Broken Symmetries in Quasi-2D Charged Systems via Dielectric Confinement

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Quasi-2D charged systems are attracting much attention because of their potential in future nanodevices. The confined geometry gives rise to new collective phases, but also brings great challenges for computational studies. We derive an analytic, fast convergent lattice summation formula for the simulation of charged particles under dielectric confinement, and demonstrate that spontaneous symmetry breaking (SSB) can be triggered solely via the substrate permittivity. Interestingly, dielectric contrast can even determine the degree of SSB in longitudinal and transverse dimensions, forming charge-separated interfacial liquids and correlated-clusters. The novel broken symmetry mechanism may shed light in understanding a variety of quasi-2D systems.

Among various long-range systems, quasi-2D charged systems are of great importance, and have caught much attention recently because of their huge potential in future nanodevices and advanced materials. Typically, quasi-2D systems are with nano-sized longitudinal thickness in z direction (usually by confinement), bulk-like and modeled as periodic in transverse xy directions [1]. Rich new collective behaviors arise in such systems, to name a few, polyelectrolyte adsorption and structure [2,3], ion transport and selectivity [4,5].

Nevertheless, in terms of the spontaneous symmetry breaking (SSB) phenomena, much existing study focuses on purely 2D and 3D systems [6-8], far less is known about quasi-2D. For bulk electrolytes or neutral plasma, it is well-known that the Coulomb potential can be dynamically screened by surrounding countercharges, leading to effectively short-range interacting particle systems [9]. The situation becomes very different in quasi-2D charged systems: their reduced symmetry (i.e., the nano-sized confinement) weakens the electrostatic screening, and correlation effect can become much more important. Clearly, this is quasi-2D specific, where simplified 2D description would fail. Yet, to the best of our knowledge, no SSB phenomena have been reported in suspension of charge- and size-symmetric, overall-neutral particle systems under dielectric confinement, without any external fields.

Another important effect associated with quasi-2D charged systems concerns the permittivity, i.e., the dielectric confinement effect. Substrate materials for nanoscale confinement can range from dielectric to metallic, and nowadays, electromagnetic metamaterials, described by permittivities that can take negative values [10,11]. For electrolytes/polymers near a single dielectric substrate, recently calculations have revealed that the dielectric surface effect can greatly deviate the systems from bulk behaviors, such as ion transport [12], polymer brush structure [5] and pattern formation in dipolar films [13]. Unfortunately, the addition of a second dielectric substrate to actually form dielectric confinement in computer simulations is far from direct-forward: simulation techniques [14-25] have made great progress over the past decades, but proper treatment of the dielectric confinement effect with satisfactory accuracy and efficiency remains challenging.

In this letter, we develop a new lattice summation formula for the Green’s function in simulating charged particles under dielectric confinement, its spectral convergence allows us to efficiently calculate the polarization field. Through computer simulations of a prototypical charge- and size-symmetric binary mixture of particles described by the primitive model [26], we demonstrate that broken symmetries arise spontaneously due to the dielectric confinement effect alone. Moreover, we discover that the substrates permittivity can even qualitatively alter the degree of SSB in longitudinal and transverse dimensions, forming charge-separated interfacial liquids and correlated-clusters. Noteworthy is that all the SSB phenomena reported here actually require the presence of two dielectric substrates, we attribute this to the complicated multiply scattered polarization field due to the layered dielectric confinement structure.

The Green’s function $G(\mathbf{r}; \mathbf{r}')$ for a doubly-periodic, dielectric confined geometry is described by the Poisson’s equation,

$$-\nabla \cdot [\epsilon(\mathbf{r}) \nabla G(\mathbf{r}; \mathbf{r}')] = \sum_{||\mathbf{m}||=0}^{\infty} \delta(\mathbf{r} - \mathbf{r}_m'), \quad (1)$$

