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# Symmetry-preserving mean field approach for electrostatics at interfaces<sup>†</sup>

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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

**We derive an instantaneous symmetry-preserving mean field equation relating the long-ranged component of the intermolecular interaction to an effective single particle potential. We verify the efficiency and accuracy of the symmetry-preserving mean field approach to treat complex nonuniform electrostatics and foresee its application to study self-assembly and disassembly processes at interfaces in many computer simulations.**

The primary purpose of theoretical and computational studies of nonuniform fluids is to obtain the dynamical, structural, and thermodynamical properties of a liquid phase in a general external field. When the long-ranged part of the intermolecular interaction plays an important role in determining these properties, there are difficulties in developing either accurate statistical mechanics theories or efficient molecular dynamics (MD) simulations and Monte Carlo techniques. Mean field approaches suggest that certain long-ranged components of the pair intermolecular interaction can be replaced by an effective single particle potential or a reconstructed molecular field that depends self-consistently on the nonuniform density that the field itself induces<sup>1,2</sup>. Recent implementation of mean field ideas in terms of the local molecular field (LMF) theory developed by Weeks and coworkers has proven successful in producing accurate results for equilibrium structure and thermodynamics for Lennard-Jones and molecular fluids<sup>2,3</sup>, and especially for complex nonuniform electrostatic systems in general<sup>4–7</sup>. However, a *controllable* way to achieve the accurate dynamics using mean field ideas has yet to be developed.

Indeed, is it possible even in principle to construct a dynamical effective single particle potential related to the long-ranged components of the pair interaction such that the system evolves in a simple but controllable way to give accurate dynamics? The existence of such a relation must certainly depend on the fluctuating instantaneous local environment of each particle in general and at first glance, it may seem hard to believe that any mean field approximation at the level of

instantaneous configurations could be controlled! In this letter, we build on ideas from the equilibrium LMF theory and introduce an appropriately chosen slowly varying dynamical variable. We show that in interfacial environments when its components in directions with different symmetries are approximated separately, this approximation can be controlled and is an efficient and practical tool to determine accurate dynamics, as well as equilibrium structure and thermodynamics.

For concreteness, we will present our ideas in the context of a simple but challenging problem of  $N$  charges confined between planar walls under an external electric field (e.g. water confined between two charged hydrophobic walls). The single particle external field is  $\phi(\mathbf{r}) = \phi(z)$  with planar symmetry. This field breaks the symmetry in the  $z$  direction and the treatment of the nonuniform electrostatics presents a particularly challenging problem because (i) it has long been recognized that the standard setup using 3D Ewald sum (Ewald3D) or the particle mesh Ewald (PME) treatment<sup>8</sup> gives inaccurate results in general<sup>6,9,10</sup> and (ii) an accurate treatment using Ewald type sums with 2D periodicity (Ewald2D)<sup>9,11–18</sup> or Lekner sum methods<sup>19–21</sup> is much more complicated and efficient methods are still under development. For this  $N$ -charge electrostatic system, the pair intermolecular interaction is a combination of a short-ranged potential  $u_s(r)$  and the long-ranged Coulomb potential. The instantaneous total potential energy felt by a test charge  $q$  at the position  $\mathbf{r}$  for a given configuration of the system ( $\bar{\mathbf{R}}$ ) is thus written as

$$U(\mathbf{r}, \bar{\mathbf{R}}) = \phi(\mathbf{r}) + \sum_j u_s(|\mathbf{R}_j - \mathbf{r}|) + \sum_j \frac{q_j q}{|\mathbf{R}_j - \mathbf{r}|}. \quad (1)$$

Accurate evaluation of  $U(\mathbf{r}, \bar{\mathbf{R}})$  at each particle's position (the self term at 0 distance is set to 0) is crucial to the dynamics. It is straightforward to determine the first two terms of  $U(\mathbf{r}, \bar{\mathbf{R}})$  but the last term usually requires the use of the Ewald type sums. When the Coulomb interaction  $1/r \equiv v_0(r) + v_1(r)$  is separated into short- and long-ranged components with  $v_1$  arising from a normalized Gaussian charge distribution with width  $\sigma$ <sup>6,7</sup>:

$$v_1(r) = \frac{1}{\pi^{3/2}\sigma^3} \int d\mathbf{r}' e^{-r'^2/\sigma^2} \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{\text{erf}(r/\sigma)}{r}, \quad (2)$$

<sup>†</sup> Electronic Supplementary Information (ESI) available: [Results for weak external fields]. See DOI: 10.1039/b000000x/

