The Symmetry-Preserving Mean Field Condition for Electrostatic Correlations in Bulk

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Accurate simulations of a condensed system of ions or polar molecules are concerned with proper handleings of the involved electrostatics. For such a Coulomb system at a charged planar interface, the Coulomb interaction averaged over the lateral directions with preserved symmetry serves as a necessary constraint in building any accurate handling that reconciles a simulated singlet charge density with the corresponding macroscopic charge/dielectric response. At present, this symmetry-preserving mean-field (SPMF) condition represented in the reciprocal space, is conjectured to be necessary for a simulated bulk system to reproduce correctly the charge structure factor of the macroscopic bulk, as well. In this work, we further examine analytically the asymptotic behavior of the charge structure factor at small wavenumbers for an arbitrary charge-charge interaction. In light of our theoretical predictions, simulations with a length of nearly 0.1 micron are carried out to demonstrate that, typical efficient methods violating the SPMF condition indeed fail to capture the exact charge correlations at small wavenumbers for both ionic and polar systems. However, for both types of systems, these existing methods can be simply amended to match the SPMF condition and subsequently to probe precisely the electrostatic correlations at all length scales.

There have been much advances regarding efficient and accurate treatments of the long-ranged electrostatics for molecular dynamics and Monte-Carlo simulations in recent years\textsuperscript{11–15}. These techniques differ from each other in various means: for bulk\textsuperscript{4,7,11,13,15} versus for interfaces\textsuperscript{8–10,14}, efficient algorithms based on existing formulations\textsuperscript{7,13,14} versus newly designed functional forms of the simulated electrostatics\textsuperscript{5,8,10}, for classical non-polarizable systems\textsuperscript{4,7,13,15} versus for systems with dielectric contrast\textsuperscript{8–10,14}, and methods well characterized by a simulation Hamiltonian in the framework of classical statistical mechanics\textsuperscript{5,10,13,14} versus others that might not be easily characterized in the same way\textsuperscript{4,11,12,15}. The development and implementation of these techniques have not only enhanced greatly our knowledge of complex Coulomb systems but also persistently called for a conceptual understanding of the intrinsic connections among the many techniques themselves from a transparent theoretical viewpoint.

The recent symmetry-preserving mean-field theory\textsuperscript{16–19} might shed some light on the connections. The core of this theory applied to the interfacial electrostatics is the so-called SPMF condition — the lateral average of the pairwise charge-charge interaction, \( \nu(\mathbf{r}) \) involved in an accurate simulation must equal that of the Coulomb interaction\textsuperscript{19}

\[ \langle \nu(\mathbf{r}) \rangle_{sp} = \frac{1}{A} \int \int dxdy \nu(\mathbf{r}) = \frac{-|z|}{2A\varepsilon_0}, \]  

where \( A = L_x L_y \) is the cross-sectional area of the simulation box and \( \varepsilon_0 \) is the vacuum permittivity. \( \langle \nu(\mathbf{r}) \rangle_{sp} \) stands for the symmetry-preserving (sp) average over the lateral directions\textsuperscript{16}. Whenever it operates on a two-dimensional (2D) Fourier series, integrations of trigonometric functions all vanish and only the first Fourier coefficient is left over\textsuperscript{19}. \( \nu(\mathbf{r}) \) can always be defined by rewriting the electrostatic energy in the simulation as\textsuperscript{14,20,21}

\[ U_{\text{elec}} = \sum_{i<j} q_i q_j \nu(\mathbf{r}_{ij}), \]  

where \( q_i \) is the charge of the \( i \)-th particle and \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) denotes the relative vector between the \( i \)-th and \( j \)-th particles.

