Stochastic Poisson-Boltzmann Equation for Charged Fluids

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The classical Poisson-Boltzmann equation (CPBE), which is a mean field theory by averaging the ion fluctuation, has been widely used to study ion distributions in charged fluids. In this study, we derive a stochastic version of the Poisson-Boltzmann equation from the field theory and recover the ion fluctuation through a multiplicative noise added in the CPBE. The stochastic Poisson-Boltzmann equation (SPBE) captures the nonlinear effect of the ion fluctuation and gives different ion distributions in the charged fluids compared to the CPBE. To solve the SPBE, we have proposed a Monte Carlo method based on the Path Integral representation. Numerical results show that the nonlinear effect of the ion fluctuation strengthens the ion diffusion into the domain and intends to distribute the ions in the fluid uniformly. The final ion distribution in the fluid is determined by the competition between the ion fluctuation and the electrostatic forces exerted by the boundaries.

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**I. INTRODUCTION**

The interaction between charged fluids and charged surfaces brings many novel phenomena, such as the condensation of DNA, aggregation of polymers, and like-charge attraction. It has been understood that the mechanism behind the phenomena is the fluctuation of ion density in the charged fluids. Even though the classical Poisson-Boltzmann equation (CPBE) has been widely used to study the ion distributions in charged fluids, it is well known that the CPBE is a mean field theory which averages the ion fluctuation and erases detail of the ion fluctuation. It is shown that such averaging is not proper in describing the ion distributions and loses the nonlinear effect of the ion fluctuation. In order to catch the nonlinear effects of the ion fluctuation in the charged fluids, a theory beyond the CPBE needs to be developed. In this study, we derive a stochastic version of the Poisson-Boltzmann equation from the field theory. This stochastic Poisson-Boltzmann equation (SPBE) recovers the ion fluctuation effects by introducing a stochastic variable. Numerical solution to the SPBE via Monte Carlo gives improved results about the nonlinear ion fluctuation over CPBE.

As a powerful tool for studying the many-body systems, the field theory has been developed in the charged fluid to understand the ion fluctuations. The field theory represents the partition function of a charged fluid in the form of functional integral. With the help of the Hubbard-Strotonovich transformation, an auxiliary field is introduced in the functional integral. All the physical properties of the fluid can be obtained from those of the auxiliary field. The saddle point solution to the functional integral is exactly the CPBE, in which the imaginary part of the auxiliary field is relevant to the electrostatic potential. However, the physical meaning of the real part of the auxiliary field has not been explored in previous studies. We will show below that the real part of the auxiliary field brings a multiplicative noise term in the SPBE and it plays an important role in catching the ion fluctuations.

In order to catch the nonlinear effects of the ion fluctuations, previous studies made expansion around the saddle point solution to the functional integral. When the coupling between the charged fluid and the interface is extremely weak, a modified Poisson-Boltzmann equation has been obtained by the one-loop expansion of the functional integral. Based on the modified Poisson-Boltzmann equation, a self-consistent theory has been developed with the help of the Gibbs variation. It has been pointed out that the self-consistent theory is only valid for this weak coupling case. It has also been pointed out that such Gibbs variation is the first order level for the perturbation variation. When the coupling between the charged fluid and the interface is extremely strong, Viral expansion for the functional integral is a reasonable tool to get the fluctuation effects. Except these two extremes, no general equation or even proper expansion has been developed yet from the functional integral when the coupling is in the intermediate range.

The difficulty to get a general theory covering the whole range of the coupling lies in the fact that the ion fluctuation in the charged fluid itself have not been well described yet. Thus, we decouple the charged fluid and the charged interfaces, and focus on the ion fluctuation in the charged fluid itself. In this way, we derive the SPBE from the field theory with a noise...
term in the equation to represent the ion fluctuation. The coupling between the fluid and the interfaces is considered as boundary conditions in solving the SPBE. Such treatment for the charged fluids is general and can be applied for various cases.

II. FIELD THEORY

The field theory has been well developed for charged fluids\textsuperscript{14,16–19}. To be self-contained, we present the field theory in this section.

We consider a charged fluid confined by solid boundaries. To illustrate the field theory clearly, the fluid consists of only two ion species with opposite charges. For the positive charges, the charge value of each ion is denoted by $z_+$ and the ion number is by $N_+$. For the negative charges, they are $z_-$ and $N_-$ respectively. We also denote the elementary positive charge by $e$. Generally, the total net charge $e z_+ N_+ - e z_- N_-$ in the fluid could be nonzero and can be compensated by external charges distributed in the solid boundaries. Thus, the total net charge of the whole system including the fluid and boundaries still could be neutral. We ignore the structures of the ions and the dielectric difference between the fluid and the solid boundaries. Therefore, the steric effect and image-charge effect are not considered in our theory. The dielectric of the system is denoted by $\varepsilon$.

