

Unveiling dielectric relaxation and shear rheology in water

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The complex dynamics of liquid water are manifested in its unique dielectric relaxation and nonlinear shear rheology. We investigate the dielectric and rheological responses of TIP4P/ε water using molecular dynamics simulations across a wide temperature range, including the deeply supercooled regime. We demonstrate that the fast secondary Debye relaxation is faithfully captured by the continuous, history-dependent hydrogen-bond lifetime, τ_{HB} , which directly accounts for the high-frequency deviation of the dielectric loss, $\varepsilon''(\omega)$, from classical Debye behavior. Unlike the history-independent intermittent lifetime $\hat{\tau}_{\text{HB}}$, which scales linearly with the primary relaxation time τ_1 and the α -relaxation time τ_α , the lifetime τ_{HB} exhibits a distinct nonlinear dependence that characterizes the local kinetic rupture of individual bonds. We establish a link between dielectric relaxation and shear thinning, revealing that the onset of thinning occurs at a critical shear rate $\dot{\gamma}_0 \lesssim 1/\tau_1 \sim 1/\tau_\alpha$, governed by the competition between the shear deformation and the slowest mode of structural relaxation. Furthermore, we explore the impact of ionic solutes on the primary relaxation time τ_1 in NaCl solutions. We find that τ_1 exhibits a nonmonotonic dependence on salt concentration, reflecting a competition between the disruption of bulk hydrogen bonds and the formation of rigid hydration shells. Our study elucidates the connection between hydrogen bonding, dielectric relaxation, and shear rheology, providing insights applicable to other tetrahedral liquids.

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I. INTRODUCTION

Understanding the dielectric properties of water and the underlying molecular relaxation mechanism remains an important problem in chemical physics [1–4]. Dielectric properties reflect the response of molecular dipoles to an applied electric field and are linked to the reorientation of water molecules [1]. It is widely known that frequency-dependent dielectric spectra, $\varepsilon(\omega)$, exhibit a characteristic peak in the dielectric loss, $\varepsilon''(\omega)$, corresponding to the cooperative reorientation of water molecules. This primary relaxation is quantified by a timescale $\tau_1 \approx 8$ –9 ps at room temperature and is traditionally described by the Debye model, which assumes a single exponential decay of the dipole correlation function [1]. However, experimental $\varepsilon''(\omega)$ results deviate from Debye predictions, exhibiting a high-frequency excess above $\approx 2 \times 10^{11}$ Hz. To account for this, a secondary fast Debye relaxation with a timescale $\tau_2 \lesssim 1$ ps has been proposed [1,5]. This rapid rate suggests a highly localized kinetic event, distinct from the collective reorientation of the bulk system.

While the primary Debye relaxation is often associated with the cooperative reorientation, the origin of the fast

secondary Debye relaxation remains debated [1]. Previous works, rooted in a two-fraction framework, attribute this mode to the fast rotations of weakly hydrogen-bonded water molecules [6]. Other proposals link it to distinct molecular motions [4,7]. Recently, the deviation from the Debye model has been traced to the global fluctuations of the hydrogen-bond network, facilitated by the hopping of structural defects [3]. Despite differing mechanistic interpretations, a consensus is emerging that hydrogen-bond dynamics lie at the heart of the fast Debye relaxation. This is supported by the picosecond-scale dynamics of hydrogen bonds, which constantly form and break on a short timescale coinciding with that of τ_2 [8–10]. Consequently, analyzing hydrogen bonding provides crucial insights into the relaxation processes of water [11–13].

Another intriguing phenomenon in water, particularly in the supercooled state, is shear thinning—the reduction in viscosity with increasing shear rate. The application of external fields, such as shear, perturbs the equilibrium structure of water [14], where molecular alignment and hydrogen-bond breaking can significantly alter the viscosity. Previous simulations have revealed a crossover from Newtonian to non-Newtonian behavior, characterized by a power-law shear-thinning regime [15,16]. However, molecular-level connection between dielectric relaxation and shear thinning remains unclear, although both phenomena are controlled by hydrogen bonds.

Furthermore, the addition of ions significantly alters the structure and dynamics of water [17,18]. Ions disrupt the hydrogen-bond network and induce the formation of

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TABLE I. Parameters for the standard TIP4P/ε water model [21].

Atom	Charge (<i>e</i>)	σ (Å)	ϵ (kJ/mol)	d_{OH} (Å)	d_{OM} (Å)	θ (°)	μ (D)
O	0	3.165	0.7732	0.9572	0.105	104.52	2.4345
H	0.527						
M	-1.054						

hydration shells, which strongly affect the orientational and translational mobility of water [18,19]. This ionic effect profoundly changes the dielectric properties of solution [6,17]. Understanding how ions affect water's dielectric relaxation is also fundamentally important [6,13,20]. However, experimental studies are often limited to a specific range of ion concentration [6].

Despite extensive research, a complete molecular picture of water's dielectric and shear response remains elusive. Critical questions persist regarding the physical origin of water's Debye relaxation, its connection to shear thinning, and their dependence on parameters such as temperature and ionic concentration. In this work, we employ classical molecular dynamics (MD) simulations of TIP4P/ε water [21] to systematically investigate dielectric relaxation and hydrogen bonding in pure water and in NaCl solutions across a wide range of concentrations. We demonstrate that the fast Debye relaxation can be faithfully described by the breakup of hydrogen bonds. The timescale of the hydrogen-bond lifetime τ_{HB} coincides with the high-frequency region where the dielectric loss $\epsilon''(\omega)$ deviates from the single-Debye prediction. To establish the connection to shear thinning, we show that the characteristic shear rate $\dot{\gamma}_0$, above which shear thinning occurs, satisfies the condition $\dot{\gamma}_0 \tau_1 \lesssim 1$. We attribute this relationship to the dynamic inhomogeneities of supercooled water. Notably, we also find that ion concentration modulates the primary relaxation time τ_1 in a nonmonotonic manner, which arises from the competition between two opposing effects: the disruption of the hydrogen-bond network and the formation of hydration shells. Our work provides crucial molecular insights into the mechanisms governing water's relaxation dynamics, establishing a close link between hydrogen bonding, dielectric relaxation, and shear rheology.

II. MODEL AND METHODS

A. Molecular dynamics simulations

The equilibrium MD simulations were performed using the LAMMPS package [22] with the TIP4P/ε water model [21], which is known for accurately reproducing the dielectric constant of water (see Table I for force fields). The simulation system consists of 500 water molecules in a cubic box. The system was equilibrated in the *NPT* ensemble at $P = 1$ atm for at least 5 ns to ensure thermal equilibrium across a temperature range of 240–450 K (specifically, $T = 240, 260, 280, 300, 330, 360, 400$, and 450 K). This was followed by production runs in the *NPT* ensemble lasting at least 20 ns, with the duration extended to 300 ns for the $T = 240$ K case to account for slower relaxation dynamics at lower temperatures. The temperature was maintained at the target value using a Noseé-Hoover thermostat with a damping parameter

of 100.0 fs. A time step of 2 fs was used for integration [5,21,23]. Long-range electrostatic interactions were treated using the particle-particle particle-mesh algorithm [24,25] with a relative force accuracy of 10^{-5} .

For the nonequilibrium shear simulations, the system consisted of 5000 water molecules in a cubic box. Shear deformation was applied in the *xz* plane with shear rates $\dot{\gamma}$ ranging from 10^{-3} to 10^{-7} fs^{-1} (corresponding to 10^{12} – 10^8 s^{-1}). The system was first equilibrated in the *NPT* ensemble at $P = 1$ atm to determine the equilibrium box size. Subsequently, the system was switched to the *NVT* ensemble while applying the shear deformation [15,16]. A steady shear flow was applied to the system by deforming the simulation box at a constant shear rate using the “fix deform” command in LAMMPS. The resulting flow field was maintained using the SLLOD equations of motion, which are the standard algorithm for simulating homogeneous shear under such conditions. We employed *NVT* ensembles for shear simulations to maintain a constant density, ensuring that the observed changes in relaxation times and viscosity are directly attributable to the shear-induced structural perturbations. While constant-pressure conditions ($NP_{yy}T$) might more closely mimic certain experimental setups, the high incompressibility of water ensures that the results in the *NVT* ensemble are representative of the steady-state rheology.

For the investigation of NaCl electrolytes at $T = 300$ K, we employ the Joung-Cheatham NaCl model [26] optimized for compatibility with the TIP4P/ε model. The force field parameters of the Joung-Cheatham model [26] are detailed in Table II. The system was constructed by adding NaCl to the pure water of 500 water molecules. A range of NaCl concentration c_s from 1 up to 6 mol/kg was investigated. The concentration was set below the solubility limit of 6.15 mol/kg.

B. Calculation of dielectric spectrum

The dielectric spectra were calculated using the polarization autocorrelation function. This method is based on the fluctuation-dissipation theorem and is the standard technique for obtaining frequency-dependent permittivity from equilibrium MD simulations. The normalized polarization autocorrelation function $\phi(\Delta t)$ is defined as

$$\phi(\Delta t) = \frac{\langle \mathbf{M}(t_0) \cdot \mathbf{M}(t_0 + \Delta t) \rangle}{\langle |\mathbf{M}(t_0)|^2 \rangle}, \quad (1)$$

where $\mathbf{M}(t_0)$ represents the total dipole moment of the system at the initial time t_0 ; the correlation function is computed as an ensemble average over all possible time origins t_0 , with every time step in the trajectory serving as a starting point.