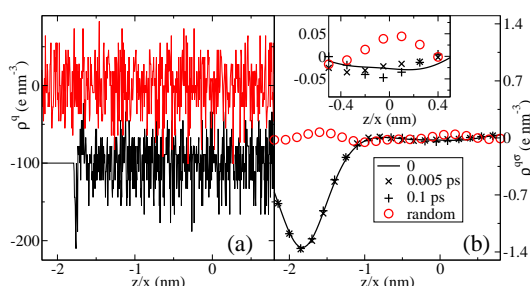
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we can *exactly* rewrite  $U(\mathbf{r}, \bar{\mathbf{R}})$  as

$$U(\mathbf{r}, \bar{\mathbf{R}}) = \phi_R(\mathbf{r}, \bar{\mathbf{R}}) + \sum_j u_s(|\mathbf{R}_j - \mathbf{r}|) + \sum_j q_j q v_0(|\mathbf{R}_j - \mathbf{r}|), \quad (3)$$

where the reconstructed configurational field is defined as  $\phi_R(\mathbf{r}, \bar{\mathbf{R}}) = \phi(\mathbf{r}) + \mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})q$  with the effective electrostatic potential  $\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})$  formed by the convolution of the instantaneous charge density  $\rho^q(\mathbf{r}, \bar{\mathbf{R}}) = \sum_j q_j \delta(\mathbf{r} - \mathbf{R}_j)$  with  $v_1(r)$

$$\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}}) = \int d\mathbf{r}' \rho^q(\mathbf{r}', \bar{\mathbf{R}}) v_1(|\mathbf{r} - \mathbf{r}'|) \equiv \int d\mathbf{r}' \frac{\rho^{q\sigma}(\mathbf{r}', \bar{\mathbf{R}})}{|\mathbf{r} - \mathbf{r}'|}. \quad (4)$$



**Fig. 1** The large-scale fluctuations of the instantaneous charge densities  $\rho^q(x/z, \bar{\mathbf{R}})$  (a) for a given configuration in a confined water system in the  $x$  or  $y$  direction (red, top, using label  $x$ ) and in the  $z$  direction at 0 time (black, bottom, using label  $z$ ) and the small-scale fluctuations of the corresponding Gaussian-smoothed charge densities  $\rho^{q\sigma}(x/z, \bar{\mathbf{R}})$  (b) from the  $x$  direction random configuration (circle) and from the  $z$  direction configuration at 0 (solid line) and later times (cross and plus).  $\phi(\mathbf{r}) = \phi(z)$  arises from the wall fixed at  $z = -2.0\text{nm}$  and an applied electric field introducing an instantaneous charge density indistinguishable from the bulk fluctuation. Note the 4 orders of magnitude difference in the vertical scale of (a) and the inset of (b).  $\sigma = 0.45\text{nm}$ .  $\rho^q(z, \bar{\mathbf{R}})$  (the black curve in(a)) has been shifted downward by 100 units.

Before making any approximation, let's examine the properties of  $\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})$  in general. In particular, what's the magnitude of  $\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})$  relative to the total electrostatic potential  $\sum_j q_j / |\mathbf{R}_j - \mathbf{r}|$  in a typical configuration? Noting the convolution defining  $v_1$ , we see that  $\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})$  exactly satisfies the Poisson's equation but with an instantaneous Gaussian-smoothed charge density  $\rho^{q\sigma}(\mathbf{r}, \bar{\mathbf{R}})$ , given by the convolution of  $\rho^q(\mathbf{r}, \bar{\mathbf{R}})$  with the Gaussian in eq. (2). Thus, we should be able to address this question by comparing the unsmoothed charge density  $\rho^q(\mathbf{r}, \bar{\mathbf{R}})$  and the Gaussian-smoothed charge density  $\rho^{q\sigma}(\mathbf{r}, \bar{\mathbf{R}})$ . We assume that the accurate dynamics can be determined (e.g. by Ewald2D type sums) for the nonuniform electrostatic system and therefore we can examine the instantaneous charge density in either the  $x$  or  $z$  direction shown in Fig. 1. Clearly, the Gaussian-smoothed instantaneous charge density with  $\sigma = 0.45\text{nm}$  is slowly varying and several orders

of magnitude smaller than the rapidly varying unsmoothed charge density. A similar observation for the magnitude of the equilibrium and Gaussian-smoothed charge densities was made in LMF theory. The remaining variations in the direction with preserved symmetry along the wall are random and would average out to 0 exactly in the ensemble averaged charge density used in LMF theory. But the  $z$  component with broken symmetry has nontrivial variations that reflect the effect of  $\phi_R$  in LMF theory<sup>6,7</sup> and we note that they are still there in each configuration as well. This suggests we may be able to capture many of the advantages and simplifications of the equilibrium LMF theory while still preserving an accurate treatment of the configurational dynamics.

