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Electrostatic interaction between two aqueous microdroplets in an apolar medium

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In an apolar medium, the electrostatic interactions between two aqueous microdroplets coated with surfactants are investigated by the mean-field theory. The electric field and ion distributions within the aqueous core are described by the Poisson-Boltzmann equation. Under Debye-Hückel approximation, the interaction energy is obtained analytically. Due to the polarization effect, the Coulomb interaction is altered by the induced multipoles in the aqueous droplet. The interaction, however, is insensitive to the ion concentration. In comparison with the Coulomb interaction, the repulsion for a pair of similarly charged droplets is reduced and the attraction for a pair of oppositely charged droplets is enhanced. More importantly, the interaction between a neutral and charged droplets is attractive. The effect of interdroplet interactions on the collision frequency is also discussed.

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I. INTRODUCTION

Microdroplets exist ubiquitously in emulsions and microemulsions. Although emulsions are kinetically stable, microemulsions are thermodynamically stable dispersions. A water-in-oil (w/o) microemulsion consists of water droplets in a continuous oil medium, stabilized by a film of amphiphiles at the droplet interface. These droplets, sometimes also called swollen reversed micelles, are approximately spherical with their diameters in the range 1–50 nm. An increasing number of scientific and technological applications are found for microemulsions, such as manufacturing nanosized particles and biocatalysis synthetic reactions in organic solvents [1–6].

The microdroplets in w/o microemulsions with ionic surfactant contain strong electrolytes, such as counterions dissociated from the surfactant shells and added inorganic salt. These ions are confined in the aqueous cores because of the low dielectric constant of the oil medium, ca. 2. To reduce the positive electrostatic free energy associated with forming a net charge in a dielectric medium, which is similar to the Born energy, one would expect that the microdroplet is electroneutral by balancing the net charge of ionic surfactant shell with that of the ions within the aqueous core. However, experimental evidences show that the exchange of materials between microdroplets can take place through collisions with temporarily merging or formation of water channels [7–9]. Since a microdroplet carries $O(10^2)$ surfactant ions and counterions, the entropic penalty of precisely matching these two large numbers is significant and comparable to the electrostatic energy. Consequently, a substantial fraction of the microdroplets acquires charges owing to the fluctuating exchange of surfactant ions at the droplet interface and the oppositely charged counterions in the aqueous interior. It has been found that the electric conductivity of w/o microemulsions, which is equivalent to that of dilute electrolyte solutions, can be explained by the migration of charged microdroplets in the applied electric field [10–12].

The w/o microemulsion can exhibit a rich variety of physical behaviors, such as clustering and percolation. The formation of various microstructures is eventually governed by the interdroplet interactions. For instance, it is generally believed that the sharp increase in electrical conductivity (over orders of magnitude), characterized as a percolation phenomenon, is associated with the formation of droplet clusters due to attractive interactions [13,14]. Besides the short-range interactions, such as the overlap of the surfactant tail region, the electrostatic interaction may also play an essential role for microstructural transformations and enhanced collisions between microdroplets. Though a microdroplet possesses no more than a few elementary charges, the resulting electric field is only weakly screened by the surrounding apolar medium. As a result, the interactions between two charged droplets can display long-range Coulomb forces. In addition, there are induced interactions between charged and neutral droplets due to the polarization of the aqueous core.

While the properties of w/o microemulsions are extensively studied by numerous experimental methods, little is known about the interdroplet interactions. The microdroplets in microemulsions are often considered as a macrofluid. The theoretical approaches developed for simple fluids are then adopted to evaluate the structure factor for various empirical models of interdroplet interactions [13,15,16]. Following this analogy, Halle and Björling [17] regarded the w/o microemulsion as a macroelectrolyte mixture based on a restricted primitive model. Then they adopted the Coulomb interactions for the interaction potential with the bulk solvent permittivity being replaced by an effective-medium permittivity. Luzar and Bratko [18] calculated the electrostatic interactions between two neutral microdroplets by means of Monte Carlo simulation. The effects of ion-ion correlations are investigated while the dielectric discontinuity is not taken into account. The correlated fluctuations in the distribution of mobile ions within electroneutral droplets give rise to attractive dispersion forces between adjacent microdroplets, which

