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Ion distributions within a microdroplet without surface charge: Fluctuation-correlation effects

Yu-Jane Sheng[1] and Heng-Kwong Tsao[2,*]
[1]*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106, Republic of China*
[2]*Department of Chemical and Materials Engineering, National Central University, Chung-li, Taiwan 320, Republic of China*

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The mean-field approach like the Poisson-Boltzmann theory predicts a trivial result that ions from a symmetric electrolyte are uniformly distributed within an aqueous microdroplet without surface charge. However, the phenomenon of an increase in surface tension due to salt addition indicates ion depletion near the air-water interface. It was believed that electrical polarization associated with dielectric differences is responsible for salt depletion. Using Monte Carlo simulations with the restrictive primitive model and Poisson equation, a depletion zone near the water-oil interface is observed. Nevertheless, without any polarization, ion depletion can still be attained near a hard interface and was theoretically predicted by the Debye-Hückel theory [Phys. Rev. E **60**, 3174 (1999)]. The nonuniform ion distribution is caused by the fluctuation-correlation effect with broken symmetry, which is furnished by the boundary.

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Aqueous microdroplets immersed in a nonpolar solvent, such as emulsions and microemulsions, have attracted much attention in recent years. The stable microdroplet is enclosed by a surfactant shell and its size ranges from a few nanometers to about one hundred. The ability of microdroplets to host nanosized particle find applications in diverse fields, for instance, materials development and biotechnology [1]. The phenomenon that a water-in-oil microemulsion displays significant electric conductivity indicates that there are ions within the aqueous core. Counterions exist due to dissociation of the ionic surfactant shell. For microdroplets surrounded by a nonionic surfactant, ions comes from added salt.

The ion distribution inside a microdroplet is often investigated through the mean-field theory like Poisson-Boltzmann (PB) equation. The counterion distribution within an aqueous droplet can be estimated, at least qualitatively, by the PB theory [2]. For a uniform surface charge density, the counterion distribution is solely determined by counterions themselves. Since the repulsions among counterions dominate, most of the counterions are expelled to the boundary of the spherical cavity. Although dielectric discontinuity does not play any role due to spherical symmetry at the mean-field level, ion fluctuations do destroy the symmetry and induce electric polarization [3]. Nevertheless, the mean-field theory predicts leading order behavior of counterion distribution.

When both coions and counterions, coming from a symmetry electrolyte, exist in the aqueous core enclosed by nonionic surfactants, the distributions of ions seems to be a trivial question at the mean-field level. Due to symmetry, the average ion distributions for coions and counterions should be the same everywhere, i.e., $\langle c_+\rangle = \langle c_-\rangle$. The $\langle \cdots \rangle$ notation denotes an ensemble average. As a result, the mean local charge density should be zero, $\langle \rho\rangle = (\langle c_+\rangle - \langle c_-\rangle)e = 0$. Here e is a fundamental charge. According to the Poisson equation, the mean electrostatic potential is thus zero everywhere, $\langle \psi\rangle = 0$. Since the electrostatic internal energy at the mean-field level is zero, $U_{el} = \frac{1}{2}\int_V \langle \rho\rangle\langle \psi\rangle dV = 0$, one would expect that the free energy of the equilibrium system is determined by the entropy. A maximum entropy is resulted if ion distributions are uniform. The aforementioned conclusion does not employ any relation between the mean local charge density and the mean electric potential.

Alternatively, one can adopt the PB approach, in which the ions are assumed to follow the Boltzmann distribution with the potential of mean force equal to the mean local electric potential. The effects of ion fluctuations and position correlation are not taken into account. Moreover, ions are treated as pointlike particles. Since the surface charge density of the microdroplet is zero, the trivial solution $\langle \psi\rangle = 0$ is resulted. Uniform ion distributions are thus obtained by the Boltzmann distribution. This conclusion agrees with that of the preceding paragraph. It is expected because the extremum of the Hamiltonian with respect to $\langle \psi\rangle$ and $\langle c_i\rangle$ leads to the PB equation [4]. In fact, the saddle point of the density functional theory [5] and exact field-theoretic formulation [6] turns out to be equivalent to the PB theory. Corrections to the mean-field theory must consider ion fluctuations and correlation.

