Applying electric field to charged and polar particles between metallic plates: Extension of the Ewald method

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We develop an efficient Ewald method of molecular dynamics simulation for calculating the electrostatic interactions among charged and polar particles between parallel metallic plates, where we may apply an electric field with an arbitrary size. We use the fact that the potential from the surface charges is equivalent to the sum of those from image charges and dipoles located outside the cell. We present simulation results on boundary effects of charged and polar fluids, formation of ionic crystals, and formation of dipole chains, where the applied field and the image interaction are crucial. For polar fluids, we find a large deviation of the classical Lorentz-field relation between the local field and the applied field due to pair correlations along the applied field. As general aspects, we clarify the difference between the potential-fixed and the charge-fixed boundary conditions and examine the relationship between the discrete particle description and the continuum electrostatics.

I. INTRODUCTION

In many problems in physics and chemistry, the electrostatic potential and field acting on each constituting particle need to be calculated. A large number of simulations have been performed to accurately estimate the long-range electrostatic interactions among charged and polar particles. The Ewald method is a famous technique for efficiently summing these interactions using the Fourier transformation. It was originally devised for ionic crystals and has been widely used to investigate bulk properties of charged and polar particles under the periodic boundary condition in three dimensions (3D). It has also been modified for filmlike systems bounded by non-polarizable and insulating regions under the periodic boundary condition in the lateral direction.

However, the Ewald method has not yet been successful when charged or polar particles are in contact with metallic or polarizable plates and when electric field is applied from outside. Such situations are ubiquitous in solids and soft matters. In idealized metallic plates, the surface charges spontaneously appear such that the electrostatic potential is homogeneous within the plates, thus providing the well-defined boundary condition for the potential within the cell. Between two parallel plates, we control the potential difference to apply an electric field. However, the electrostatic interaction between the surface charges and the particles within the cell is highly nontrivial. On the other hand, such surface changes are nonexistent for the magnetic interaction.

Each charged particle between parallel metallic plates induces surface charges producing a potential equivalent to that from an infinite number of image charges outside the cell. If a charged particle approaches a metal wall, it is attracted by the wall or by its nearest image. Some mathematical formulae including these image charges in the Ewald sum were presented by Hautman et al. and by Perram and Ratner. In the same manner, for each dipole in the cell, an infinite number of image dipoles appear. A dipole close to a metal surface is attracted and aligned by its nearest image. Accounting for these image dipoles, Klapp performed Monte Carlo simulations of 500 dipoles interacting with the soft-core potential, but without applied electric field, to find wall-induced ordering. The image effect is also relevant in electrrohydrodynamical fluids between metallic plates.

Inclusion of the image effect in molecular dynamics simulations of molecules near a conducting or polarizable surface is still challenging in a variety of important problems. Moreover, the effects of applied electric field remain largely unexplored on the microscopic level, while the continuum electrostatics is well established. For example, the local electric field acting on a dipole is known to be different from the applied electric field in dielectrics and polar fluids, where the difference is enlarged in highly polarizable systems. In contrast, a number of microscopic simulations have been performed on the effect of uniform magnetic field for systems of magnetic dipoles.

In this paper, we hence aim to develop an efficient Ewald method to treat charged and polar particles between parallel metallic plates accounting for the image effect, where we apply an electric field with an arbitrary size. In the Ewald sum in this case, we can sum up the terms homogeneous in the lateral $xy$ plane but inhomogeneous along the normal $z$ axis into a simple form and can calculated them precisely. This one-dimensional part of the electrostatic energy yields one-dimensional (laterally averaged) electric field along the $z$ axis for each particle.

Using our scheme, we present some numerical results under applied electric field, including the soft-core pair interaction and the wall-particle repulsive interaction. We confirm that accumulation of charges and dipoles near metallic walls gives rise to a uniaxially symmetric, homogeneous interior region. We also examine formation of ionic crystals and that of dipole chains under electric field. Here, we are interested in the mechanisms of dipole alignment near metallic walls, which are caused by the image interaction or by the applied electric field. We shall also see that the classical local field relation is much violated in our dipole systems because of strong...
pair correlations along the applied field.

The organization of this paper is as follows. In Sec.II, we will extend the Ewald scheme for charged particles between metallic plates and clarify the difference between two typical experiments at a fixed potential difference and at fixed surface charges. In Sec.III, we will further develop the Ewald scheme for point-like dipoles between metallic plates under applied electric field. In these two sections, we will present some numerical results.

II. CHARGED PARTICLES

We consider \( N \) charged particles in a cell. Their positions and charges are \( r_i \) and \( q_i \) (\( 1 \leq i \leq N \)). We assume the charge neutrality condition,

\[
\sum_i q_i = 0. \tag{2.1}
\]

In terms of the electrostatic energy \( U = U(r_1, \ldots, r_N) \), the electrostatic force on particle \( i \) is given by

\[
F_i^e = q_i F_i = -\frac{\partial}{\partial r_i} U, \tag{2.2}
\]

where \( E_i \) is the electric field on particle \( i \). There can also be neutral particles interacting with charged ones.

A. Ewald method for charged particles in the periodic boundary condition

When the bulk properties of charged particle systems are calculated, the periodic boundary condition is usually assumed in molecular dynamics simulation. In a \( L \times L \times L \) cell, the electrostatic energy is written as

\[
U_p = \frac{1}{2} \sum_{m} q_i q_j \frac{1}{|r_{ij} + Lm|}, \tag{2.3}
\]

where \( r_{ij} = r_i - r_j \) is the relative positional vector, \( m = (m_x, m_y, m_z) \) is a 3D vector with three integer components, and the self terms \((j = i \text{ and } m = (0,0,0))\) are excluded in the summation \( \sum_{i,j} \). Here, \( E_i \) is obtained from Eq.(2.2) with \( U = U_p \).

In the Ewald method, the Coulomb potential \( q_i q_j/r \) is divided into the short-range part \( q_i q_j \psi_s(r) \) and the long-range part \( q_i q_j \psi_l(r) \), where

\[
\psi_s(r) = \text{erfc}(\gamma r), \quad \psi_l(r) = \text{erf}(\gamma r). \tag{2.4}
\]

The inverse \( \gamma^{-1} \) is an adjustable potential range. For \( r \gg \gamma^{-1} \), we have \( \psi_s \propto r^{-1} \). For \( r \ll \gamma^{-1} \) it is finite as

\[
\psi_l(r) = (2/\sqrt{\pi})(1 - \gamma^2 r^2/3 \cdots). \tag{2.5}
\]

As is well-known, \( U_p \) is written as

\[
U_p = \sum_{m} \sum_{i,j} \frac{q_i q_j}{|r_{ij} + Lm|} - \frac{1}{L^3} \sum_{\nu \neq 0} \sum_{i,j} \frac{q_i q_j}{\sqrt{\pi}} \Psi_k(k) e^{i k \cdot r_{ij}} + \frac{2\pi}{3 L^3} \sum_{i} |q_i r_i|^2, \tag{2.7}
\]

where the second term is equal to \(-\sum_{i} \frac{\rho_i^2 \psi_0(0)/2} \), and the last two terms arise from \( \sum_{m} \sum_{i,j} q_i q_j \psi_k(|r_{ij} + Lm|)/2 \) including the self part. Use is made of the Fourier transformation \( \psi_i(r) = (2\pi)^{-3} \int d\mathbf{k} \Psi_i(k) e^{i \mathbf{k} \cdot \mathbf{r}} \), where

\[
\Psi_i(k) = 4\pi \exp[(-k^2/4\gamma^2)/k^2]. \tag{2.8}
\]

In the third term, \( \mathbf{k} \) is discretized as

\[
\mathbf{k} = (2\pi/\ell)(\nu_x, \nu_y, \nu_z), \tag{2.9}
\]

and the term with \( \nu = (\nu_x, \nu_y, \nu_z) = (0,0,0) \) is excluded, where \( \nu_x, \nu_y, \) and \( \nu_z \) are integers \((0, \pm 1, \pm 2, \cdots)\). This discretization stems from the summation over \( m \) in Eq.(2.3). The last term in Eq.(2.7) arises from the \( k \)-integration at small \( |k| \lesssim L^{-1} \). However, it is negligible without overall polarization or for \( \sum_i q_i r_i \equiv 0 \). See Appendix A for the derivation of the last two terms.