The frequency-dependent dielectric response can be related to the time correlation of polarization fluctuations through

TABLE II. Parameters for the Joung-Cheatham NaCl solution model [26].

Lennard-Jones	σ (Å)	ε (kJ/mol)	Charge	q (e)
Na ⁺ -Na ⁺	2.160	1.4752	Na ⁺	+1.0
Cl ⁻ -Cl ⁻	4.830	0.0536	Cl ⁻	-1.0
Na ⁺ -Cl ⁻	3.495	0.2811		
Na ⁺ -O	2.6625	1.0681		
Cl ⁻ -O	3.9975	0.2035		
O-O	3.165	0.7732	O	0.0
			H	+0.527
			M	-1.054

linear-response theory [27]. The relationship between the dielectric constant and the time derivative of the polarization correlation function is given by

$$\frac{\varepsilon(\omega) - 1}{\varepsilon(0) - 1} = \int_0^\infty \left(-\frac{d\phi(t)}{dt} \right) \exp(-i\omega t) dt, \quad (2)$$

where $\varepsilon(0)$ is the static dielectric constant and ω is the angular frequency. $\varepsilon(0)$ is computed from the dipole moment fluctuations using the following formula:

$$\varepsilon(0) = 1 + \frac{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{3\varepsilon_0 V k_B T}, \quad (3)$$

where $\langle \mathbf{M}^2 \rangle$ is the mean squared dipole moment, $\langle \mathbf{M} \rangle^2$ is the squared mean dipole moment, V is the simulation box volume, k_B is the Boltzmann constant, T is the temperature, and ε_0 is the vacuum permittivity. For nonpolarizable rigid water models such as TIP4P/ε model, the high-frequency limit is taken as $\varepsilon_\infty = 1$.

However, direct calculation of $\varepsilon(\omega)$ based on the integrals in Eq. (2) is generally inaccurate in numerical calculations. We choose to fit $\phi(t)$ with a double-exponential Debye model, and the analytical expression offers a well-defined route to determine $\varepsilon(\omega)$. Specifically, the dielectric spectra were obtained from the fitted $\phi(\Delta t)$ curve, including primary Debye relaxation and high-frequency excess from hydrogen bonding:

$$\phi(t) = A_1 \exp(-t/\tau_1) + A_{HB} \exp(-t/\tau_{HB}). \quad (4)$$

Here, τ_{HB} is the hydrogen-bond lifetime defined as the average duration of hydrogen-bond existence. It is computed directly from the simulation trajectory by tracking the persistence time of each bond, thereby providing a physically rigorous value. The relaxation time τ_1 , along with the amplitude coefficients A_1 and A_{HB} , are fitting parameters obtained by employing the non-negative least squares (NNLS) method to fit $\phi(t)$. Based on the fitting of $\phi(t)$, the frequency-dependent dielectric constant $\varepsilon(\omega)$ can be analytically derived. The integral in Eq. (2) can be evaluated for each exponential component. For a single mode $\exp(-t/\tau)$, the integral is

$$\int_0^\infty \exp(-t/\tau) \exp(-i\omega t) dt = \frac{1}{1/\tau + i\omega}. \quad (5)$$

Applying this result to the fitted $\phi(t)$, the complex dielectric spectrum becomes

$$\varepsilon(\omega) = 1 + (\varepsilon(0) - 1) \left[\frac{A_1/\tau_1}{1/\tau_1 + i\omega} + \frac{A_{HB}/\tau_{HB}}{1/\tau_{HB} + i\omega} \right]. \quad (6)$$

The real part of $\varepsilon(\omega)$, which represents the dielectric storage, can be expressed as

$$\varepsilon'(\omega) = 1 + (\varepsilon(0) - 1) \left[\frac{A_1}{1 + (\omega\tau_1)^2} + \frac{A_{HB}}{1 + (\omega\tau_{HB})^2} \right]. \quad (7)$$

The imaginary part of $\varepsilon(\omega)$, which represents the dielectric loss, can then be calculated as

$$\varepsilon''(\omega) = (\varepsilon(0) - 1) \left[\frac{A_1\omega\tau_1}{1 + (\omega\tau_1)^2} + \frac{A_{HB}\omega\tau_{HB}}{1 + (\omega\tau_{HB})^2} \right]. \quad (8)$$

C. Hydrogen-bond lifetime τ_{HB}

Hydrogen bonds were identified using geometric criteria [9,28]. A hydrogen bond is considered to exist between two water molecules when the following conditions are simultaneously satisfied: (1) the distance between two oxygen atoms is less than 3.5 Å and (2) the angle H-D-A is less than 30°, where the D represents the donor oxygen atom, and the A represents the acceptor oxygen atom [9,28].

We determine the connectivity between water molecules at each time step, creating an $n \times n$ boolean matrix (1 for bonded, 0 for not bonded). The hydrogen-bond lifetime τ_{HB} was defined as the average duration of consecutive bonded states for all molecule pairs across the whole trajectory. This definition ensures that τ_{HB} characterizes the continuous persistence of hydrogen bonds, and we show it provides a timescale relevant to the fast secondary dielectric relaxation mode.

D. α -relaxation time

The α -relaxation time τ_α is the characteristic timescale for the decay of self-density correlations in a liquid. This timescale is determined from the self-intermediate scattering function, $F_s(q, t)$, defined as

$$F_s(q, t) = \langle \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \rangle, \quad (9)$$

where $\mathbf{r}_j(t)$ denotes the position of the j th molecule at time t . The relaxation time τ_α is extracted using the condition $F_s(q, \tau_\alpha) = e^{-1}$. Following the previous work [29], the magnitude of the wave vector $\mathbf{q}$ is chosen as the first peak of the static structure factor $S(q)$.

E. Water structure descriptors

1. Orientational order parameter θ

The angular descriptor θ is defined based on the local arrangement around each oxygen atom. For a given central oxygen atom, only neighboring oxygen atoms within 3.3 Å (the minimum after the first peak in the oxygen-oxygen radial distribution function) are considered. The descriptor θ is calculated as the average of all angles formed between pairs of adjacent oxygen atoms and the central oxygen atom. If the central oxygen atom has n neighboring oxygen atoms, there are $C_n^2 = n(n-1)/2$ angles to be averaged [30]. The parameter θ reflects orientational order within the first coordination shell [31,32].

2. Translational order parameter ζ

The structural descriptor ζ is defined as

$$\zeta = r_2 - r_1, \quad (10)$$

where r_2 is the distance from the central oxygen atom to the nearest oxygen atom that does not form a hydrogen bond and r_1 is the distance from the central oxygen atom to the farthest oxygen atom that forms a hydrogen bond [30]. The descriptor ζ captures translational order of the second coordination shell [33].

3. Dipolar ordering parameter $\cos \beta$

To quantify the orientation of water's dipoles around ions, a descriptor denoted as β is introduced. For a central ion, β represents the angle between two vectors: (1) the dipole moment vector $\vec{\mu}$ of a water molecule in the solvation shell and (2) the radial vector $\vec{r}$ connecting the central ion to the oxygen atom of the water molecule. Water molecules within the first solvation shell—identified by the first minimum in the $\text{Na}^+ - \text{O}$ or $\text{Cl}^- - \text{O}$ radial distribution function (RDF)—are considered. The descriptor β quantifies the orientation of water's dipole moments relative to the radial vector pointing from the ion to the oxygen atom.

F. Calculation of shear viscosity

During the nonequilibrium MD simulations, we apply a shear deformation in the xz plane and computed the viscosity from the corresponding stress tensor component σ_{xz} according to the relation

$$\eta = \frac{\langle \sigma_{xz} \rangle}{\dot{\gamma}}, \quad (11)$$

where $\langle \sigma_{xz} \rangle$ is the average off-diagonal component of the stress tensor under steady shear and $\dot{\gamma}$ is the applied shear rate. The stress tensor components were computed using the virial expression during the nonequilibrium MD simulation. The stress tensor was calculated for each atom using the compute stress/atom command in LAMMPS [22], which implements the Irving-Kirkwood formulation. The details of how LAMMPS computes the stress tensor under periodic boundary conditions are described in Refs. [34,35].

G. Dielectric relaxation function in ionic solutions

In ionic solutions, the dielectric relaxation function is evaluated using a nonequilibrium approach based on the response to a static external electric field E_x (assume it is applied in the x direction) [36,37]. The dielectric relaxation function is defined as

$$\phi(\Delta t) = \frac{\langle (P_x(t_0) - P_x^0)(P_x(t_0 + \Delta t) - P_x^0) \rangle_{t_0}}{\langle (P_x(t_0) - P_x^0)^2 \rangle_{t_0}}. \quad (12)$$

Here, P_x^0 is the steady-state polarization induced by a small static field E_x within the linear-response regime, defined as

$$P_x^0 = M_x/V, \quad (13)$$

where M_x is the x component of the total dipole moment and V is the volume of the system.