where $\mathbf{r}, \mathbf{r}' \in [0, L_x] \times [0, L_y] \times [0, L_z]$ are the target and source locations within the simulation box, $\mathbf{r}_m' = \mathbf{r}' + m_x L_x \hat{x} + m_y L_y \hat{y}$ accounts for the periodic replicas along x and y directions, with $\mathbf{m} = (m_x, m_y)$ the 2D lattice vector, $m_x, m_y \in \mathbb{Z}$. Importantly, $\epsilon(\mathbf{r})$ is the material-specific, spatially varying dielectric constant, as is depicted in Fig. 1. Finally, we have the dielectric interface conditions, i.e., the continuity of $G(\mathbf{r}; \mathbf{r}')$ and $\epsilon(\mathbf{r}) \partial G(\mathbf{r}; \mathbf{r}')/\partial z$ across $z = 0$ and $L_z$, and the free-space boundary condition (FBC) as $z \to \pm \infty$. Note that for charges under dielectric confinement, proposing the
The solvent medium with dielectric permittivity \( \epsilon \) is illustrated in Fig. 1. Schematic depiction of a quasi-2D charged system, the dielectric confinement effect is illustrated from the Image Charge Method (ICM) view point. The grey region represents the solvent medium with dielectric permittivity \( \epsilon \), orange and green regions represent upper and lower substrate with dielectric permittivity \( \epsilon' \). Red and blue circles surrounded by solid lines are actual charged particles of the doubly-periodic system, while those surrounded by dotted lines are their images reflected by dielectric interfaces.

To gain insight in the role of dielectric confinement in quasi-2D systems, we start our discussion with the classic Image Charge Method (ICM). Consider a point charge \( q \) located in a medium with dielectric constant \( \epsilon \), and near a single planar substrate with dielectric constant \( \epsilon' \), the polarization potential can be equivalently expressed as the Coulomb potential generated by an image charge located with mirror-symmetry, and magnitude \( q_{img} = \gamma q \). The dimensionless coefficient \( \gamma = (\epsilon - \epsilon')/\epsilon + \epsilon' \) quantifies the strength of polarization. Usually, \( |\gamma| \leq 1 \) for materials with positive permittivities, but the upper bound can be further lifted for metamaterials because of their stronger polarizability, characterized by negative permittivity values [27, 28]. Based on the ICM, the Green’s function in Eq. (1) can be further constructed via a multiple reflection process, resulting in an infinite image charge series, which is also schematically illustrated in Fig. 1. Note that when \( |\gamma| \leq 1 \), the image reflection series is convergent; but when \( |\gamma| > 1 \), it will be divergent and thus the reflective ICM approach would fail. Due to this divergence difficulty, current simulation studies in the \( |\gamma| > 1 \) regime is still limited to a single dielectric substrate [19].

Our new approach overcomes this divergence issue via a proper renormalization strategy, which allows us to extensively explore the dielectric confinement effect in all possible \( \gamma \) regimes, especially the less explored scenario of metamaterial substrates.

The dielectric confinement effect turns out to be physically interesting even when only two charged particles are present. In Fig. 2, we plot the electrostatic force \( F_x \) between two likely charged particles as a function of their center-to-center distance \( \Delta x \), with varying values of \( \gamma \) ranging from \(-10\) to \(+10\). The two particles are symmetric both in charge and size (same valence \( \nu \), diameter \( \tau_0 \)), placed at \( \mathbf{r}_1 = (15\tau_0, 15\tau_0, \tau_0) \) and \( \mathbf{r}_2 = (15\tau_0 + \Delta x, 15\tau_0, \tau_0) \) inside a box of size \( 30\tau_0 \times 30\tau_0 \times 2\tau_0 \). The electrostatic energy of the two-particle system can be written as \( U_{elec} = (\nu e_0)^2 G(\mathbf{r}_1, \mathbf{r}_2) \), with the Green’s function \( G \) defined in Eq. (1) and the Bjerrum length \( \ell_B = e_0^2/(4\pi \epsilon k_B T) \) characterizing the electrostatic coupling strength of the solvent, with \( e_0 \) the elementary charge, \( k_B \) the Boltzmann constant, and \( T \) for temperature. The electrostatic force thus can be defined as \( F_x = -\partial U_{elec}/\partial x \), a positive value of \( F_x \) indicates repulsion and negative represents attraction. Surprisingly, we observe from Fig. 2 a continuous transition from like-charge attraction (LCA) into repulsion and then even oscillatory interaction as \( \gamma \) increases from \(-10\) to \(+10\). This shows a clear dominance of the dielectric confinement effect over the bare Coulomb repulsion at a wide range of particle separations, particularly in the \( |\gamma| > 1 \) regimes. This phenomenon can be understood from the induced surface charge density profiles. Because of symmetry, in the insets of Fig. 2 we examine the induced charge density \( \sigma(\mathbf{r}) \) on the bottom substrate when \( \gamma = 10 \) or \( \gamma = -10 \), where red/blue represents positive/negative charges, respectively. For the case \( |\gamma| < 1 \), we also validate our method with ICM, results can be found in supplementary information (SI) [29].
point. Note that many studies have shown that likely charged nanoparticles can attract each other due to polarization, but attraction often occurs under either charge- or size-asymmetric settings [30–32]. Thus the LCA and oscillation phenomena reported here are both new, which may further influence the collective behavior of charged particles under dielectric confinement.