A. Partition function

We start from the canonical partition function of the system

$$Q = \frac{1}{N_+! N_-! \lambda_+^{N_+} \lambda_-^{N_-}} \prod_{i=1}^{N_+} d\vec{r}_i \prod_{j=1}^{N_-} d\vec{r}_j e^{-\beta H + \int d\vec{r} \bar{h}(\vec{r}) \rho(\vec{r})}. \quad (1)$$

Here, $\lambda_+$ and $\lambda_-$ are the de Broglie wavelengths for the positive charges and the negative ones respectively. $\vec{r}_i$ is the position vector of the $i$-th ion and $d\vec{r}_i$ is the infinitesimal volume for the integration. $\beta$ is the inverse temperature. In the exponent, the Coulomb energy is

$$H = \frac{e^2}{2} \int d\vec{r} d\vec{r}' \rho(\vec{r}) C(\vec{r}, \vec{r}') \rho(\vec{r}'). \quad (2)$$

It is expressed in terms of the Green function $C(\vec{r}, \vec{r}')$, which satisfies the equation $-\nabla_r \cdot [\varepsilon \nabla_r C(r, r')] = \delta(r-r')$. The ion density of the positive charges is denoted by $c_+$ and the ion density of the negative ones is by $c_-$, with $c_\pm(\vec{r}) = \sum_{i=1}^{N_\pm} \delta(\vec{r} - \vec{r}_i)$. The net charge density then can be expressed by $\epsilon \rho(\vec{r}) = e \sigma(\vec{r}) + e(z_+ c_+ - z_- c_-)(\vec{r})$ with $e(\vec{r})$ the external charge density in the solid boundaries. $\rho(\vec{r})$ is the net ion density in the fluid with the elementary positive charge for each ion. The function $h(\vec{r})$ introduced in the exponent is to generate the averaged ion density through $\langle \rho(\vec{r}) \rangle = \frac{\partial \ln Q}{\partial h(\vec{r})}|_{h=0}$.

Now we apply the Hubbard-Stratonovich transformation on the partition function $Q$ and introduce an auxiliary field $\xi$. Denoting the imaginary unit by $i$, we obtain

$$Q = \frac{1}{Z_c} \int [D\xi] e^{-\int d\vec{r} \left[ \frac{1}{2} \nabla_r \cdot [\varepsilon \nabla_r \xi(\vec{r})] + [ie\sqrt{\sigma}(\vec{r}) - h(\vec{r})] \right] + N_+ \lambda^+ + N_- \lambda^-}. \quad (3)$$

with

$$\Lambda_+ = \int d\vec{r} e^{-iz_+ [ie\sqrt{\sigma}(\vec{r}) - h(\vec{r})]}, \quad \Lambda_- = \int d\vec{r} e^{iz_- [ie\sqrt{\sigma}(\vec{r}) - h(\vec{r})]},$$

$$Z_c = \int [D\xi] e^{-\frac{1}{2} \int d\vec{r} d\vec{r}' \xi(\vec{r}) C(\vec{r}, \vec{r}') \xi(\vec{r}')}}. \quad (4)$$

We denote the chemical potential of positive charges by $\mu_+$ and the chemical potential of negative ones by $\mu_-$. The grand canonical partition function then is obtained through $\Xi = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} Q(N_+, N_-) \mu_+^{N_+} \mu_-^{N_-}$. For convenience, we use the Bjerrum length $l_B^e = \frac{e^2}{\epsilon \sigma}$ in standard units and introduce our length scale $l_B = 4\pi l_B^e$ to scale all the lengths. The Bjerrum length $l_B^e$ equals 7Å for water at room temperature. We rewrite $\vec{r}/l_B$ by $r$, $\epsilon \sqrt{\beta \sigma}$ by $\phi$ and $\sigma l_B^e$ by $\sigma$. We also define $w_+ = \mu_+ l_B^3 / \lambda_+$, $w_- = \mu_- l_B^3 / \lambda_-$. Then the grand canonical partition function $\Xi$ reads

$$\Xi = \frac{1}{Z_c} \int [D\phi] e^{\int dr [A_1(r) + A_2(r) + A_3(r) + A_4(r)]}. \quad (5)$$

with

$$A_1(r) = -\frac{1}{2} [\nabla_r \phi(\vec{r})]^2, \quad A_2 = [h(r) - i \phi(\vec{r})] \sigma, \quad A_3(r) = w_+ e^{i \phi(r)} - h(r), \quad A_4(r) = w_- e^{-i \phi(r)} - h(r). \quad (6)$$

Clearly, the partition function $\Xi$ is a functional of the auxiliary field $\phi(r)$.