III. RESULTS AND DISCUSSION

A. Calculation of dielectric spectra

We first analyze the dielectric relaxation in TIP4P/ε water at room temperature of $T = 300$ K. The polarization autocorrelation function $\phi(t)$ can be accurately captured by a dual-exponential decay, $\phi(t) = A_1 \exp(-t/\tau_1) + A_{\text{HB}} \exp(-t/\tau_{\text{HB}})$ [Fig. 1(a)]. We find the fitted slow timescale, $\tau_1 = 13.2$ ps, is close to the experimental primary Debye relaxation time $\tau_1 \approx 8\text{--}9$ ps, given the known slight overestimation by the TIP4P/ε model [5]. The calculated τ_1 agrees with the value reported in Ref. [5]. The faster timescale, $\tau_{\text{HB}} \approx 0.27$ ps, is defined as the average lifetime of hydrogen bonds, as detailed in Sec. II C. The timescale of the secondary Debye relaxation agrees with prior experimental works [39–41].

The analytical form of $\phi(t)$ allows for the direct calculation of the real component of the dielectric spectrum $\epsilon'(\omega)$ [Fig. 1(b)] and the imaginary component of the dielectric spectrum $\epsilon''(\omega)$ [Fig. 1(c)] via Eqs. (7) and (8), respectively. Figure 1(b) presents the frequency dependence of the real part of the dielectric constant at $T = 300$ K. The dielectric response $\epsilon'(\omega)$ (black line) shows a primary relaxation drop around $f \approx 10^{10}$ Hz, which corresponds to the main peak in the imaginary part $\epsilon''(\omega)$ [Fig. 1(c)]. As shown in Fig. 1(c), the calculated $\epsilon''(\omega)$ (black line) qualitatively reproduces the primary features of the experimental data (blue line) up to 10^{12} Hz, notably exhibiting a high-frequency excess that deviates from the standard Debye model with a single relaxation mode. The main peak, centered around $f \approx 10^{10}$ Hz (corresponding to $1/\tau_1$), is attributed to the slower, primary structural relaxation. This peak dominates the spectrum and reflects the collective, cooperative reorientation of the entire hydrogen-bond network. A high-frequency excess is visible above $f \approx 2 \times 10^{11}$ Hz, which directly coincides with the secondary peak (corresponding to $1/\tau_{\text{HB}}$). Thus, our result supports the interpretation that the high-frequency excess in $\epsilon''(\omega)$ is attributed to the rapid breaking of hydrogen bonds characterized by the timescale τ_{HB} . The qualitative agreement between the calculated $\epsilon''(\omega)$ and experimental data [5] also supports the dual-exponential description of $\phi(t)$ (up to 10^{12} Hz) and indicates that the history-dependent hydrogen-bond lifetime τ_{HB} represents the characteristic

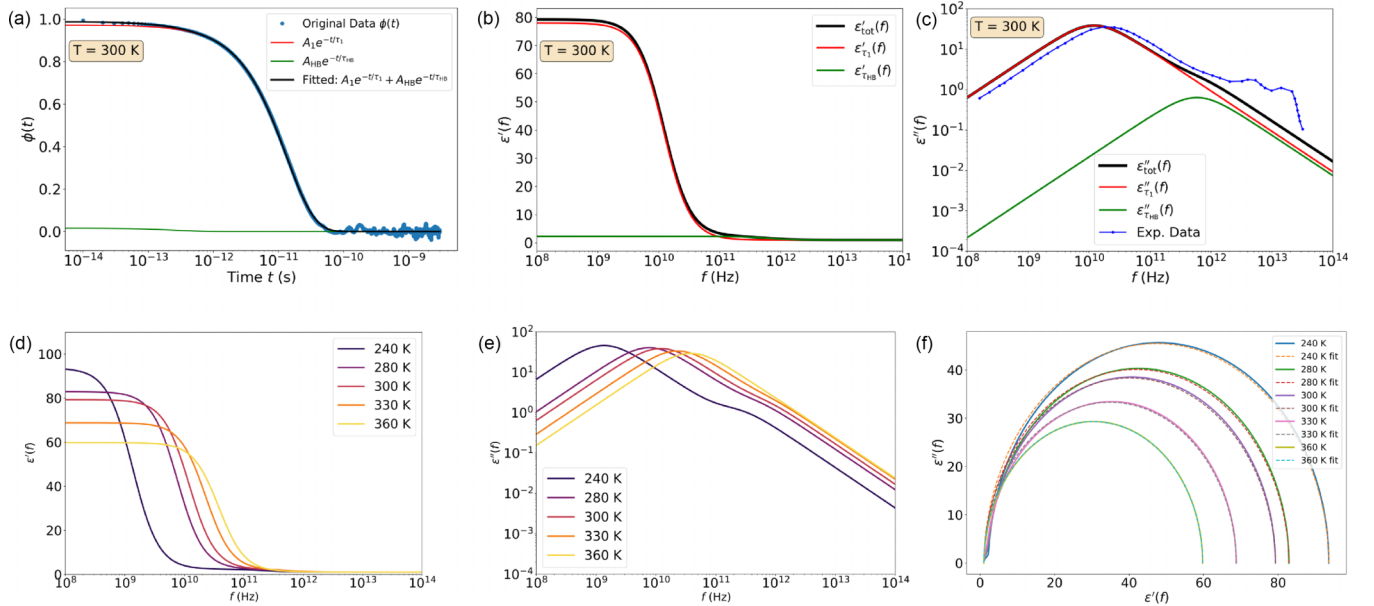


FIG. 1. Polarization autocorrelation function $\phi(t)$ and complex dielectric spectra of TIP4P/ ϵ water [21] at $T = 300$ K and temperature dependence of the complex dielectric spectrum. (a) The original data for $\phi(t)$ at $T = 300$ K and its fit via the NNLS method, decomposed into two relaxation modes with characteristic times τ_1 and τ_{HB} . (b) Display of the real part of the complex dielectric spectrum $\epsilon'(f = \omega/2\pi)$, separated into contributions from the relaxation modes of τ_1 (red line) and τ_{HB} (green line). (c) Display of the imaginary part of the complex dielectric spectrum $\epsilon''(f = \omega/2\pi)$ (black line), separated into contributions from the relaxation modes of τ_1 (red line) and τ_{HB} (green line), alongside the experimental data (blue line) [5]. (d), (e) Real and imaginary parts of the complex dielectric spectrum at different temperatures (240–360 K). (f) Cole-Cole representation (ϵ'' vs ϵ') [38] of the dielectric response at different temperatures (240–360 K).

timescale of the secondary Debye relaxation. We note that the experimental spectrum exhibits additional features at even higher frequency ($f \approx 10^{13}$ Hz), which originates from librational and vibrational modes of water. These high-frequency molecular motions are not captured by the rigid, nonpolarizable TIP4P/ ϵ water model employed in this study.

The evolution of the dielectric response across the temperature range of 240–360 K, as illustrated in Figs. 1(d)–1(e), reveals several key features of water's dynamics. As the temperature decreases, the primary relaxation step shifts to lower frequencies. This shift reflects the significant slowing of structural dynamics as water enters the supercooled regime. Simultaneously, the static dielectric constant, $\epsilon_s = \epsilon'(\omega \rightarrow 0)$, increases significantly as T drops toward 240 K. The peaks in the imaginary spectrum also shift toward the low-frequency regime at lower temperatures. Across the wide range of temperatures (240 and 280 K; Fig. S1 in the Supplemental Material [42]), the dielectric relaxation in supercooled water is consistently governed by the same underlying mechanisms: slow, cooperative water reorientation (τ_1) and fast, localized hydrogen-bond dynamics (τ_{HB}). Notably, the peak broadening observed at 240 K [Fig. 1(e)] suggests an increase in dynamical heterogeneity as the system approaches a deeply supercooled state. This broadening highlights the essential role of the secondary Debye relaxation mode, characterized by the hydrogen-bond lifetime τ_{HB} , in determining the overall shape of the dielectric spectrum $\epsilon''(\omega)$ at low temperatures. The corresponding Cole-Cole plots are also shown in Fig. 1(f). In Cole-Cole representation, the dielectric function is often

fitted as

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}, \quad (14)$$

where α ($0 \leq \alpha < 1$) is the Cole-Cole parameter that quantifies the deviation from the Debye relaxation ($\alpha = 0$). Upon lowering the temperature, we find that the value of α gradually increases, confirming a gradual deviation from the ideal Debye relaxation.