The key idea of our method in efficiently solving for the Green’s function Eq. (1) is originated from Ewald-splitting, but tailored for quasi-2D systems. Instead of using a spherical symmetric Gaussian cloud, we decompose the Dirac \( \delta(\cdot) \) in a cylindrical symmetric manner, i.e.,

\[
\delta(r) = \left[ \frac{\delta(r) - \alpha}{\pi} e^{-\alpha r^2} \delta(z) \right] + \frac{\alpha}{\pi} e^{-\alpha r^2} \delta(z),
\]

with \( \rho = (x, y) \), \( r = \sqrt{x^2 + y^2} \), and the choice of \( \alpha \) will be determined by considerations of computational efficiency. Here we choose \( \alpha = \sqrt{N/(L_x L_y)} \) similar to the standard 3D Ewald summation. Physically, Eq. (3) can be understood as screening the point charge only in the transverse directions, which is sufficient for quasi-2D systems. It also avoids the subtle situation of Gaussian charge cloud overlapping the substrates.

Based on the splitting strategy Eq. (4), the Green’s function can be decomposed into short- and long-range components, i.e., \( G := G_1 + G_2 \) with

\[
G_1(r; r') = -\sum_m \int_0^\infty \frac{1}{2\pi \epsilon_0} g(\kappa, z; z') \times \left(1 - e^{-\pi \kappa r^2}\right) J_0(\kappa \hat{\rho}_m) \kappa d\kappa,
\]

\[
G_2(r; r') = -\sum_k \frac{1}{L_x L_y} g(k, z; z') e^{-\pi \kappa^2} e^{ik \hat{\rho}},
\]

where \( \hat{\rho} = \rho - \rho' \), \( k = (k_x, k_y) = (\frac{2\pi m_x}{L_x}, \frac{2\pi m_y}{L_y}) \) and \( J_0 \) the 0-th order Bessel function. One can show that \( G_1 \) and \( G_2 \) shares the same coefficients \( g(k; z, z') \), given by (See SI [29] for more detailed derivations)

\[
g(k; z, z') = \frac{\Gamma_0(k)}{2k^2} \left[ \Gamma_1 e^{k(z'-z-L_z^2)} + \Gamma_2 e^{-k(z'+z)} + \Gamma_3 e^{-k|z'-z|} + \Gamma_4 e^{k|z'-z| + 2L_z^2} \right], \quad \text{for } k > 0
\]

where \( \Gamma_0(k) = 1/[(\epsilon - \epsilon')^2 e^{-2kL_z} - (\epsilon + \epsilon')^2] \), \( \Gamma_1 = \Gamma_2 = (\epsilon^2 - \epsilon'^2) \), \( \Gamma_3 = (\epsilon + \epsilon')^2 \) and \( \Gamma_4 = (\epsilon - \epsilon')^2 \).

Eq. (6) diverges as \( k \to 0 \), the 0-th mode need to be treated carefully. Physically, it corresponds to proposing the proper FBC as \( z \to \pm \infty \) so that the divergent image charge series (as depicted in Fig. 1) can be renormalized. For \( k = 0 \), it is understood that the electric field should be a function of \( z \) only, hence \( \hat{E}_{k\to0}(z \to +\infty) \) and \( \hat{E}_{k\to0}(z \to -\infty) \) are both constants so as to satisfy Gauss’s law. The divergence issue thus can be properly renormalized, which leads us to

\[
g(k = 0, z; z') = -\frac{|z - z'|}{2}. \quad (7)
\]

Physically, Eq. (7) implies that for \( k = 0 \), confined source charge acts as a uniformly charged plate.

