Molecular dynamics simulation of water under electric field: 
Dielectric response and dynamics after field reversal

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We study water between parallel metal walls under applied electric field accounting for the image effect at $T = 298$ K. The electric field due to the surface charges serves to attract and orient nearby water molecules, while it tends to a constant determined by the mean surface charge density away from the walls. We examine the dielectric response to find Stern boundary layers and a bulk region. The dielectric constant can then be calculated in the bulk region. We also examine the local electric field on each molecule and its fluctuation distribution. The average local field considerably deviates from the classical Lorentz field. However, if we suppose a nanometer-size sphere around each molecule, the local field contribution from its exterior is nearly equal to that from the continuum electrostatics. As a nonequilibrium problem, we investigate the dynamics after a reversal of applied field, where we observe large rotational jumps breaking the hydrogen-bond network. The molecules undergoing these jumps form hydrogen-bonded clusters heterogeneously distributed in space.

I. INTRODUCTION

In physics and chemistry, we need to accurately estimate the long-range electrostatic interactions among charged and polar particles. To this end, a large number of simulations have been performed and the Ewald method is a famous technique for efficiently summing these interactions using the Fourier transformation. It has been used to investigate the bulk properties of charged and polar particles under the periodic boundary condition in three dimensions (3D Ewald). It has also been modified for film-like systems under the periodic boundary condition in the lateral directions (2D Ewald). Several groups have performed simulations of dipole systems in electric field between parallel metal walls. However, not enough efforts have been made on dynamics, where applied electric field can be nonstationary. Such nonequilibrium situations are ubiquitous and are of great scientific and practical importance. Hence, this paper aims to give a general scheme of treating water under electric field and investigate the dielectric relaxation after field reversal.

Hautman et al developed a 3D Ewald method assuming parallel, smooth metal walls, where the constant potential condition is satisfied at the metal walls ($z = 0$ and $H$) and the periodic boundary condition is imposed along the $x$ and $y$ axes. In this case, each charged particle in the cell induces surface charges producing a potential equivalent to that from an infinite number of image charges outside the cell. Perram and Ratner found some relations on these image charges. In the same scheme, Klapp treated dipoles interacting with the soft-core potential to find wall-induced ordering. The present authors extended this 3D Ewald method for charged and polar particles to examine surface effects, ionic crystals, dipole chains, and local electric field. In this paper, we use this method for water.

We also mention other methods. Shelley and Patey assumed empty (vacuum) slabs outside the cell, which the particles cannot enter due to the repulsive wall potentials. If the regions $-d_{em} < z < 0$ and $H < z < H + d_{em}$ are empty, the 3D Ewald method can be used with period $H + 2d_{em}$ along the $z$ axis. Also with empty slabs, Yeh and Berkowitz applied electric field accounting for the local field from net polarization. They found that the computing time with this 3D Ewald method was ten times faster than that with the 2D Ewald method. With such empty regions, however, charged or polar particles are effectively in contact with neutral, non-polarizable walls. Siepmann and Sprik assumed atomic particles forming a crystal and interacting with water molecules via a model potential at the surface. They varied charges of these atoms continuously to maintain the constant potential condition in metal. This model was used to study water and ions between electrodes with the aid of the 2D Ewald method.

Surface charges increase locally as charges or dipoles in the liquid region approach a metal wall. As a result, water molecules are adsorbed and oriented near a metal wall. They form a Stern surface layer even without ions, where the electric potential changes appreciably on a microscopic length. It also follows that the surface charges exhibit significant in-plane fluctuations with a correlation length $\xi_s$. We shall see that the electric field due to these surface charges tends to be uniform in the bulk where the distances from the walls much exceed $\xi_s$.

We are not aware of previous microscopic calculations to check the validity of the classical theory of dielectrics. Hence, we calculate the average and fluctuations of the local electric field $E_k^{loc}$ acting on each molecule $k$. In particular, we consider a nanometer-size sphere surrounding each molecule. In our simulation, the local field contribution from the sphere interior consists of an average (a deviation from the classical Lorentz field) and large fluctuations ($\sim e/\sigma^2$ with $\sigma \sim 3$ Å), while that from the sphere exterior is obtained from the continuum electrostatics.
electrostatics with small fluctuations.

We also present a first study of water in nonequilibrium, where the polarization relaxes after a reversal of applied electric field. In our simulation, rotational jumps with large angle changes play a major role in the relaxation. These largely rotated molecules form clusters causing breakage and reorganization of the hydrogen bond network. In previous simulations on water, collective hydrogen-bond dynamics was studied at \( T \approx 300 \) K\(^{20}\) and marked dynamic heterogeneities were observed in translation and rotation in supercooled states\(^{21}\).

The organization of this paper is as follows. In Sec. II, we will reexamine the Ewald scheme for water between metal walls. In Sec. III, we will calculate the dielectric response and the local electric field. In Sec. IV, simulation results on field reversal will be presented. In Appendix A, we will give an expression for the local electric field on water molecules composed of three charge points. In Appendix B, we will devise a microscopic expression for the polarization density \( \mathbf{p}(\mathbf{r}) \), which is convenient for theoretical study of water.

II. THEORETICAL BACKGROUND

In our system, \( N = 2400 \) water molecules are in a \( L \times L \times H \) cell with metal plates at \( z = 0 \) and \( H \). We impose the periodic boundary condition along the \( x \) and \( y \) axes. The walls at \( z = 0 \) and \( H \) are assumed to be smooth and structureless for simplicity. We apply electric field under the fixed-potential condition.

A. Water model. We use the TIP4P/2005 model\(^{22}\), where each water molecule \( k \) has three charge points \( r_{kH1}, r_{kH2}, \) and \( r_{kM} \) with charges \( q_{H1}, q_{H1}, \) and \( q_{M} = -2q_{H} \), respectively, where \( q_{H} = 0.5564e \). The point \( r_{kM} \) is slightly shifted from the oxygen point \( r_{kO} \) along \( \mathbf{n}_k \), where \( \mathbf{n}_k \) is the unit vector along the bisector of the H-O-H triangle. Its dipole moment vector is given by

\[
\mathbf{\mu}_k = q_H (r_{kH1} + r_{kH2} - 2r_{kM}) = \mu_0 \mathbf{n}_k, \tag{2.1}
\]

where \( \mu_0 = 2.305 \)D. See Appendix A for more details.

The total potential \( U \) consists of three parts as

\[
U = U_m + \frac{1}{2} \sum_{k \neq \ell} u_{LJ}(|r_{kO} - r_{\ellO}|) + \sum_k [u_w(z_{kO}) + u_w(H - z_{kO})], \tag{2.2}
\]

where \( U_m \) is the total electrostatic energy, \( u_{LJ} \) is the Lennard-Jones potential among the oxygen atoms, and \( u_w \) is the wall potential of the oxygen atoms:

\[
u_{\text{LJ}}(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^{12}, \tag{2.3}
\]

\[
u_w(z) = C_0 (\sigma / z)^6 - C_3 (\sigma / z)^3 \tag{2.4}
\]

We set \( \epsilon = 93.2k_B, \sigma = 3.1589\AA , C_9 = 2\pi\epsilon/45, \) and \( C_3 = 15C_9/2. \) Due to \( u_w(z) \) the distances of any charge positions from the walls at \( z = 0 \) and \( H \) are larger than 1 Å. The density and the orientation of water molecules near a wall sensitively depend on the form of \( u_w \). In this paper, we do not treat realistic surface states of water, on which a number of papers have been published\(^{11-13,23,24}\).