B. Ewald method for charged particles between metallic plates under applied electric field

As in Fig.1, we consider a \( L \times L \times H \) parallel plate geometry, where the plates at \( z = 0 \) and \( H \) are both metallic. For simplicity, they are assumed to be smooth and structureless. Then we may apply electric field \( E_0 \) perpendicularly to the plates. We assume the periodic boundary condition along the \( x \) and \( y \) axes with lateral length \( L \). In the semi-infinite case \( 0 < z < \infty \) with a metal plate at \( z = 0 \), a charge \( q_i \) at \( \mathbf{r}_i = (x_i, y_i, z_i) \) induces an image charge at

\[
\mathbf{r}_i = (x_i, y_i, -z_i), \tag{2.10}
\]

with the opposite strength \(-q_i \). For small \( z_i \), the particle \( i \) is attracted by its image with the force \(-\partial \psi_1/\partial z_i = -q_i^2/(2z_i^2) \), so the image potential is of the form,

\[
\psi_1(z) = -q_i^2/4z_i. \tag{2.11}
\]

Experimentally, the potential difference between the two plates can be controlled and can even be non-stationary. In this paper, we adopt the fixed-potential boundary condition and write the electrostatic potential away from the particle positions \( \mathbf{r} \neq \mathbf{r}_j \) as

\[
\Phi(r) = \phi(r) - E_0 z. \tag{2.12}
\]
The electric field away from the particle positions is $E = E_\alpha e_z - \nabla \phi$, where $e_z$ is the unit vector along the z axis. We assume that the charged particles are repelled from the walls at close distances and that no ionization occurs on the walls. Then, the excess potential $\phi$ in Eq.(2.12) satisfies the boundary condition,

$$\phi(x, y, 0) = \phi(x, y, H) = 0. \quad (2.13)$$

From the bottom to the top, the potential difference is

$$\Delta \Phi = \Phi(x, y, 0) - \Phi(x, y, H) = H E_\alpha. \quad (2.14)$$

In the region $0 < z < H$, $\phi(r)$ is the solution of the Poisson equation under the boundary condition (2.13),

$$- \nabla^2 \phi = 4\pi \sum_j q_j \delta(r - r_j). \quad (2.15)$$

To calculate $\phi(r)$, we consider its 2D Fourier expansion,

$$\phi = \frac{4\pi}{L^2} \sum_{\nu_\perp} \sum_j q_j G_k(z, z_j) e^{i(k_x x + k_y y)} , \quad (2.16)$$

where $\nu_\perp = (\nu_x, \nu_y)$ and $(k_x, k_y) = (2\pi/L) (\nu_x, \nu_y)$ with $\nu_x$ and $\nu_y$ being integers. From Eq.(2.15) the Green function $G_k(z, z')$ satisfies

$$(k^2 - \partial^2 / \partial z'^2) G_k(z, z') = \delta(z - z'), \quad (2.17)$$

where $k = (k_x^2 + k_y^2)^{1/2}$. Here, $G_k(0, z') = G_k(H, z') = 0$ from Eq.(2.13), so we solve Eq.(2.17) as

$$G_k(z, z') = \frac{1}{2k} e^{-k|z-z'|} - \frac{1}{2k \sinh(kH)} \left[ \sinh(kH)e^{-k(H-z')} + \sinh(kH - kz)e^{-kz} \right] , \quad (2.18)$$

which has the symmetry $G_k(z, z') = G_k(z', z)$. The first term in Eq.(2.18) arises from the 2D Fourier transformation of the direct Coulomb interaction, while the second term is induced by the surface charges on the metallic surfaces. Note that the term with $k_x = k_y = 0$ is included in Eq.(2.16), which give rise to a term independent of $x$ and $y$. From Eq.(2.18) the long wavelength limit $G_0(z, z') = \lim_{k \to 0} G_k(z, z')$ becomes

$$G_0(z, z') = (z + z' - |z - z'|)/2 - zz'/H. \quad (2.19)$$

To find image charges, we further use the expansion $1/\sinh(kH) = 2\sum_{n \geq 0} e^{-kH(2n+1)}$ in Eq.(2.18) to obtain

$$G_k(z, z') = \frac{1}{2k} \sum_n \left[ e^{-|k|z-z'+2Hn} - e^{-|k|z+z'+2Hn} \right] , \quad (2.20)$$

where $n = 0, \pm 1, \pm 2, \cdots$. Since $2\pi \exp(-k|z|)/k = \int dxdy \exp(ik_x x + ik_y y)/r$, substitution of the above expansion into Eq.(2.16) yields $\phi(r)$ in the following superposition of Coulomb potentials,

$$\phi = \sum_m \sum_j \frac{q_j}{|r - r_j + h|} - \sum_m \sum_j \frac{q_j}{|r - \bar{r}_j + h|} , \quad (2.21)$$

where $m = (m_x, m_y, m_z)$ with integer components and

$$h = (Lm_x, Lm_y, 2Hm_z). \quad (2.22)$$

For each charge $q_j$ at $r_j = (x_j, y_j, z_j)$ in the cell, we find image charges with the opposite strength $-q_j$ at $(x_j, y_j, -z_j - 2Hn) \ (n = 0, \pm 1, \cdots)$, giving rise to the second term in Eq.(2.21). We call them O-image charges. We also find those with the same strength $q_j$ at $(x_j, y_j, z_j - 2Hn) \ (n = \pm 1, \cdots)$ in the first term in Eq.(2.21), which are called S-image charges. We may now construct the electrostatic energy $U_m$ as

$$U_m = \frac{1}{2} \sum_{m, j} \left( \sum_{i,j} \frac{q_i q_j}{|r_{ij} + h|} - \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{|\bar{r}_{ij} + h|} \right) - E_\alpha \sum_i q_i z_i , \quad (2.23)$$

where $\bar{r}_{ij} = r_i - \bar{r}_j = (x_i - x_j, y_i - y_j, z_i + z_j)$. In $\sum_{ij}$, we exclude the self term with $j = i$ for $m = (0, 0, 0)$. The direct image potential (2.11) is included in the second term.

To obtain the Ewald representation, we divide the Coulomb potentials into the short-range and long-range parts as in Eq.(2.4). We then find

$$U_m = \sum_m \left[ \sum_{i,j} \frac{q_i q_j}{2} \psi_s(|r_{ij} + h|) - \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{2} \psi_s(|\bar{r}_{ij} + h|) \right]$$

$$- \sum_i \frac{q_i^2}{\sqrt{n}} + U_m^\ell - E_\alpha \sum_i q_i z_i , \quad (2.24)$$

where the first term is the short-range part and $U_m^\ell$ is the long-range part (including the self terms) given by

$$U_m^\ell = \sum_m \sum_{i,j} \frac{q_i q_j}{2} \left[ \psi_{\ell}(|r_{ij} + h|) - \psi_{\ell}(|\bar{r}_{ij} + h|) \right]$$
From the first line \( U_m^i \) vanishes as \( z_i \) (or \( z_j \)) tends to 0 or \( H \), while the first term in Eq.(2.24) diverges in this limit since it contains \( v_1(z_i) \) in Eq.(2.11). In Eq.(2.25) the wave vector \( k \) is discretized as
\[
k = \pi(2\nu_x/L, 2\nu_y/L, \nu_z/H),
\]
(2.26)
where \( \nu_x, \nu_y \), and \( \nu_z \) are integers. The summation is over \( \nu = (\nu_x, \nu_y, \nu_z) \) with \( \nu_{\perp} = (\nu_x, \nu_y) \neq (0,0) \). Note that the contribution from \( \nu = (\nu_x, \nu_y, \nu_z) = (0, 0, 0) \) has been excluded in the periodic case in Eq.(2.7).

In Eq.(2.25) the term involving \( K_0(z, z') \) arises from the one-dimensional contributions with \( \nu_z = \nu_y = 0 \) and \( \nu_x \neq 0 \), where the contribution from \( \nu = (0, 0, 0) \) vanishes in the present case. In Appendix B, requirement of \( K_0(0, z') = K_0(H, z') = 0 \) will yield
\[
K_0(z, z') = \int_0^H dz G_0(z, u) [\varphi(u - z') - \varphi(u + z')]
\]
(2.27)
in terms of \( \varphi(z) \) in Eq.(2.5). Here, \( \varphi(z) = \varphi(-z) \) and \( \int_0^H dz \varphi(z) = 1/2 \). For \( \gamma H \gg 1 \), we have \( \varphi(z) \approx \varphi(z) \) for \( |z| \ll H \). The second line of Eq.(2.27) is the Fourier expansion, indicating the symmetry \( K_0(z, z') = K_0(z', z) \).

From Eqs.(2.24) and (2.25) we may calculate the electric field \( E_i \) on particle \( i \) using Eq.(2.2). The contribution from the first term in Eq.(2.24) is written as \( E_i^0 \), that from the first term in Eq.(2.25) as \( E_i^f \), and that from the remaining terms as \( E_i^d \). Then
\[
E_i = E_i^0 + E_i^f + E_i^d.
\]
(2.29)

The first line of Eq.(2.30) tends to a well-defined limit in the continuum theory in Appendix C. The last term of Eq.(2.25) is expressed as \( (4H/\pi L^2) \sum_{n \geq 1} e^{-(\pi n^2/2H)^2} J_n^2 \).

\[\text{C. Surface charges}\]

In the parallel plate geometry, real charges are those within the cell and the excess electrons on the metal surfaces at \( z = 0 \) and \( H \). The image charges are introduced as a mathematical convenience.