B. Auxiliary field $\phi(r)$

The auxiliary field $\phi(r)$ is a complex field and can be decomposed by two real fields $\phi_R$ and $\phi_I$ as $\phi = \phi_R + i \phi_I$. The term relevant to $\phi_R$ in Eq. (6) is quadratic $-\frac{1}{2} [\nabla_r \phi_R(\vec{r})]^2$. In the functional integral Eq. (7), the quadratic term of $\phi_R$ appears in the exponent of

$$B(\phi_R) = e^{\frac{1}{2} \int dr [\nabla_r \phi_R(\vec{r})]^2}. \quad (7)$$

To show the physical meaning of $B(\phi_R)$, we take one dimension fluid as an example. We discrete $B(\phi_R)$ as

$$B(\phi_R) = e^{-\sum_n \frac{(\phi_{n+1} - \phi_n)^2}{\Lambda_n^2}}. \quad (8)$$
with $\Delta$ the width of discrete mesh. $\phi_{R,n}$ means $\phi_R(r)$ at the $n$-th discrete lattice and behaves as a Gaussian function. Compared to $\phi_R$, the term involving $\phi_I$ in $A_1$ of Eq.\ref{eq:10} takes the form $\exp\left[\sum_n \frac{(\phi_I + 1 - \phi_I) z}{2\Delta}\right]$ that is not Gaussian by lacking the minus in the exponent. Thus, $\phi_R$ instead of $\phi_I$ can be interpreted as the Gaussian white noise, which is originated from the thermal fluctuation. It will be shown later that $\phi_R$ really brings a noise term in the SPBE. Due to the Gaussian nature, $\phi_R$ takes zero at the saddle point solution to the partition function $\Xi$.

We set $\hbar = 0$ and solve the functional derivative equation $\Delta \Xi/\delta \phi = 0$ to get the saddle point solution that reads ( neglecting the $r$ variable in $\sigma$ and $\phi$ fields)

$$-\nabla^2 [i\phi] = \sigma + z_+ w_+ e^{-z_+ [i\phi]} - z_- w_- e^{-z_- [i\phi]}.$$  

(9)

In order to understand the above equation, we apply $< \rho(\vec{r}) > = \frac{\partial \ln \Xi}{\partial \phi(\vec{r})}|_{\phi=0}$ to get the ion density of the charged fluid

$$< \rho(\vec{r}) > = < \sigma + z_+ w_+ e^{-z_+ [i\phi]} - z_- w_- e^{-z_- [i\phi]} >.$$  

(10)

In the above equation, $\sigma$ is the density of ions in solid boundaries. The second term means the density of the positive-charged ions in the fluid with unit charge per ion, and the third term is the density of negative-charged ions. Thus, the right hand side of Eq.\ref{eq:10} is understood as the net ion density for one measure of the ion fluctuation. If we drop $\phi_R$ because $\phi_R = 0$ at the saddle point solution and only keep $i\phi_I$, the CPBE is recovered from Eq.\ref{eq:10}. The imaginary part $-\phi_I$ is then interpreted as the electrostatic potential.

Since $\phi_I$ and $\phi_R$ have the same dimension and $-\nabla \phi_I$ is the electrostatic force to drift ions, $\nabla \phi_R$ can be regarded as the stochastic thermal force to diffuse ions. The physical meaning of the real part $\phi_R$ of the auxiliary field has long been missing in previous research works. In the self-consistent theory, the Gaussian assumption has been applied to average the fluctuation of the auxiliary field with $\phi_R$ disappearing in the theory\textsuperscript{15,19}. Such Gaussian assumption, though widely used for quantitative treatment of the fluctuations\textsuperscript{20}, has never been verified and it veils the role of $\phi_R$. Now we uncover that $\phi_R$ is the source of the Gaussian noise.

### III. SPBE

It is observed in Eq.\ref{eq:10} that the magnitude of $\phi_R$ fluctuating in the charged fluid is small in the scale of $\Delta$. In order to derive the SPBE, we make an assumption that the thermal fluctuation in the charged fluid is very weak and brings small change of $\phi_R$ among discrete lattice sites. This assumption means that the stochastic thermal force for diffusion of ions is less than the electrostatic force on the moving ions, namely $|\nabla \phi_R| \ll |\nabla \phi_I|$. The ion distribution in the fluid mainly depends on the mean field potential, and the nonlinear thermal fluctuation only perturbs the distribution.

#### A. Equation

We set $\hbar = 0$ and substitute $\phi = \phi_R + i\phi_I$ into $A_3$ and $A_4$ of Eq.\ref{eq:10}. Thus, we have $A_3(r) = w_+ e^{-z_+ |\phi_R-\phi_I|}$ and $A_4(r) = w_- e^{-z_- |\phi_R-\phi_I|}$. Due to the small magnitude of $\phi_R$ in our assumption, $A_3$ and $A_4$ can be expanded to the second order, reading

$$A_3(r) = w_+ e^{z_+ |\phi_I|} \left(1 - z_+ i\phi_R + \frac{z_+^2}{2} |\phi_R|^2\right),$$

$$A_4(r) = w_- e^{-z_- |\phi_I|} \left(1 + z_- i\phi_R + \frac{z_-^2}{2} |\phi_R|^2\right).$$  