B. Electrostatic energy and image charges. We explain the electrostatics of water between parallel metallic plates at \( z = 0 \) and \( H \). Let \( r_i = (x_i, y_i, z_i) \) and \( r_j = (x_j, y_j, z_j) \) denote the \( 3N \) charge positions \( r_{kH1}, r_{kH2}, \) and \( r_{kM} \) (\( 1 \leq k \leq N \)). The electrostatic potential \( \Phi(\mathbf{r}) \) outside the charge positions \( r \neq r_i \) satisfies the metallic boundary condition,

\[
\Phi(x, y, 0) = 0 \quad \Phi(x, y, H) = -\Delta \Phi = -E_a H, \tag{2.5}
\]

where \( \Delta \Phi \) is the applied potential difference and \( E_a = \Delta \Phi / H \) is the applied electric field. From Eq.(2.5), \( \Phi(\mathbf{r}) \) is expressed in terms of image charges as

\[
\Phi = \sum_m \sum_j \left[ \frac{q_j}{|\mathbf{r} - \mathbf{r}_j + \mathbf{h}|} - \frac{q_j}{|\mathbf{r} - \mathbf{r}_j + \mathbf{h}|} \right] - E_a z, \tag{2.6}
\]

where \( \mathbf{r}_j = (x_j, y_j, -z_j) \) and

\[
\mathbf{h} = (L_{mx}, L_{my}, 2Hm_z) \tag{2.7}
\]

with \( m_x, m_y, \) and \( m_z \) being integers \((0, \pm 1, \pm 2, \ldots.)\). For each real charge \( q_j \) at \( \mathbf{r}_j = (x_j, y_j, z_j) \) in the cell, we find images with the same charge \( q_j \) at \( (x_j, y_j, z_j - 2Hm_z) \) \((m_z = \pm 1, \cdots)\) and those with the opposite charge \(-q_j \) at \((x_j, y_j, -z_j - 2Hm_z) \( (m_z = 0, \pm 1, \cdots) \) outside the cell. Due to the summation over \( m_z \) the metallic boundary conditions (2.5) is satisfied.

The electrostatic energy \( U_m \) at fixed \( E_a \) is given by\(^{22}\)

\[
U_m = \frac{1}{2} \sum_m \sum_{ij} \left[ \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{h}|} - \frac{q_i q_j}{|\mathbf{r}_{ij} + \mathbf{h}|} \right] - E_a M_z, \tag{2.8}
\]

where \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \) and

\[
M_z = \sum_i q_i z_i = \sum_k \mathbf{n}_k \tag{2.9}
\]

is the total polarization along the \( z \) axis. In \( \sum'_{ij} \) in Eq.(2.8), we exclude the self term with \( j = i \) for \( h = (0, 0, 0) \). For infinitesimal changes \( \mathbf{r}_i \rightarrow \mathbf{r}_i + d\mathbf{r}_i \) and \( E_a \rightarrow E_a + dE_a \), the incremental change of \( U_m \) in Eq.(2.8) is of the following differential form,

\[
dU_m = -\sum_i q_i \mathbf{E}_i \cdot d\mathbf{r}_i - M_z dE_a, \tag{2.10}
\]

where \( \mathbf{E}_i = -q_i \mathbf{\partial} U_m / \partial \mathbf{r}_i \) is the local electric field acting on charge \( i \).

The first term in Eq.(2.8) is periodic in 3D with respect to \( x_i \rightarrow x_i \pm L, y_i \rightarrow y_i \pm L, \) and \( z_i \rightarrow z_i \pm 2H \) due to the summation over \( h \). Thus, it can be calculated with the 3D Ewald method. So far, a few groups have performed simulations on the basis of \( U_m \) in Eq.(2.8)\(^{25,26}\). In the Ewald method, the Coulomb potential \( \frac{q_i q_j}{r} \) is divided
2.2Å

\[
\text{FIG. 1. (Color online) Three typical configurations of a water molecule, whose oxygen atom is separated by 2.2Å from a metal wall without applied electric field. Image potential } U_{ik} \text{ in Eq.(2.13) is calculated to be (a) } -1.06 \times 10^{-13} \text{ erg, (b) } -1.63 \times 10^{-13} \text{ erg, and (c) } -1.23 \times 10^{-13} \text{ erg.}
\]

\[
\text{where } n_z = \cos \theta \text{ with } \theta \text{ being the angle between the polarization direction and the z axis. H-down orientation (b) has the lowest electrostatic energy and most frequently appears without applied electric field, leading to a surface potential change } \Phi_{ik}^{0} \text{ in Eq.(3.19).}
\]

\[
\text{into the long-range part } q_i q_j \psi(r) \text{ and the short-range part } q_i q_j \psi_s(r) \text{ with}
\]

\[
\psi(r) = \text{erf}(\gamma r) / r, \quad \psi_s(r) = [1 - \text{erf}(\gamma r)] / r. \tag{2.11}
\]

where \text{erf}(u) is the error function and \gamma^{-1} represents the potential range of \psi_i(r). It follows the Poisson equation

\[
-\nabla^2 \psi(r) = 4\pi \varphi(x) \varphi(y) \varphi(z),
\]

where

\[
\varphi(z) = (\gamma / \sqrt{\pi}) \exp(-\gamma^2 z^2) \tag{2.12}
\]

is the 1D Gaussian distribution with \int dz \varphi(z) = 1. In this paper, we set \gamma = 0.85 / \sigma = 2.7 / \text{nm.}

It is well-known that the image interaction grows when a charge or a dipole approaches a wall. For a water molecule \(k\) near the bottom wall at \(z = 0\), the following image potential grows in \(U_m:\)

\[
U_{ik} = -\sum_{\alpha \neq \beta} \frac{q_\alpha q_\beta}{2|\mathbf{r}_{k\alpha} - \mathbf{r}_{k\beta}|}, \tag{2.13}
\]

where \(\alpha, \beta = M, H1, H2\). In Fig.1, typical molecular configurations are illustrated, where we give the corresponding \(U_{ik}\) without applied field. In Sec.IIIb, we shall see that water molecules near a metal wall form a Stern layer where the H-down orientation (b) most frequently appears near a metal wall. On real metal surfaces, such orientation ordering is induced by excess electrons.\(^{[13]}\)

**C. Surface charges.** The image charges are introduced as a mathematical convenience. The real charges are those in the cell and the surface charges on the metal walls. Here, we examine the effects of the latter in detail.

The surface charge densities are written as \(\sigma_0(r_\perp)\) at \(z = 0\) and \(\sigma_H(r_\perp)\) at \(z = H\), where \(r_\perp = (x, y)\). Since the charges in the cell are expelled from the walls due to the wall potentials, \(\sigma_0\) and \(\sigma_H\) are expressed in terms of \(E_z(x, y, z) = -\partial \Phi / \partial z\) as

\[
\sigma_0 = E_z(x, y, 0) / 4\pi, \quad \sigma_H = -E_z(x, y, H) / 4\pi. \tag{2.14}
\]

We consider their lateral mean surface charges,

\[
\bar{\sigma}_0 = \frac{1}{L^2} \int dS_0(r_\perp), \quad \bar{\sigma}_H = \frac{1}{L^2} \int dS_H(r_\perp), \tag{2.15}
\]

where \(dS = dx dy\) and \(0 < x, y < L\). From Eq.(B4) in Appendix B, these mean values exactly satisfy\(^{[77]}\)

\[
\bar{\sigma}_0 = -\bar{\sigma}_H = E_a / 4\pi + M_z / V. \tag{2.16}
\]

We write the potential from the surface charges as \(\Phi_s\) and divide it into two parts,

\[
\Phi_s(r) = -4\pi \bar{\sigma}_0 z + \phi_s(r). \tag{2.17}
\]

The first term arises from the mean surface charges. The second contribution \(\phi_s\) is due to the surface charge deviations, which will be estimated in Sec.III.