B. Two-state features of TIP4P/ ϵ water

To demonstrate the presence of two distinct structural motifs in TIP4P/ ϵ water, we use a two-order-parameter approach based on the translational order parameter ζ and the orientational order parameter θ [30]. Here, ζ is defined as the difference between the minimum distance to a non-hydrogen-bonded neighbor and the maximum distance to a hydrogen-bonded neighbor [33], while θ represents the average angle formed between an oxygen atom and its neighboring oxygens [31,32]. We analyze the bivariate distribution $P(\zeta, \theta)$ for TIP4P/ ϵ water [Fig. 2(a)]. Consistent with findings in TIP4P/2005 water [30], we observe two distinct peaks separated by a pronounced valley, highlighting the two-state character of TIP4P/ ϵ water. The peak near $\zeta \approx 0.5$ Å and $\theta \approx 109^\circ$ corresponds strongly to hydrogen-bonded (S -state) water. These molecules form tetrahedral structures through four hydrogen bonds. The second peak signifies the less bonded (ρ -state) water. These molecules are characterized by three hydrogen bonds but possess a higher local density. At lower temperatures of 240 and 280 K (Fig. S2 in the

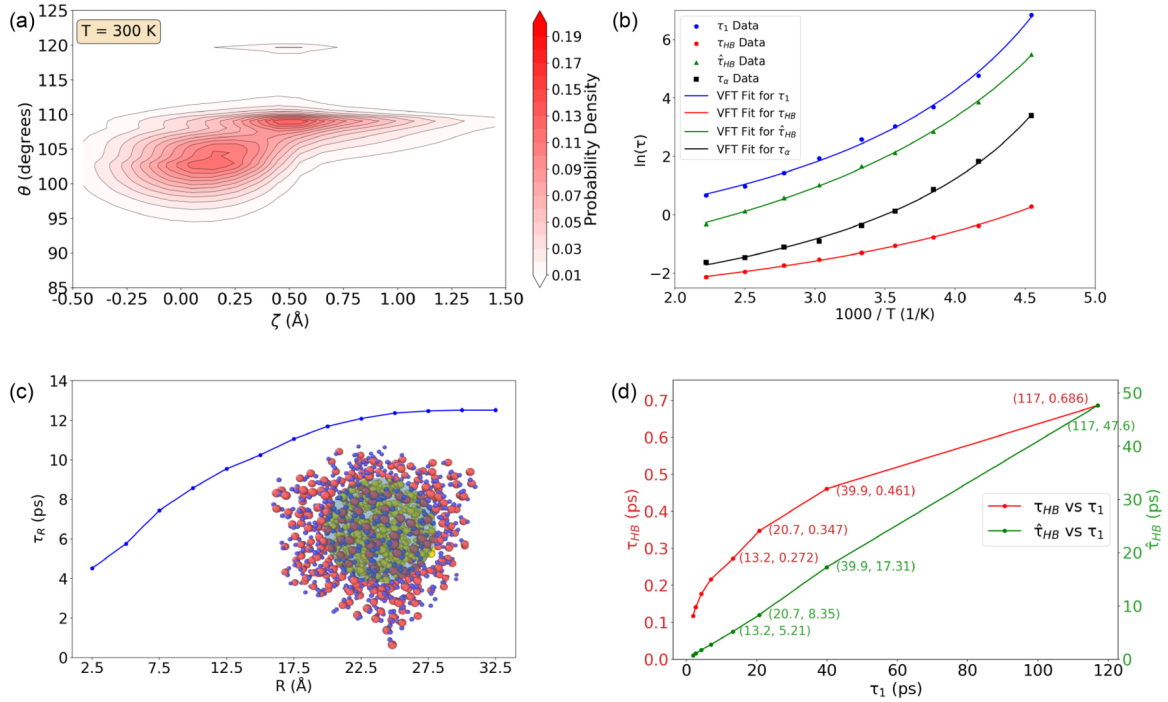


FIG. 2. Structural and dynamical properties of TIP4P/ε water. (a) Probability distribution $P(\zeta, \theta)$ at $T = 300$ K, showing the existence of two structural states (S state and ρ state) of TIP4P/ε water. (b) Temperature dependence of τ_1 , τ_{HB} , $\hat{\tau}_{HB}$, and τ_α from $T = 220$ K to $T = 450$ K. The timescales were fitted using the Vogel-Fulcher-Tammann equation [Eq. (16)]. (c) Characteristic time τ_R vs radius R , calculated from the autocorrelation function of the total dipole moment of all neighbor molecules within a sphere of radius R around the central water. (d) Correlation between τ_1 and hydrogen-bond lifetimes τ_{HB} and $\hat{\tau}_{HB}$ [definition based on correlation function $c(t)$ [23]].

Supplemental Material [42]), the probability density becomes more concentrated around the S state, indicating a higher fraction of strongly hydrogen-bonded molecules. This shift in population clearly demonstrates that the tetrahedral ordering becomes stronger as the temperature decreases [43–45]. We have also evaluated the tetrahedral order parameter q [46], which is widely used to characterize tetrahedral ordering, for our water model. The corresponding statistical distributions of $f(q)$ (Fig. S3 in the Supplemental Material [42]) collectively show that decreasing temperature strongly favors the highly ordered, stable tetrahedral S state, consistent with the two-state picture identified from our analysis of order parameters ζ and θ .

C. Secondary Debye relaxation and hydrogen bonding kinetics

In previous works [23], the correlation function

$$c(t) = \frac{\langle h(0)h(t) \rangle}{\langle h(0)^2 \rangle} \quad (15)$$

has been used to characterize hydrogen-bond dynamics. In this definition, $h(t)$ is a binary variable indicating the existence of a hydrogen bond at time t . The correlation function measures the probability that a bond present at $t = 0$ is also present at time t , regardless of any intermediate breaking and reformation events. This corresponds to a history-independent correlation function, which defines the intermittent hydrogen-bond lifetime $\hat{\tau}_{HB}$.

In this work, we adopt a history-dependent definition of the hydrogen-bond lifetime, denoted as τ_{HB} , in which

the lifetime is defined as the duration over which a hydrogen bond remains continuously intact, terminating at the first breaking event. Consistently, we examine the frequency of hydrogen-bond breaking and reformation events f_{HB} (Fig. S4 in the Supplemental Material [42]). This provides a support for distinguishing the history-dependent and history-independent definitions of hydrogen-bond lifetime, as the latter allows for bond reformation events that can lead to a higher estimation of the kinetic lifetime.

We compare the timescales of τ_{HB} , $\hat{\tau}_{HB}$, τ_1 , and τ_α across a wide range of temperatures [Fig. 2(b); see Table S1 in the Supplemental Material [42] for data]. To quantify the temperature dependence, we fit these relaxation times to the Vogel-Fulcher-Tammann (VFT) equation:

$$\tau(T) = \tau_\infty \exp\left(\frac{DT_{VFT}}{T - T_{VFT}}\right), \quad (16)$$

where τ_∞ , D , and T_{VFT} are fitting parameters (Table S2 in the Supplemental Material [42]). As seen in Fig. 2(b), the VFT equation successfully captures the super-Arrhenius behavior of the primary relaxation time (τ_1), α -relaxation time (τ_α), and the history-independent hydrogen-bond lifetime ($\hat{\tau}_{HB}$) [23]. This super-Arrhenius divergence is a signature of glassy dynamics in supercooled water, where the thermal activation energy is not constant; rather, it increases significantly as the temperature decreases.

In contrast, the history-dependent hydrogen-bond lifetime τ_{HB} shows a dynamic behavior with a much smaller thermal activation energy that is close to the Arrhenius behavior. The Arrhenius model fit for τ_{HB} shows an activation

energy of 0.08 eV, which is approximately the energy barrier required for the hydrogen bond to break. This systematic deviation across temperatures clearly demonstrates that the local hydrogen-bond breaking process (τ_{HB}) remains decoupled from the slow, cooperative restructuring process (τ_1). The timescale τ_{HB} reflects an elementary, thermally activated barrier-crossing event which is responsible for the secondary Debye relaxation mode, whereas τ_1 and τ_α reflect the relaxation of the collective hydrogen-bond network.

Interestingly, $\hat{\tau}_{\text{HB}}$ exhibits a near-linear relationship with τ_1 [Fig. 2(d)] and τ_α , namely, $\hat{\tau}_{\text{HB}} \sim \tau_1 \sim \tau_\alpha$, consistent with the findings in previous works [23,47]. In contrast, τ_{HB} is significantly shorter than τ_1 —typically by approximately two orders of magnitude—confirming that the fundamental bond breaking process occurs on a much faster timescale than the collective dipolar relaxation. We find τ_{HB} shows a distinctly nonlinear dependence on τ_1 [Fig. 2(d)]. This difference arises from the distinct definitions of hydrogen-bond lifetime: $\hat{\tau}_{\text{HB}}$ is obtained from a history-independent correlation function, whereas τ_{HB} is based on the continuous (history-dependent) bond lifetime. These results clarify the relationship between the local hydrogen-bond dynamics and the slow, collective relaxation. The different temperature dependences (Arrhenius for τ_{HB} and super-Arrhenius for $\hat{\tau}_{\text{HB}}$ and τ_α) are also consistent with the findings in the previous simulation work where the simple point-charge water model was used [47]. Furthermore, we find that using the history-independent $\hat{\tau}_{\text{HB}}$ to fit the polarization autocorrelation function $\phi(t)$ results in a poor description of the dielectric relaxation (Fig. S5 in the Supplemental Material [42]). This further confirms that $\hat{\tau}_{\text{HB}}$ is an inadequate descriptor for the secondary Debye relaxation. Overall, these results support that the hydrogen-bond lifetime τ_{HB} is the relevant timescale governing the rapid, localized molecular motions responsible for the high-frequency excess in $\epsilon''(\omega)$. This substantiates the molecular picture where the secondary Debye relaxation corresponds to the rapid breaking kinetics of local hydrogen bonding, distinct from the collective dipolar relaxation that governs $\hat{\tau}_{\text{HB}}$.

We remark that the choice of simulation recording frequency also influences the calculated hydrogen-bond lifetime. At 300 K, for example, a low recording resolution of 100 fs yields $\tau_{\text{HB}} \approx 1$ ps, 3–4 times longer than $\tau_{\text{HB}} \approx 0.27$ ps obtained when recording every 1 fs. This indicates that the recording resolution is a key factor that must be considered, as lower frequencies fail to capture the fast hydrogen-bond breaking and reforming events. We also verify that an integration time step of 2 fs yields results consistent with those using 1 fs, showing a negligible impact on the calculated $\phi(t)$ [Fig. S5(e) in the Supplemental Material [42]].