In contrast to surfactant solutions, it has been known that the surface tension of an aqueous inorganic salt solution tends to increase with increasing concentration [7,8]. According to the Gibbs-Duhem (GD) equation and criterion of thermodynamic stability, an increase in surface tension requires a negative adsorption. In other words, a deficiency of electrolyte is indicated near the air-water interface despite the mean-field prediction of uniform ion distributions. Wagner in 1924 believed that electric polarization of the air-water interface induces an effective surface charge. Since the electrostatic ‘‘image’’ force is repulsive, ions are repelled from the interface [8]. On the basis of the reversible work theorem [9], the ion distribution is related to the potential of mean force, which is approximated by the electric potential established by the image charge corresponding to a fixed ion. The screening effect in the electrolyte solution can be accounted for by using the linearized PB equation. Extended by Onsager and Samaras (OS), explicit formulas were obtained and

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*Email address: hktsao@cc.ncu.edu.tw

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accounted reasonably well for the observed surface tension at low electrolyte concentrations. Recently, following the same scheme, Levin considered the finite size effect near the interface and employed a canonical calculation. The agreement between the analytical result and experiment can be extending to relatively high concentrations [8]. Nonetheless, this method is not self-consistent.

In this Letter we intend to examine ion distributions of a 1-1 electrolyte within a spherical drop based on Monte Carlo simulations. For an unbounded domain, which involves bulk electrolytes, long-range interactions and dielectric mismatch cause difficulties in performing the calculations. On the other hand, the ions distributed within an aqueous sphere bounded by low dielectric materials could provide an ideal example for the study of the effects of polarization, ion fluctuations, and correlation.

The interior of the droplet is modeled as a spherical cavity of radius R with N_+ coions and N_- counterions. The surface of the cavity is assumed to be smooth with a uniform charge density $\sigma=(N_- - N_+)/4\pi R^2$. We resort to a restricted primitive model that is simple but captures the main features of an electrolyte solution. The solvent is represented by a continuum medium of uniform dielectric constant $\epsilon_{r,i}$ (≈ 80) surrounded by an oil medium with $\epsilon_{r,o}$ (≈ 2). The ions are represented as hard spheres of diameter a ($\approx 0.2-0.4$ nm). The charge of the ion is located at the center of the hard sphere and each of the ions is made up of a material with the same dielectric constant as the solvent. These charges locate at positions $\{\mathbf{x}_j\}$ with charges $\{q_j\}$, where $j=1,\ldots,(N_- + N_+)$. The space charge distribution is related to the electric potential by the Poisson equation subject to the condition that the electric potential and its normal derivative are continuous across the interface,

$$\nabla\cdot[\epsilon_r(\mathbf{r})\epsilon_0\nabla\psi(\mathbf{r})]=-\sum_{j=1}^{N_- + N_+} q_j\delta(\mathbf{r}-\mathbf{x}_j), \qquad (1)$$

where ϵ_0 is the permittivity of a vacuum. The electric potential inside the droplet produced by the surface charge is constant, $\sigma R/\epsilon_0\epsilon_{r,o}$, and is irrelevant in determining the ion distribution. Because of the linearity associated with Eq. (1), the electric potential is simply the sum of those caused by each ion. The solution of Eq. (1) due to the ion j at $\mathbf{x}_j$ inside a dielectric sphere can be expressed analytically, $\psi_j(\mathbf{r})=(q_j/4\pi\epsilon_{r,i}\epsilon_0)(1/|\mathbf{r}-\mathbf{x}_j|)+\psi_j'(\mathbf{r};(\epsilon_{r,o}/\epsilon_{r,i}))$ [3,10]. Here $\psi_j'(\mathbf{r})$ denotes the image contribution due to dielectric differences.