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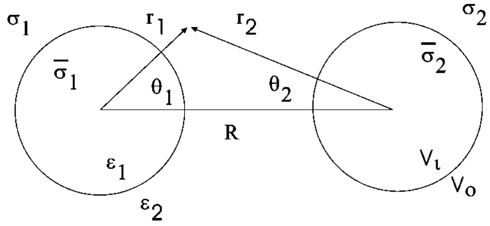

FIG. 1. Coordinate system for the electrostatic interactions between two aqueous microdroplets immersed in an apolar medium.

are of comparable magnitude to the classical van der Waals interactions.

In this paper the electrostatic interactions between two microdroplets are investigated by the mean-field theory. Since there are no mobile charges in the apolar phase, the electrostatic potential must satisfy the Laplace equation. Within the microdroplet, the distribution of mobile ions can be described by the sophisticated statistical mechanical theories such as the integral equations (e.g., MSA and HNC) and molecular simulations. However, the Poisson-Boltzmann (PB) equation, despite its drawbacks (such as finite ion size effects), is possibly the simplest model in depicting the ion distribution and the electric field inside a sphere [19]. The results are often accurate at low enough ion concentrations [20,21]. The nonlinear nature of the PB equation, nevertheless, renders the problem analytically intractable except for simplest geometries. Thus, the solution is usually displayed in a numerical form. Lack of analytical expressions makes it strenuous to analyze the systems from every possible aspect in an orderly manner. In the present work, we adopt the Debye-Hückel approximation, which leads to a linearized PB equation. When the electrostatic potential is low enough, the linearized PB equation should be adequate to describe the electric field within the aqueous core. We expect that the linearized PB equation can provide us with the detailed insight into the electrostatic interactions of this system and reveal important features of the problem.

The paper is organized as follows. In Sec. II the governing equations and boundary conditions for two microdroplet interactions are introduced. Two fundamental problems are considered in Sec. III, including cases of common and difference charge densities. The analytical solutions of electric potentials inside and outside the microdroplet are obtained. The electrostatic free energy and interaction energy are then calculated in Sec. IV. Finally, the induced interactions between neutral and charged microdroplets and the effects of interdroplet interactions on the collision frequency are discussed.

II. FORMULATION

Consider two aqueous droplets with dielectric constant ε_1 immersed in an oil environment with dielectric constant ε_2, as shown in Fig. 1. The center-to-center separation between the two spherical droplets is R. The surface of the droplet k $(k=1,2)$ carries charges with density σ_k and there are mobile ions enclosed in the droplet of radius a. These ions are dissociated either from the surface or the added electrolytes. Without charges in the oil phase, the electric potential ϕ_o satisfies the Laplace equation

$$\nabla^2\phi_o=0 \quad \text{for} \;\; r_1>a \;\; \text{and} \;\; r_2>a. \tag{1}$$

Within the aqueous core, by assuming the ions follow the Boltzmann distribution, one has

$$n_\pm(\mathbf{r})=n_\pm^0\exp\left\{-\frac{z_\pm e}{k_BT}[\phi_i(\mathbf{r})-C_k]\right\}, \tag{2}$$

where $n_\pm$ and $z_\pm$ are the concentrations and valency of the positive and negative ions, respectively. $n_\pm^0$ are the reference concentrations corresponding to the electric potential inside the droplet $\phi_i=C_k$. k_B stands for the Boltzmann constant, T for the absolute temperature, and e for the fundamental charge, 1.6×10^{-19} C. Since the zero potential is chosen at infinity, the reference potential associated with the droplet k, C_k, must be dependent upon the interparticle distance R.

