rotations of “mobile” molecules. The fast mode was interpreted as a fast dipolar reorientation process attributed to undercoordinated water in [20], etc. The fraction of molecules that form only two hydrogen bonds with their neighbors is reported to be 3.6% at room temperature [21]. This seems to be in agreement with the results of decomposition of experimental dielectric spectra. However, the coordination analysis performed in [21] reveals a smooth fraction distribution ranging from undercoordinated molecules forming only 2 H bonds to overcoordinated molecules with 5 H bonds, while the dielectric spectrum shows *only two* resolved dielectric modes. Although the structural scenario has the right to

TABLE I. Characteristic times, frequencies, and static dielectric constants τ_1 , τ_2 , and τ_{50} are characteristic times of the main dielectric mode, fast mode, and band at 50 cm^{-1} , respectively. Δ_1 , Δ_2 , and Δ_{50} are their amplitudes. f_L and f_R are peak positions of librational and translational bands. ϵ_s is static permittivity.

T(K)	τ_1 (ps)	τ_2 (ps)	τ_{50} (ps)	Δ_2/Δ_1	Δ_{50}/Δ_1	f_L (cm^{-1})	f_R (cm^{-1})	ϵ_s
240	41.0	2.5	0.11	0.05	0.09	580	230	73
250	31.0	2.0	0.11	0.05	0.09	570	230	69
260	17.0	1.6	0.12	0.06	0.08	560	240	66
280	9.0	1.2	0.12	0.07	0.07	550	240	61
300	5.4	0.9	0.12	0.08	0.06	530	250	57
320	3.8	0.7	0.13	0.08	0.05	520	260	52
330	3.0	0.6	0.14	0.09	0.06	500	270	49
340	2.6	0.5	0.14	0.09	0.07	500	270	48

exist, we are inclined to accept a different explanation for the fast dielectric mode.

Scenario 2 is *dynamical*. Under this hypothesis, we apply a general (albeit simplified) model of dielectric relaxation to liquid water, specifically—reorientations of fixed axis dipoles in a double well effective potential. The central assumption behind this is that the orientation of the dipole moment of a central water molecule surrounded by four closest neighbors in the local structures of liquid water has several preferential directions. Thus, there exist several quasiequilibrium orientations (in the simplest case two) with fixed dipole directions and the bistability (multistability) of orientations originates naturally from the process of H-bond breaking and making in the course of changing H-bond partners.

The rotational motion of rotators in 3D space in the double well potential, $V(\theta)/kT = -2\sigma(\cos\theta)^2$, where $\sigma = V_0/2kT$, gives rise to three fundamental modes [22]. Their characteristic times can be approximately given as: (a) the relaxation time of the main dielectric process τ_1 , resulting from thermally activated escape of molecules from the wells, which is strongly temperature dependent, just as any activation process

$$\tau_1 \sim \tau \frac{\sqrt{\pi}}{2\sigma^{1.5}} e^{2\sigma} \quad (2)$$

(b) the intrawell relaxation time τ_2 , which is temperature dependent via the temperature dependence of the dynamic viscosity

$$\tau_2 \sim \tau \frac{1}{4\sigma} \quad (3)$$

and (c) the period of rotational inertial oscillations inside the potential wells τ_L , normally referred to as librations

$$\tau_L \sim \sqrt{\frac{I}{4\sigma kT}} \quad (4)$$

where $\tau = \zeta/2kT$, $\zeta = 4\pi\eta a^3/kT$, a is the radius of the particle, I is the moment of inertia, η is the dynamic viscosity [23]. The approximations (a)–(c) are valid if $2\sigma > 3$ [22]. We computed the dynamic viscosity using the following empirical relation $\eta(T) = A \times 10^{B/(T-C)}$, where $A = 2.414 \times 10^{15}$ Pa·s, $B = 247.8$ K, and $C = 140$ K. In Fig. 4, the values τ_1 , τ_2 , and τ_L computed using the above relations (lines) together with those derived with MD simulation (symbols) are shown as a function of temperature.

Although agreement is merely qualitative, such a simplified description for rotations in the bistable cosine potential, nevertheless, captures all the essential aspects of reorientational dynamics in liquid water as well as their temperature evolution. Thus, the fast relaxation process can be accounted for without introducing a fraction of mobile, undercoordinated, or weakly bound molecules. If the fast mode resulted from a fraction of mobile molecules,

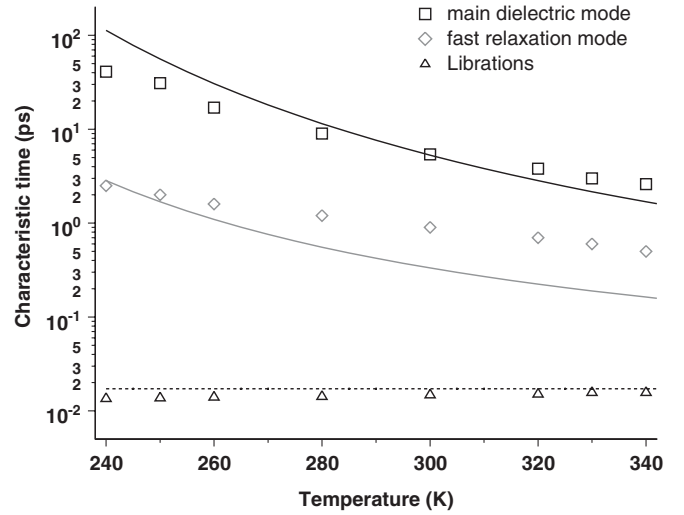


FIG. 4. Temperature effect on dielectric relaxation times in liquid water. Values obtained with MS simulation are shown by the symbols. Estimates derived by using the model of fixed axis rotators in the double well cosine potential are shown by the solid lines.

there should be at least some coupling to translations, which is not the case, as no indication of such a mode can be found in the spectra of center-of-mass velocity ACFs, and the fast dielectric relaxation appears purely rotational. In contrast to the *structural* scenario, where only a small fraction of molecules is considered to participate in the fast relaxation, the *dynamical* scenario assumes that (almost) all molecules in the bulk water make contributions to it. The dynamical approach to fast relaxation strongly supports the hypothesis of large angle jumps as the primary mechanism of reorientations in liquid water [24]. From which it follows that molecules remain in quasiequilibrium states on the duration of the waiting period between jumps, during which the *intrawell* relaxation takes place, while the main relaxation mode results from thermally activated jumps in the course of breaking and making *H* bonds.

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