In the 2D Fourier series, we set

\[
\Delta \sigma_0(r_\perp) = \sigma_0(r_\perp) - \bar{\sigma}_0 = \sum_{k \neq 0} \sigma_{0k} e^{ik \cdot r},
\]

\[
\Delta \sigma_H(r_\perp) = \sigma_H(r_\perp) - \bar{\sigma}_H = \sum_{k \neq 0} \sigma_{Hk} e^{ik \cdot r}, \tag{2.18}
\]

where \(k = (2\pi / L)(n_x, n_y) \neq (0, 0)\) with \(n_x\) and \(n_y\) being integers. The Fourier components are calculated as

\[
\sigma_{0k} = -\frac{1}{L^2} \sum_{j} q_j \sin(hk - k \cdot j) / \sin(hk),
\]

\[
\sigma_{Hk} = -\frac{1}{L^2} \sum_{j} q_j \sin(k \cdot j) / \sin(hk), \tag{2.19}
\]

where \(k = |k| \neq 0\) and the summation over \(m_z\) in Eq.(2.7) has been performed to give the hyperbolic sine functions. The potential deviation \(\phi_s\) is expressed as

\[
\phi_s = \sum_{m_\perp} \int dS' \left[ \frac{\Delta \sigma_0(r_\perp')}{|r - r' + Lm_\perp|} + \frac{\Delta \sigma_H(r_\perp')}{|r - r'' + Lm_\perp|} \right]
\]

\[
= \sum_{k \neq 0} 2\pi \frac{k}{L} \left[ \sigma_{0k} e^{-kz} + \sigma_{Hk} e^{k(z-H)} \right] e^{ik \cdot r_\perp}. \tag{2.20}
\]

In the first line, \(dS' = dx' dy', \ r_\perp' = (x', y')\), \(r' = (x', y', 0)\), \(r'' = (x', y', H)\), and \(m_\perp = (m_x, m_y, 0)\) with \(m_x\) and \(m_y\) being integers. The second line is the 2D Fourier expansion of the first line, where we use the 2D integral \(\int dS e^{ik \cdot r_\perp} / r = 2\pi e^{-kz} / k\).

The total potential \(\Phi(r) (r \neq r_j)\) in Eq.(2.6) arises from the changes in the cell and those on the walls as

\[
\Phi = \sum_{m_\perp j} \frac{q_j}{|r - r_j + Lm_\perp|} + \phi_s(r) - 4\pi \bar{\sigma}_0 z, \tag{2.21}
\]
which also follows if we substitute Eq.(2.19) into the second line of Eq.(2.20). The summation over \( \mathbf{m}_\perp \) in the first term ensures the lateral periodicity. From Eq.(2.9) \( \phi_s(\mathbf{r}) \) is also written in terms of the image potentials as

\[
\phi_s = \sum_{\mathbf{m}} \sum_j \left[ q_j \left( 1 - \delta_{m,0} \right) \frac{1}{|\mathbf{r} - \mathbf{r}_j + \mathbf{h}|} - \frac{q_j}{|\mathbf{r} - \mathbf{r}_j + \mathbf{h}|} \right] + 4\pi M_z \frac{z}{V}, \tag{2.22}
\]

where \( \delta_{mn} \) is the Kronecker delta and \( \mathbf{h} \) is expressed as Eq.(2.7). The first term in Eq.(2.22) is the sum of the image potentials. Far from the walls, we shall see that it is mostly canceled by the second term \( (\propto M_z) \), leading to small \( \phi_s \) (see Sec.III).

Using Eq.(2.22), we rewrite the electrostatic potential energy \( U_m \) in Eq.(2.8) using \( \phi_s \) as

\[
U_m = \frac{1}{2} \sum_{\mathbf{m}_\perp} \sum_{i,j} \left| q_i q_j \right| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{Lm}_\perp|} + \sum_j \frac{1}{2} \phi_s(\mathbf{r}_j) - 2\pi M_z^2 \frac{\sigma_s}{V} - E_\text{s} M_z, \tag{2.23}
\]

The third term \( (\propto M_z^2) \) in Eq.(2.23) is a large mean-field contribution to \( U_m \). As a result, the local field \( E_i \) in Eq.(2.10) is divided as

\[
E_i = E_i^d + E_s(\mathbf{r}_i) + 4\pi \sigma_0 e_z. \tag{2.24}
\]

The \( E_i^d \) arises from the charges in the cell and \( E_s(\mathbf{r}) \) from the surface charge deviations so that

\[
E_i^d = \sum_{\mathbf{m}_\perp} \sum_j q_j g(\mathbf{r}_i - \mathbf{r}_j + \mathbf{Lm}_\perp), \tag{2.25}
\]

\[
E_s(\mathbf{r}) = -\nabla \phi_s(\mathbf{r}). \tag{2.26}
\]

where \( \nabla_i = \partial / \partial \mathbf{r}_i \) and \( g(\mathbf{r}) = -\nabla r^{-1} = r^{-3}\mathbf{r} \). Use has been made of the relation \( \nabla_i \sum_j q_j \phi_s(\mathbf{r}_j) = -2q_i E_s(\mathbf{r}_i) \). The third term in Eq.(2.24) arises from the mean surface charge, where \( e_z \) is the unit vector along the \( z \) axis.

Yeh and Berkowitz\textsuperscript{10} used the 3D Ewald method with empty slabs\textsuperscript{13} under applied electric field, where \( E_s \) is replaced by \( E_s + 4\pi M_z \frac{\sigma_s}{V} \) in the equations of motion. Their simulation is justified by Eq.(2.23) provided that \( \phi_s \) is negligible far from the walls.

III. EQUILIBRIUM STATES UNDER ELECTRIC FIELD

We performed MD simulation using \( U_m \) in Eq.(2.8) with the 3D Ewald. The molecule number is \( N = 2400 \) and the cell dimensions are \( L = 41.5 \text{Å} \) and \( H = 44.7 \text{Å} \) with volume \( V \approx 77 \text{nm}^3 \). The mass density is 1.01 g/cm\(^3\). The temperature is at \( T = 298 \text{K} \).

A. Effects of surface charges. In Fig.2, we present snapshots of the surface charge deviations \( \Delta \sigma_0(x,y) \) in (a) and \( \Delta \sigma_H(x,y) \) in (b) with \( \Delta \Phi = 1.9 \text{V} \) or \( E_a = 0.42 \text{V/Å} \), so the bottom (top) wall is positively (negatively) charged with \( \sigma_0 / e = 0.44/\text{nm}^2 \). Here, the fluctuations of \( \Delta \sigma_H \) are larger than those of \( \Delta \sigma_0 \), because the protons can be closer to the top wall than the oxygen atoms to the bottom wall in the present model. (See Fig.10 for examples of the molecular configurations close to the bottom wall.) We also show a cross-sectional snapshot of \( \phi_s(x, L/2, z) \) in the \( xz \) plane in (c) and \( |E_s(x, y, 2.1 \text{Å}| \) in the \( xy \) plane in (d).