The surface charge densities are given by \( \sigma_0(x, y) = E_z(x, y, 0)/4\pi \) at \( z = 0 \) and \( \sigma_H(x, y) = -E_z(x, y, H)/4\pi \) at \( z = H \), where \( E_z(x, y, z) = -\partial\Phi/\partial z \). From Eq.(2.18) we obtain their 2D Fourier expansions,
\[
\sigma_0 = E_a \frac{1}{4\pi} - \frac{1}{L^2} \sum_{\nu_{\perp}} \sum_j q_j \frac{\sin (kH - k_{\nu_z} j)}{\sin (kH)},
\]
\[
\sigma_H = -E_a \frac{1}{4\pi} - \frac{1}{L^2} \sum_{\nu_{\perp}} \sum_j q_j \frac{\sin (k_{\nu_z} j)}{\sin (kH)},
\]
(2.32)
Here, \( \nu_{\perp} = (\nu_x, \nu_y) \), \( k = (k_x, k_y, 0) = (2\pi/L)(\nu_x, \nu_y, 0) \), and \( \exp[i k \cdot (r - r_{\perp})] = \exp[i(k_x(x - x_{\perp}) + i(k_y(y - y_{\perp}))] \) as in Eq.(2.16). The total electric charges on the bottom and top surfaces \( Q_0 \) and \( Q_H \) are the surface integral of \( \sigma_0(x, y) \) and that of \( \sigma_H(x, y) \), respectively. In Eq.(2.32) we thus pick up the terms with \( \nu_{\perp} = (0, 0) \) to obtain
\[
Q_0 = -Q_H = \frac{1}{4\pi} L^2 E_a + \frac{1}{H} \sum_j q_j z_j.
\]
(2.33)

See the counterpart (C6) in the continuum theory in Appendix C.

Under the periodic boundary condition in the \( xy \) plane, the excess potential \( \phi(r) \) in Eq.(2.16) is rewritten as
\[
\phi = \sum_{m_x, m_y} \left[ \sum_j \frac{q_j}{|r - r_{\perp} + Lm|} + \phi_s (r + Lm) \right],
\]
(2.34)
where \( m = (m_x, m_y, 0) \). The excess charge densities \( \Delta \sigma_0(x, y) = \sigma_0(x, y) - E_a/4\pi \) and \( \Delta \sigma_H(x, y) = \sigma_H(x, y) + E_a/4\pi \) in the plane \( 0 < x, y < L \) induce the potential contribution,
\[
\phi_s = \int dr' \frac{\Delta \sigma_0(x', y')}{|r - r_{\perp}'|} + \frac{\Delta \sigma_H(x', y')}{|r - r_{\perp}' + H e_z|},
\]
(2.35)
where \( r_{\perp}' = (x', y', 0) \) is on the bottom and \( r_{\perp}' + H e_z = (x', y', H) \) is on the top with \( 0 < x', y' < L \).

\[\text{D. Fixed-potential and fixed-charge conditions}\]

In the fixed-potential condition, it is convenient to use the electrostatic energy \( U_m = U_m(r_1, \ldots, E_a) \) depending on the positions and the applied electric field \( E_a \). For
infinitesimal changes $r_i \to r_i + dr_i$, and $E_o \to E_0 + dE_o$, Eq.(2.23) yields the differential form of $U_m$ as

$$dU_m = - \sum_i q_i E_i \cdot dr_i - \sum_i q_i z_i dE_o,$$  \tag{2.36}

where use has been made of Eq.(2.33). Note that $Q_0$ is a dynamical variable at fixed $Q_H$.

However, we may also suppose experiments where the surface changes, $Q_0$ and $Q_H$, are fixed as illustrated in Fig.1. For simplicity, we assume $Q_H = -Q_0$, where we do not consider ionization of the surfaces. In this fixed-charge condition, the charged particles and the two plates constitute a closed system. See Appendix C for the continuum theory for these two boundary conditions.

Let $U_c = U_c(r_1, \cdots, Q_0)$ be the electrostatic energy appropriate for the fixed-charge condition, which includes the contribution from the excess electrons on the metal surfaces. For infinitesimal changes $r_i \to r_i + dr_i$ and $Q_0 \to Q_0 + dQ_0$, $U_c$ should be changed as

$$dU_c = - \sum_i q_i E_i \cdot dr_i + H E_o dQ_0,$$  \tag{2.37}

where $E_a$ is a dynamic variable at fixed $Q_0$. The expressions for $E_i$ are the same in the two cases at fixed $E_a$ and at fixed $Q_0$. Then, from Eqs.(2.36) and (2.37), $U_c$ and $U_m$ are related by

$$U_c = U_m - H L^2 E_a^2/8\pi + H E_o Q_0.$$  \tag{2.38}

This relation holds generally for mixtures of charged and polar particles (see Eqs.(3.19) and (C15)).

E. Numerical example of charged particles between metallic plates under applied electric field

1. Model and method

This subsection presents results of molecular dynamics simulation of two-component charged particles between metallic plates at the fixed-potential condition. The numbers of the two species are $N_1 = N_2 = 500$ and the charges are $q$ and $-q$. All the particles have a common mass $m$ and a common diameter $\sigma$. The average density is $n_0 = (N_1 + N_2)/HL^2 = 0.57\sigma^{-3}$ and the cell dimensions are $H = L = 12\sigma$.

The total potential energy consists of three parts as

$$U_{\text{tot}} = U_m + \sum_{i>j} v_s(r_{ij}) + \sum_i v_w(z_i).$$  \tag{2.39}

Here, $v_s(r)$ is the soft-core pair potential,

$$v_s(r) = 4\epsilon (\sigma/r)^{12} - C_0,$$  \tag{2.40}

where $\epsilon$ is the interaction energy and $C_0$ ensures the continuity of the potential at $r = r_s^\text{cut}$. That is, $v_s(r) = 0$ for $r > r_s^\text{cut}$. This cut-off length $r_s^\text{cut}$ was set equal to $4\sigma$. We also truncated the short-range part of the electrostatic interaction in Eq.(2.24) at $4\sigma$. The $v_w(z)$ is the repulsive potential from the walls written as

$$v_w(z) = w \exp(-z/\xi) + w \exp(- (H - z)/\xi),$$  \tag{2.41}

and $v_w$ is soft-core-like with $\xi = 0.01\sigma$ and $w = \epsilon^{40}\epsilon$. As a result, the minimum of $z_i$ and $H - z_i$ was about $0.4\sigma$ in our simulation. The charge size is set equal to $q = 5(\epsilon/\sigma)^{1/2}$. Then the typical magnitude of the Coulomb interaction among the particles is $q^2 n_0^{1/3} \sim 20\epsilon$ per particle, while that of the image interaction is about 10$\epsilon$ for $z_i \sim 0.5\sigma$ from Eq.(3.7). Hereafter, units of length, density, potential, electric field, and electric charge are $\sigma$, $\sigma^{-3}$, $(\epsilon/\sigma)^{1/2}$, $(\epsilon/\sigma^3)^{1/2}$, and $(\epsilon/\sigma)^{1/2}$, respectively. The temperature $T$ is in units of $\epsilon/k_B$.

In $U_m$ in Eq.(2.24), we set $\gamma = 0.5$ and the summation over $k$ is in the region $k \leq k_c = 18\pi/\lambda$. From the second line of Eq.(2.30) we calculated the one-dimensional electric field $E_0^n$ retaining the terms up to $n = 18$, for which there is virtually no error since $\exp(-2n\pi\gamma H^2) \sim 10^{-10}$ at $n = 18$. If we calculate $E_0^n$ from the first line of Eq.(2.30) using the error function, the difference between these two calculations is at most of order $10^{-7}$ for our examples.

The particles obey the equations of motions,

$$m \frac{d^2}{dt^2} r_i = - \frac{\partial}{\partial r_i} U_{\text{tot}}.$$  \tag{2.42}

We measure time in units of

$$\tau_0 = (m/\epsilon)^{1/2}\sigma.$$  \tag{2.43}

Starting with a high temperature liquid state, we changed $T$ to a final value and waited for a time about $10^4$ to realize an equilibrium state. We attached a thermostat to all the particles in this initial preparation, but it was switched off in taking data.

2. Charged particles at $T = 1$: Screening effect

In Figs.2 and 3, we show simulation results in liquid at $T = 1$ for $\Delta \Phi = 1$ and 10. In Fig.2(a)-(a'), snapshots of the particles are given. In Fig.2(b)-(b'), cross-sectional densities $\langle n_1(z) \rangle$ and $\langle n_2(z) \rangle$ are displayed, which show accumulation of the negative (positive) charges near the wall at $z = 0$ ($z = H$). They are defined as follows. Let $\Delta N_\alpha(z) = \sum_{j_L \in \alpha} \theta(z_j - z) \theta(z + \Delta z - z_j)$ be the particle numbers in layers $[z, z + \Delta z] (z = n\Delta z$ with $n = 0, 1, \cdots)$ for the two species $\alpha = 1, 2$. The $\theta(u)$ is the step function being 1 for $u > 0$ and 0 for $u \leq 0$. In this subsection, we set $\Delta z = H/100 = 0.12$, which is much smaller than the particle size. The laterally averaged densities for the two species are given by

$$\langle n_\alpha(z) \rangle = \langle \Delta N_\alpha(z, t) \rangle / L^2 \Delta z.$$  \tag{2.44}