(11)

We substitute Eq.\ref{eq:11} in Eq.\ref{eq:10}, and rewrite $\Xi$ as

$$\Xi = \frac{1}{Z e^w} \int [D\phi_R] [D\phi_I] e^{i\int \left(T_1 + i\phi_I T_2 + \frac{1}{2} |\phi_R|^2 T_3\right)}.$$  

(12)

with

$$T_1 = \frac{1}{2} [\nabla \phi_I]^2 - \frac{1}{2} [\nabla \phi_R]^2 + \sigma \phi_I + w_+ e^{z_+ \phi_I} + w_- e^{-z_- \phi_I},$$

$$T_2 = \nabla^2 \phi_I - \sigma - z_+ w_+ e^{z_+ \phi_I} + z_- w_- e^{-z_- \phi_I},$$

$$T_3 = z_+^2 w_+ e^{z_+ \phi_I} + z_-^2 w_- e^{-z_- \phi_I}.$$  

(13)

Here, integral by parts has been applied to transform $\nabla \phi_R \cdot \nabla \phi_I$ to $-\phi_R \nabla^2 \phi_I$. Since $T_3$ is positive, it is $|\phi_R|^2 = -\phi_R^2$ on the exponent of Eq.\ref{eq:12} that guarantees the low probability of the ion fluctuation with large $\phi_R$, which is consistent to our assumption that $\phi_R$ is small for the expansion of Eq.\ref{eq:11}. We drop off the second term in $T_1$ of Eq.\ref{eq:13} by applying our assumption of $|\nabla \phi_R| \ll |\nabla \phi_I|$. In this way, only $i\phi_I T_2 + \frac{1}{2} |\phi_R|^2 T_3$ in the exponent of Eq.\ref{eq:12} is relevant to $\phi_R$.

Before we derive the SPBE, we firstly study the property of the term $i\phi_I T_2$ by dropping off the quadratic term $\frac{1}{2} |\phi_R|^2 T_3$ in the exponent. The functional integral $\int [D\phi_R] e^{i\int \phi_I T_2}$ in Eq.\ref{eq:12} leads to a functional $\delta(T_2)$. That means $\phi_I$ is governed by a differential equation $T_2 = 0$, which is exactly the mean field theory CPBE. In order to consider the nonlinear effects of the ion fluctuation, we should keep the quadratic term $\frac{1}{2} |\phi_R|^2 T_3$ in the exponent and figure out the stochasticity from the term.

We discrete the quadratic term in space by

$$e^{i\int \phi_I T_2} = e^{\sum_n \Delta x_n^+ i\phi_{R,n} + \Delta x_n^- i\phi_{N,n}}.$$  

(14)

Here, $\Delta$ is the volume of discrete mesh in 3D system, which can be reduced to be the area in 2D and the width
in 1D. \( T_{3,n} \) means the value of \( T_3 \) at the \( n \)-th lattice site, similar to the notation of \( \phi_{\,R,n} \). We introduce a variable \( \alpha \) at each lattice site and apply Hubbard-Stratonovich again to get

\[
e^{-\sum_n \frac{\Delta T_{3,n}}{2} \left[ i \phi_{\,R,n} \right]^2} = \int [D\alpha] e^{-\sum_n \alpha_n^2 e^{-\sum_n i \sqrt{\Delta T_{3,n}} \phi_{\,R,n} \alpha_n}} \tag{15}
\]

with \([D\alpha] = \prod_n \frac{d\alpha_n}{\sqrt{2\pi}}\). The partition function Eq. (12) now becomes

\[
\Xi = \frac{1}{Z_c} \int [D\phi_R][D\phi_I][D\alpha] e^{\sum_n \left[ -\frac{\alpha_n^2}{2} + \Delta T_{1,n} \right]}
\times \sum_n i \phi_{\,R,n} \left[ \sqrt{\Delta T_{3,n}} \alpha_n + \Delta T_{2,n} \right] \tag{16}
\]

The functional integral \( \int [D\phi_R] e^{\sum_n i \phi_{\,R,n} \left[ \sqrt{\Delta T_{3,n}} \alpha_n + \Delta T_{2,n} \right]} \) in the above \( \Xi \) leads to a functional \( \delta(\sqrt{\Delta T_{3,n}} \alpha_n + \Delta T_{2,n}) \) at each lattice, just like what we have done on the term \( i \phi_R \) in the last paragraph. The \( \delta \) functional means the system is governed by a equation \( \sqrt{\Delta T_{3,n}} \alpha_n + \Delta T_{2,n} = 0 \) at each lattice. We map the temporal noise in the theory of stochastic process to a spatial noise in our study by introducing a variable \( \eta_n \) to replace \( \alpha_n / \sqrt{\Delta} \) in the \( \delta \) functional. Further, we use \( \psi \) to replace \( -\phi_I \) in the equation to represent the electrostatic potential. Finally, we obtain the SPBE explicitly as

\[
- \nabla^2 \psi = \sigma + z_r \, w_+ \, e^{-z_r \, \psi} - z_- \, w_- \, e^{z_- \, \psi} - \sqrt{z_r^2 \, w_+ \, e^{-z_r \, \psi} + z_-^2 \, w_- \, e^{z_- \, \psi}} \eta. \tag{17}
\]