In \( N \) particle simulations, the long-range component \( G_2 \) can be efficiently computed, because 1) fast convergence due to the prefactor \( e^{-\frac{z^2}{\kappa}} \); and 2) unlike Ewald2D method [33–35] which scales as \( O(N^2) \) since its reciprocal part is not separable, here \( G_2 \) can be computed as fast as Ewald3D since it only involves exponential terms which is separable, e.g., \( e^{ik\rho_i - \rho_j} = e^{ik\rho_i} e^{-ik\rho_j} \). However, computing the short-range part \( G_1 \) is challenging, since \( J_0(z) \) decays slowly \((z^{-1}\text{ as } z \to \infty)\) and is oscillatory. To avoid numerically evaluating \( G_1 \) directly, we introduce the Hankel transform \( \mathcal{F} \), \( \mathcal{F}[f(r)] = 2\pi\int_0^\infty f(r) J_0(2\pi\kappa r) rdr = g(\kappa) \), and its inverse transform \( \mathcal{F}^{-1}[g(\kappa)] = 2\pi\int_0^\infty g(\kappa) J_0(2\pi\kappa r) rdk = f(r) \). Based on the useful fact that

\[
\left\{ \frac{1}{\sqrt{a^2 + r^2}}, \frac{e^{-2\pi\kappa r}}{\kappa} \right\}
\]

is a Hankel transform pair, we are able to extract the slowly decaying component of \( G_1 \) analytically,

\[
G_1 = \sum_m \sum_{i=1}^4 \int_0^\infty |A_i(\kappa)| e^{-\frac{z^2}{\kappa}} + B_i(\kappa) e^{-2\kappa L_z^2} |e^{a_i(z, z')}| \times J_0(\kappa |\rho - \rho_m|) d\kappa + C_i/\sqrt{a_i(z, z')^2 + \rho_m^2}.
\]

where \( a_i \) are index coefficients of four exponential terms same as Eq. (10) so that \( a_i \in \{-2L_z, 0\} \); \( A_i(\kappa) \), \( B_i(\kappa) \) and \( C_i \) are other coefficients with detailed expressions given in SI [29]. Clearly, all integrands in Eq. (8) are now associated with an exponential decay prefactor, a recently developed Gauss quadrature scheme can be applied to achieve optimal spectral accuracy [34]. Furthermore, due to the short-range nature of \( G_1 \), the computational cost can be reduced to \( O(N) \) in a simulation by combining with neighbor-list algorithms. Compared to existing Ewald3D-based methods [14, 15, 37], our approach is tailored for quasi-2D and thus do not need any artificial vacuum zones in \( z \) and correction terms. Compared to other grid-based methods [38, 39], our approach has its natural merit since we do not require numerical discretization and solving linear systems. Particularly, it overcomes the divergence issue for \( |\gamma| > 1 \), which allows us to investigate the less explored metamaterial confinement cases.

We examine a prototypical quasi-2D charged system, namely binary mixture of charged particles described by the primitive model. The system contains \( N/2 \) cations and \( N/2 \) anions, each particle with same diameter \( \gamma_0 \) and valence \( \pm 1 \) and is thus overall charge neutral. Assume
In all the Molecular Dynamics (MD) simulations performed, we fix $N = 100$ and box size $30\gamma_0 \times 30\gamma_0 \times 10\gamma_0$, yielding a particle volume fraction of $5.8 \times 10^{-3}$. The Bjerrum length for the solvent medium is set to be $\ell_B = 3.5\gamma_0$. Temporal integration is performed via the Velocity-Verlet algorithm provided by LAMMPS [40] and temperature is controlled via Anderson thermostat with stochastic collision frequency $\omega = 0.1$. To isolate electrostatic effect, the reduced temperature $T_r$ is defined as $T_r = k_B T / U_{\text{coul}}$, where $U_{\text{coul}} = \varepsilon_0^2 / (4 \pi \varepsilon \ell_B)$ and we maintain $\varepsilon_{\text{LJ}} = k_B T$ for both particle-particle and particle-substrate interactions. Then, without loss of generality, we are able to investigate the impact of dielectric confinement by adjusting only two parameters ($\gamma$ and $T_r$).

In the $|\gamma| \leq 1$ regime, extensive simulation works have been done recently [23, 24] and no SSB phenomenon has been found, i.e., the density distributions of cations $\rho_+(r)$ and anions $\rho_-(r)$ always maintain symmetries of the system, given by 1) cross symmetry in the confined space: $\rho_+(r) = \rho_-(r)$, 2) longitudinal symmetry: $\rho_\pm(x, y, z) = \rho_\pm(x, y, L_z - z)$, and 3) transverse symmetry: $\rho_\pm(x, y, z) = \rho_\pm(x', y', z)$. Our simulations give symmetric results for $|\gamma| \leq 1$, consistent as previous investigations (details are documented in SI [29]). In the following discussions we will focus on the strongly polarizable cases of $|\gamma| > 1$, where SSB phenomena arise.