The equilibrium configuration are obtained by Monte Carlo simulations according to the standard Metropolis method [11]. The electrostatic internal energy is calculated with the help of solving the Poisson equation. When the ion p moves from $\mathbf{x}_p^o$ to $\mathbf{x}_p^n$, the internal energy change of the system is given by $\Delta U_{el}=U_{el}^n-U_{el}^o=q_p[\Psi(\mathbf{x}_p^n)-\Psi(\mathbf{x}_p^o)]+q_p[\psi_p'(\mathbf{x}_p^n)-\psi_p'(\mathbf{x}_p^o)]$ with $\Psi(\mathbf{x}_j)=\Sigma_{k\neq j}\psi_k(\mathbf{x}_j)$. The term in the second bracket in ΔU_{el} calculations designates electric polarization acting on the ion p itself. It is missing in Ref. [3] but does not affect their conclusion. The domain in the present system is finite and the correction to the Coulomb interaction is correctly treated by accounting for the polarization effect. In the simulation, the infinite series of Legendre polynomials are truncated after the first 50 terms.

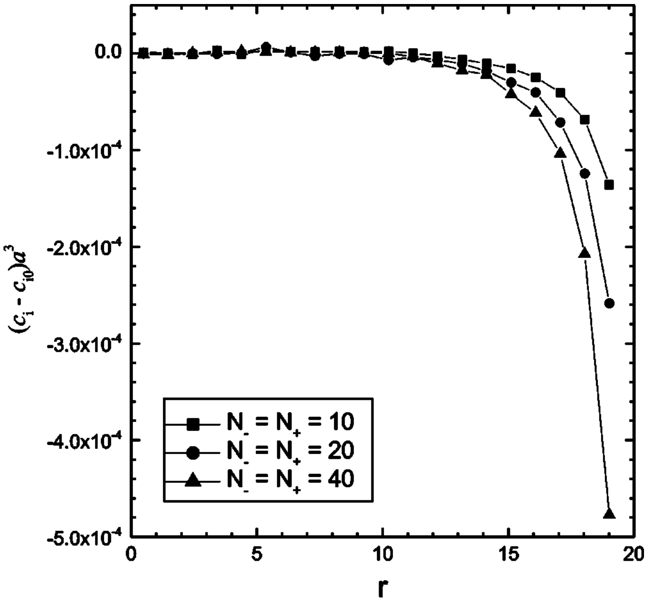

FIG. 1. The variation of ion concentrations with radial position for three salt concentrations with $R=20a$ and $\epsilon_{r,o}/\epsilon_{r,i}=0.025$. The concentrations in the center are $c_{i,0}a^3=3.60\times10^{-4}$, 7.15×10^{-4}, and 1.41×10^{-3}, respectively. Here $a=0.4$ nm.

Figure 1 demonstrates the variation of ion concentrations with radial position for three salt concentrations, $N_+=N_-=10$, 20, and 40. The surface charge density is $\sigma=0$ and the radius of the microdroplet is $R=20a$ for $\epsilon_{r,o}/\epsilon_{r,i}=0.025$. The diameter of ions is $a=0.4$ nm. The concentration profile is relative to the ion concentration at the center, $(c_i-c_{i0})a^3<0$. This consequence confirms that the distribution of ions from a symmetric salt is inhomogeneous inside the droplet with an electroneutral surface. Moreover, it exhibits the depletion of salt near the interface, which becomes more significant with increasing the salt concentration. Note that rescaling the volume fraction difference by the volume fraction in the center cannot collapse three salt distributions into a single profile. This result is consistent with experimental observations of surface tension increment with increasing concentration ($d\gamma/dc>0$). Furthermore, based on GD equation, we calculate $d\gamma/dc=1.43$ dyn/(cm·M) for $N_\pm=10$, which agrees quite well with the experimental data and OS limiting law, 1.75. Evidently, the mean-field theory fails to predict this phenomenon. However, is electric polarization the necessary condition for nonuniform ion distributions, as suggested by Wagner?