The electric potential inside the droplet ϕ_i can then be determined by the PB equation,

$$\nabla^2\phi_i=-\frac{\rho(\mathbf{r})}{\varepsilon_1\varepsilon_0} \quad \text{for} \;\; r_1\leqslant a \;\; \text{or} \;\; r_2\leqslant a, \tag{3}$$

with

$$\rho(\mathbf{r})=(n_+z_++n_-z_-)e, \tag{4}$$

where ε_0 is the permittivity of a vacuum. Under the Debye-Hückel approximation, Eq. (3) can be simplified as

$$\nabla^2\phi_i=\kappa_k^2(\phi_i-C_k-\lambda_k) \quad \text{for} \;\; k=1,2, \tag{5}$$

where

$$\kappa_k^2=\frac{(n_+^0z_+^2+n_-^0z_-^2)e^2}{\varepsilon_1\varepsilon_0k_BT} \tag{6}$$

and

$$\lambda_k=\frac{n_+^0z_++n_-^0z_-}{n_+^0z_+^2+n_-^0z_-^2}\,\frac{k_BT}{e}. \tag{7}$$

The Debye-Hückel parameter κ_k^2 and λ_k (or $n_\pm^0$) can be decided by the total positive and negative ions within the droplet k. For the case of counterions only, $\lambda_k=k_BT/z_ce$, where z_c is the valency of counterions.

The governing equations (1) and (5) are subject to the following conditions:

$$\phi_o=\phi_i \quad \text{at} \;\; r_k=a, \tag{8}$$

$$\varepsilon_1\varepsilon_0\boldsymbol{\nabla}\phi_i\cdot\mathbf{n}_i+\varepsilon_2\varepsilon_0\boldsymbol{\nabla}\phi_o\cdot\mathbf{n}_o=-\sigma_k \quad \text{at} \;\; r_k=a, \tag{9}$$

$$\phi_o\rightarrow0 \quad \text{at} \;\; r_k\rightarrow\infty, \tag{10}$$

$$\phi_i \;\; \text{is finite} \quad \text{at} \;\; r_k=0, \tag{11}$$

and

$$\varepsilon_1\varepsilon_0\int_{A_k}\nabla\phi_i\cdot\mathbf{n}_i dA_k=-4\pi a^2\overline{\sigma_k}\quad\text{for}\quad k=1,2,\qquad(12)$$

where $\mathbf{n}_i$ ($\mathbf{n}_o$) is the inwardly (outwardly) directed normal vector. The first two boundary conditions (8) and (9) express that the electric potential and its normal derivative are continuous across the oil-water boundary. The third condition (10) comes from choosing the origin of the potential to be at infinity. The last condition (12) represents the total mobile charges within the droplet k, $-4\pi a^2\overline{\sigma_k}$. Note that we express the total number of mobile ions within a droplet in terms of an area charge density $\overline{\sigma_k}$. When $\overline{\sigma_k}=\sigma_k$, the droplet is electroneutral. However, it is not necessary that $\overline{\sigma_k}$ equals σ_k because the droplet can possess net charges.

The fact that the total numbers of positive (or negative) ions in the droplet 1 can differ from those in droplet 2 leads to different values of κ^2 in the linearized PB equation (3). This would complicate the analysis. In this study, for simplicity, we assume $\kappa_1=\kappa_2=\kappa$ ($\lambda_1=\lambda_2=\lambda$) and then the problem is always represented by two fundamental problems, which can be resolved analytically.

III. TWO FUNDAMENTAL PROBLEMS

For two spherical droplets of the same radius, the charges associated with the droplet k can be characterized by the two area charge densities, σ_k and $\overline{\sigma_k}$. To simplify the analysis, we express the area charge densities of the droplets in terms of common charge density σ_c ($\overline{\sigma_c}$) and the difference charge density σ_d ($\overline{\sigma_d}$),

$$\sigma_c=\frac{1}{2}(\sigma_1+\sigma_2),\quad \overline{\sigma_c}=\frac{1}{2}(\overline{\sigma_1}+\overline{\sigma_2})\qquad(13)$$

and

$$\sigma_d=\frac{1}{2}(\sigma_1-\sigma_2),\quad \overline{\sigma_d}=\frac{1}{2}(\overline{\sigma_1}-\overline{\sigma_2}).\qquad(14)$$

Since the Laplace equation, the linearized PB equation, and the boundary conditions are all linear, now we have two fundamental problems. The first case is two droplets of the same area charge densities, σ_c and $\overline{\sigma_c}$, and the second one is two droplets possessing oppositely charged area densities, i.e., $\pm(\sigma_d,\overline{\sigma_d})$. The electric potentials driven by the common and difference charge densities can be evaluated independently and then superimposed to give the electric potential of the system. In other words, solutions to the case of common charge density ($\sigma_1=\sigma_2$) and the case of difference charge density ($\sigma_1=-\sigma_2$) are to be used to construct the solution for two microdroplets of arbitrary charges.