The SPMF condition is necessary for a finite simulation consist of a few thousands to billions of particles to reproduce the charge/dielectric response of the corresponding macroscopic Coulomb system (\( \sim 10^{21} \) particles)\textsuperscript{19}. To illustrate this statement precisely, let us consider an example of mobile ions confined between two macroscopic plate electrodes with fixed surface charges, \( \pm \sigma \). In this model system, the mobile ions driven by the electric field must form a nontrivial interfacial region around each electrode. At thermal equilibrium under normal conditions, the fixed surface charge of each electrode (\( \pm \sigma \)) should be screened completely by the compensating mobile surface charge (\( \mp \sigma \)) resulting from the integration of the equilibrium singlet charge density over the corresponding interfacial region, such that, mobile ions in the bulk region feel no net electrostatic force on average. In a numerical simulation employing \( \nu(\mathbf{r}) \) for the charge-charge interaction under the usual 2D periodic boundary condition (PBC), the SPMF condition becomes necessary and sufficient for producing the exact compensating surface charge, \( \mp \sigma \). On the other hand, the condition is necessary but insufficient for producing the detailed variation of the equilibrium singlet charge density along the \( z \) direction. However, as long as \( \nu(\mathbf{r}) \) differs from \( \nu_{\text{Ewald}}(\mathbf{r}) \) involved in the formally exact Ewald-2D sum method\textsuperscript{20,22,24} by a slowly varying long-ranged component, the SPMF theory has suggested that interfacial structure, thermodynamics as well as dynamics in the \( z \) direction can often be obtained accurately from the approximated but much more efficient method\textsuperscript{16}. In terms of \( \nu(\mathbf{r}) \), all existing methods for interfacial electrostatics can be classified into three categories: the formally exact Ewald-2D method and its efficient algorithms, approximated SPMF methods (e.g.\textsuperscript{25,26} and more in ref.\textsuperscript{19}), and other methods which vio-
late the SPMF condition but could be amended to work well for interfaces\[19\].

While the guiding constraint, Eq. (1), and the associated SPMF theory provide a transparent analysis of the interfacial electrostatics, the question arises as to whether or not the electrostatics in the bulk phase could be simply analyzed as well. Since the equilibrium singlet charge density in bulk vanishes for \( q = \pm 1 \) and \( q = -1 \) separated at \( d \) interacting through the laterally averaged Coulomb interaction (left), the quadratic infinite boundary term (middle) and the periodic series (right) of Eq. (4), respectively. Any potential (black) produced by the pair is the sum of the two individual potentials (colored). The dash lines indicate the periodic images of the pair.

The electric potential produced by this quadratic term for a pair of unit charges (\( q = \pm 1 \)) is a constant proportional to the distance between the two charges in the prescribed direction (see Fig. 1). Each quadratic term in an instantaneous configuration thus adds up to contribute a constant electric field proportional to the non-periodic (itinerant) total dipole moment. Being the reality of a non-periodic quantity, the itinerant dipole moment possesses no translational invariance and becomes ill-defined upon the PBC transform of any non-zero charge. As such, the quadratic infinite boundary term, as its name says, must be merely responsible for the effect of the macroscopic boundary, which is deemed irrelevant to any well-defined bulk property such as \( S(k) \) of Eq. (3).

When focusing on the translationally invariant electrostatic correlations under the full PBC, one might exclude the non-periodic term and subsequently conjecture that the pairwise interaction accounting for an accurate \( S(k) \) with \( k = (0,0,2\pi k_z/L_z) \) satisfies necessarily,

\[
\langle \nu(r) \rangle_{sp} = \frac{1}{V} \sum_{k_z \neq 0} e^{ikz},
\]

which defines the SPMF condition for the electrostatics in the bulk phase. Similar constraints apply to symmetry-preserving averages in other directions for the purpose of determining precisely \( S(k) \) at the corresponding wave vectors. Noting that \( 1/(\varepsilon_0 k^2) \) is the 3D Fourier transform of the Coulomb interaction and \( \langle \rangle_{sp} \) removes all the 3D Fourier coefficients associated with \( e^{ikr} \) subject to \( k_x \neq 0 \) or \( k_y \neq 0 \), this SPMF condition suggests essentially that, any chosen lateral average of \( \nu(r) \) represented in the reciprocal space must equal that of the Coulomb interaction such that the finite simulation under the 3D PBC is able to reproduce correctly the macroscopic charge correlations in the corresponding normal direction of the reciprocal space.