To that end, let us consider how accurately the Coulomb interactions in the Hamiltonian (and hence the associated forces) have to be determined to achieve the realistic dynamics. MD simulation studies using different number of particles and different initial conditions clearly have different energies and forces for each instantaneous configuration but still yield at least consistent results for equilibrium properties. This suggests that the dynamics in molecular simulation or arguably in reality as well should be insensitive to the tiny random forces remaining even after Gaussian-smoothing in the  $x$  direction (more generally in the directions with no broken symmetry).

The above discussion thus suggests a simple and physically suggestive approximation where the small-scale fluctuations of  $\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})$  in the  $x$  and  $y$  direction with preserved symmetries are integrated out

$$\mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}}) \simeq \langle \mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}}) \rangle_{\text{sp}} \equiv \frac{\int dX_1 \cdots dX_N dY_1 \cdots dY_N \mathcal{V}_R(\mathbf{r}, \bar{\mathbf{R}})}{\int dX_1 \cdots dX_N dY_1 \cdots dY_N} = \mathcal{V}_R(z, \bar{Z}), \quad (5)$$

where  $\langle \rangle_{\text{sp}}$  is the symmetry-preserving operator defined as the normalized integration over the degrees of freedom in the directions with no broken symmetry. The effective field  $\mathcal{V}_R(z, \bar{Z})$  does not depend on the small-scale degrees of freedom ( $x$  or  $y$ ) any more and is exactly given by

$$\mathcal{V}_R(z, \bar{Z}) = \int d\mathbf{r}' \rho_s^q(z', \bar{Z}) v_1(|\mathbf{r} - \mathbf{r}'|), \quad (6)$$

with the instantaneous singlet charge density in the  $z$  direction defined as  $\rho_s^q(z, \bar{Z}) \equiv \frac{1}{A} \sum_{j=1}^N \delta(z - Z_j)$ , where  $A$  is the unit area of the  $N$  charges and we have simply ignored or more formally averaged out the fluctuating contribution in  $x$  and  $y$  direction.

Using  $v_1 = \text{erf}(r/\sigma)/r$  as in eq. (2),  $\mathcal{V}_R(z, \bar{Z})$  can be written explicitly as

$$\mathcal{V}_R(z, \bar{Z}) = \frac{-\sigma}{A} \sum_{j=1}^N q_j \left[ \pi v_j \text{erf}\left(\frac{v_j}{2}\right) + 2\sqrt{\pi} e^{-v_j^2/4} \right], \quad (7)$$

where  $v_j = 2|z - Z_j|/\sigma$ . However, even with this simplification the evaluation of  $\mathcal{V}_R(z, \bar{Z})$  in eq. (7) for all charges still

requires the calculation of all relative vectors in the  $z$  direction which is time costly ( $\sim O(N^2)$ ). To make the approximation useful in practice, we now show that  $\mathcal{V}_R(z, \bar{Z})$  can be accurately rewritten as a rapidly convergent expansion whose evaluation is as efficient as that of a single particle potential ( $\sim O(N)$ ). This important simplification is possible because the smoothness of  $\mathcal{V}_R(z, \bar{Z})$  allows one to obtain a rapidly convergent expansion using an orthogonal basis where only a small number of terms are needed to achieve high accuracy:

$$\mathcal{V}_R(z, \bar{Z}) = \sum_m C_m(z) T_m(\bar{Z}). \quad (8)$$

In practise, a few terms of eq. (8) related to each coordinate (not the distance between two) of the instantaneous configuration  $\bar{Z}$  are computed once for all charges. The expansion formula then yields the potentials and forces after the coefficients  $C_m(z)$  at each specific particle are determined. This expansion decouples  $z$  and  $Z_j$  to make an efficient calculation of  $\mathcal{V}_R(z, \bar{Z})$  practical ( $\sim O(N)$ ) and shares the same advantage as doing LMF theory with the exact  $\phi_R(z)$  as a static external potential<sup>6,7</sup>.