Here, \( \eta \) is a Gaussian noise due to the Gaussian distribution \( e^{-\frac{\alpha_n^2}{2}} \) of \( \alpha \) in Eq. (15). It is a function of position in the charged fluid with correlation \( \langle \eta(r) \eta(r') \rangle = \delta(r - r') \). Except the last term, the other part in Eq. (17) is exactly the CPBE. For the general case where the charged fluid contains various ionic species \((k = 1, 2, \ldots)\), the SPBE reads

\[
- \nabla^2 \psi = \sigma + \sum_k a_k z_k w_k e^{-a_k z_k \psi} - \sqrt{\sum_k z_k^2 w_k e^{-a_k z_k \psi}} \eta \tag{18}
\]

with \( a_k = +1 \) for positive charges and \( a_k = -1 \) for negative charges.

**B. Charge conservation**

In Eq. (18), the parameters \( w_k \) have not been determined yet. According to the CPBE, \( w_k \) should be the bulk ion density of the \( k \)-th ionic species. However, such treatment brings a problem that charges in the fluid are not conserved. The total ion number \( \int dr w_k e^{-a_k z_k \psi} \) is not always equal to the total ion number \( \int dr w_k \) in bulk.

This charge conservation problem has been pointed out in our reported work. Several methods have been proposed to guarantee the charge conservation. Here, we adopt the following method for the numerical calculation.

The charge conservation in the fluid means the total ion number must not be changed no matter what is the distribution of the ion density. We note the bulk density by \( M_k \) for the \( k \)-th ionic species. The charge conservation requires \( \int dr w_k e^{-a_k z_k \psi} = M_k \int dr \). Since \( w_k \) depends on the chemical potential that is constant in equilibrium, we have \( w_k \) as

\[
w_k = \frac{M_k}{\int dr e^{-a_k z_k \psi}}. \tag{19}
\]

The integrations are over the total computational domain.

**C. Boundary condition**

The coupling between the interface and the fluid is taken into account by the boundary condition (BC) of the SPBE. Three BCs have been used. The first BC is the Dirichlet BC, in which the electrostatic potentials are fixed at the interfaces between the fluid and the solid boundaries. Such BC is also known as \( \zeta \) potential BC in colloidal science. The second BC is the Neumann BC, in which the derivative of electrostatic potential with respect to spatial coordinate is fixed at the interfaces. The last BC is the Robin BC, which is the mixture of the Dirichlet BC and Neumann BC.

It has been observed in some experiments that the BCs at the interfaces are not fixed but depend on the experimental conditions in bulk. For example, \( \zeta \) potential or the interface charges vary when the ion densities or PH values in the fluid are changed. To treat such variation of BCs, several models have been proposed, such as the charge regulation model and the potential trap model.

In this study, for illustration purpose, we only apply the Dirichlet BC to solve our SPBE. We propose a Monte Carlo method based on path integral representation for the solving. The studies on other BCs are not in the scope of this work.

**IV. NUMERICAL CALCULATION**

The SPBE has a multiplicative noise in Eq. (15). The white noise \( \eta \) is coupled to a function of the electrostatic potential, which means any change of the electrostatic potential can be fed back to itself through the noise. To solve this equation, we propose a Path Integral Monte
Carlo (PIMC) method. It is a Monte Carlo method based on path integral representation. For clarity, we reduce our system to be one dimensional along $x$ axis. The one dimensional PIMC method described in this study can be easily extended to two dimensional or three dimensional systems.

A. Path Integral representation

We propose the PIMC for a general stochastic equation

$$-\frac{d^2\psi}{dx^2} = f(\psi) - g(\psi)\eta. \quad (20)$$

We introduce a function $K(x) = \frac{1}{2} \frac{d\omega}{dx}$ to transform the above equation to two first order differential equations

$$\frac{dK}{dx} + K^2 \frac{dg}{d\psi} + f(\psi) \frac{g(\psi)}{g(\psi)} - \eta = 0, \quad (21)$$

$$\frac{d\psi}{dx} = gK. \quad (21)$$

After such transformation, the noise term appearing in the stochastic equation is additive instead of multiplicative. We use $h(K, \psi)$ to represent $K^2 \frac{dg}{d\psi} + f(\psi) \frac{g(\psi)}{g(\psi)}$ for simple notation and note $dW$ by $dW$. Then, we discrete the first equation of Eq. (21) in Stratonovich sense as

$$K_n - K_{n-1} + \frac{(h_n + h_{n-1})\Delta}{2} = W_n - W_{n-1}. \quad (22)$$

The Jacobian determinant for the variable transformation reads

$$\frac{dW_n}{dK_n} = 1 + K_n \frac{dg_n}{d\psi_n} \Delta \cong e^{K_n \frac{dg_n}{d\psi_n} \Delta}. \quad (23)$$