Fig. 3(a) documents the cation/anion density profiles in $z$ with $\gamma = 10$ and reduced temperature $T_r = 0.1$, 1 and 10. It clearly shows, for the first time, the SSB force and longitudinal symmetries are broken. The inset plot shows a snapshot configuration for $T_r = 1$ after equilibrium, cations and anions separate spontaneously and forming charge-separated liquids on the opposing substrates. We also observe the loss in symmetry varies continuous as a function of temperature, i.e., the mixing rate of cations and anions can be controlled via increasing $T_r$. Videos displaying the MD trajectories for the charge separating process are documented in SI.

To understand the spontaneous charge separation mechanism, in Fig. 3(b) we plot the electrostatic force $F_z$ on each particle from 4000 independent snapshot configurations at $T_r = 1$ after equilibrium, where dashed lines indicate the potential of mean force $F_z$. Clearly, $F_z$ is repulsive at short range but attractive if a particle leaves away from the substrate. The location $F_z = 0$ also corresponds to the peak of density profiles in Fig. 3(a). Interestingly, though both substrates are overall neutral, they behave effectively as charged surfaces due to polar-
FIG. 4. Cluster formation when $\gamma = -10$. (a) Structure of equilibrium stats, red balls for cations can blue balls for anions. (b) Force in $x$ direction for two cations on $z = 0.48\tau_0$ plane. The subfigure shows the structure of one cluster from (a). (c) Average force $\bar{F}_x$ from one cluster to its partner, when there is a shift in $x$ direction presented by $\Delta x$.

To further understand why liquid phases are formed in transverse directions, in Fig. 3(c) we plot $F_x$ between two cations as a function of separation $\Delta x$ with $z = 0.48\tau_0$, which is the interfacial liquid formation plane. Clearly, the cations are repulsive over the range $\Delta x \in [0, 15\tau_0]$, which is enhanced by dielectric confinement, leading to the formation of 2D liquids. Note that the oscillatory behavior observed in Fig. 2 still exists, but it occurs at long distance and is not strong enough to make an impact.

While the interfacial liquid phase breaks the longitudinal symmetry, the dielectric confined system can further break the transverse symmetry when $\gamma = -10$. Fig. 4(a) shows a typical snapshot configuration after equilibrium with $\gamma = -10$ and $T_r = 1$, where clusters are formed by likely-charged particles near the substrates (videos displaying the MD trajectories for the cluster formation process are documented in SI). Each cluster is hexagonal close packed with gylation radius $R_g \sim 1.5\tau_0$, the top view of a typical cluster is shown in the inset of Fig. 4(b).

To understand the cluster formation mechanism, in Fig. 4(b) we examine $F_x$ between two cations as a function of separation $\Delta x$ with $z = 0.48\tau_0$, which is the cluster formation plane. Consistent with previous observation in Fig. 4 LCA arises over the range $\Delta x \in [0.5\tau_0, 5\tau_0]$, leading to the surprising cluster formation phenomenon for likely-charged particles.

Interestingly, we find that the clusters on opposing substrates are strongly correlated, i.e., there is a one-to-one “pairing” between the opposing clusters. In Fig. 4(c) we plot the average electrostatic force $\bar{F}_x$ exerts on each cluster when two already paired clusters are shifted by a distance $\Delta x$ from each other. Clearly, $\bar{F}_x$ is always attractive, thus the clusters will be pulled back if shifted, forming stable opposing pairs. Experimentally, similar clustering phenomena have been reported for colloidal particles at air-water interfaces \[41-43\], but the phenomena reported here solely via dielectric confinement effect is clearly of different physical origin.

In summary, using a newly developed lattice summation method that permits simulations of dielectric confined quasi-2D charged systems, we are able to extensively explore the role of dielectric confinement effect. For a prototypical overall neutral charged system, it is discovered for the first time that spontaneous symmetry breaking can be induced and even modulated via the substrate polarizability alone. Our approach also provides a powerful tool for efficient and accurate simulation for a broad range of quasi-2D systems, with wide applications in future nanotechnology. Future plan includes further improve our method into an $O(N)$ algorithm \[44\], and an open source implementation in LAMMPS \[10\].

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