The effect of the polarization can be turned off by eliminating dielectric differences. As shown in Fig. 2(a), a depletion of ions near the boundary can still be attained for $\epsilon_{r,o}=\epsilon_{r,i}$ with $R=10a$. Since the boundary is purely a hard wall, it proves that electric polarization is not a necessary condition for inhomogeneous distributions. The depletion zone is roughly in the region $7a\lesssim r\leqslant 9.5a$, which can be differentiated from the ion-free region unmistakably. Although a dense fluid of hard spheres displays a certain struc-

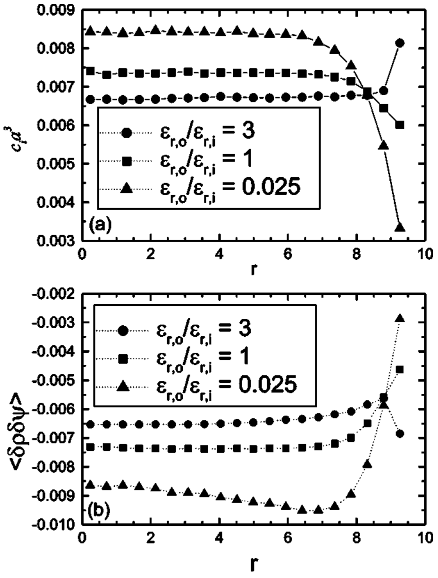

FIG. 2. (a) The variation of ion concentrations with radial position for three ratios of dielectric constants with $R=10a$ and $N_+=N_-=25$. Here $a=0.2$ nm. (b) The variation of dimensionless internal energy density, $\langle \delta\rho\,\delta\psi\rangle$, with radial position.

ture near the hard interface, it is not the case here because of low volume fraction of ions, i.e., $c_{\pm}a^3 \ll 1$. As Coulomb interactions between ions are turned off, a uniform distribution is obtained in our simulations. An additional evidence, which can strengthen this conclusion, is the distribution of pseudoion pairs, which interact with each other through a short-range square-well potential with the depth $\varepsilon_{++}=\varepsilon_{--}=-\varepsilon_{+-}<0$. Again, a depletion of pseudoions near the hard interface can be clearly observed. Consequently, the depletion of ions does not necessarily originate from interactions between the ions and the interface.

Despite the failure to obtain depletion of ions, the mean-field theory does give a correct result of the mean electric potential, $\langle \psi\rangle = 0$, as shown in Fig. 3(a). Moreover, in accordance with the Poisson equation, $\langle c_+\rangle = \langle c_-\rangle$. Nevertheless, the standard deviation of the electric potential, $\langle \psi^2\rangle^{1/2}$, is $O(kT)$ large. The contribution associated with ion fluctuations often gives the next order correction to the mean-field outcome. The substantial electric potential fluctuation in the present condition implies that it dominates over the mean-field result, which is a saddle point. Therefore, one has to look for the explanation of nonuniformity beyond the mean-field theory, i.e., the fluctuation-correlation effect. Since an inhomogeneous ion distribution represents a decrease in entropy, the equilibrium distribution corresponding to the free energy minimum requires a decrease in the internal energy due to ion fluctuation correlation. In other words, one must have $U_{el}=\frac{1}{2}\int_V \langle(\delta\rho)(\delta\psi)\rangle d\mathbf{r}^3<0$, where δx stands for the fluctuation from the mean $\langle x\rangle$. Figure 2(b) shows the variation of $\langle(\delta\rho)(\delta\psi)\rangle$, scaled by kT/a^3, with radial position. As anticipated, the two fluctuation quantities are negatively correlated. Since the electric potential is related to positions of ions, this consequence can be attributed to the fluctuation-correlation effect.

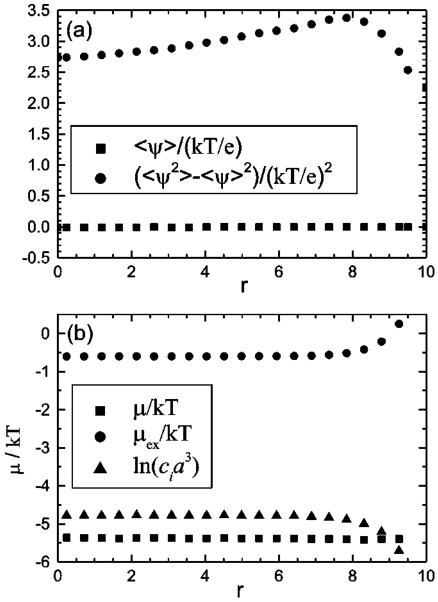

FIG. 3. (a) The variation of the dimensionless electric potential and its variance with radial position. (b) The variation of chemical potential with radial position for $\epsilon_{r,o}/\epsilon_{r,i}=0.025$ with $R=10a$ and $N_+=N_-=25$. Here $a=0.2$ nm.