Here, $\frac{dg_n}{d\psi_n}$ means the derivative of the function $g(\psi)$ with respect to $\psi$ at the $n^{th}$ lattice. The probability for one electrostatic potential path starting from $\psi_0$ at $x_0$ to $\psi_N$ at $x_N$ is

$$P(\psi_N, x_N | \psi_0, x_0)$$

$$= \int [D\psi] [DW] \delta(\psi - \psi_0) \delta(\psi - \psi_N) \delta(\frac{d\psi}{dx} - gK) e^{-f_\omega^N \frac{1}{2} \eta^2 dx}$$

$$= \int [D\psi] [DK] \delta(\psi - \psi_0) \delta(\psi - \psi_N) \delta(\frac{d\psi}{dx} - gK) e^{f dx(K \frac{d\psi}{dx} - \psi \frac{d\psi}{dx} + K^2 \frac{dg}{d\psi} \frac{d\psi}{dx} + \frac{1}{4} (\frac{dg}{d\psi})^2)}. \quad (24)$$

Here, $[DW] = \prod_n \frac{dW_n}{2\sqrt{\pi}\Delta}$, $[D\psi] = \prod_n d\psi_n$ and $[DK] = \prod_n \frac{dK_n}{2\sqrt{\pi}\Delta}$. The action in the path integral is represented by $L$ as

$$L = \int dx \{ K \frac{d\psi}{dx} - \frac{1}{2} \left( \frac{dK}{dx} + K^2 \frac{dg}{d\psi} \frac{d\psi}{dx} \right) + f(\psi) \frac{g(\psi)}{g(\psi)} \}, \quad (25)$$

which will be used for the Metropolis algorithm later.

B. PIMC

For our reduced one-dimensional fluid, the two interfaces are set at $x = 0$ and $x = b$ respectively. The charged fluid is confined in $0 < x < b$. For illustration, the charged fluid contains only one ionic species and the ions are positive. For the fluid, we have $\sigma = 0$ in Eq. (18). Considering the charge conservation Eq. (19), we express the SPBE in an explicit form according to Eq. (18). It reads

$$-\frac{d^2\psi}{dx^2} = zBMe^{-2\psi} - \theta \sqrt{\frac{2bMe^{-2\psi}}{dx^2}} \eta. \quad (26)$$

In this equation, the charge is always conserved for the solution. Comparing to Eq. (20), we have $f(\psi) = \frac{zBMe^{-2\psi}}{dx^2}$ and $g(\psi) = \theta \sqrt{\frac{2bMe^{-2\psi}}{dx^2}}$. A parameter $\theta$ is introduced in $g(\psi)$ to control the intensity of noise. $\theta = 0$ is for the CPBE while $\theta = 1$ is for the SPBE. Practically, we will take $\theta = 0.01$ instead of $\theta = 0$ for the CPBE in the numerical study.

We discrete the computational domain from $x = 0$ to $x = b$ by $N$ slices. The discrete lattice sites are indexed from 0 to $N$. The 0-th and the N-th lattice sites are fixed at the boundaries and have their potentials of $\psi_0$ and $\psi_N$, respectively. Before sampling the paths, we need to initialize the potential path for the start. It does not matter which potential path is used for the initialization. The Markovian process of noise will lose its memory in the sampling.

We denote the old potential path by $\psi^{old}$ and the new one by $\psi^{new}$. In the sampling, for site $n$ we generate $\psi^{new}$ on this site by $\psi^{new}_n = \psi^{old}_n + \Delta \psi(2\omega - 1)$. Here, $\Delta \psi$ is the step magnitude for the moving of $\psi$ and $\omega$ is a random number with uniform distribution in the range $[0, 1]$. Now the new path $\psi^{new}$ is generated from $\psi^{old}$ by replacing $\psi^{old}$ with $\psi^{new}$ and keeping $\psi^{old}$ intact. Similarly, we can sample numerous $K$ paths for the calculation. However, the accept ratio of the new $K$ paths is governed by the factor $\eta^2 = \frac{1}{2} \left( \frac{dg}{d\psi} \frac{d\psi}{dx} + K^2 + (\frac{dg}{d\psi})^2 \right)$. That means the new $K$ paths can be accepted only if they satisfy $K = \frac{1}{2} \frac{dg}{d\psi}$. Otherwise, they will be rejected. Therefore, we can get the new $K$ path directly from $\psi^{new}$ through the second equation in Eq. (21).