D. Primary Debye relaxation and local dipole correlations

To investigate the collective nature of the primary Debye relaxation, we analyze the relaxation dynamics of the local dipole moment $\mathbf{M}_R$ within defined spatial regions. Simulations were performed in a cubic box with a side length of $a = 35.6$ Å, containing 1500 water molecules. The local dipole moment $\mathbf{M}_R$ centered on a reference water molecule was defined as the vector sum of the dipole moments of all water molecules located within a cutoff distance R from

that central molecule. The total local dipole moment at each time step was calculated as the ensemble average over all possible central molecules. The autocorrelation function of $\mathbf{M}_R(t)$ was then computed following the same procedure used for the polarization autocorrelation function $\phi(t)$. The local relaxation time, τ_R , was obtained by fitting the local dipole autocorrelation function using the same two-exponential form as Eq. (4), ensuring consistency with the definition of the primary Debye relaxation time τ_1 .

We find τ_R increases systematically with increasing R [Fig. 2(c)], indicating the presence of long-range correlations within the water. Importantly, the value of τ_R reaches saturation at approximately $R = 25$ Å (with a saturated value of $\tau_R \approx 13.2$ ps, which is in close agreement with the primary dielectric relaxation time τ_1). This suggests that the primary Debye relaxation is indeed a collective, cooperative process involving a large ensemble of molecules within a characteristic size of $R \approx 25$ Å.

E. Non-Newtonian shear-thinning behavior

The viscosity of water has been a subject of extensive study. Much less is known, however, about the shear effects on viscosity, especially in the supercooled state. Critically, the connection between shear response and dielectric response remains largely unexplored, although both phenomena are governed by the structural relaxation of hydrogen bonds. Here, we connect the dielectric timescale and the rheological timescale.

Figure 3(a) shows the shear viscosity η of water at $T = 240$ K and $T = 300$ K as a function of the shear rate $\dot{\gamma}$. The simulation results clearly demonstrate the characteristic behavior of many complex fluids: When the shear rate ($\dot{\gamma}$) is low, the viscosity (η) stays constant, known as Newtonian behavior. However, when the shear rate is higher, the viscosity goes down, which is known as shear-thinning (or non-Newtonian) behavior. We fitted the shear viscosity η using the following formula [49,50]:

$$\frac{\eta}{\eta_N} = \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^2 \right]^{\frac{n-1}{2}}, \quad (17)$$

where η_N is the viscosity at very low shear rates, $\dot{\gamma}_0$ is a characteristic shear rate where the fluid behavior transitions from constant viscosity (η_N) to decreasing viscosity (shear thinning), and n is a number that quantifies the strength of the shear-thinning effect. For $T = 240$ K, the fit gives $\dot{\gamma}_0 = 4.453 \times 10^9 \text{ s}^{-1}$ and $n = 0.502$, while for $T = 300$ K, we find $\dot{\gamma}_0 = 6.266 \times 10^{10} \text{ s}^{-1}$ and $n = 0.668$. Since a smaller n indicates stronger shear thinning, this shows that the supercooled water is more susceptible to structural breakdown under high shear than the ambient-temperature water. The critical shear rate $\dot{\gamma}_0$ decreases dramatically by an order of magnitude as the temperature is lowered from 300 to 240 K. This is consistent with the primary Debye relaxation time τ_1 increasing sharply in the supercooled regime.

The shear thinning is rooted in the disruption of the hydrogen-bond network. As shown in Fig. 3(d), the average number of hydrogen bonds per molecule n_{HB} drops significantly as the shear rate increases. We find a significant fraction

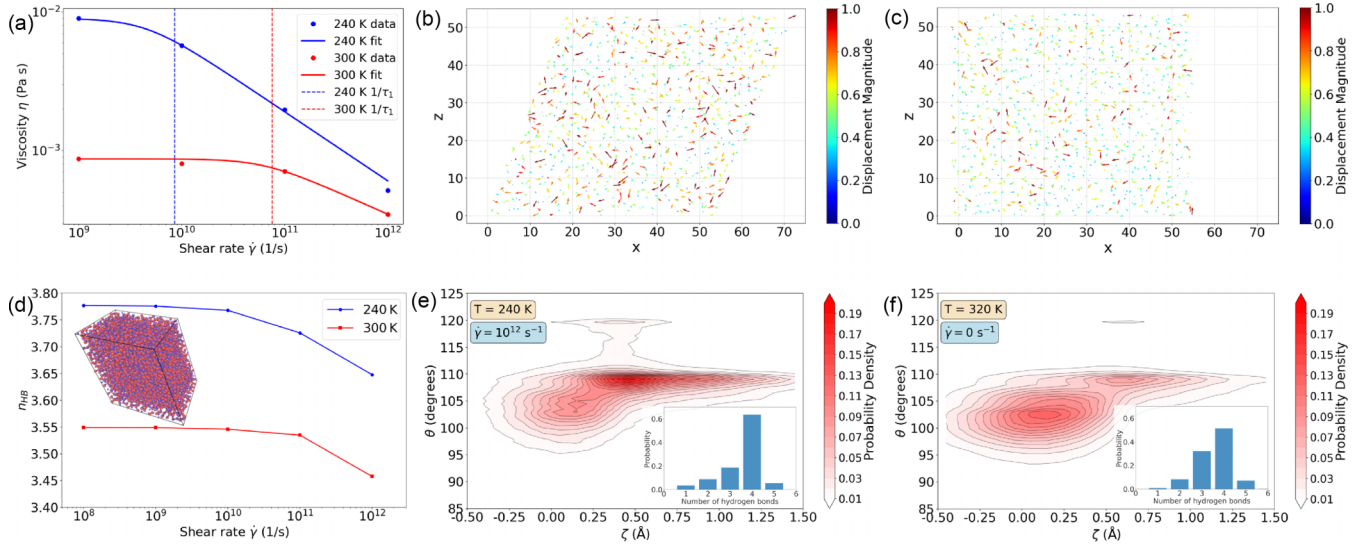


FIG. 3. Rheological response and characterization of water under shear. (a) Shear viscosity η as a function of shear rate $\dot{\gamma}$ at 240 and 300 K. Solid lines represent fits from Eq. (17); dashed lines indicate $1/\tau_1$. Particle displacement maps at 240 K during a time interval of 150 fs under a shear rate of 10^{12} s^{-1} [panel (b)] and under zero shear [panel (c)], colored by displacement magnitude, revealing dynamic heterogeneity in the supercooled water. (d) Average number of hydrogen bonds per molecule n_{HB} vs $\dot{\gamma}$ at 240 and 300 K, with an inset showing the simulation configuration at high shear. Probability distribution $P(\zeta, \theta)$ under high shear at 240 K [panel (e)] and under zero shear at 320 K [panel (f)], with insets showing the distribution of hydrogen-bond counts per water molecule. The viscosity in panel (e) is approximately $5.2 \times 10^{-4} \text{ Pa s}$, which is similar to that in panel (f) [48].

of water molecules become strongly aligned with the flow direction (Fig. S6 in the Supplemental Material [42]), which is responsible for the shear thinning. Importantly, the shear rate at which n_{HB} begins to drop is close to the onset point of shear thinning. This indicates that the strong shear is sufficient to disrupt the hydrogen-bond structure, leading to a reduction in η .

F. Connection between dielectric relaxation timescale and rheological timescale

The characteristic frequencies $1/\tau_1$ are calculated to be approximately $8.5 \times 10^9 \text{ s}^{-1}$ for 240 K and $7.6 \times 10^{10} \text{ s}^{-1}$ for 300 K. The values of $1/\tau_1$ are in the same order of magnitude as the fitted critical shear rates, $\dot{\gamma}_0$ (e.g., $4.45 \times 10^9 \text{ s}^{-1}$ at 240 K). This agreement supports the physical picture that the onset of shear thinning (characterized by $\dot{\gamma}_0$) is intrinsically linked to the molecular reorientation timescale (τ_1).

The breakdown of Newtonian behavior occurs when the shear rate $\dot{\gamma}$ becomes comparable to the primary relaxation time, namely, $\dot{\gamma}_0 \lesssim 1/\tau_1 \sim 1/\tau_\alpha$. We find that τ_α is proportional to the primary dielectric relaxation time τ_1 [Fig. 2(b)], despite their distinct definitions. This physical picture aligns with the relation $\dot{\gamma}_0 \sim 1/\tau_\alpha$ observed in glass-forming liquids [51]. Consequently, the observed relation $\dot{\gamma}_0 \lesssim 1/\tau_1 \sim 1/\tau_\alpha$ emerges from a universal mechanism, suggesting that the onset of shear thinning in supercooled water is fundamentally governed by the competition between the slowest mode of intrinsic structural relaxation and the shear deformation.