A. Common charge density ($\boldsymbol{\sigma_1=\sigma_2=\sigma_c}$, $\boldsymbol{\overline{\sigma_1}=\overline{\sigma_2}=\overline{\sigma_c}}$)

The Laplace equation can be solved in spherical coordinates by the method of separation of variables. Since the electric potential decreases to zero at large distances from the droplet, only the decaying harmonics are retained: one based on the (r_1, θ_1) coordinate system and the other on (r_2, θ_2), as defined in Fig. 1. Owing to the azimuthal symmetry and using the method of twin spherical harmonic expansions, the solution of the Laplace equation (1) for ϕ_o is given by

$$\phi_o=\sum_{n=0}^{\infty} f_n\left[\left(\frac{a}{r_1}\right)^{n+1}P_n(\cos\theta_1)+\left(\frac{a}{r_2}\right)^{n+1}P_n(\cos\theta_2)\right].\qquad(15)$$

Since the potential distributions around both droplets are identical, only one set of the coefficients f_n is necessary. To apply the boundary condition at the surface of either droplet to determine the coefficients f_n, we transform one of the multipole expansions into the other set of spherical coordinates through an addition theorem of Legendre functions derived by Hobson [22],

$$\left(\frac{1}{r_k}\right)^{n+1}P_n(\cos\theta_k)=\left(\frac{1}{R}\right)^{n+1}\sum_{q=0}^{\infty}\binom{n+q}{q}\times\left(\frac{r_{3-k}}{R}\right)^{q}P_q(\cos\theta_{3-k})\quad\text{for}\quad r_{3-k}<R.\qquad(16)$$

The general solution of the linearized PB equation for ϕ_i can be expressed in terms of the modified spherical Bessel function of the first and third kind. Inside the spheres the potential must be finite at $r=0$ and thus the general form reduces to

$$\phi_i(r_k,\theta_k)=\sum_{n=0}^{\infty}a_n i_n(\kappa r_k)P_n(\cos\theta_k)+C+\lambda,\qquad(17)$$

where $i_n(x)$ is related to the modified Bessel function of half integer order $I_{n+1/2}(x)$ by $i_n(x)=\sqrt{(\pi/2x)}I_{n+1/2}(x)$.

Using Eqs. (15)–(17), a system of linear equations for $\{f_n, a_n, C\}$ is obtained from Eqs. (8)–(12) according to the orthogonality property associated with the Legendre polynomials. First of all, the coefficient a_0 is determined by the boundary condition (12),

$$a_0=\frac{\overline{\sigma_c}}{\kappa\varepsilon_1\varepsilon_0 i_0'(\kappa a)},\qquad(18)$$

where $i_n'(x)$ means the derivative $d[i_n(x)]/dx$. The rest of the coefficients can be found by applying the boundary conditions (8) and (9),

$$a_n i_n(\kappa a)+(C+\lambda)\delta_{n0}=f_n+\sum_{m=0}^{\infty} f_m\binom{m+n}{n}\left(\frac{a}{R}\right)^{m+n+1},\qquad(19)$$

and

$$a_n i_n'(\kappa a)=\frac{\varepsilon_2}{\kappa a\varepsilon_1}\left[-(n+1)f_n+n\sum_{m=0}^{\infty}f_m\binom{m+n}{n}\times\left(\frac{a}{R}\right)^{m+n+1}\right]+\frac{\sigma_c}{\kappa\varepsilon_1\varepsilon_0}\delta_{n0}, \tag{20}$$

where $\delta_{nm}=1$ for $n=m$, $\delta_{nm}=0$ otherwise.