After obtaining the new path $\psi^{new}$, we make the integration of $\int dx e^{-z\psi^{new}}$ over the system as the denominator in Eq. (26). In this way, the functions $f(\psi^{new})$ and $g(\psi^{new})$ in Eq. (20) are updated. This step is very important for the charge conservation respecting each new path. By using the new functions $\psi$, $K$, $f$ and $g$, we calculate the action $L^{new}$ according to Eq. (26).

Since the random numbers generated for $\psi$ are uniform, the detailed balance requires that the accept ratio...
for the new path is

$$A_r = e^{L_{new}} / e^{L_{old}}. \quad (27)$$

Then Metropolis algorithm is applied for the accept ratio. If $A_r > 1$ is true, the new path $\psi_{new}$ is accepted. If not, generate a random number $A_q$ in the range of $[0,1]$ uniformly. If $A_r > A_q$ is true, accept the new path. If not again, the new path is rejected and the old path must be restored.

In practice, the PIMC runs from the 1st lattice to the $(N - 1)^{th}$ lattice. And then return to the 1st lattice again for many cycles. After reaching the equilibrium, the paths then are used for statistical calculations.

V. RESULTS AND DISCUSSIONS

In this section, we will compare the results from CPBE and SPBE. In our SPBE, the electrostatic potential has been renormalized by $1/\beta$ which is $26\text{meV}$ at room temperature. All the lengths have been scaled by $l_B$, which is $88\text{Å}$ for water at room temperature. As mentioned above, Eq. (26) is used in this study with $\vartheta = 0.01$ for the CPBE and $\vartheta = 1$ for the SPBE.

We take $M = 0.04$ and $z = 1$, which corresponds to $1 \times 10^{-4}\text{mol/L}$ of electrolyte and the Debye length of such system is $5l_B$. The length $b$ of the charged fluid is set to be 20 and the potentials at boundaries are set to be $\psi_0 = -2$ and $\psi_N = 0$ respectively. We present the electrostatic potentials in Fig.1(a). For the CPBE, the potential goes up from $\psi_0 = -2$ at $x = 0$ to $\psi_N = 0$ at $x = b$ as a continuous convex function. However, the SPBE shows that the potential goes up from $\psi_0 = -2$ as a convex function and then behaves as a concave function before reaching $\psi_N = 0$. There exists a segment in the SPBE curve to transit the convex function to the concave function. The existence of the transition segment is the feature of the nonlinear effects of the ion fluctuation that has been captured by the SPBE, and is to distinguish the SPBE from the CPBE. The transition segment is in the domain instead of close to the interfaces and the potential gradient is small in the segment compared to the large potential gradient close to the interfaces.

In Fig.1(b), we present the ion density $<\rho> = <\frac{e^{\beta \psi + i - i}}{\beta d\psi}>$. It shows that the positive charges of both the CPBE and the SPBE concentrate close to the interface at $x = 0$ due to the negative potential $\psi_0$ and then decay with $x$ up to the interface at $x = b$. But we can find detailed differences between the CPBE and SPBE. In the CPBE result, the ion density decays in the same manner as a continuous concave function. However, in the SPBE curve the ion density experiences a transition from a concave function to a convex function. Compared to the CPBE result, the SPBE result has a low ion density at the interface $x = 0$ but a high density in the center of domain. The two curves cross at the Debye length $5l_B$.

The ion distribution is determined by the competition between the ion fluctuation and the electrostatic force applied by the interfaces. The ion fluctuation increases the entropy of the system and intends to disperse the ions uniformly in the whole domain. Eventually, the dispersion of the ions into the domain is balanced by the electrostatic force provided by the boundaries, forming the final ion distribution. In the CPBE, the ion fluctuation is averaged as the mean field effect balanced by the electrostatic force. Such averaging misses the nonlinear effect of the ion fluctuation. The multiplicative noise in the SPBE Eq. (26) has captured the nonlinear effect of the ion fluctuation around the mean field solution. Such nonlinear effect strengthens the dispersion of ions into...
When the domain to increase the entropy of the whole system are dispersed away from the interfaces and enter into the domain. Similar to the conclusion of Fig. 1, the ions density close to the interfaces but increases it in the interface at the potential drop attracts more ions close to the interfaces. It is expected that the increasing electrostatic force is exerted by the potential drop over the nonlinear ion fluctuation and no transition segment could be observed in the curve, meaning that the nonlinear effect of the ion fluctuation is strengthened. Fig. 2(b) is an overview of the ion density for various \( \vartheta \). For clarity, we plot the data of Fig. 2(b) in Fig. 2(c) and Fig. 2(d) with different ranges. It is shown in the figures that the increasing of \( \vartheta \) decreases the ions density close to the interfaces but increases it in the domain. Similar to the conclusion of Fig. 1, the ions are dispersed away from the interfaces and enter into the domain to increase the entropy of the whole system when \( \vartheta \) increases to enhance the nonlinear effects of the ion fluctuation.