Hereafter, $\langle \cdots \rangle$ represents the average over a time interval with width $10^3$. 
In Fig. 2(c)-(c'), we display the laterally averaged (local) electric field along the \( z \) axis calculated from

\[
\langle E_z \rangle(z) = \sum_j \frac{\langle E_{zj} \rangle(z) \theta(z_j - z) \theta(z + \Delta z - z_j)}{\Delta N(z)}, \tag{2.45}
\]

where \( q_j E_{zj} = -\partial U_m / \partial z_j \) and \( \Delta N(z) = \Delta N_1(z) + \Delta N_2(z) \). We can see that \( \langle E_z \rangle(z) \) exhibits sharp peaks near the walls but tends to zero in the interior. This screening is achieved only by one or two layers of the accumulated charges. In the same manner, replacing \( E_{zj} \) in Eq. (2.45) by \( E_{zj}^1, E_{zj}^2 \), and \( E_j^0 \) in Eq. (2.29), we may define the lateral averages \( \langle E_{zj}^1 \rangle(z), \langle E_{zj}^2 \rangle(z), \) and \( \langle E_j^0 \rangle(z) \), respectively. For the examples in this subsection, we find \( \langle E_j^0 \rangle(z) \cong 0 \) (less than 0.01) so that

\[
\langle E_z \rangle(z) \cong \langle E_{zj}^1 \rangle(z) + \langle E_{zj}^2 \rangle(z). \tag{2.46}
\]

In Fig. 2(c)-(c'), \( \langle E_j^0 \rangle(z) \) more smoothly varies than \( \langle E_z \rangle(z) \) and tends to zero far from the walls, while

\[
\langle E_{zj}^1 \rangle(z) \text{ exhibits sharp peaks near the walls and oscillates around zero far from the walls.}
\]

In Fig. 3, we show snapshots of the particles in the two layers \( 0 < z < 1 \) and \( 2 < z < 2 \). For \( \Delta \Phi = 1 \), cations and anions are both attracted to the wall due to the image interaction. For \( \Delta \Phi = 10 \), only anions are attached in the first layer, but cations are richer in the second layer.

We also rewrite Eq. (2.33) as

\[
Q_0 / qL^2 = E_0 / 4\pi q + \sum_j q_j z_j / qH^2, \tag{2.47}
\]

where the second term is the areal density of excess cations at the top (with \( z_j \cong H \)) and is larger than the first term for strong screening. The data in Figs. 2(a)-(a') give \( E_0 / 4\pi q, \sum_j q_j z_j / qH^2 \) = (0.0013, 0.106) for \( \Delta \Phi = 1 \) and (0.0013, 0.426) for \( \Delta \Phi = 10 \).

3. Charged particles at \( T = 0.2 \): Ionic crystals

In Figs. 4 and 5, we show simulation results in crystal at \( T = 0.2 \). For \( \Delta \Phi = 0 \) the cations and anions form a square lattice, as is well known for salts such as NaCl, from the first layer. However, for \( \Delta \Phi = 100 \), we can see a hexagonal structure in the first layer \( 0 < z < 1 \) and a square lattice for \( z > 2 \), where the structure changes over in the second layer \( 1 < z < 2 \). In this case, the first layer is composed of anions only and the second layer is anion-rich, as can also be seen in Fig. 4(b'). In the lower plates of Fig. 5, the surface charge density \( \sigma_0(x, y) \) varies nearly in one direction as a result of the complex charge distributions in the first few layers.

In addition, we examine Eq. (2.47). From the data in Figs. 4(a)-(a') we have \( E_0 / 4\pi q, \sum_j q_j z_j / qH^2 \) = 0.0013, 0.0106 for \( \Delta \Phi = 1 \) and (0.0013, 0.426) for \( \Delta \Phi = 10 \).
III. POLAR PARTICLES

In this section, we consider $N$ polar particles at positions $r_j$ and with dipole moments $\mu_j$. The derivatives of the electrostatic energy $U$ give the electrostatic force $F_i^e$ and the electric field $E_i$ on dipole $i$ as

$$ F_i^e = -\frac{\partial}{\partial r_i} U, \quad E_i = -\frac{\partial}{\partial \mu_i} U, $$

which are used in the equations of motions. There can also be neutral and charged particles.

We first consider the electrostatic energy in the periodic boundary condition (3.2), which is written as $U_p^d$. Here, there is no applied electric field. In Eq.(2.3) we replace $q_i$ by $\mu_i \cdot \nabla_j$, where $\nabla_i = \partial/\partial r_i$. Then, we obtain

$$ U_p^d = \frac{1}{2} \sum_{i,j}^{m'} (\mu_i \cdot \nabla_i)(\mu_j \cdot \nabla_j) \frac{1}{|r_{ij} + Lm|}. $$

From Eq.(2.7) the Ewald representation is given by

$$ U_p^d = \frac{1}{2} \sum_{m} \sum_{i,j}^{m'} (\mu_i \cdot \nabla_i)(\mu_j \cdot \nabla_j) \frac{1}{|r_{ij} + Lm|} + \frac{1}{2L^3} \sum_{k} \sum_{i,j}^{m'} (\mu_i \cdot \nabla_i)(\mu_j \cdot \nabla_j) \Psi_k(|k|) e^{i|k|r_i} = \sum_{i} \frac{2\gamma^3}{3\sqrt{\pi}} |\mu_i|^2 + \frac{2\pi}{3L^3} \sum_{j} |\mu_j|^2. $$

In the first term, we introduce the tensor $\hat{w}_s(r)$ by

$$ \hat{w}_s(r) = -\nabla \nabla \psi_s(r) = B(r) \hat{I} - C(r) \frac{1}{r^2} rr, $$

where $\hat{I}$ is the unit tensor and

$$ B(r) = \psi_s(r)/r^2 + 2\pi \varphi_3(r) / r^2, $$
$$ C(r) = 3B(r) + 4\pi \varphi_3(r), $$

with $\varphi_3(r) = \varphi(x)\varphi(y)\varphi(z)$ (see Eq.(2.5)). The third term in Eq.(3.3) is the counterpart of the second term in Eq.(2.7) following from the small-$r$ expansion (2.6).
B. Ewald method for dipoles between metallic plates under applied electric field

We consider $N$ dipoles between metallic parallel plates under applied electric field $E_a$. The electrostatic potential $\Phi$ is written as Eq. (2.12). For each dipole $\mu_i = (\mu_{x_i}, \mu_{y_i}, \mu_{z_i})$ at $r_i = (x_j, y_j, z_j)$, there arise S-image dipoles at $(x_i, y_i, z_i - 2Hn)$ with the same moment $\mu_i$ (where $n \neq 0$) and O-image dipoles at $(x_i, y_i, -z_i - 2Hn)$ with the moment,

$$\hat{\mu}_i = (-\mu_{x_i}, -\mu_{y_i}, \mu_{z_i}).$$

If a dipole at position $r_i$ approaches the bottom wall, it is acted by the image electric field $-\partial v_i^d / \partial r_i = -(2z_i)^{-3}(\mu_i - 3z_i e_z)$, leading to the interaction energy,

$$v_i^d(z_i, \theta_i) = [\mu_i \cdot \hat{\mu}_i - 3 \mu_{z_i} z_i] / 2(2z_i)^3 = -\mu_i^2 / (1 + \cos^2 \theta_i) / 16z_i^3,$$

where $\cos \theta_i = \mu_{z_i} / |\mu_i|$ with $\theta_i$ being the angle of $\mu_i$ with respect to the $z$ axis. This image interaction energy is negative grows for $z_i$. By their images, dipoles are attracted to the walls and tend to be parallel ($\theta_i = 0$) or antiparallel ($\theta_i = \pi$) to the $z$ axis. From the formulae in the previous section, we obtain the counterparts by replacing $q_j$ by $\mu_j \cdot \nabla_j$ for S-image charges and $-q_j$ by $\mu_j \cdot \nabla_j$ for O-image charges, where $\nabla_j = \partial / \partial r_j$. As a result, Eq. (2.21) leads to the excess potential $\phi(r)$ for $r \neq r'$ in the form,

$$\phi = \sum \sum' \nabla_j \cdot \left[ \frac{\mu_j}{|r - r_j + h|} + \frac{\hat{\mu}_j}{|r - r_j + h|} \right],$$

which surely vanishes at $z = 0$ and $H$. The total electrostatic energy in the fixed-potential condition is written as $U_m^d$. From Eq. (2.23), we find

$$U_m^d = \frac{1}{2} \sum \sum' \left[ \frac{\mu_j}{|r - r_j + h|} + \frac{\hat{\mu}_j}{|r - r_j + h|} \right] - E_a \sum \mu_{z_i},$$

where the self-interaction terms are removed in $\sum'_{i,j}$ and $h$ is given by Eq. (2.22). The direct image interaction energy in Eq. (3.7) is included in the above expression.