To examine the thermal fluctuations of the surface charges, we introduce their structure factors by

\[
\Delta \sigma_0^2 = L^2 e^{-2} \langle |\sigma_0 k| \rangle^2, \quad \Delta \sigma_H^2 = L^2 e^{-2} \langle |\sigma_H k| \rangle^2 \tag{3.1}
\]

where \( k = |k| \) is the wave number and \( e = 23.82(e\sigma)^{1/2} \) is the elementary charge. In this section, the symbol \( \langle \cdots \rangle \) denotes the time average over 6 ns, which is taken as the equilibrium average. In terms of these quantities, the
To our small system, however, this formula is not applicable. In fact, the right hand side of Eq.(3.4) coincides with the numerical curve in Fig.2(f) only for \( z \sim 2\AA \) and \( H - z \sim 2\AA \).

**B. Average 1D polarization and potential.** In Appendix B, we will give the microscopic expression for the polarization density \( p(r) \). In our 1D geometry, we examine the average polarization along the \( z \) axis,

\[
P(z) = \langle p_z(r) \rangle = \frac{1}{L^2} \sum_j \langle q_j \theta(z - z_j) \rangle,
\]

where \( \theta(u) \) is the step function being 0 for \( u \leq 0 \) and 1 for \( u > 0 \). We may then define the average Poisson electric potential \( \Psi(z) \) and field \( \mathcal{E}(z) = -d\Psi/dz \) as

\[
\Psi(z) = -4\pi \langle \bar{\sigma}_0 \rangle z + 4\pi \int_0^z dz' P(z'),
\]

\[
\mathcal{E}(z) = 4\pi \langle \bar{\sigma}_0 \rangle - 4\pi P(z).
\]

where \( \langle \bar{\sigma}_0 \rangle \) is the average of \( \sigma_0 \). In our case, the temporal fluctuations of \( \bar{\sigma}_0 \) are very small and we need not distinguish between \( \sigma_0 \) and \( \langle \bar{\sigma}_0 \rangle \). Taking the average of Eq.(2.16) gives

\[
\langle \bar{\sigma}_0 \rangle = -\langle \bar{\sigma}_H \rangle = E_a/4\pi + \int_0^H dz P(z)/H,
\]

where \( \int_0^H dz P(z) = \langle M_z \rangle / L^2 \). From Eq.(3.6), \( \Psi \) satisfies

\[
\Psi(0) = 0, \quad \Psi(H) = -E_aH,
\]

and

\[
\frac{d^2 \Psi(z)}{dx^2} = 4\pi \frac{dP(z)}{dz} = -\frac{4\pi}{L^2} \sum_j \langle q_j \delta(z - z_j) \rangle.
\]

The quantities in Eq.(3.9) are nonvanishing only near the walls. Note that \( P, \Psi, \) and \( \mathcal{E} \) correspond to the polarization, electric potential, and electric field in the continuum electrostatics for \( L \gg \xi_A \). We define the effective dielectric constant of a film by

\[
\varepsilon_{\text{eff}} = 4\pi \langle \bar{\sigma}_0 \rangle / E_a = 1 + 4\pi \langle M_z \rangle / V E_a.
\]

In Fig.3, (a) \( 4\pi P(z) \) and (b) \( \Psi(z) \) are displayed for \( \Delta\Phi = 0 \) and 1.9 V. Here, there appear Stern boundary layers near the walls, whose thickness is \( d \approx 4.5\AA \). Remarkably, outside the layers \( z > d \) and \( H - z > d \), a homogeneous state is realized, where \( P(z) \) and \( \mathcal{E}(z) \) assume constant values,

\[
P(z) \cong P_b, \quad \mathcal{E}(z) \cong E_b = 4\pi (\langle \bar{\sigma}_0 \rangle - P_b).
\]

The thickness of the bulk region is \( H - 2d (\approx 3.5 \text{ nm here}) \). We can then determine the bulk dielectric constant by

\[
\varepsilon = 4\pi \langle \bar{\sigma}_0 \rangle / E_b = 1 + 4\pi P_b / E_b.
\]

In the bulk region, \( \Psi(z) \) behaves linearly as

\[
\Psi(z) \cong -E_b z + A_0,
\]
we can see considerable nonlinear dielectric response between 0.42 V and 0.82 V, as shown in Fig.3(d), we also have $\Phi_{00}^W = 0.46(\varepsilon/\sigma)^{1/2} (= 0.09 V)$, $C_+ = 1.0/nm (= 11\mu F/cm^2)$, $C_- = 1.4/nm (= 14\mu F/cm^2)$ for small $\Delta \Phi$. Thus, $\ell_w = 8\ nm \sim 2\ H$. As a result, we have $E_w/E_b \approx \varepsilon/\varepsilon_{eff} \sim 3$ for our small system. In contrast, in our recent paper, we applied electric field to point dipoles interacting with the soft-core potential to obtain $\ell_w \sim 2\sigma \sim 0.1H$ and $\varepsilon_{eff} \approx \varepsilon$.

Previously, Huntam et al.\textsuperscript{[45]} obtained $\Phi_{00}^W \sim 0.58 V$, $C_+ = 12.4\mu F/cm^2$, and $C_- = 10.5\mu F/cm^2$ at 300 K using the SPC model of water. They estimated the effective dielectric constant from Eq.(3.10) to find $\varepsilon_{eff} \approx 12$ in one example. Yeh and Berkowit\textsuperscript{[29]} found $\varepsilon$ similar to ours. Willard et al.\textsuperscript{[46]} obtained $\varepsilon$ similar to ours, $\Phi_{00}^W \sim 0.8 V$, $C_+ \approx 520\mu F/cm^2$, and $C_- \approx 8.39\mu F/cm^2$, using the SPC/E model of water and the Siepmann-Sprik model of electrodes.\textsuperscript{[43]}

In these simulations, water molecules are strongly adsorbed and oriented on metal walls, leading to larger $\Phi_{00}^W$ than ours, but the surface electric length $\ell_w$ may be estimated to be of order 10 nm as in our case.

### C. Local electric field

As will be shown in Appendix A, the local electric field on molecule $k$ is a linear combination of those at the constituting charged points $r_j$. For the TIP4P/2005 model, we have

$$E_{k}^{loc} = \frac{1}{2}(1 + b_M)(E_{kH1} + E_{kH2}) - b_M E_{kM},$$

(3.22)

where $b_M = 0.208$. In the bulk region, the average of its $z$ component $E_{zk}^{loc}$ is related to the bulk average field $E_b$ and polarization $P_b$ in Eq.(3.11) in the form,

$$E_{loc} = \langle E_{zk}^{loc} \rangle = E_b + 4\pi\gamma_{loc} P_b,$$

(3.23)

where $\gamma_{loc}$ is called the Lorentz factor. In our simulation, averaging over the molecules in the region $0.3H < z_{kG} < 0.7H$, we find $\gamma_{loc} \approx 0.58$ for all $\Delta \Phi$ investigated (see Table 1 for $\Delta \Phi = 0.19$ and 1.9 V).