As discussed above, the ion distribution is determined by the competition between the ion fluctuation and the electrostatic force applied by the interfaces. In our BC, the electrostatic force is exerted by the potential drop between interfaces. It is expected that the increasing of the potential drop attracts more ions close to the interface at \( x = 0 \) and weakens the nonlinear effects of the ion fluctuation dispersing ions into the bulk as well. This scenario is confirmed by Fig. 3. We fix \( M = 0.04 \), \( z = 1 \) and \( \psi_N = 0 \) in this SPBE calculation, but vary \( \psi_0 \) to change the potential drop on the charged fluid. For comparison, we normalize all the potential data into the same plot range, shown in Fig. 3(a). After the normalization, the three curves have the same start point of \( \psi_0 = -2 \). It shows that the curve of \( \psi_0 = -10 \) behaves different to the other two curves and no such transition segment could be observed in the curve, meaning that the nonlinear effect of the ion fluctuation has been suppressed by the high potential drop. Such phenomena has also been reflected in the ion density shown in Fig. 3(b). Since the ion densities close to the interfaces have different scales for the three curves, we plot the main part of the data in Fig. 3(b) for comparison. Results show that the high potential drop of \( \psi_0 = -10 \) really attracts more ions close to the interface and less ion density could be found in the domain for \( \psi_0 = -10 \) than the other two cases. In this way, the high potential drop of \( \psi_0 = -10 \) dominates over the nonlinear ion fluctuation and no transition segment could be found in the ion density curve.

Finally, we study the effect of the ion bulk density

FIG. 2. Solutions to Eq. (26) by varying \( \vartheta \). Nonlinear effect of the ion fluctuation is enhanced with the increasing of the intensity of the multiplicative noise which is controlled by \( \vartheta \). (a) Electrostatic potentials. (b) Overview of the ion densities with various \( \vartheta \), which are replotted in (c) and (d) with different ranges for clarity.
$M$ on the ion fluctuation by the SPBE equation. We set the potential drop as $\psi_0 = -2$ and $\psi_N = 0$, and vary $M$. $z = 1$ is still fixed. When the ion bulk density in the system increases, the probability for the ions to interact with each other is enhanced. Therefore, it is easier for the ions to distribute in the system uniformly with the larger $M$. This point is revealed in Fig. 4. In the Fig. 4(a), the largest ion bulk density $M = 0.1$ has the smallest potential gradient at the transition segment in the three cases, showing that the ions distribute much more uniformly in the domain for the larger ion bulk density. Fig. 4(b) is for the distribution of the ion density. We have scaled the data in the same plot range for comparison. It shows in Fig. 4(b) that the increasing of the ion bulk density strengthens the nonlinear ion fluctuation and weakens the electrostatic force as well. Thus, the nonlinear effect of higher ion bulk density leads to a much more uniform distribution of ions in the higher ion density case, such as in the case of $M = 0.1$.

VI. CONCLUSION

In the charged fluid, the ion distribution is determined by the competition between the ion fluctuation and the electrostatic force applied by the boundaries. The CPBE has been applied to study the ion distribution. It averages the ion fluctuation, and misses the nonlinear effects of the ion fluctuation, which is not enough to describe the ion distribution precisely. Based on the field theory, we have derived the SPBE with a multiplicative noise added into the CPBE. The multiplicative noise captures the nonlinear effect of the ion fluctuation. To solve the SPBE, we have proposed a Path Integral Monte Carlo method to sample the potential paths.

Results show that the nonlinear ion fluctuation strengthens the dispersion of ions away from the interfaces into the domain to increase the entropy of the charged fluid. The increasing of the electrostatic force by the boundaries enhances the attraction of ions to the interfaces and weakens the nonlinear effect of the ion fluctuation.

FIG. 3. Influence of the potential drop on the charged fluid. $\psi_N = 0$ is fixed while $\psi_0$ is varied to get various potential drops. (a) The electrostatic potentials with various potential drops are scaled in the same plot range for comparison. (b) Ion densities.

FIG. 4. Influence of the ion bulk density $M$ on the charged fluid. (a) Electrostatic potentials. (b) Ion densities with various $M$ are scaled in the same plot range for comparison.
fluctuation. On the other side, the increasing of the ion bulk density enhances the nonlinear ion fluctuation and weakens the electrostatic forces by the boundaries.

The SPBE obtained in this work is independent on the coupling between the charged fluid and interfaces, and focuses on the ion fluctuation of the charged fluid itself. The coupling is taken into account in the solution as the boundary conditions. Thus, this SPBE is general and can be applied to various cases. As we have mentioned, the steric effect is missing in the SPBE. For the charged fluid with a high ion density, we need to implement the steric effect in the equation to capture the proper effect of the ion fluctuation. This issue is still under our research.

Footnotes:

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