The Ewald representation of $U_m^d$ reads

$$U_m^d = \frac{1}{2} \sum \sum \left[ \frac{\mu_j}{|r - r_j + h|} \right] \cdot \mu_j + \frac{1}{2} \sum \sum \left[ \frac{\hat{\mu}_j}{|r - r_j + h|} \right] \cdot \mu_j + \frac{1}{2} \sum \sum \left( \frac{\Psi_k(k)}{4} \right) (k \cdot \mu_j \hat{n} + e^{ik \cdot r_j} \hat{\mu}_j)$$

$$+ V_m^d = E_a \sum \mu_{z_i}.$$  

The first and second terms represent the short-range part with $\bar{w}_s$ given in Eq. (3.4). The third term has appeared in Eq. (3.3). In the fourth long-range term, the summation is over $\nu = (\nu_x, \nu_y, \nu_z)$ with $\nu_\perp = (\nu_x, \nu_y) \neq 0$ and $k$ is given by Eq. (2.26). The fifth term $V_m^d$ arises from the contributions with $k_x = k_y = 0$. From Eqs. (2.25), (2.27), and (B4), we find

$$V_m^d = \frac{2\pi}{L^2} \sum \mu_{z_i} \mu_{z_j} \left[ \hat{\varphi}(z_i - z_j) + \hat{\varphi}(z_i + z_j) - \frac{1}{H} \right]$$

$$= \frac{4\pi}{HL^2} \sum_{n \geq 1} e^{-\pi n / 2H} K_n^2,$$

where $K_n$ depends on $z_1, z_2, \cdots$ as

$$K_n = \sum \mu_{z_j} \cos \left( \frac{\pi n z_j^i}{2} \right).$$

The electric field $E_i$ on dipole $i$ can be calculated from Eq. (3.10). That is, the contribution from the first and second terms, that from the third and fourth terms, and that from the fifth and sixth terms are written as $E_i^{d_1}, E_i^{d_2}, E_i^{d_3},$ and $E_i^{d_4} e_z$, respectively. Then,

$$E_i = E_i^{d_1} + E_i^{d_2} + E_i^{d_3} e_z.$$  

From Eq. (3.11) $E_i^{d_3}$ is expressed as

$$E_i^{d_3} = E_a - \frac{4\pi}{L^2} \sum \mu_{z_j} \left[ \hat{\varphi}(z_i - z_j) + \hat{\varphi}(z_i + z_j) - \frac{1}{H} \right]$$

$$= - \frac{8\pi}{HL^2} \sum_{n \geq 1} e^{-\pi n / 2H} K_n \cos \left( \frac{\pi n z_i^i}{2} \right).$$

In the first line, if the particles $j (\neq i)$ are randomly distributed in the cell, the second term vanishes, and the self term with $j = i$ is of order $\mu_{z_i}^2 / L^2$. Thus, if the boundary disturbances do not extend into the interior in a thick and wide cell, we have $E_i^{d_3} \approx 0$ (see Table 1 below). The first line of Eq. (3.14) is consistent with Eq. (C5) in Appendix C.

C. General relations for dipoles between metallic plates under applied electric field

By replacing $q_j$ by $\mu_j \cdot \nabla_j$ in Eq. (2.32), we obtain the surface charge densities, $\sigma_0(x, y)$ at $z = 0$ and $\sigma_H(x, y)$ at $z = H$, in the 2D Fourier expansions,

$$\sigma_0 = \frac{E_a}{4\pi} - \frac{1}{L^2} \sum \sum \mu_{z_j} \nabla_j \left( \frac{\sin(kH - kz_j)}{\sin(kH)} \right) e^{i \hat{k} \cdot (r - r_j)},$$

$$\sigma_H = \frac{E_a}{4\pi} - \frac{1}{L^2} \sum \sum \mu_{z_j} \nabla_j \left( \frac{\sin(kz_j)}{\sin(kH)} \right) e^{i \hat{k} \cdot (r - r_j)},$$

(3.15)
where $\mathbf{v}_\perp = (v_x, v_y)$ and $\mathbf{k} = (2\pi \nu_x/L, 2\pi \nu_y/L, 0)$. Integrating $\sigma_0$ and $\sigma_\nu$ in the planar region $0 < x, y < L$ yields the total electric charges on the metallic surfaces,

$$Q_0 = -Q_H = \frac{1}{4\pi} \int \mathbf{E}_a + \frac{1}{H} \sum_j \mu_{iz}.$$  \tag{3.16}

See Eq.(C6) for the counterpart in the continuum theory.

The electrostatic energy $U_m^{\text{el}}$ in Eq.(3.9) is relevant under the fixed-potential condition, depending on $\mathbf{r}_1, \cdots, \mathbf{r}_N, \mathbf{\mu}_1, \cdots, \mathbf{\mu}_N$, and $E_a$. As the counterpart of Eq.(3.36), Eq.(3.1) leads to its differential form,

$$dU_m^{\text{el}} = -\sum_i (\mathbf{F}_i^e \cdot d\mathbf{r}_i + E_i \cdot d\mathbf{\mu}_i) - \sum_i \mu_{iz} dE_a.$$  \tag{3.17}

Under the fixed-charge condition, on the other hand, relevant is the electrostatic energy $U_m^{\text{el}}$ satisfying

$$dU_c^{\text{el}} = -\sum_i (\mathbf{F}_i^e \cdot d\mathbf{r}_i + E_i \cdot d\mathbf{\mu}_i) + HE_a dQ_0.$$  \tag{3.18}

As in Eq.(3.38), $U_c^{\text{el}}$ and $U_m^{\text{el}}$ are related by

$$U_c^{\text{el}} = U_m^{\text{el}} - HL^2 E_a^2/8\pi + HE_a Q_0.$$  \tag{3.19}

D. Numerical example for dipoles between metallic plates under applied electric field

1. Model and method

Next, we present results of molecular dynamics simulation of one-component spherical dipoles with number $N = 1000$ between parallel metallic plates in the fixed-potential condition. As in Eq.(3.39), the total potential energy is written as

$$U_{\text{tot}} = U_m^{\text{el}} + \sum_{i>j} v_s(r_{ij}) + \sum_i v_w(z_i),$$  \tag{3.20}

where $U_m^{\text{el}}$ is given by Eq.(3.10), $v_s(r)$ by Eq.(4.0), and $v_w(z)$ by Eq.(2.41). We cut off $v_s(r)$ and the short-range part of the electrostatic interaction in Eq.(3.10) at $r = 4\sigma$. In terms of $\sigma$ and $\epsilon$ in $v_s(r)$, units of length, density, potential, electric field, electric charge, and dipole moment are $\sigma$, $\sigma^{-3}$, $(\epsilon/\sigma)^{1/2}$, $(\epsilon/\sigma^3)^{1/2}$, $(\epsilon^2)^{1/2}$, and $(\epsilon^3)^{1/2}$, respectively. The temperature is in units of $\epsilon/k_B$. The average density $n_0 = N/HL^2$ is chosen to be 0.19, 0.38, and 0.57. We set $H = L$; then, the cell dimension is $L = 17.4, 13.8,$ and 12.0, respectively.

In $U_m^{\text{el}}$, we set $\gamma = 0.65$ and the summation over $k$ is in the region $k \leq k_c = 18\pi/L$. In $E_m^{\text{el}}$ in Eq.(3.14), the terms up to $n = 18$ are picked up. The dipole moment has a fixed magnitude $\mu_0$ and is expressed as

$$\mathbf{\mu}_i = \mu_0 \mathbf{n}_i,$$  \tag{3.21}

where $\mathbf{n}_i$ is the unit vector representing the direction of polarization. In this subsection, we set $\mu_0 = 2(\epsilon^2)^{1/2}$, for which our system is highly polarizable with large dielectric constants.

The total kinetic energy is assumed to be of the form,

$$K_{\text{tot}} = \sum_i \frac{m}{2} |\mathbf{\dot{r}}_i|^2 + \sum_i \frac{I_1}{2} |\mathbf{\dot{n}}_i|^2,$$  \tag{3.22}

where $\mathbf{\dot{r}}_i = d\mathbf{r}_i/dt$, $\mathbf{\dot{n}}_i = d\mathbf{n}_i/dt$, and $I_1$ is the moment of inertia. Regarding dipoles as spheres with diameter $\sigma$, we set $I_1 = m\sigma^2/10$. The Newton equations of motions for $\mathbf{r}_i$ and $\mathbf{n}_i$ are written as

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\frac{\partial}{\partial \mathbf{r}_i} U_{\text{tot}},$$  \tag{3.23}

$$I_1 \mathbf{n}_i \times \frac{d^2 \mathbf{n}_i}{dt^2} + \mathbf{\mu}_i \times \frac{\partial}{\partial \mathbf{\mu}_i} U_{\text{tot}},$$  \tag{3.24}

where $\mathbf{\dot{n}}_i \cdot d^2 \mathbf{n}_i/dt^2 = -|\mathbf{\dot{n}}_i|^2$ from $\mathbf{\dot{n}}_i \cdot \mathbf{\dot{n}}_i = 0$. The total energy $U_{\text{tot}} + K_{\text{tot}}$ is conserved in time.

2. Highly polarizable liquids

In Fig.6, we show snapshots of spherical dipoles for $n_0 = 0.19$ and 0.38 in liquid at $T = 1$ under $\Delta \Phi \neq 1$ and 10. The colors of the spheres represent their polarization directions according to the color maps in Fig.7. We can...
see gradual orientation enhancement with increasing \(\Delta \Phi\).

For \(n_0 = 0.19\), chainlike associations are conspicuous, whose lengths increase with increasing \(\Delta \Phi\). For small \(\Delta \Phi\) a large number of dimers appear.