In the classical theory of dielectrics,\textsuperscript{[17],[19]} the space is divided into the exterior and interior of a sphere around each dipole $k$. Then, the contribution to $E_{k}^{loc}$ from the dipoles in the exterior has been assumed to be the mean field $E_b + 4\pi P_b/3$ along the $z$ axis. Here, we suppose a sphere with radius $R = 12.6\ A$ around the center of mass $r_{kG}$ of molecule $k$. For $0.3H < z_{kG} < 0.7H$, Eqs.(2.25) and (3.22) yield the local field contribution from the charges $j$ inside the sphere in the form,

$$E_{k}^{in} = \sum_{\alpha,\beta,\ell \neq k} \theta(R - |r_{kG} - r_{jG}|)A_{ij}q_j g(r_i - r_j),$$

(3.24)

where $\theta(u)$ is the step function, $i = ka$, and $j = \ell\beta$ with $\ell \neq k$ and $\alpha, \beta = H1, H2$. The coefficients $A_{ij}$ are $A_{H1} = A_{H2} = (1 + b_M)/2$ and $A_M = -b_M$ from Eq.(3.22). Then, the local field contribution from the sphere exterior is equal to the difference $E_{k}^{loc} - E_{k}^{in}$ and its mean field average is $(E_b + 4\pi P_b/3)\epsilon_z$. Thus, from the classical theory\textsuperscript{[17],[19]} the following deviation should be very small:

$$F_{k}^{loc} = E_{k}^{loc} - E_{k}^{in} - (E_b + 4\pi P_b/3)\epsilon_z.$$  

(3.25)
If this deviation is negligible, Eq.(3.23) gives
\[ \gamma_{\text{loc}} = 1/3 + E_{\text{in}}/4\pi P_b, \] (3.26)
where \( E_{\text{in}} = \langle E_{\text{in}}^r \rangle \) is the average in the bulk. Our simulation indicates \( E_{\text{in}}/4\pi P_b \cong 0.25 \).

We further divide the dipolar field \( E_i^d \) on charge \( i \) in Eq.(2.24) into the long-range part \( E_{i}^{dL} \) and the short-range part \( E_{i}^{ds} \) replacing \( 1/r \) by \( \psi_i(r) \) and \( \psi_a(r) \) in Eq.(2.11), respectively. Then, we have
\[ E_{i}^{dL} = \sum_{m} \sum_{j} q_j g_\ell(r_i - r_j + Lm_\perp), \] (3.27)
\[ E_{i}^{ds} = \sum_{m} \sum_{j} q_j g_s(r_i - r_j + Lm_\perp), \] (3.28)
where \( g_\ell(r) = -\nabla \psi_i(r) \) and \( g_s(r) = -\nabla \psi_s(r) \).

From Eq.(3.22), the contributions of \( E_{i}^{dL} \) and \( E_{i}^{ds} \) to \( E_{\text{local}} \) are given by the linear combinations \( E_{k}^{dL} = \sum \alpha A_\alpha E_{\alpha}^{dL} \) and \( E_{k}^{ds} = \sum \alpha A_\alpha E_{\alpha}^{ds} \). In Appendix C, we will express \( E_{i}^{dL} \) in terms of the polarization density deviation,
\[ \delta p(r) = p(r) - P(z)e_z, \] (3.29)
where \( p(r) \) is defined in Eq.(B3) and \( P(z) \) in Eq.(3.5).

Some calculations yield
\[ E_{i}^{dL} = -\sum_{m_\perp} \int d^3r' \bar{\ell}_\ell'(r_i - r' + Lm_\perp) \cdot \delta p(r') \]
\[ -4\pi \int_0^{\infty} dz' \varphi(z' - z_i) P(z') e_z, \] (3.30)
where the integral \( \int d^3r' \) is within the cell, \( \bar{\ell}_\ell'(r) = -\nabla \psi_i(r) \) is the long-range dipolar tensor (see Appendix C), and \( \varphi(z) \) is the normalized Gaussian distribution in Eq.(2.12). We notice that the second term in Eq.(3.30) and the last term in Eq.(2.24) mostly cancel, leading to \( E_{i}^{dL} + 4\pi \langle \sigma_0 \rangle e_z \sim E_a \) in the bulk region (see Fig.4(a)).

We calculated the averages of the \( z \) components of \( E_{\text{local}}^L, E_{\text{local}}^p, E_{\text{local}}^d, \) and \( E_{\text{local}}^{ds} \) for the molecules with their centers of mass in the bulk region (0.3H < \( z_{KG} \) < 0.7H). In Fig.4(a), we write them as \( E_{\text{local}}^L, E_{\text{local}}^p, E_{\text{local}}^d, \) and \( E_{\text{local}}^{ds} \), respectively. We can see that \( E_{\text{local}}^d + 4\pi \langle \sigma_0 \rangle e_z \) is close to \( E_a \) in accord with the discussion below Eq.(3.30). In (b), we show that \( F_{\text{local}} = E_{\text{local}}^L - E_a - 4\pi P_b/3 \) is almost zero and \( E_{\text{local}} - E_{\text{local}}^{ds} - E_a \) is at most 10% of \( E_a \). The former indicates smallness of \( F_{\text{local}}^E \) in Eq.(3.25).

In (c) and (d) of Fig.3, we display the equilibrium probability distributions for the \( z \) components of \( E_{\text{local}}^L \) and \( F_{\text{local}}^E \) in the bulk. They are written as
\[ P_{\text{local}}(E) = \langle \sum_{k \in \text{bulk}} \delta(E_{Z_{kG}} - E)/N_{\text{bulk}} \rangle, \] (3.31)
\[ P_{L}(E) = \langle \sum_{k \in \text{bulk}} \delta(F_{Z_{kG}} - E)/N_{\text{bulk}} \rangle, \] (3.32)
where the molecules with 0.3H < \( z_{KG} \) < 0.7H are summed with \( N_{\text{bulk}} \) being their number. Including the case of \( \Delta \Phi = 0 \), the distribution of \( E_{\text{local}}^L \) is broad with width greater than 15 V/\( \text{nm} \), while that of \( F_{\text{local}}^E \) is narrow with width less than 1 V/\( \text{nm} \). Note that the bulk average of \( E_{Z_{kG}}^L \) is 0.48 and 4.3 V/\( \text{nm} \) for \( \Delta \Phi = 0.19 \) and 1.9 V, respectively. These values also follow from the relation \( E_{\text{local}} = \int dE P_{\text{local}}(E)E \). It is worth noting that a charge \( e \) separated by \( \sigma \) creates an electric field with size \( e/\sigma^2 \) = 14 V/\( \text{nm} \). Previously, similar electric field fluctuations in water were calculated\(^{22}\) because they are relevant in ionic dissociation reactions and vibrational spectroscopic response.