Indeed, an analytical expansion of  $\mathcal{V}_R(z, \bar{Z})$  by a Fourier series using a dimensionless parameter  $\zeta$  exists<sup>18</sup>

$$C_m(z) = \frac{\sigma \zeta}{A} \frac{e^{-(m\zeta)^2}}{(m\zeta)^2} \exp\left[i \frac{2m\zeta}{\sigma} z\right], \quad (9)$$

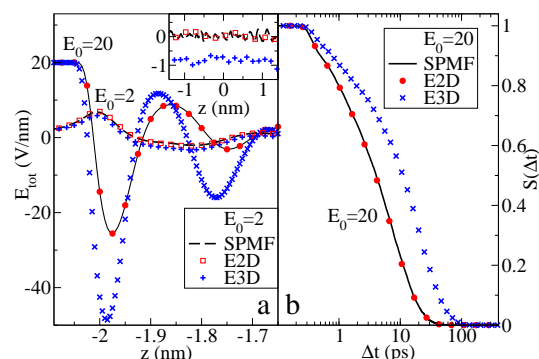
and

$$T_m(\bar{Z}) = \sum_{j=1}^N q_j \exp\left[i \frac{2m\zeta}{\sigma} Z_j\right]. \quad (10)$$

The choice of the parameter  $\zeta$  has to be related to the ratio between  $\sigma$  and  $L_z$ , the  $z$  direction length that the system spans. Further, it has been proved that the rigorous error bound of the above expression scales as  $e^{-(\pi/\zeta - L_z/\sigma)^2}$ <sup>18</sup>. For a given value of  $\zeta$ , because the coefficients of eq. (9) again decrease as the Gaussian function, contributions from terms with a large  $m$  is obviously negligible. Indeed, the most important term is the  $m = 0$  term linearly proportional to the  $z$  direction total dipole moment  $C_0(z)T_0(\bar{Z}) = z \frac{4\zeta}{A\sigma} \sum_{j=1}^N q_j Z_j - \frac{2\zeta}{A\sigma} \sum_{j=1}^N q_j Z_j^2$ . This simple first term states that when the system has a permanent dipole,  $\mathcal{V}_R(z, \bar{Z})$  persists and the proper treatment of the long-ranged component becomes more important which is consistent with the previous observations<sup>6,9,10</sup>.

This completes the presentation of the essential ideas in this mean field approach at the instantaneous level for electrostatics. The present approach using the dynamical effective field  $\mathcal{V}_R(z, \bar{Z})$  instead of its ensemble average  $\mathcal{V}_R(z) \equiv \langle \mathcal{V}_R(z, \bar{Z}) \rangle$  (see e.g. eq. 7 of ref.<sup>7</sup>) used in LMF theory thus makes fewer approximations and is more general than LMF approach because the self-consistent process to determine  $\mathcal{V}_R(z)$  in LMF theory is now done instantaneously. Moreover, it is closely related to the various Ewald2D algorithms<sup>9,17</sup>. The dynamical

effective field in eq. (7) is exactly equivalent to the singular term of the Ewald2D sum (e.g.<sup>18</sup>). Furthermore, Lindbo and Tornberg<sup>17</sup> and Pan and Hu<sup>18</sup> have recently shown that the singular term of the Ewald2D sum can be either numerically or analytically expanded to the form of eq. (8) which enables an efficient calculation. On the other hand, LMF theory suggests that when  $\sigma$  is appropriately chosen (e.g.  $\sigma \geq 0.45\text{nm}$  for water confined between walls), the long-ranged component can be replaced by the effective single-particle potential. Therefore, the present approach is a combination of the previous excellent developments toward efficient simulations of electrostatics from both the Ewald2D sum<sup>9,11,17,18</sup> and the mean field approach<sup>7</sup>. Because the symmetry-preserving approximation of eq. (5) reveals the essential physical meaning of neglecting the component of the Fourier space term of the Ewald2D sum<sup>9,11</sup>, we call the present method symmetry-preserving mean field approach (SPMF).



**Fig. 2** The internal electric fields  $E_{\text{tot}}$  and the survival probabilities  $S(\Delta t)$  for  $E_0 = 20\text{V/nm}$  (solid line, filled circle and cross) and  $E_0 = 2\text{V/nm}$  (dash line, open square and plus) from SPMF (solid or dash line), the Ewald2D method (filled circle or open square) and the Ewald3D method (cross or plus) respectively. Inset blows up the values of  $E_{\text{tot}}$  at  $E_0 = 2\text{V/nm}$  in the middle region. LMF method<sup>7</sup> works as efficient as SPMF for  $E_{\text{tot}}$  but it might be challenging to obtain  $S(\Delta t)$  using current versions of LMF.