In the top panels of Fig.8, we display particle configurations near the bottom wall in the two layers, \(0 < z < 1\) and \(1 < z < 2\), and the surface charge density \(\sigma_0(x,y)\) in Eq.(3.15). In these cases, dipoles are accumulated on the walls and are aligned along the \(z\) axis. For \(\Delta \Phi = 1\), the image interaction (3.7) is strong enough to induce the alignment both in the parallel and antiparallel directions along the \(z\) axis. For \(\Delta \Phi = 10\) those aligned along the \(z\) axis increase. In the bottom panels of Fig.8, the surface charge density in Eq.(3.15) are written, which are highly heterogeneous and fluctuating in time.

In Figs.9(a)-(a'), we display the laterally averaged density \(\langle n \rangle(z)\) defined as in Eq.(2.44), where we write two curves for \(\Delta z = H/100 = 0.138\) and \(H/20 = 0.69\). We recognize that the interior away from the walls is in a homogeneous, uniaxial equilibrium state under electric field for \(H \gg 1\). In Table 1, we can see that the bulk density \(\bar{n}\) in the interior is slightly smaller than \(n_0\).

Using the decomposition (3.13) of the local field \(E_z\), we define the laterally averaged electric fields \(\langle E_z \rangle(z)\), \(\langle E_{y(z)}^{\parallel} \rangle(z)\), \(\langle E_{y(z)}^{\perp} \rangle(z)\), and \(\langle E^{\text{mix}} \rangle(z)\) as in Eq.(2.45). Hereafter, \(\langle \cdots \rangle\) represents the average over a long time inter-

**TABLE I.** Data for 1000 spherical dipoles in liquid at \(T = 1\) in a \(L \times L \times H\) cell (\(H = L\)) under applied potential difference \(\Delta \Phi = HE_{\text{av}} = 1\) and 10 for three densities \(n_0 = 0.19, 0.38,\) and 0.57. Here, \(\bar{n}, \mu_x,\) and \(\bar{p}_z = \bar{n}\mu_z\) are bulk values in the interior. Also given are bulk values of \(\langle E_z^n \rangle(z)\) and \(\langle E_y \rangle(z)\), dielectric constant \(\varepsilon_0\) in Eq.(3.30), local field factor \(\gamma_e\) in Eq.(3.31), polarizability \(\alpha_0 = \bar{\mu}_z/E_{\text{av}}\).

\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\(n_0\) & \(E_{\text{av}}\) & \(Q_0\) & \(\langle E_{\text{mix}} \rangle\) & \(\bar{n}/n_0\) & \(\mu_x\) & \(4\pi p_z\) & \(\varepsilon_0\) & \(\gamma_e\) & \(\alpha_0\) \\
\hline
0.19 & 0.058 & 11.6 & 0.060 & 0.88 & 0.18 & 0.37 & 0.42 & 7.4 & 0.97 & 0.43 \\
0.19 & 0.58 & 78.5 & 0.65 & 0.91 & 1.20 & 2.02 & 2.88 & 5.5 & 0.88 & 0.42 \\
0.38 & 0.073 & 23.0 & 0.069 & 0.95 & 0.30 & 1.36 & 0.82 & 19.6 & 0.55 & 0.37 \\
0.38 & 0.73 & 115 & 0.80 & 0.97 & 1.46 & 6.81 & 4.45 & 10.3 & 0.55 & 0.33 \\
0.57 & 0.083 & 40.5 & 0.069 & 0.97 & 0.48 & 3.29 & 1.55 & 40.6 & 0.45 & 0.31 \\
0.57 & 0.83 & 143 & 0.95 & 0.98 & 1.62 & 11.36 & 5.89 & 14.7 & 0.45 & 0.26 \\
\hline
\end{tabular}
val with width $10^3$. Along the $z$ axis we thus have
\begin{equation}
\langle E_z \rangle = \langle E_{zs}^d \rangle + \langle E_{zd}^d \rangle + \langle E_{zd}^{\ell} \rangle.
\end{equation}
(3.25)
If the boundary layers are much thinner than $H$, we have
\begin{equation}
\langle E_{zd}^{\ell} \rangle \approx E_a
\end{equation}
in the interior (see the sentences below Eq.(3.14)). For the examples in Table 1, we can indeed see $\langle E_{zd}^{\ell} \rangle \approx E_a$. Furthermore, we find that $\langle E_{zd}^d \rangle$ is of the same order as $E_a$. In the bulk region of our example, the short-range contribution $\langle E_{zs}^d \rangle$ is dominant in the right-hand side of Eq.(3.25), typically being about 90% of $\langle E_z \rangle$, so that
\begin{equation}
\langle E_z \rangle \approx \langle E_{zs}^d \rangle.
\end{equation}
(3.26)
We also define the lateral average of the polarization,
\begin{equation}
\langle p_z \rangle = \frac{1}{2\pi} \int_0^{2\pi} d\theta \langle \theta | \partial_z - z \rangle \partial_z \langle z + \Delta z - z \rangle.
\end{equation}
(3.27)
We plot $\langle E_z \rangle$ in Fig.9(b)-(b') and $\langle p_z \rangle$ in Fig.9(c)-(c') for $\Delta z = H/100$ and $H/20$, where the curves are more smooth for larger $\Delta z$. In the interior, they assume the bulk average values with small fluctuations. In Table 1, we give the average bulk values of $\langle E_z \rangle$, $\langle E_{zd}^{\ell} \rangle$, and $4\pi E_a^2$ at $T = 1$ for three densities $n_0 = 0.19, 0.38$, and 0.57 under $\Delta \Phi = 1$ and 10.

In terms of the polarization variable,
\begin{equation}
\hat{p}(r) = \sum_i \mu_i \delta(r_i - r),
\end{equation}
(3.28)
we have
\begin{equation}
\langle p_z \rangle = \frac{1}{2\pi} \int_0^{2\pi} d\theta \langle \theta | \partial_z - z \rangle \partial_z \langle z + \Delta z - z \rangle.
\end{equation}
Averaging over the particles in the interior and over a long time yields the bulk average polarization,
\begin{equation}
\bar{p}_z = \langle \hat{p}_z \rangle = \bar{n} \bar{\mu}_z,
\end{equation}
(3.29)
where $\bar{p}_z$ is the average of $\mu_z$ in the interior. We define the effective dielectric constant by
\begin{equation}
\varepsilon_e = 1 + 4\pi \bar{p}_z / E_a.
\end{equation}
(3.30)
In Table 1, $\varepsilon_e$ is much larger than unity, increasing with increasing $n_0$ and decreasing with increasing $E_a$. Note that $\bar{p}_z$ approaches its maximum $\mu_0 = 2$ for $\Delta \Phi = 10$, where the system is in the nonlinear response regime. Furthermore, since $E_i$ is the local electric field, its lateral average $\langle E_z \rangle$ along the $z$ axis is related to the applied electric field $E_a$ and the local polarization $\bar{p}_z$ by
\begin{equation}
\langle E_z \rangle = E_a + 4\pi \gamma_e \bar{p}_z,
\end{equation}
(3.31)
in the bulk region. The second term represents the Lorentz field with $\gamma_e$ being the local field factor. The classical value of $\gamma_e$ is 1/3. However, in Table 1, $\gamma_e$ considerably exceeds 1/3. It increases with decreasing $n_0$ but is rather insensitive to $E_a$. We may also introduce the polarizability $\alpha_e = \bar{p}_z / \langle E_z \rangle$. Then, $\varepsilon_e$ satisfies
\begin{equation}
\frac{\varepsilon_e - 1}{1 + \gamma_e(\varepsilon_e - 1)} = 4\pi \bar{n} \alpha_e,
\end{equation}
(3.32)
which nicely holds in Table 1. The Clausius-Mossotti formula follows for $\gamma_e = 1/3$. Here, we should suppose a thick cell $(H \gg 1)$ to avoid the boundary effect in the relations (3.30) and (3.31), though our system size is still not large enough.

In the case, the classical local field relation breaks down because of strong pair correlations along the $z$ axis. To explain this, we assume a large homogeneous interior region in liquid for large $H$ and $L$. We define the pair correlation functions $\langle g(r, \theta) \rangle$ and $g_p(r, \theta)$ by
\begin{equation}
\langle \hat{n}(r_0) \hat{n}(r_0 + r) \rangle = \hat{n} \delta(r) + n^2 g(r, \theta),
\end{equation}
(3.33)
\begin{equation}
\langle \hat{\bar{p}}_z(r_0) \hat{\bar{p}}_z(r_0 + r) \rangle = \bar{n} \bar{p}_z \delta(r) + \bar{n} g_p(r, \theta),
\end{equation}
(3.34)
where $\hat{n}(r) = \sum_i \delta(r_i - r)$ is the density variable and $\hat{\bar{p}}_z(r)$ is defined in Eq.(3.28). These relations are independent of $r_0$ from the translational invariance. The $g(r, \theta)$ and $g_p(r, \theta)$ depend only on $r$ and $\theta = \cos^{-1}(r/|r|)$ from the rotational invariance around the $z$ axis. For $r \gg 1$, we have $g(r, \theta) \to 1$ and $g_p(r, \theta) \to \bar{p}_z$. Also from the invariance with respect to the inversion $r \to -r$, they are even functions of $\pi/2 - \theta$ and we notice
\begin{equation}
\langle \hat{n}(r_0) \hat{\bar{p}}_z(r_0 + r) \rangle = \langle \hat{\bar{p}}_z(r_0) \hat{n}(r_0 + r) \rangle = 0.
\end{equation}
(3.35)
In Fig.10, we plot $g(r, \theta)$ and $g_p(r, \theta)/\bar{p}_z$ for $T = 1$, $n_0 = 0.38$, and $\Delta \Phi = 10$. They exhibit first peaks at $r \approx 1.1$ and second peaks at $r \approx 2.2$. They are maximized for $\cos \theta = \pm 1$, so the associated dipoles are on the average oriented along the $z$ axis. However, this tendency is not clearly visualized in Fig.6(d) at $n_0 = 0.38$, while it is evident in Fig.6(b) at $n_0 = 0.19$. For ferromagnetic fluids, similar behavior of the pair correlation function $g(r, \theta)$ was theoretically examined numerically and calculated.