While the critical shear rate ($\dot{\gamma}_0$) and the inverse primary relaxation time ($1/\tau_1$) are in the same order of magnitude, we also find that the product $\dot{\gamma}_0 \tau_1$ is consistently less than 1, especially in the supercooled state ($\dot{\gamma}_0 \tau_1 \approx 0.5$). This systematic

deviation can be explained by the dynamic heterogeneity of supercooled water [Figs. 3(b) and 3(c)]. Comparing systems under high shear [$\dot{\gamma} = 10^{12} \text{ s}^{-1}$; Fig. 3(b)] and zero shear [Fig. 3(c)], we observe that the system under shear exhibits strong dynamic heterogeneity, characterized by domains of fast and slow mobilities forming flowing bands [52,53]. This suggests that the overall onset of shear thinning ($\dot{\gamma}_0$) is controlled by the relaxation dynamics of the slowest domains in the supercooled water. Since the measured τ_1 is an average that includes these faster and slower regions, the critical shear rate $\dot{\gamma}_0$ appears lower than the $1/\tau_1$ prediction. This implies that dynamic heterogeneity is essential for the rheological response of supercooled water, providing a crucial molecular explanation for the observed deviation from the $1/\tau_1$ prediction. Similar behavior has been reported for shear thinning in a deeply supercooled melt [54].

We also compare the structural properties of water under two distinct conditions that yield equivalent macroscopic viscosity ($\eta \approx 5.2 \times 10^{-4} \text{ Pa s}$): (1) $T = 240 \text{ K}$ under high shear ($\dot{\gamma} = 1 \times 10^{12} \text{ s}^{-1}$) and (2) $T = 320 \text{ K}$ under zero shear. While applying strong shear has a similar macroscopic effect to increasing temperature—both reduce viscosity—the underlying molecular structures are very different. In the high-shear, low-temperature case [Fig. 3(e)], the S state remains the dominant species; here, viscosity reduction is driven by a mechanical force directly aligning water molecules with the flow direction (Fig. S6 in the Supplemental Material [42]) while maintaining the energetically favored S -state structure. Conversely, at high temperature 320 K [Fig. 3(f)], the fraction of the ρ state increases; the viscosity reduction is driven by enhanced thermal activations. Therefore, despite the similar viscosity η , the microscopic populations of local bonding are distinct under mechanical and thermal

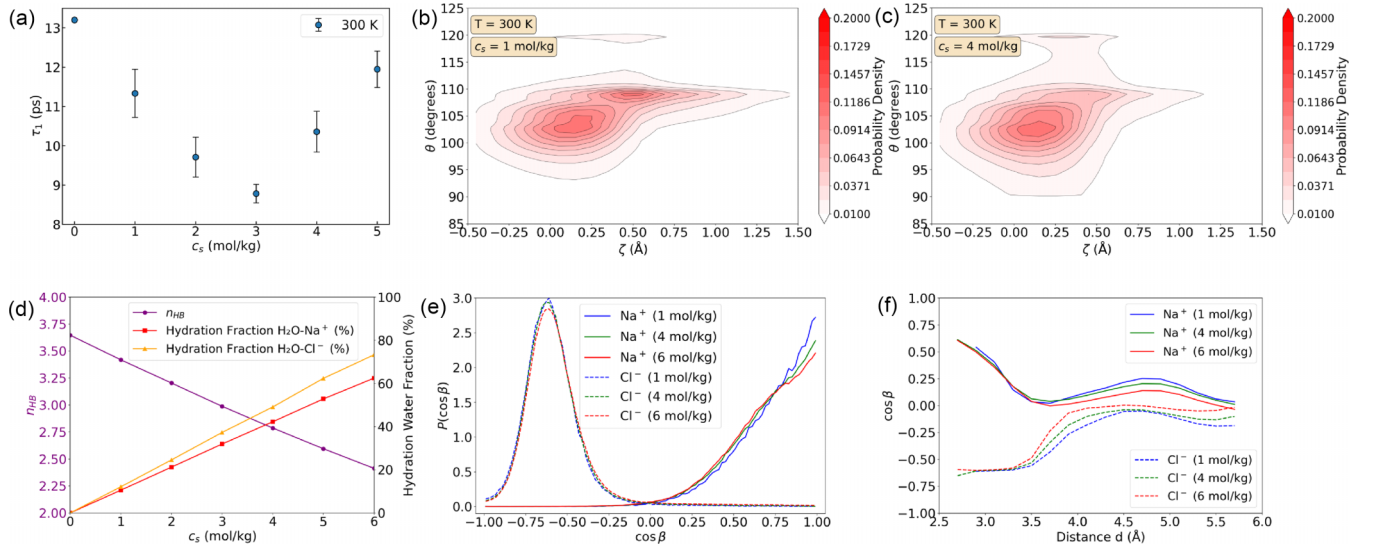


FIG. 4. Ions-regulated dielectric relaxation in aqueous NaCl solutions at 300 K. (a) Salt concentration c_s dependence of the primary Debye relaxation time τ_1 . Probability distribution $P(\zeta, \theta)$ of structural descriptors ζ and θ at 300 K for salt concentrations of $c_s = 1$ mol/kg [panel (b)] and $c_s = 4$ mol/kg [panel (c)]. (d) Average number of hydrogen bonds n_{HB} and the fraction of hydration water molecules (around Na^+ and Cl^-) as functions of c_s . (e) Probability distribution $P(\cos \beta)$ of the orientational order parameter $\cos \beta$ (see Sec. II E) for water molecules within the first shell of Na^+ and Cl^- ions at varying concentrations. (f) Distance-dependent orientational order parameter $\cos \beta$ for water around Na^+ and Cl^- across different concentrations.

perturbation. This highlights that shear thinning is a unique, nonequilibrium process of structural breakdown, which is not merely an equivalent shift to a higher-temperature equilibrium state.

G. Impact of ions on dielectric relaxation

Finally, we study the impact of adding ions (NaCl solutions) on the primary dielectric relaxation time, τ_1 , in aqueous solutions under $T = 300$ K. To measure τ_1 , we employ a nonequilibrium approach based on the response to a static external electric field E_x applied along the x direction. The electric fields E_x are within the linear-response regime where the accumulated dipole moment in the x direction depends linearly on E_x (Fig. S7 in the Supplemental Material [42]). This nonequilibrium method accounts for the collective ionic correlations in electrolyte solutions [36,37]. Interestingly, we find instead of a monotonic decrease, the primary dielectric relaxation time, τ_1 , exhibits a nonmonotonic dependence on NaCl concentration c_s [Fig. 4(a)]. The τ_1 initially decreases and then reaches a minimum extending from approximately $c_s = 3$ mol/kg, after which τ_1 increases for higher concentrations. The nonmonotonic behavior of the primary dielectric relaxation time τ_1 with increasing NaCl concentration was not reported in previous experiments [6], which is likely due to the limited range of salt concentrations.

This non-monotonic behavior can be understood as the result of two competing effects, which are illustrated in Fig. 4(d). On the one hand, as the salt concentration increases, the hydrogen-bond network is disrupted, leading to a decrease in the average number of bonds per water n_{HB} . This reduction in structural ordering tends to accelerate molecular reorientation and thus shorten τ_1 . On the other hand, as more

ions are added, an increasing fraction of water molecules become part of the hydration shells around Na^+ and Cl^- ions [Fig. 4(d)]. These hydration shell water molecules experience strong electrostatic interactions with ions and exhibit orientational ordering, which significantly slows down their rotational dynamics.

As shown in Figs. 4(b) and 4(c), the local water ordering undergoes a significant change upon salt addition. At low salt concentration ($c_s = 1$ mol/kg), both the S state and the ρ state are significantly populated. However, as the NaCl concentration increases to $c_s = 4$ mol/kg, the probability density shifts markedly toward the ρ state, which then becomes the dominant species. This observation clearly indicates that the addition of ions disrupts the stable, tetrahedral network characteristic of pure water, promoting the formation of less structured local environments and thus decreasing the value of τ_1 . The dominance of the ρ state in the highly concentrated regime confirms that the system shifts toward a more disordered state (indicated by the decrease in n_{HB}). While the reduction in n_{HB} tends to speed up dynamics, this effect is ultimately overcome by the strong binding of water molecules to the ions in their hydration shells, which significantly hinders the reorientation of those specific molecules and leads to the increase in τ_1 .

H. Ionic solvation structure

We analyze the orientational ordering of water molecules within the first solvation shell by examining the order parameter $\cos \beta$ defined as the vector product between the water's dipole moment vector (μ) and the radial vector ($\mathbf{r}$) connecting the ion to the water oxygen atom. The distribution $P(\cos \beta)$ reveals different solvation for the cation Na^+ and the

anion Cl^- [Fig. 4(e)]. The probability distribution for $\cos \beta$ is sharply peaked near $\cos \beta \approx 1$ ($\beta \approx 0^\circ$). This indicates that the water dipoles are preferentially oriented to maximize interaction: The oxygen atom points directly toward the Na^+ ion. This arrangement creates a stable alignment where the dipole vector is aligned with the radial vector. As the concentration increases, the $\cos \beta$ distribution broadens and shifts toward lower values (closer to 0). This suggests increased disorder in the water orientation due to the influence of competing electrostatic fields from neighboring ions, disrupting the ordered structure around Na^+ ions.