### IV. FIELD REVERSAL

Now, we present results on the relaxation after field reversal at \( T = 298 \text{ K} \), where the applied potential \( \Delta \Phi \) (field \( E_a \)) is changed from \(-1.9 \text{ V} \) (\(-0.42 \text{ V/nm}\)) to 1.9 V (0.42 V/\( \text{nm} \)) at \( t = 0 \). The system was in equilibrium for \( t < 0 \) and transient behaviors follow for \( t > 0 \) on a timescale of \( \tau_r \). We assume that the relaxation time in the metal walls is much faster than \( \tau_r \). Then, \( \Delta \Phi \) can be changed instantaneously, while the polarization in the liquid increases continuously. In Fig.5, we illustrate microscopic time-evolution of reorientation of seven water molecules in a very short time interval of 0.27 ps. We can see very complex rotational motions, where large angle changes occur cooperatively in a short time interval\(^{20,25}\). Previously, Laage et al\(^{22}\) detected sudden, large-amplitude rotations of water molecules in...
their simulation in equilibrium as a relevant reorientation mechanism. However, in water at room temperatures, the thermal fluctuations are large. Thus, we performed 50 independent runs to produce Figs. 6 and 7 and the bottom panels of Fig. 8. In this section, $(\cdots)$ denotes taking the nonequilibrium average over these 50 runs.

**A. Results of 1D profiles.** In (a) and (b) of Fig. 6, we show 1D profiles of $4\pi P(z,t)$ in Eq. (3.5) and $\Psi(z,t)$ in Eq. (3.6) at $t = 0.001, 1.5$, and 6 ps. We can see that the film is divided into Stern layers and a bulk region even in transient states. In (c), we give $4\pi \langle \sigma_0(t) \rangle$, $4\pi P_b(t)$, and $4\pi \langle M_z(t) \rangle / V$ vs $t$. Here, Eqs. (2.16) and (3.11) hold, so $4\pi \langle \sigma_0(t) \rangle(t)$ increases by $2 \times 0.42$ V/nm discontinuously at $t = 0$ from Eq. (2.16). These quantities are very close since $E_a$ and $E_b(t)$ are much smaller. In (d), we give the average of the $z$ component of the polarization direction $\vec{n}_k(t)$ in Eq. (2.1), denoted by $\langle n_z \rangle(t)$, for the molecules in the three regions $z_{4G} < 0.1H$, $z_{4G} > 0.9H$, and $0.1H < z_{4G} < 0.9H$. The relaxations near the walls and in the bulk are similar because the adsorption is weak in our simulation. Also displayed are $E_b(t)$ in (e) and $\Phi^{\sigma}(t)$ and $\Phi^{\pi}(t)$ in (f). The quantities in (c)-(f) ultimately relax exponentially. For example, at long times, we have

$$
\langle M_z(t) \rangle - \langle M_z(\infty) \rangle \propto \exp(-t/\tau_r),
$$

where $\tau_r = 2.84$ ps at $T = 298$ K.

**B. Big rotational jumps and hydrogen-bonded clusters.** In water, large orientational changes of the dipoles are accompanied by breakage and reorganization of hydrogen bonds.
FIG. 8. (Color online) Largely rotated (LR) molecules satisfying Eq.(4.2) at (a) $t = 1.5$ and (b) $3$ ps (left), among which selected are those forming hydrogen-bonded clusters with sizes exceeding 2 at (a’) $t = 1.5$ and (b’) $3$ ps (right). The $z$ axis is in the vertical direction. Cross-sectional snapshots at (a”) $t = 1.5$ and (b”) $3$ ps (bottom), where displayed are molecules with their centers of mass in the shaded region with thickness 6 Å in (a) and (b).

of the hydrogen-bond network. This suggests that large angle changes are relevant in the relaxation after a reversal of strong applied field, which can in fact be seen in Fig.5 and Fig.7(b). Thus, we consider largely rotated (LR) molecules with angle jumps determined by

$$n_{zk}(t) - n_{zk}(0) > 0.8,$$  \hspace{1cm} (4.2)

where $n_{zk}(t) = \cos \theta_{k}(t)$ is the $z$ component of the polarization direction $\mathbf{n}_{k}(t)$ in Eq.(2.1) with $\theta_{k}(t)$ being the angle with respect to the $z$ axis. We define the big-jump fraction by

$$\phi_{M}^{jump}(t) = \langle \sum_{k \in \text{jump}} [n_{zk}(t) - n_{zk}(0)] \rangle \mu_{0}/\Delta M(t),$$  \hspace{1cm} (4.3)

where the summation is over $k$ satisfying Eq.(4.2). In the denominator, we set $\Delta M(t) = \mu_{0} \langle \sum_{k \in \text{jump}} [n_{zk}(t) - n_{zk}(0)] \rangle$, where the summation is over all $k$. It is equal to the total polarization change $\langle M_z(0) \rangle - \langle M_z(t) \rangle$ (see Fig.6(c)). In Fig.6(a), this fraction is small at very short times but soon exceeds 0.6 for $t > 0.5$ ps. Therefore, for $t > 0.5$ ps, the relaxation is governed by these big rotational jumps.

At $T = 298$ K, the timescales of reorientation and reorganization of the hydrogen bonds are both very rapid and it is difficult to capture the dynamics quantitatively. Here, we regard that an intermolecular O-H pair is hydrogen-bonded if their distance is shorter than 2.4 Å (since the pair correlation function $g_{OH}(r)$ for intermolecular O and H pairs exhibits a sharp minimum at this distance). Then, for the tetrahedral structure, the hydrogen bond number $m_{k}$ for molecule $k$ is ideally 4 (two for its oxygen atom and two for its protons), but its thermal average $\langle m_{k} \rangle$ at $T = 298$ K is about 3.8 in our model. In Fig.6(b), we plot the fractions of the LR molecules with $m_{k} = m$ at time $t$ expressed as

$$\phi_{HB}^{jump}(m, t) = \langle \sum_{k \in \text{jump}} \delta_{mm_{k}(t)}/N_{jump}(t) \rangle,$$  \hspace{1cm} (4.4)

where $N_{jump}(t)$ is the number of the molecules satisfying Eq.(4.2) at time $t$. We can see that $\phi_{HB}^{jump}(3, t)$ decays from 0.48 at $t = 0.1$ ps to the equilibrium value $\phi_{HB}(3) = 0.27$ with a relaxation time of 1.3 ps (a half of $\tau_{c}$ in Eq.(4.1)), while there is no increase in $\phi_{HB}^{jump}(5, t)$ from the equilibrium value $\phi_{HB}(5) = 0.10$. Note that $\phi_{HB}(4) \approx 0.63$ in equilibrium. Here, $\phi_{HB}^{jump}(m, t)$ rapidly approaches the equilibrium distribution $\phi_{HB}(m)$ and the deviation $\phi_{HB}^{jump}(m, t) - \phi_{HB}(m)$ is not large except for very small $t(<0.1$ ps), though breakage of a few hydrogen bonds are needed for each big rotational jump.

In Fig.8, we present snapshots of the LR molecules satisfying the jump condition (4.2) in the left panels at $t = 1.5$ and 3 ps. Among these molecules, we pick up those belonging to hydrogen-bonded clusters with member numbers exceeding 2 in the right panels. In the bottom panels, cross-sectional snapshots at these times are displayed. These snapshots indicate that large rotational jumps occur heterogeneously in the form of hydrogen-bonded clusters, which is conspicuous even at $T = 298$ K.