From Eq.(3.10), the short-range part of the local field in the interior is given by
\begin{equation}
\langle E_{zd}^d \rangle \approx -\sum_i m_i \cdot \nabla_s (|r_{ij}|).
\end{equation}
(3.36)

Here, if we set $g_p(r, \theta) = \bar{p}_z$, the right-hand side becomes $4\pi \bar{p}_z/3$ from Eq.(3.35). Use of Eq.(3.26) yields the correction to the classical value in the form,
\begin{equation}
\gamma_e = 1 - \frac{1}{3} \int \frac{dr}{4\pi} [C(r) \cos^2 \theta - B(r)] |g_p(r, \theta)/\bar{p}_z - 1|.
\end{equation}
(3.37)
For our examples in Table 1, this formula reproduces the numerical values of $\gamma_e$ within errors of order 10%.

3. Dipole chains

For ferromagnetic colloids with permanent dipoles, chain formation was predicted and has been studied
Comparison of these two energies yields a crossover potential difference about 20, in accord with Fig. 11.

In Fig. 12, we show dipole configurations for \( n_0 = 0.57 \) under two potential differences \( \Delta \Phi = 0 \) and 10. At this high density, a hexagonal lattice (with defects) appears on the walls, extending between the top and the bottom in the form of chains. For \( \Delta \Phi = 0 \), the cross-sectional configurations in the middle are glassy. We can see that the chains are somewhat curved, broken, branched, or entangled. In the left panel of Fig. 13, the mean-square displacement \( M(t) = \langle |r_i(t + t_0) - r_i(t_0)|^2 \rangle \) grows to saturate at a plateau value (\( \sim 0.1 \)) for \( t \gtrsim 1 \) in units of \( \tau_0 \) in Eq. (2.43), which are common for the particles near the walls and those in the middle. In \( M(t) \) the average over \( t_0(< 10^4) \) is taken. We can also see a tendency of segregation between the chains parallel to the z axis and those antiparallel to the z axis. On the other hand, for \( \Delta \Phi = 10 \), the fraction of the chains parallel to the z axis increases and the orientational fluctuations decrease, where \( \langle \mu_z \rangle_{\text{all}} = 1.17 \) and \( \langle \mu_z \rangle_{\text{wall}} = 0.99 \) (see Eq. (3.38)). In this more ordered state, collective configuration changes are appreciable for \( t \gtrsim 100 \). In the right panel of Fig. 13, this leads to very slow growth of \( M(t) \).
IV. SUMMARY AND REMARKS

In summary, we have extended the Ewald method for charged and polar particles between metallic plates in a $L \times L \times H$ cell, aiming to apply electric field $E_a$ to these systems. In this problem, we should account for an infinite number of image charges and dipoles outside the cell. With this method, we have presented some results of molecular dynamics simulation.

In the previous papers by Hautman et al.\cite{13} by Perram and Ratner\cite{14}, and by Klapp\cite{15}, the conventional 3D Ewald method for periodic systems was applied to a doubly expanded $L \times L \times 2H$ cell, where the three axes were formally equivalent. Our scheme is essentially the same as theirs, but we have treated the $z$ direction differently from the lateral directions. In particular, we have divided the terms in the long-range part of the Ewald sum into those inhomogeneous in the $xy$ plane (with nonvanishing $k_x$ or $k_y$) and those homogeneous in the $xy$ plane but inhomogeneous along the $z$ axis (with $k_x = k_y = 0$ and $k_z \neq 0$) in Eqs.(2.25) and (3.10). The latter one-dimensional terms can be summed up into simple forms in Eqs.(2.27) and (3.11), yielding the one-dimensional electric field $E^i_{\rm o}$ in Eqs.(3.30) and (3.14). In our simulations, we have calculated $E^i_{\rm o}$ very accurately. For dipole systems, $E^i_{\rm o} \approx E_a$ far from the walls for thick cells.

In applying electric field between metallic plates, we may control the potential difference $\Delta \Phi = HE_a$ or the surface charge $Q_0$. The electrostatic energy has been written as $U_{\rm m}$ or $U_{\rm d}$ in the fixed-potential condition and as $U_e$ or $U_{\rm ed}$ in the fixed-charge condition, where $U_{\rm m}$ and $U_e$ ($U_{\rm ed}$ and $U_{\rm d}$) are related by the Legendre transformation as in Eqs.(2.38) and (3.19). In the continuum electrostatics in Appendix C, we have also introduced the free energies $F_{\rm m}$ and $F_{\rm e}$ for these two cases\cite{13,14}.

Some remarks are given below.

(1) We have assumed stationary applied field, but we may assume a time-dependent field $E_a(t)$ and examine various nonequilibrium phenomena. For example, when $\Delta \Phi$ was changed from 0 to 100, we observed complex dynamics of charged particles from the crystal in Fig.4(a) to that in Fig.4(a'). We also mention that melting due to electric field was observed in charged colloidal crystal\cite{16}.

(2) We have assumed spherical dipoles, but real molecules are nonspherical and undergo hindered rotations. This feature should be included in future simulations. We should also consider mixtures of ions and nonspherical polar molecules bounded by metallic plates, where the ion-dipole interaction is crucial\cite{17}.

(3) The classical result $\gamma_e = 1/3$ for the local field factor follows for a spherical cavity\cite{18,19}, leading to the Clausius-Mossotti formula for the dielectric constant (see Eq.(3.32)). However, $\gamma_e$ becomes one of the depolarization factors for an ellipsoidal cavity\cite{20} so it is sensitive.
to the environment around each dipole. In our case, γ increases due to the pair correlations along the applied field as in Eq. (3.37). More systematic simulations are needed on this aspect.

(4) Various systems such as charged polymers, proteins, and water molecules should exhibit interesting behaviors close to metal surfaces without and with applied fields. The ion distributions themselves are strongly influenced by the image interaction.

(5) It is of great interest to examine the electric field influenced the image interaction.

\[ \sum_{\alpha \beta} \frac{1}{r_{ij}} (r_{ij} + Lm) \]

where \( \epsilon \) is a positive small number (not to be confused with the energy \( \epsilon \) in \( v_s(r) \) in Eq. (2.40)). The summation yields \( \sum_{m} \exp(i k \cdot Lm) = \zeta(Lk_x)\zeta(Lk_y)\zeta(Lk_z) \), where

\[ \zeta(u) = \sum_{m_x=0, \pm 1, \ldots} \exp[i m_x u - \epsilon |m_x|] \]

\[ \approx 2\epsilon/|\epsilon|^2 + 2(1 - \cos(u)) \]

For \( Lk > 1 \), \( \Psi_\ell(k) \) is finite, so we may replace \( \zeta(Lk_\alpha) \) by 2π \( \sum_{\nu, \alpha \neq 0} \delta(Lk_\alpha - 2\nu k_\alpha) \), where \( \alpha = x, y, z \). For \( Lk \leq 1 \), we may set \( \zeta(Lk_\alpha) = 2\epsilon/|\epsilon|^2 + 2L^2k_\alpha^2 \). Thus, \( U^\ell_p \) becomes

\[ U^\ell_p = \frac{1}{2} \int \Psi_\ell(k) \zeta(Lk_x)\zeta(Lk_y)\zeta(Lk_z) \sum_{i,j} q_i q_j e^{i k \cdot r_{ij}} \]

\[ = \frac{1}{2L^3} \sum_{k \neq 0} \Psi_\ell(k) \sum_{i,j} q_i q_j e^{i k \cdot r_{ij}} \]

\[ + \int \frac{16\pi e^3 \sum_{i,j} q_i q_j e^{i k \cdot r_{ij}} - 1 - e^{-i k \cdot r_{ij}}}{k^2(\epsilon^2 + L^2k_x^2)(\epsilon^2 + L^2k_y^2)(\epsilon^2 + L^2k_z^2)} \]  

(A3)

The first term coincides with the third term in Eq.(2.7) with \( k = 2\pi L^{-1}(\nu_x, \nu_y, \nu_z) \neq (0, 0, 0) \). The second term arises from \( k \lesssim L^{-1} \), where \( \exp[i k \cdot r_{ij}] \approx 1 \) for \( i \approx k \cdot r_i \) and \( \exp[-i k \cdot r_{ij}] \approx 1 \) for small \( k \). Furthermore, \( k_n k_\beta \) may be replaced by \( (k^2/3)\delta_{\alpha \beta} \) from the angle integration of \( k \), leading to the fourth term in Eq.(2.7).