The solvation structure for the Cl^- anion is distinct. The $\cos \beta$ distribution for Cl^- peaks sharply at $\cos \beta \approx 0.6$ ($\beta \approx 53.1^\circ$). This angle, $\beta \approx 53.1^\circ$, is remarkably close to half of the H-O-H angle of a water molecule ($104.52^\circ/2 \approx 52.3^\circ$). This geometry implies that the most probable configuration is one where one of the water's hydrogen atoms points directly toward the Cl^- ion. The water's dipole moment vector is thus oriented at an angle relative to the ion-oxygen radial vector, resulting in the observed peak at $\cos \beta \approx 0.6$.

This difference in preferred orientation is fundamental: The smaller Na^+ cation maximizes interaction by aligning the water dipole moment along the radial vector, whereas the larger Cl^- anion favors a geometry where a single positively charged hydrogen atom interacts directly with the anion's electron density. This distinction is consistent with the classification of the Na^+ solvation shell as ionic type and the Cl^- solvation shell as van der Waals type, as reported in previous work [55], confirming the distinct nature of ion-water interactions for Na^+ and Cl^- .

I. Concentration-dependent orientational ordering

The orientational influence of the central ion (Na^+ or Cl^-) on the water dipole moment is examined by analyzing the average $\langle \cos \beta \rangle$ as a function of the ion-oxygen distance [Fig. 4(f)]. For both ions, we find $\langle \cos \beta \rangle$ decreases steadily with increasing distance, indicating that the orientational influence weakens outside the first solvation shell. For Na^+ , $\langle \cos \beta \rangle$ decays from a high positive value toward zero, vanishing near the first Na^+ -O RDF minimum (~ 3.3 Å; Fig. S8 in the Supplemental Material [42]). Crucially, the orientational ordering within the first solvation shell remains largely unaffected by increasing salt concentration, as the strong electrostatic forces ensure maximal alignment regardless of neighboring ions. The primary effect of increasing salt concentration is therefore to reduce the ordering of the second solvation shell, effectively truncating the ion's influence to shorter distances. The Cl^- anion also exhibits a concentration dependence in the range of its orientational ordering. For Cl^- , the $\langle \cos \beta \rangle$ profile at high concentration (6 mol/kg) decays to $\langle \cos \beta \rangle \approx 0$ at a shorter distance compared to the low-concentration profile [Fig. 4(f)]. This demonstrates that the influence of Cl^- ion on water's orientational ordering is screened at higher concentrations.

J. Model limitations

We remark that the TIP4P/ε model [21] lacks nuclear quantum nature and polarizability effects [56], which become

increasingly important in the supercooled regime and potentially affect hydrogen-bond dynamics [28]. Nevertheless, the model's demonstrated accuracy in reproducing experimental dielectric spectra across a wide frequency range supports the robustness of our findings. We therefore expect our qualitative picture—which links the primary Debye relaxation to shear rheology and the secondary Debye relaxation to history-dependent hydrogen bonding—to be robust. However, future studies with polarizable or quantum models will be crucial for refining quantitative predictions.

We also note that a recent Car-Parrinello MD study revealed that water molecules characterized by strong local tetrahedral order exhibit higher dipole moments [57]. This suggests that these structural motifs could affect the relaxation phenomena, as molecular reorientation rates likely differ between the two motifs. While the TIP4P/ε model used in our study is a rigid, non-polarizable model with fixed charges that does not explicitly fluctuate individual molecular dipoles based on the local environment, it was parametrized to accurately reproduce the experimental static dielectric constant of water and effectively captures the ensemble-averaged polarization response. Notably, similar to TIP4P/2005 water in our recent study [58], we find that the tetrahedral (*S*-state) water molecules exhibit stronger orientational correlations between the central dipole and its four nearest neighbors compared to the *ρ*-state water molecules. The persistence of short-range correlations suggests that these tetrahedral units form a locally polar structural motif. Thus, although the classical water model does not explicitly fluctuate individual molecular dipoles based on the local environment, as observed in *ab initio* study [57], it effectively captures the enhanced local dipolar correlations by the tetrahedral coordination [58]. Future work could further investigate the roles of the two distinct structural motifs in water's dielectric relaxation dynamics.

IV. CONCLUSION

In conclusion, we systematically explore the dielectric relaxation of liquid water and its response to shear deformation using MD simulations with TIP4P/ε model [21]. We demonstrate that the polarization autocorrelation function $\phi(t)$ exhibits a double-exponential decay, governed by two distinct relaxation processes: the slow, collective orientational reorientation of water molecules (τ_1) and the fast, structural relaxation associated with hydrogen-bond breaking (τ_{HB}). This mechanistic interpretation is validated by the double-peak structure in the imaginary part of the complex dielectric spectrum, $\varepsilon''(\omega)$, which accounts for the high-frequency excess. By defining the hydrogen-bond lifetime based on its continuous existence, we reveal a nonlinear dependence of τ_{HB} on τ_1 , whereas the previously reported relation $\hat{\tau}_{\text{HB}} \sim \tau_1$ [23] arises from the use of history-independent definition of hydrogen-bond lifetime. We find τ_{HB} is significantly shorter than τ_α . While τ_{HB} characterizes the local rupture of individual hydrogen bonds, τ_α represents the collective structural relaxation associated with the escape of molecules from their local cages. This structural process is intrinsically linked to the emergence of dynamical heterogeneity observed in the supercooled state, where the disparity between local bond breaking events and collective reorganization becomes more

pronounced. We also demonstrate that the primary dielectric relaxation time τ_1 is proportional to τ_α in water, despite their distinct physical origins—the former associated with dipolar reorientation and the latter with density correlations. Their proportionality suggests that both processes are governed by the same underlying structural rearrangement of the hydrogen-bond network.

We also examine the rheological behavior in liquid water. Shear thinning becomes pronounced when the applied shear rate $\dot{\gamma}$ far surpasses the intrinsic reorientation rate, i.e., $\dot{\gamma}\tau_1 \gg 1$. Under this condition, the hydrogen-bond network is perturbed, leading to decreased viscosity. The onset of shear thinning occurs at a shear rate $\dot{\gamma}_c$ slightly below the inverse of the primary Debye relaxation time τ_1 , which is attributed to the dynamic heterogeneity. In the supercooled state, water is not kinetically uniform. It consists of coexisting regions of fast-relaxing (high-mobility) and slow-relaxing (low-mobility) molecules. The shear thinning is triggered when shear rate $\dot{\gamma}_0$ begins to disrupt the structure of the slowest-relaxing domains. Our observation made in supercooled water also aligns with the relation $\dot{\gamma}_c \sim 1/\tau_\alpha$ for glass-forming liquids [51].

Furthermore, the structural response of water to external shear is fundamentally distinct from its response to temperature. While both a high-shear rate (e.g., 10^{12} s^{-1} at 240 K) and a high temperature (320 K at zero shear) exhibit similar macroscopic viscosities, they achieve this through different water structural organization. The high-shear case maintains a higher fraction of tetrahedral S states, with structure broken primarily by applied shear force, inducing alignment of water. In contrast, the high temperature promotes the formation of ρ states due to increased thermal fluctuations.

Finally, we reveal that the impact of ions on dielectric relaxation time τ_1 in NaCl solutions stems from two competing effects. The introduction of ions disrupts the existing hydrogen-bond network, reducing the overall structural ordering and effectively accelerating τ_1 . As concentration rises, an increasing fraction of water becomes tightly bound and restricted within the hydration shells around the Na^+ and Cl^- ions. This strong constraint decelerates τ_1 and slows down relaxation dynamics. The observed broad plateau signifies the concentration range where the fluidity gained from hydrogen-bond disruption is balanced by the kinetic constraint by hydration.

By linking water's structure, dielectric relaxation, and shear rheology, our work clarifies several key aspects of its dynamic complexity, with broader implications for understanding other tetrahedral liquids.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

- [1] D. C. Elton, The origin of the Debye relaxation in liquid water and fitting the high frequency excess response, *Phys. Chem. Chem. Phys.* **19**, 18739 (2017).
- [2] U. Kaatz, Water, the special liquid, *J. Mol. Liq.* **259**, 304 (2018).
- [3] I. Popov, P. B. Ishai, A. Khamzin, and Y. Feldman, The mechanism of the dielectric relaxation in water, *Phys. Chem. Chem. Phys.* **18**, 13941 (2016).
- [4] A. Y. Zasetsky, Dielectric relaxation in liquid water: Two fractions or two dynamics? *Phys. Rev. Lett.* **107**, 117601 (2011).
- [5] J. H. Ryu, J. W. Yu, T. J. Yoon, and W. B. Lee, Understanding the dielectric relaxation of liquid water using neural network potential and classical pairwise potential, *J. Mol. Liq.* **397**, 124054 (2024).
- [6] R. Buchner, J. Barthel, and J. Stauber, The dielectric relaxation of water between 0 °C and 35 °C, *Chem. Phys. Lett.* **306**, 57 (1999).
- [7] T. Fukasawa, T. Sato, J. Watanabe, Y. Hama, W. Kunz, and R. Buchner, Relation between dielectric and low-frequency Raman spectra of hydrogen-bond liquids, *Phys. Rev. Lett.* **95**, 197802 (2005).
- [8] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, New York, 1969).
- [9] Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson, and A. Nilsson, The structure of the first coordination shell in liquid water, *Science* **304**, 995 (2004).
- [10] C. J. Fecko, J. D. Eaves, J. J. Loparo, A. Tokmakoff, and P. L. Geissler, Ultrafast hydrogen-bond dynamics in the infrared spectroscopy of water, *Science* **301**, 1698 (2003).
- [11] F. H. Stillinger, Water revisited, *Science* **209**, 451 (1980).
- [12] F. W. Starr, J. K. Nielsen, and H. Eugene Stanley, Fast and slow dynamics of hydrogen bonds in liquid water, *Phys. Rev. Lett.* **82**, 2294 (1999).
- [13] A. L. Benavides, J. L. Aragones, and C. Vega, Consensus on the solubility of NaCl in water from computer simulations using the chemical potential route, *J. Chem. Phys.* **144**, 124504 (2016).
- [14] L. Onsager, Electric moments of molecules in liquids, *J. Am. Chem. Soc.* **58**, 1486 (1936).
- [15] I. de Almeida Ribeiro and M. de Koning, Non-Newtonian flow effects in supercooled water, *Phys. Rev. Res.* **2**, 022004(R) (2020).
- [16] Y. Gao, J. Wu, Y. Feng, J. Han, and H. Fang, Structural effects of water clusters on viscosity at high shear rates, *J. Chem. Phys.* **160**, 104502 (2024).