It turns out to be informative to examine the existing methods for bulk electrostatics in terms of Eq. (5). The pairwise

\[
S(k) = \frac{1}{V} \sum_{ij} q_i q_j \langle e^{ikr_{ij}} \rangle,
\]

where \( V = L_xL_yL_z \) is the volume of the cubic simulation cell. \( S(k) \) at \( k = 2\pi(k_x/L_x, k_y/L_y, k_z/L_z) \) with \( k_x, k_y \) and \( k_z \) all integers, probes the charge correlation at the discrete wave vector that is compatible with the reciprocal lattice of the finite simulation cell. Correspondingly, the averaged Coulomb interaction represented in the reciprocal space is known to be a combination of a non-periodic quadratic term and a periodic Fourier series\[\[18, 19\].

\[
-\frac{|z|}{2\varepsilon_0A} = -\frac{z^2}{2\varepsilon_0V} + \frac{1}{V} \sum_{k_z \neq 0} e^{ikz},
\]

where \( k = |k| \) with \( k \) specified to be \( (0,0,2\pi k_z/L_z) \) normal to the \( xy \) plane. Eq. (4) is valid up to a constant for any \( z \in [-L_z, L_z] \). The quadratic term, previously called the infinite boundary term, identifies with the excluded \( k \to 0 \) term of the periodic series, provided that the divergence caused by \( 1/k \) and \( 1/k^2 \) are all removed\[20\].

FIG. 1. The electric potentials (top) and the corresponding electric fields (bottom) produced by a pair of unit charges (red solid lines for \( q = +1 \) and blue solid lines for \( q = -1 \)) separated at \( d \) interacting through the laterally averaged Coulomb interaction (left), the quadratic infinite boundary term (middle) and the periodic series (right) of Eq. (4), respectively. Any potential (black) produced by the pair is the sum of the two individual potentials (colored). The dash lines indicate the periodic images of the pair.
interaction of the well known Ewald3D sum method with the
tinfoil boundary condition (e3dtf) reads
\[ \rho^{\text{e3dtf}}(r) = \tau^{\text{3D}} + \frac{1}{V} \sum_{k \neq 0} e^{ik \cdot r} \frac{\nu_{sp}(k \cdot r)}{\varepsilon_0 k^2}, \] (6)

which indeed satisfies Eq. (5) (up to the constant \( \tau^{\text{3D}} \)) in any
direction. The e3dtf method is therefore considered to be for-
mally exact for probing the electrostatic correlations in the
reciprocal space. This shift of perspective resolves the long-
time concern regarding the artificial anisotropy introduced by
the e3dtf method[1, 2, 30], charge correlations in the recipro-
cal space under the 3D PBC are as isotropic as they are on
the 3D hypersurface of a 4D sphere[30]. In another word, any
anisotropy introduced by \( \rho^{\text{e3dtf}}(r) \) in the real space won’t be
problematic any more once the quantity of interest is com-
peted properly by the inverse Fourier transform of the corre-
ponding \( k \)-dependent ensemble average. When the Ewald3D
sum is associated with other boundary conditions that depend
on the itinerant dipole moment[16, 31, 32]. Caillol has argued
that the itinerant dipole moment is a decoupled collective vari-
able that behaves as an independent harmonic oscillator for an
electrolyte[32], which well supports our exclusion of the re-
dundant non-periodic infinite boundary term.

Distinct pairwise interactions involved in other useful meth-
ods in principle violate the SPMF condition. As an example,
the recent zero-multipole (zm) method introduces deformed
Coulomb interactions, \( \nu(r l, \alpha) \) parameterized by the order of
the multipole moment \( l \) and the damping factor \( \alpha \). Its
3D Fourier transform, which is the Fourier coefficient of the cor-
corresponding pairwise interaction, differs (d) from \( 1/(\varepsilon_0 k^2) \)
by
\[ \hat{\nu}_d(k l, \alpha) = 1/(\varepsilon_0 k^2) - \hat{\nu}(k l, \alpha). \] (7)