**Appendix B: Derivation of Eq.(2.27)**

In Eq.(2.25) \( K_0(z, z') \) is given by

\[ K_0(z, z') = \frac{1}{4\pi} \int dx dy \sum_{m} [\psi_e(|r - r'| + h)] \]

\[ - \psi_f(|r - r'| + h)], \]  

(B1)

where \( r = (x, y, z) \), \( r' = (x', y', z') \), and \( r'' = (x'', y'', z'') \). After integrating in the region \( 0 < x, y < L \), the right hand side of Eq.(B1) becomes a function of \( z \) and \( z' \) independent of \( x' \) and \( y' \). We then twice differentiate \( K_0(z, z') \) with respect to \( z \) and use the relation \( \nabla^2 \psi_e(r) = -4\pi \varphi(x) \varphi(y) \varphi(z) \), where \( \varphi(x) \) is defined by Eq.(2.5). Some calculations yield

\[ \frac{\partial^2}{\partial z^2} K_0(z, z') = -\varphi(z - z') + \hat{\varphi}(z + z'), \]  

(B2)

where \( \varphi(z) \) is defined by Eq.(2.28). The above relation is integrated to give Eq.(2.27) under \( K_0(0, z') = K_0(H, z') = 0 \). Furthermore, Eqs.(2.19) and (2.27) give

\[ \frac{\partial K_0(z, z')}{\partial z'} = \int_0^z du [\hat{\varphi}(u + z') + \hat{\varphi}(u - z')] - \frac{z}{H}, \]  

(B3)

\[ \frac{\partial^2 K_0(z, z')}{\partial z \partial z'} = \hat{\varphi}(z + z') + \hat{\varphi}(z - z') - 1 \frac{1}{H}, \]  

(B4)

where we have used \( \int_0^H du [\hat{\varphi}(u + z') + \hat{\varphi}(u - z')] = 1 \).

**Appendix C: Continuum theory of electrostatics**

We compare the results in the text and those of continuum electrostatics.\[11,22\] We consider charged particles in a polar medium between parallel metallic plates under applied electric field \( E_\alpha \). The system is in the region \( 0 < x, y < L \) and \( 0 < z < H \). We assume \( L \gg H \) to neglect the edge effect. We do not assume the (artificial) periodic boundary condition in the \( x \) and \( y \) axes.

In this appendix, the physical quantities are smooth functions of space after spatial coarse-graining. In addition to the electrostatic potential \( \Phi(r) = \varphi(r) - E_\alpha z \), we introduce the charge density \( \rho(r) \) and the polarization \( p(r) \). The electric field \( E = -\nabla \Phi = E_\alpha e_z - \nabla \varphi \) and the electric induction \( D = E + 4\pi p \) are defined. For simplicity, we assume the overall charge neutrality condition \( \int dr \rho = 0 \) without ionization on the walls. Hereafter, the integral \( \int dr \) is performed within the cell.

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From the relation $\nabla \cdot \mathbf{D} = 4\pi \rho$, we may define the effective charge density by

$$\rho_e = \rho - \nabla \cdot \mathbf{p}, \quad \text{(C1)}$$

which satisfies $\nabla \cdot \mathbf{E} = -\nabla^2 \phi = 4\pi \rho_e$. Let $\rho_{e\mathbf{k}}(z) = \int \, dr \, e^{-i\mathbf{k} \cdot \mathbf{r}} \rho_e$ be the 2D Fourier transformation in the $xy$ plane, where $\mathbf{k} = (k_x, k_y)$ and $\mathbf{r}_\perp = (x, y)$. As in Eq.(2.16), the excess potential $\phi$ is written as

$$\phi(r) = 4\pi \int_0^H dz' G_k(z, z') \rho_{e\mathbf{k}}(z') e^{i\mathbf{k} \cdot \mathbf{r}_\perp}, \quad \text{(C2)}$$

where $\int_\mathbf{k} = (2\pi)^{-2} \int dk_x dk_y$ and the Green function $G_k(z, z')$ is given in Eq.(2.18).

First, we consider the lateral averages $(0 < x, y < L)$,

$$\bar{\phi}(z) = \int dx dy \, \phi / L^2, \quad \bar{p}_z(z) = \int dx dy \, p_z / L^2,$$

$$\bar{p}(z) = \int dx y \, \rho / L^2, \quad \bar{p}_e(z) = \int dx dy \, \rho_e / L^2. \quad \text{(C3)}$$

Then, we find $\bar{\rho}_e = \bar{\rho} - \bar{p}_z / dz$ and Eq.(C2) becomes

$$\bar{\phi}(z) = 4\pi \int_0^H du G_0(x, u) \bar{\rho}_e(u), \quad \text{(C4)}$$

where $G_0(z, z')$ is given in Eq.(2.19). The average electric field $\bar{E}_z(z) = E_a - d\bar{\phi}(z) / dz$ is calculated as

$$\bar{E}_z(z) = -4\pi \bar{p}_z(z) + 4\pi Q_0 / L^2 + 4\pi \int_0^z du \bar{\rho}(u). \quad \text{(C5)}$$

The total surface charge at $z = 0$ is denoted by $Q_0$; then, that at $z = H$ is $Q_H = -Q_0$. From Eq.(C4) we obtain

$$Q_0 = \frac{L^2}{4\pi} E_a + \frac{1}{H} \int dr [\rho(r) + p_z(r)]. \quad \text{(C6)}$$

This formula corresponds to Eqs.(2.33) and (3.16). The above relation itself readily follows if we set $\rho = \nabla \cdot \mathbf{D} / 4\pi$ in the integral $\int dr \, z \rho$.

Second, we consider the electrostatic energy $U_m$ in the fixed-potential condition. Its discrete versions are in Eqs.(2.23) and (3.9). The continuum version reads

$$U_m = \int dr \left[ \frac{1}{2} \rho_e \phi - E_a (z \rho + p_z) \right]. \quad \text{(C7)}$$

For small incremental changes ($\rho \rightarrow \rho + \delta \rho$, $\mathbf{p} \rightarrow \mathbf{p} + \delta \mathbf{p}$, ...), $U_m$ in Eq.(C7) is changed as

$$\delta U_m = \int dr [\Phi \delta \rho - \mathbf{E} \cdot \delta \mathbf{p} - (z \rho + p_z) \delta E_a], \quad \text{(C8)}$$

which corresponds to Eqs.(2.36) and (3.17). On the other hand, the electrostatic energy $U_e$ in the fixed-charge condition should satisfy

$$\delta U_e = \int dr (\Phi \delta \rho - \mathbf{E} \cdot \delta \mathbf{p}) + H E_a \delta Q_0, \quad \text{(C9)}$$

which is the counterpart of Eqs.(2.37) and (3.18). Then, $U_e$ and $U_m$ are related by Eq.(2.38), leading to

$$U_e = U_m - \frac{HL^2}{8\pi} E_a^2 + H E_a Q_0 = \int dr \frac{|\mathbf{E}|^2}{8\pi}. \quad \text{(C10)}$$

Third, we remark on the polarization $\mathbf{p}$. So far it has been treated as an independent variable. Without ferroelectric order, $\mathbf{p}$ is usually related to $\mathbf{E}$ by

$$\mathbf{p} = \chi \mathbf{E}, \quad \text{(C11)}$$

in the linear response regime. From $\mathbf{D} = \varepsilon \mathbf{E}$, the electric susceptibility $\chi$ and the dielectric constant $\varepsilon$ are related by $\varepsilon = 1 + 4\pi \chi$. In this situation, we may introduce the following free energy contribution,

$$F_p = \int dr \frac{1}{2\chi} |\mathbf{p}|^2, \quad \text{(C12)}$$

which is an increase in the free energy due to mesoscopic ordering of the constituting dipoles. The polarization free energy is needed to examine the thermal fluctuations of $\mathbf{p}$.

We then treat the sum, $F_m = U_m + F_p$ or $F_e = U_e + F_p$, as the electrostatic free energy in the fixed-potential or fixed-charge condition. Since its functional derivative with respect to $\mathbf{p}$ is given by $-\mathbf{E} + \chi^{-1} \mathbf{p}$ from Eqs.(C8), (C9), and (C12), its minimization yields Eq.(C11). Eliminating $\mathbf{p}$, we rewrite $F_m$ and $F_e$ as

$$F_m = \int dr \rho \Phi - \frac{\varepsilon}{8\pi} |\mathbf{E}|^2 + \frac{HL^2}{8\pi} E_a^2, \quad \text{(C13)}$$

$$F_e = \int dr \frac{\varepsilon}{8\pi} |\mathbf{E}|^2. \quad \text{(C14)}$$

The second term in $F_m$ in Eq.(C13) is a constant at fixed $E_a$, so we may redefine the electrostatic free energy as

$$F_m' = F_m - \frac{HL^2}{8\pi} E_a^2 = F_e + Q_0 (\partial F_e / \partial Q_0), \quad \text{(C15)}$$

which is the Legendre transform of $F_e$. The two expressions, $F_m'$ and $F_e$, have both been used in the literature. In the Ginzburg-Landau scheme, Yaakov et al. used $F_m'$ and one of the present authors used $F_e$ for ions in a mixture solvent, where $\varepsilon$ depends on the local solvent composition and is inhomogeneous.
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