- [17] K. Heinzinger, Computer simulations of aqueous electrolyte solutions, *Physica B+C* **131**, 196 (1985).
- [18] K. J. Tielrooij, N. Garcia-Araez, M. Bonn, and H. J. Bakker, Cooperativity in ion hydration, *Science* **328**, 1006 (2010).
- [19] F. M. Coelho and L. F. M. Franco, The interplay between dynamics and structure on the dielectric tensor of nanoconfined water: Surface charge and salinity effect, *J. Phys. Chem. B* **128**, 11759 (2024).
- [20] R. Cota, N. Ottosson, H. J. Bakker, and S. Woutersen, Evidence for reduced hydrogen-bond cooperativity in ionic solvation shells from isotope-dependent dielectric relaxation, *Phys. Rev. Lett.* **120**, 216001 (2018).
- [21] R. Fuentes-Azcatl and J. Alejandro, Non-polarizable force field of water based on the dielectric constant: TIP4P/ ϵ , *J. Phys. Chem. B* **118**, 1263 (2014).
- [22] A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. In't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, *et al.*, LAMMPS—A flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales, *Comput. Phys. Commun.* **271**, 108171 (2022).
- [23] P. Zarzycki and B. Gilbert, Temperature-dependence of the dielectric relaxation of water using non-polarizable water models, *Phys. Chem. Chem. Phys.* **22**, 1011 (2020).
- [24] R. W. Hockney and J. W. Eastwood, *Computer Simulation Using Particles* (IOP Publishing, Bristol, 1988).
- [25] J. Yuan, H. S. Antila, and E. Luijten, Particle–particle particle–mesh algorithm for electrolytes between charged dielectric interfaces, *J. Chem. Phys.* **154**, 094115 (2021).
- [26] I. S. Joung and T. E. Cheatham III, Determination of alkali and halide monovalent ion parameters for use in explicitly solvated biomolecular simulations, *J. Phys. Chem. B* **112**, 9020 (2008).
- [27] D. van der Spoel, P. J. van Maaren, and H. J. C. Berendsen, A systematic study of water models for molecular simulation: Derivation of water models optimized for use with a reaction field, *J. Chem. Phys.* **108**, 10220 (1998).
- [28] A. Luzar and D. Chandler, Effect of environment on hydrogen bond dynamics in liquid water, *Phys. Rev. Lett.* **76**, 928 (1996).
- [29] E. Guillaud, S. Merabia, D. de Ligny, and L. Joly, Decoupling of viscosity and relaxation processes in supercooled water: A molecular dynamics study with the TIP4P/2005f model, *Phys. Chem. Chem. Phys.* **19**, 2124 (2017).
- [30] Z. Yu, R. Shi, and H. Tanaka, A unified description of the liquid structure, static and dynamic anomalies, and criticality of TIP4P/2005 water by a hierarchical two-state model, *J. Phys. Chem. B* **127**, 3452 (2023).
- [31] A. V. Muthachikavil, G. M. Kontogeorgis, X. Liang, Q. Lei, and B. Peng, Structural characteristics of low-density environments in liquid water, *Phys. Rev. E* **105**, 034604 (2022).
- [32] A. V. Muthachikavil, G. Sun, B. Peng, H. Tanaka, G. M. Kontogeorgis, and X. Liang, Unraveling thermodynamic anomalies of water: A molecular simulation approach to probe the two-state theory with atomistic and coarse-grained water models, *J. Chem. Phys.* **160**, 154505 (2024).
- [33] J. Russo and H. Tanaka, Understanding water's anomalies with locally favoured structures, *Nat. Commun.* **5**, 3556 (2014).
- [34] A. P. Thompson, S. J. Plimpton, and W. Mattson, General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions, *J. Chem. Phys.* **131**, 154107 (2009).
- [35] T. W. Sirk, S. Moore, and E. F. Brown, Characteristics of thermal conductivity in classical water models, *J. Chem. Phys.* **138**, 064505 (2013).
- [36] S. J. Cox and M. Sprik, Finite field formalism for bulk electrolyte solutions, *J. Chem. Phys.* **151**, 064506 (2019).
- [37] I. Skarmoutsos and S. Mossa, Length scales in electrolytes, *J. Chem. Phys.* **163**, 054502 (2025).
- [38] M. Neumann, Dielectric relaxation in water. Computer simulations with the TIP4P potential, *J. Chem. Phys.* **85**, 1567 (1986).
- [39] D. S. Venables and C. A. Schmuttenmaer, Far-infrared spectra and associated dynamics in acetonitrile–water mixtures measured with femtosecond THz pulse spectroscopy, *J. Chem. Phys.* **108**, 4935 (1998).
- [40] H. Yada, M. Nagai, and K. Tanaka, Origin of the fast relaxation component of water and heavy water revealed by terahertz time-domain attenuated total reflection spectroscopy, *Chem. Phys. Lett.* **464**, 166 (2008).
- [41] A. Beneduci, Which is the effective time scale of the fast Debye relaxation process in water? *J. Mol. Liq.* **138**, 55 (2008).
- [42] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/rfks-j3yr> for the information about additional characterization of water structure and dynamics.
- [43] H. Tanaka, Simple physical explanation of the unusual thermodynamic behavior of liquid water, *Phys. Rev. Lett.* **80**, 5750 (1998).
- [44] H. Tanaka, Simple physical model of liquid water, *J. Chem. Phys.* **112**, 799 (2000).
- [45] H. Tanaka, Thermodynamic anomaly and polyamorphism of water, *Europhys. Lett.* **50**, 340 (2000).
- [46] J. R. Errington and P. G. Debenedetti, Relationship between structural order and the anomalies of liquid water, *Nature (London)* **409**, 318 (2001).
- [47] F. W. Starr, J. K. Nielsen, and H. E. Stanley, Hydrogen-bond dynamics for the extended simple point-charge model of water, *Phys. Rev. E* **62**, 579 (2000).
- [48] Ł. Baran, C. A. Dicu-Gohoreanu, and L. G. MacDowell, How important is the dielectric constant in water modeling? Evaluation of the performance of the TIP4P/ ϵ force field and its compatibility with the Joung–Cheatham NaCl model, *J. Chem. Phys.* **163**, 054504 (2025).
- [49] P. J. Carreau, Rheological equations from molecular network theories, *Trans. Soc. Rheol.* **16**, 99 (1972).
- [50] V. Jadhao and M. O. Robbins, Probing large viscosities in glass-formers with nonequilibrium simulations, *Proc. Natl. Acad. Sci. USA* **114**, 7952 (2017).
- [51] H. Mizuno, A. Ikeda, T. Kawasaki, and K. Miyazaki, Universal mechanism of shear thinning in supercooled liquids, *Commun Phys* **7**, 199 (2024).
- [52] A. Furukawa, K. Kim, S. Saito, and H. Tanaka, Anisotropic cooperative structural rearrangements in sheared supercooled liquids, *Phys. Rev. Lett.* **102**, 016001 (2009).
- [53] H. Tanaka, Structural origin of dynamic heterogeneity in supercooled liquids, *J. Phys. Chem. B* **129**, 789 (2025).
- [54] V. Lubchenko, Shear thinning in deeply supercooled melts, *Proc. Natl. Acad. Sci. USA* **106**, 11506 (2009).
- [55] R. Shi, A. J. Cooper, and H. Tanaka, Impact of hierarchical water dipole orderings on the dynamics of aqueous salt solutions, *Nat. Commun.* **14**, 4616 (2023).

- [56] Y. Nagata, R. E. Pool, E. H. G. Backus, and M. Bonn, Nuclear quantum effects affect bond orientation of water at the water-vapor interface, *Phys. Rev. Lett.* **109**, 226101 (2012).
- [57] I. Skarmoutsos, G. Franzese, and E. Guardia, Using Car-Parrinello simulations and microscopic order descriptors to reveal two locally favored structures with distinct molecular dipole moments and dynamics in ambient liquid water, *J. Mol. Liq.* **364**, 119936 (2022).
- [58] J. Yuan, K. Qiu, G. Sun, and H. Tanaka, Competing hydrogen-bond orders drive water's anomalous surface tension, *Nat. Commun.* **17**, 1498 (2026).