In Fig.9(a), we illustrate a cluster composed of 11 LR molecules (which is the largest one at $t = 1.5$ ps in a simulation run). Here, the orientations $\mathbf{n}_{k}(t)$ of these molecules exhibit rapidly varying thermal fluctuations, so we consider the time averag of their $z$ components,

$$\bar{n}_{zk}(t) = \int_{t-\Delta t}^{t} dt' n_{zk}(t')/\Delta t.$$  \hspace{1cm} (4.5)

In Fig.9(b), setting $\Delta t = 0.015$ ps, we plot $\bar{n}_{zk}(t)$ vs $t$ for 8 members depicted in (a). We can see these molecules have undergone simultaneous big rotational jumps in a time interval of 1 ps. In Fig.9(c), as functions of $t$, we
(c) Number of largely rotated molecules (total) and that of largely rotated molecules belonging to H-bonded clusters with sizes exceeding 2. In (d), we plot the average maximum cluster size $\bar{m}(t)$ and mean cluster size $\bar{m}(t)$ vs $t$.

show the total number of the LR molecules and that of the LR molecules belonging to hydrogen-bonded clusters with sizes exceeding 2. In (d), we plot the average maximum cluster size $m_{\text{max}}(t)$ and mean cluster size $\bar{m}(t)$.

$$\bar{m}(t) = \frac{\sum_{m>2} N_m(t)m^2}{\sum_{m>2} N_m(t)m},$$

where $N_m(t)$ is the number of the clusters with size $m$.

It is worth noting that irregular chain-like, dynamic heterogeneities have been observed numerically in supercooled water. In our case of electric field reversal, we have detected similar clusters even at $T = 298$ K.

C. Orientational change in Stern layer. In Fig.10, we show time-evolution of the molecules in the bottom Stern layer ($0 < z_{\text{SG}} < d = 4.5$ Å), which are heterogeneously distributed on the plane and are connected by hydrogen bonds. These molecules are partially connected by the hydrogen bonds. See Fig.6(c) for the behavior of the time-dependent average $\langle \cos \theta \rangle = \langle n_{zk} \rangle$ near the walls, which is not much different from that in the bulk. In addition, the molecules in the Stern layers stay there on a timescale of 5 ps in our model (not shown in this paper). We note that the dynamics of more strongly adsorbed water molecules on a realistic metal wall should be investigated in future.

V. SUMMARY AND REMARKS

We have studied a system of 2400 water molecules under electric field between metal walls, using the TIP4P/2005 model and the 3D Ewald method. Main results in this paper are as follows.

(i) In Sec.IIIA, we have expressed the electric potential due to the surface charges as the sum of the uniform part $-4\pi \tilde{q}_0 z$ and the deviation $\phi_s$ as in Eq.(2.17) with $\phi_s$ being expressed microscopically as in Eq.(2.22). Remarkably, $\phi_s$ tends to zero away from the walls as demonstrated by Fig.2 and Eqs.(3.2)-(3.4). This means that we can calculate the bulk properties of water under electric field assuming a uniform surface charge distribution. This result supports the method of Yeh and Berkowitz.

(ii) In Sec.IIIB, we have examined 1D average profiles in the range $0 < z < H$ starting with the average polarization $P(z)$ in Eq.(3.5). We have found Stern boundary layers with thickness $d = 4.5$ Å and a homogeneous bulk region with thickness $H - 2d$. The ratio between the bulk polarization $P_b$ and the bulk electric field $E_b$ yields the bulk dielectric constant $\varepsilon$ in Eq.(3.12). Though the layer thickness $d$ itself is short, the surface effect on the dielectric response is determined by the ratio $\ell_{\phi}/H$, where $\ell_{\phi}$ is a surface electric length of order 10 nm in Eq.(3.16).

In addition, we have found a surface potential change $\Phi_{00}^w = 0.09$ V at $\Delta \Phi = 0$ in Eq.(3.19) due to the preferred H-down molecular orientation in Fig.1(b). However, our numerical value of $\Phi_{00}^w$ is considerably smaller.
than those in the previous simulations because its size sensitively depends on the wall-water interaction. (iii) In Sec.IIIC, we have calculated the local field $E^\text{loc}_k$ on each molecule $k$ to obtain its average and its fluctuation distribution in Fig.4. We have confirmed that the local field contribution from its interior fluctuates strongly around an average about $0.25 \times 4\pi P_b$ with large fluctuations with sizes of order 15 V/nm.

(iv) In Sec.IV, we have examined the dynamics after a field reversal of strong applied field. Due to the presence of the hydrogen-bond network, the relaxation is governed by big rotational jumps, as demonstrated in Fig.7, where the jump criterion is given by Eq.(4.2). These big jumps occur in the form of hydrogen-bonded clusters as in Fig.8 and Fig.9(a).

(v) We have obtained the microscopic expression for the molecular local electric field $E^\text{loc}_k$ in Appendix A and that for the polarization density $\mathbf{p}(\mathbf{r})$ in Appendix B.

Some remarks are given below.

(1) We should further check the validity of a number of mean-field predictions in the classical theory of dielectrics using microscopic simulation. In particular, we should examine the short-range orientational correlation in electric field. In fact, it gave rise to a deviation of the Lorentz factor $\gamma_{\text{loc}}$ from 1/3 in our previous simulation on point dipoles.[9] (2) There are a number of important nonequilibrium situations under applied electric field, including the case of an oscillating field. We should also perform simulations of electrolytes between electrodes. (3) Marked dynamic heterogeneities are well-known in the translational and rotational dynamics in glassy states of anisotropic particles.[21][22] Dynamics of supercooled polar liquids under applied electric field is of great interest.

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**Appendix A: Local electric field for water**

In the TIP4P/2005 model,[22] a water molecule is treated as a rigid isosceles triangle. For a molecule $k$, we write the positions of its oxygen atom and two protons as $\mathbf{r}_{kO}$, $\mathbf{r}_{kH1}$, and $\mathbf{r}_{kH2}$, respectively. Here, $q_{\text{OH}} = |\mathbf{r}_{kH1} - \mathbf{r}_{kO}| = |\mathbf{r}_{kH2} - \mathbf{r}_{kO}| = 0.957 \text{ Å}$ and the angle between $\mathbf{r}_{kH1} - \mathbf{r}_{kO}$ and $\mathbf{r}_{kH2} - \mathbf{r}_{kO}$ is $\theta_{\text{HOH}} = 104.5^\circ$. So $a_{\text{HH}} = |\mathbf{r}_{kH1} - \mathbf{r}_{kH2}| = 2a_{\text{OH}} \sin(\theta_{\text{HOH}}/2) = 0.844 \text{ Å}. For each ion, the charges are at the proton positions with $q_\text{H} = 0.5564e$ and at another position $M$,

$$r_{kM} = r_{kO} + a_{\text{OM}} \mathbf{n}_k$$  \hfill (A1)

with $q_\text{M} = -2q_\text{H}$ and $a_{\text{OM}} = 0.1546\text{Å}$. The elementary charge is $e = 23.82(e\sigma)^{1/2}$. The $\mathbf{n}_k$ is the unit vector from $r_{kO}$ to the midpoint of the proton positions,

$$\mathbf{r}_{kH} = \frac{1}{2}(\mathbf{r}_{kH1} + \mathbf{r}_{kH2})$$  \hfill (A2)