For three typical sets of parameters: \( l = 0 \) (zm0), \( l = 2 \) and
\( \alpha = 0 \) (zm2), and \( l = 3 \) and \( \alpha = 0 \) (zm3)[5, 6]. The remaining
Fourier coefficients read explicitly
\[ \hat{\nu}_d(k 2, 0) = \frac{15}{\varepsilon_0 k^2} \frac{(3 - k_c^2) \sin k_c - 3k_c \cos k_c}{k^2 k_c^3}, \] (9)

where \( k_c = kr_c \) with \( r_c \) the cutoff distance, and
\[ \hat{\nu}_d(k 3, 0) = \frac{105}{\varepsilon_0 k^2} \frac{(15 - 6k_c^2) \sin k_c - (15 - k_c^2)k_c \cos k_c}{k^2 k_c^4}, \] (10)

respectively. \( \hat{\nu}_d(k l, \alpha) \) is nonzero unless both \( \alpha = 0 \) and
\( r_c \rightarrow \infty \). To match the SPMF condition in a prescribed
(e.g. \( z \)) direction for the general case of finite \( \alpha \) and \( r_c \), the
amended zero-multipole (azm) method must include an extra
electrostatic term
\[ U_{extra} = \sum_{i<j} q_i q_j \nu_{sp}(z_{ij} l, \alpha), \] (11)

where \( \nu_{sp}(z l, \alpha) \) sums over the remaining Fourier coeffi-
cients in the direction with preserved symmetry as in Eq. (5)
\[ \nu_{sp}(z l, \alpha) = \frac{1}{V} \sum_{k \neq 0} \hat{\nu}_d(k l, \alpha) e^{ikz}. \] (12)

Besides, both electrostatic terms corresponding to \( \nu_{sp}(z l, \alpha) \)
and \( \nu_{sp}(y l, \alpha) \) can be added to retain isotropy and subse-
quently match the SPMF condition in all three directions.

It is possible to examine analytically the influence of the
different pairwise interactions on the charge structure factor,
\( S(k) \) for both ionic and polar systems. Because vari-
ous methods have been successful in probing the short-ranged
correlations[5, 6, 11, 12, 15], which is related to \( S(k) \) at rela-
tively large wavenumbers, deficiencies of the pairwise interac-
tion violating the SPMF condition must be evident when
one computes \( S(k) \) at small wavenumbers that reflect other-
wise the long-ranged correlations. For a conducting ionic fluid
interacting through the Coulomb force, the seminal work of
Stillingler and Lovett argued that \( S(k) \) has the universal form
at small wavenumbers[53]
\[ S(k) = 0 + \varepsilon_0 k^2 \cos \lambda k + O(k^4), \] (13)

where \( k_b \) is the Boltzmann constant and \( T \) is the tem-
perature. This exact asymptotic form of course agrees with the
well known Debye-Huckel limit[29]
\[ S(k) = \frac{k_b T \varepsilon_0}{\lambda^2} + \hat{\nu}(k l, \alpha) \varepsilon_0, \] (14)

where \( \hat{\nu}(k l, \alpha) = 1/(\varepsilon_0 k^2) \) and \( \lambda \) is the Debye length defined
through \( \lambda^2 = k_b T \varepsilon_0 / I \) given by the sum of squares of charges divided by the volume. Both forms in Eqs. (13) and (14) characterize the charge correlations in the conducting fluid — any fixed charge is com-
pletely screened by the surrounding mobile charges as a con-
sequence of the divergence of \( \hat{\nu}(k l, \alpha) \) at \( k \rightarrow 0 \). This com-
plete screening effect is irrespective of any details of the short-
ranged non-electrostatic interaction.

In a simulation employing otherwise the deformed
Coulomb interaction, the asymptotic behavior of \( S(k) \) can be readily obtained by replacing \( \hat{\nu}(k l, \alpha) \) in Eq. (14) with \( \hat{\nu}(k l, \alpha) \),
which however remains finite at \( k \rightarrow 0 \) for finite \( \alpha \) and \( r_c \).
Therefore, any short-ranged pairwise interaction must lead to an
incomplete screening which gives the divergence of the screen-
ing function, \( S(k)/k^2 \) at \( k \rightarrow 0 \):
\[ \frac{S(k)}{k^2} = \frac{k_b T \varepsilon_0}{\lambda^2 k^2 + \hat{\nu}(k l, \alpha) \varepsilon_0 k^2} + O(k^2). \] (15)

When the simulation box is large enough to evaluate \( S(k) \)
of Eq. (13) at a sufficient small \( k \), \( S(k)/k^2 \) for the simulated
conducting fluid must approach the infinite.