We now numerically demonstrate the efficiency and accuracy of SPMF for extended simple point charge (SPC/E)<sup>22</sup> water confined between two hydrophobic Lennard-Jones (LJ) walls<sup>23</sup> under a strong ( $E_0 = 20\text{V/nm}$ ) or a weak electric field ( $E_0 = 2\text{V/nm}$ ). The systems are equilibrated using NVT ensemble at  $T=298\text{K}$  followed by a productive NVE simulation of 1.2ns using a relatively smaller time step  $\Delta t = 0.5\text{fs}$  to ensure the conservation of total energy. The two walls are fixed at  $z = \pm 2.25\text{nm}$ . Three types of methods, SPMF, the Ewald2D method<sup>18</sup> and the Ewald3D method with an artificial empty space of about 10nm have been used to treat the nonuniform electrostatics. SPMF is more than an order of magnitude faster than the other two methods in the present setup and in general SPMF ( $O(N)$ ) must be much more efficient than the regular

PME method ( $O(N \log N)$ ) for the electrostatics at interfaces.

As was known previously<sup>9,10</sup>, an accurate treatment of the nonuniform electrostatics becomes very important when the system responds to a strong external electric field. Indeed, Fig. 2 (a) shows that, at  $E_0 = 20\text{V/nm}$ , the total internal electric field,  $E_{\text{tot}}(z)$  defined as  $E_{\text{tot}}(z) = E_0 + \int_{-\infty}^z dz' \langle \rho_s^q(z', \bar{Z}) \rangle$  from SPMF overlaps that from the Ewald2D method but differs significantly from that from the Ewald3D method. More importantly, Fig. 2 (b) shows that the present method of SPMF reproduces the survival probability (see e.g.<sup>24,25</sup>) of the oxygen atom in the interfacial region,  $S(\Delta t) = P(z(\Delta t) < z_b | z(0) \geq z_0)$ <sup>25</sup>, where the barrier position  $z_b = 1.92\text{nm}$  and the well position  $z_0 = 2.0\text{nm}$  are determined from the local minimum and maximum of the oxygen density distribution close to the interface. This agreement for  $S(\Delta t)$  reflects the advantage of SPMF using  $\mathcal{V}_R(z, \bar{Z})$  rather than LMF using  $\langle \mathcal{V}_R(z, \bar{Z}) \rangle$ <sup>7</sup>.

To further check the validity of SPMF we compute the radial angle distribution. This depends on the distance between the oxygen atoms in two molecules and their relative orientation<sup>26</sup>  $g(r, \theta) = \frac{1}{N_c} \sum_{i \neq j}^{N_c} \langle \delta(r - r_{ij}) \delta(\theta - \theta_{ij}) \rangle$ , where  $N_c$  is the number of the oxygen atoms contained in the same interfacial region of  $z \geq z_b$ .  $g(r, \theta)$  is normalized to 1 at large distances and reduces to the usual radial distribution function in the bulk region<sup>26</sup>. The contour plot in Fig.1 of the Supplementary Information (SI) shows that SPMF works well for the correlated structural features.

Traditionally the regular Ewald3D method and its PME alternatives (e.g.<sup>8</sup>) are used for complex nonuniform electrostatics and often produce reasonable results from MD simulation. Indeed, for the weak electric field  $E_0 = 2\text{V/nm}$ , the Ewald3D method using the present conservative setup works equally well for both the survival probability and the correlated structure (see Fig.2 and Fig.3 in SI). However, other properties might be very sensitive and require a very accurate treatment of the 2D electrostatics even in the weak field case. The inset of Fig. 2 (a) shows that  $E_{\text{tot}}$  from SPMF/Ewald2D reaches a fluctuating value around but in average very slightly above zero in the bulk region while the Ewald3D method gives the corresponding result of a negative plateau value. The averaged slightly positive value explains the dielectric property of bulk water saying that the internal total electric field,  $E_{\text{tot}}$  inside water under a weak external electric field is proportional to  $E_0$  with a very small coefficient  $1/\epsilon_0$  (experimental value  $\epsilon_0 \simeq 80$  for bulk water). However, the use of the Ewald3D method violates this essential thermodynamical argument about the dielectric response in bulk water.

Obviously, the present SPMF approach shares the same advantage of the computational efficiency and speed gains as the LMF approach does<sup>7</sup>. Moreover, the analytical expression of the effective field in eqs. (8), (9) and (10) makes no difficulty in coding the simple SPMF algorithm in any leading MD simulation engines. We believe that SPMF with the advantages

inherited from LMF and with the additional merits from simplifying the Ewald2D method can be used to study a large variety of liquid systems at interfaces.

This work was supported by National Natural Science Foundation of China (grant no.91127015). I am indebted to Prof. John Weeks for helpful discussions and his suggestions for how to present this work.

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