Thus, $\mathbf{r}_{kH} - r_{kO} = a_d \mathbf{n}_k$ with $a_d = a_{\text{OH}} \cos(\theta_{\text{HOH}}/2) = 0.5859\text{Å}$. The dipole is expressed as in Eq.(2.1) with $\mu_0 = 2q_\text{H}(a_d - a_{\text{OM}}) = 3.62(e\sigma^3)^{1/2} = 2.305 \text{ D}$. Next, we shift the charge positions $\mathbf{r}_j$ infinitesimally by $d\mathbf{r}_j$ with the molecular shape held unchanged. Their images outside the cell are also shifted by the same amounts. The change in the electrostatic energy in Eq.(2.8) is rewritten at fixed $E_\text{A}$ as

$$dU_m = -\sum_k [F^e_k \cdot d\mathbf{r}_G + F^e_k \cdot d\mathbf{r}_H + E^\text{loc}_k \cdot d\mathbf{r}_M].$$  \hfill (A3)

where we introduce the center of mass and the relative positional vector between two protons by

$$r_{kG} = \frac{8}{9}r_{kO} + \frac{1}{18}(r_{kH1} + r_{kH2}),$$ \hfill (A4)

$$\mathbf{r}_k = r_{kH1} - r_{kH2}.$$ \hfill (A5)

For each water molecule $k$, the conjugate electric forces to $r_{kG}$ and $\mathbf{r}_k$ are given by

$$F^e_k = q_H(E_{kH1} + E_{kH2} - 2E_{kM}),$$ \hfill (A6)

$$F^e_k = \frac{1}{2}q_\text{H}(E_{kH1} - E_{kH2}).$$ \hfill (A7)

The $E^\text{loc}_k$ in Eq.(A3) is the local electric field on water molecule $k$, which is conjugate to $\mathbf{r}_M$. It is expressed as in Eq.(3.22) with $b_M = (a_{\text{OM}} - a_d)/a_d = 0.208$.

**Appendix B: Microscopic expressions for polarization density and Poisson electric potential**

We give a microscopic expression for the polarization density $\mathbf{p}(\mathbf{r})$ in terms of the charged positions $\mathbf{r}_j$ for polar molecules (with $\sum_j q_j = 0$). We assume that $\mathbf{p}$ is related to the microscopic charge density $\rho(\mathbf{r})$ by

$$-\nabla \cdot \mathbf{p} = \rho = \sum_j q_j \delta(\mathbf{r} - \mathbf{r}_j).$$ \hfill (B1)

We introduce the following 3D symmetrized $\delta$-function,

$$\hat{\delta}(\mathbf{r}; \mathbf{r}_1, \mathbf{r}_2) = \int_0^1 d\lambda \delta(\mathbf{r} - \lambda \mathbf{r}_1 - (1 - \lambda) \mathbf{r}_2),$$ \hfill (B2)

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are particle positions. This $\delta$-function is nonvanishing only on the line segment connecting $\mathbf{r}_1$.
and \( r_2 \). It is known to appear in the microscopic expression for the local stress tensor \(^{28}\) for the TIP4P/2005 model \(^{22}\) using the relation \((r_1 - r_2) \cdot \nabla \delta (r; r_1, r_2) = \delta (r - r_2) - \delta (r - r_1)\), we find \( p \) explicitly as

\[
p(r) = \sum_k \frac{q_k}{2} \left[ \hat{\delta}(r; r_{kH1}, \bar{r}_{kH}) - \hat{\delta}(r; r_{kH2}, \bar{r}_{kH}) \right] \xi_k \\
+ \sum_k \delta (r; \bar{r}_{kH}, r_{kM}) \mu_k, \tag{B3}
\]

where \( \bar{r}_{kH} \), \( \xi_k \), and \( \mu_k \) are defined by Eqs.(A2), (A5), and (2.1), respectively. We then find the total polarization \( M = \int dr p(r) = \sum_k \mu_k \). Without ions, the electric field \( E = -\nabla \Phi \) away from the charge positions satisfies

\[
\nabla \cdot (E + 4\pi p) = 0. \tag{B4}
\]

We obtain Eq.(2.16) by multiplying \( z \) to the above relation and integrating in the cell.

To calculate the average polarization \( P(z) \) in Eq.(3.5), we introduce the laterally integrated polarization,

\[
M_L(z) = \int dz dy p_z(r). \tag{B5}
\]

Then, \( P(z) = \langle p_z(r) \rangle = \langle M_L(z) \rangle / L^2 \). The total polarization along the \( z \) axis in Eq.(2.9) is given by \( M_z = \int_0^dz M_L(z) \). This \( M_z(z) \) is obtained from Eq.(B3) if we replace \( \delta (r; r_1, r_2) \) by the 1D symmetrized \( \delta \)-function,

\[
\int_0^1 d\lambda \delta (z - \lambda z_1 - (1 - \lambda) z_2) \\
= [\theta(z - z_1) - \theta(z - z_2)] / (z_2 - z_1), \tag{B6}
\]

where \( \theta(u) \) is the step function. We then find

\[
M_L(z) = -q_H \sum_k \left[ \theta(z - z_{kH1}) + \theta(z - z_{kH2}) \\
-2\theta(z - z_{kM}) \right], \tag{B7}
\]

which leads to Eq.(3.5).

**Appendix C: Long-range dipolar field**

Here, we derive Eq.(3.30). In \( E^{dl}_{\perp} \) in Eq.(3.27) the self terms \((j = i \text{ for } m_{\perp} = 0)\) can be included because \( \psi_i(0) \) is finite. From Eq.(3.27) we have

\[
E^{dl}_{\perp} = \sum_{m_\perp} \int dr' \rho(r') g_{\perp}(r_i - r' + L m_{\perp}), \tag{C1}
\]

where \( \rho(r) = \sum_q g_q \delta (r - r_q) \) is the charge density. We use \( p(r) \) in Eq.(B3), which is related to \( \rho(r) \) by Eq.(B1). Since \( p(r) \) vanishes at \( z = 0 \) and \( H \) due to the wall potentials, we find

\[
E^{dl}_{\perp} = -\sum_{m_\perp} \int dr' \hat{w}_{\perp}(r_i - r' + L m_{\perp}) \cdot p(r'), \tag{C2}
\]

where \( \hat{w}_{\perp}(r) = -\nabla \nabla \psi_i(r) \) is calculated as

\[
\hat{w}_{\perp}(r) = \left[ \frac{1}{r^3} - B(r) \right] \hat{I} - \frac{3}{r^5} - C(r) \right] \frac{1}{r^2} \hat{r} \hat{r}. \tag{C3}
\]

Here, \( \hat{I} \) is the unit tensor and

\[
B(r) = \psi_x(r)/r^2 + 2\pi \varphi_3(r)/\gamma^2 r^2, \\
C(r) = 3B(r) + 4\pi \varphi_3(r), \tag{C4}
\]

where \( \varphi_3(r) = \varphi(x)\varphi(y)\varphi(z) = (\gamma/\sqrt{\pi})^3 \exp(-\gamma^2 r^2) \) is the normalized 3D Gaussian distribution (see Eq.(2.12)).

Let us replace \( p(r') \) by \( P(z') e_z \) in Eq.(C2). Then, only the \( z \) component is nonvanishing, where the \( z \) component of \( \hat{w}_{\perp}(r' - r'' \perp) \) may further be replaced by \(-\left(\nabla' \right)^2 \psi_i(r' - r'') = 4\pi \varphi_3([r' - r'']) \) with \( \nabla' = \partial / \partial r' \) and \( r'' = r_i + L m_{\perp} \). Integration of the resultant expression in the \( x'y' \) plane yields Eq.(3.30).

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