Similar things happen to a molecular fluid with a dielectric
constant (relative permittivity) of \( \varepsilon_r (\varepsilon_r \geq 1) \). \( \lambda^2 k^2 \) in Eq. (13)
is substituted with \( 1/(\varepsilon_r - 1) \)
\[ \frac{S(k)}{k^2} = \frac{k_b T \varepsilon_0}{1/(\varepsilon_r - 1) + \hat{\nu}(k l, \alpha) \varepsilon_0 k^2} + O(k^2), \] (16)
of the screening effect of the Coulomb force. Violation of the SPMF condition leads to improper behaviors of charge correlations characterized by $S(k)/k^2$ at small wavenumbers. In light of these theoretical predictions, we carry out simulations of the model ionic fluid[36] at $T = 5000 K$ and the SPC/E water[37] at $T = 298.15 K$ with one length of the simulation box 930 Å and 939.6 Å, respectively. In the zm2/zm3 methods, $r_c = 30 Å$ and $r_c = 12 Å$ for the ionic fluid and the water respectively. In the zm0 method, $\alpha = 1/4.5 Å^{-1}$ as in other simulations of water[36][38][39]. The ionic strengths $I = 0.00859 e^2 Å^{-3}$ and $I = 0.0359 e^2 Å^{-3}$ for the ionic fluid and the water respectively. The Debye length of the ionic fluid is $\lambda = 0.526 Å$. Complete details of the simulations are available to the public[40].

Figs. 2 and 3 display the computed $S(k)$ and $S(k)/k^2$ at discrete wavenumbers for both systems. At extremely large $k$, $S(k)$ approaches the corresponding ionic strength indicating the self-correlation. In addition, the damped oscillation of $S(k)$ for the SPC/E water approaches the intra-molecular correlation

$$
\frac{S(k)}{T} \sim 1 + \frac{4q_0 q_H \sin(kd_{OH})}{q_{sum} kd_{OH}} + \frac{2q_0^2 \sin(kd_{HH})}{kd_{HH}},
$$

where $q_0$, $q_H$, $d_{OH}$ and $d_{HH}$ are the parameters of charges and bond lengths in the SPC/E model[37][40]. $q_{sum} = q_0^2 + 2q_H^2$, is the sum of the squares of the charges in one molecule. $S(k)$ from all methods are indistinguishable at the wavenumbers corresponding to distances ($2\pi/k$) smaller than the local correlation lengths. However, distinct features between the SPMF condition satisfied and violated methods are found at small $k$ for both the ionic fluid and the water. These characteristics are in excellent agreement with the analytical predictions from Eqs. (15) and (16) with $\hat{\nu}(k|l, \alpha)$ determined by Eqs. (7) to (10) and the specified parameters of the systems.

In conclusion, the SPMF condition provides a simple concept to connect the electrostatic correlations among Coulomb and simulated Coulomb systems. Exceptions are simulations employing techniques that are not well represented by a pairwise interaction. These useful methods include the local maxwell approach[4], the random batch method[15][41] and the fast growing machine-learning techniques[11][12]. While analytic understandings of the mentioned methods have yet to be achieved, the present work suggests that it is convenient to validate them by calculating correlations in the reciprocal space such as $S(k)$, the usual structure factor and intermediate scattering functions[29]. We note that numerical evidence does show that the local maxwell approach behaves correctly at small wavenumbers[4]. Further investigations at all wavelengths for both time-averaged and time-displaced correlations are expected. We finally hope that the SPMF condition for interfacial and bulk electrostatics helps to provide a simple starting point when developing methods to simulate a complex condensed phase.

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