In addition to ion fluctuations and correlation, the necessary condition for nonuniform distributions also require broken symmetry, which can be furnished by an interface. For a cavity containing *one* species only, the effect of the hard interface on the distribution is apparent even in the dilute limit. Near the interface, the depletion of the particle is observed for an attractive potential. On the contrary, the surface excess of the particle is attained for a repulsive potential. These results are obtained in our simulations for a square-well potential and can be explained by a similar concept associated with surface tension. The surface tension arises from the differences between the environment around a molecule in the bulk and near the interface. The broken symmetry in the vicinity of the interface causes unbalance forces acting on a molecule. It gives rise to an effective interaction between the particle and hard surface, which can be easily determined from the interparticle potential. In the present case of ion pairs, it is not clear whether the effective interaction is attractive or not, according to Coulomb interactions. Nevertheless, the interface does lead to broken symmetry of the screening effect.

It should be emphasized that at the mean-field level, the polarization effect does not come into play due to either zero local mean charge density or spherical symmetry. Within the PB scheme, a broken symmetry of geometry can bring in the polarization contribution for the case of counterions only but not for salt solutions. As a consequence, for the latter, the manifestation of the polarization effect near the boundary must be introduced by virtue of ion fluctuations. In fact, a counterion and a coion cannot occupy the same location at the same time. Therefore, electric polarization always plays a significant role even though the mean local charge density is zero at the mean-field level. As demonstrated in Fig. 2(a), for the same salt concentration, electric polarization couples considerably with the fluctuation-correlation effects. As

$\epsilon_{r,o}/\epsilon_{r,i}=3$, a surface excess of ions is obtained. For a microdroplet containing both salt and counterions dissociated from the charged surface, the ion distributions become asymmetric, as predicted by the PB theory. However, one can observe a peak near the interface due to polarization. This cannot be obtained from the mean-field theory and will vanish for large enough value of $(N_-+N_+)/R$ (small Debye length).

In this study, the volume fraction of ions are small and the point ion assumption seems valid. When fluctuations are included, nevertheless, hard-core interactions have to be included to prevent counterion and coion collapse. This makes theoretical approaches much more complicated. In Wagner's approach, ion fluctuations are circumvented and the polarization force is induced by the insertion of a fixed charge. It is somewhat similar to the Widom's method for calculating the chemical potential, which is simply the reversible work needed to add such an ion to the electrolyte solution [12],

$$\frac{\mu}{kT}=\ln c_{\pm}+\frac{\mu_{ex}}{kT}=\ln\left[\frac{c_{\pm}(\mathbf{r})}{\langle\exp(-\Delta U_{el}(\mathbf{r})/kT)\rangle}\right]=\text{const.} \tag{2}$$

As shown in Fig. 3(b), in our simulations, the total chemical potential μ is essentially constant everywhere while the excess chemical potential μ_{ex} reflects ion distributions near the interface. In Widom's method, a ''ghost'' charge is randomly inserted to evaluate the potential of mean force but the test particle does not disturb the system at all. However, the ionic atmosphere in the vicinity of the fixed charge is polarized in Wagner's approach.

Recently, a Debye-Hückel (DH) theory that neglects the nonlinear effects is generalized to planar interfacial geometries [13]. The formulation goes beyond the mean-field (PB) approach and accounts for fluctuations and correlations on a Gaussian level. As $\epsilon_{r,o}=\epsilon_{r,i}$, the potential of mean force at contact is repulsive and reads $(\ell_B\kappa/3)kT$. Here ℓ_B denotes the Bjerrum length and κ^{-1} the Debye length. Under the condition in Fig. 2(a), i.e., $c_{i0}=1.53$ *M*, DH predicts a substantial depletion and the ratio of surface to bulk concentration is 0.38. Nevertheless, a weak depletion (0.82) is obtained in our simulation. Since the salt concentration is high, the effects of finite size and nonlinearity may come into play.

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