Apparently, the electric potential and hence the coefficients vary with the separation R. When $R\to\infty$, the above result reduces to that associated with an isolated droplet,

$$f_0^*=\frac{\Delta\sigma_c a}{\varepsilon_2\varepsilon_0},\quad C^*=\frac{\Delta\sigma_c a}{\varepsilon_2\varepsilon_0}-\frac{\overline{\sigma_c}}{\kappa\varepsilon_1\varepsilon_0}\frac{i_0(\kappa a)}{i_0'(\kappa a)}-\lambda \tag{21}$$

and

$$f_n^*=a_n^*=0\quad\text{for } n\geqslant 1. \tag{22}$$

where $\Delta\sigma_c=\sigma_c-\overline{\sigma_c}$. For a neutral droplet, $\Delta\sigma_c=0$. This result can serve as a leading order solution and is denoted by a superscript "*."

For a finite separation R, Eqs. (19) and (20) can also be solved analytically by the iteration method. Let a_n, f_n, and C be expressed in terms of an infinite series,

$$a_n=\sum_{i=0}^{\infty}a_n^{(i)},\quad f_n=\sum_{i=0}^{\infty}f_n^{(i)},\quad\text{and } C=\sum_{i=0}^{\infty}C^{(i)}. \tag{23}$$

The leading terms $a_n^{(0)}$, $f_n^{(0)}$, and $C^{(0)}$ can be easily chosen as those associated with an isolated droplet, which are independent of R. That is,

$$a_n^{(0)}=a_n^*,\quad f_n^{(0)}=f_n^*,\quad\text{and } C^{(0)}=C^*. \tag{24}$$

Substituting Eq. (24) into Eqs. (19) and (20) and using Eq. (24) yields the following recurrence relations for $k\geqslant 1$:

$$a_n^{(k)}i_n(\kappa a)+C^{(k)}\delta_{n0}=f_n^{(k)}+\sum_{m=0}^{\infty}f_m^{(k-1)}\binom{n+m}{n}\left(\frac{a}{R}\right)^{m+n+1} \tag{25}$$

and

$$a_n^{(k)}i_n'(\kappa a)=\frac{\varepsilon_2}{\kappa a\varepsilon_1}\left[-(n+1)f_n^{(k)}+n\sum_{m=0}^{\infty}f_m^{(k-1)}\binom{n+m}{n}\times\left(\frac{a}{R}\right)^{m+n+1}\right]. \tag{26}$$

According to Eqs. (18) and (26), one has

$$a_0^{(k)}=0\quad\text{and}\quad f_0^{(k)}=0\quad\text{for } k\geqslant 1. \tag{27}$$

The solutions for $f_n^{(k)}$ and $C^{(k)}$ are then given by

$$f_n^{(1)}=-\Theta_n\left(\kappa a;\frac{\varepsilon_2}{\varepsilon_1}\right)f_0^{(0)}\left(\frac{a}{R}\right)^{n+1},\quad n\geqslant 1, \tag{28}$$

$$f_n^{(k)}=-\Theta_n\left(\kappa a;\frac{\varepsilon_2}{\varepsilon_1}\right)\sum_{m=1}^{\infty}f_m^{(k-1)}\binom{n+m}{n}\left(\frac{a}{R}\right)^{n+m+1}\quad\text{for } k\geqslant 2, \tag{29}$$

and

$$C^{(k)}=\sum_{m=0}^{\infty}f_m^{(k-1)}\left(\frac{a}{R}\right)^{m+1},\quad\text{for } k\geqslant 1, \tag{30}$$

where

$$\Theta_n\left(\kappa a;\frac{\varepsilon_2}{\varepsilon_1}\right)=\left[1-\frac{\varepsilon_2}{\varepsilon_1}\frac{n}{\kappa a}\frac{i_n(\kappa a)}{i_n'(\kappa a)}\right]\Big/\left[1+\frac{\varepsilon_2}{\varepsilon_1}\frac{n+1}{\kappa a}\frac{i_n(\kappa a)}{i_n'(\kappa a)}\right]. \tag{31}$$

Note that $-1<\Theta_n<1$. For $\varepsilon_2\ll\varepsilon_1$, Θ_1 is essentially 1.

B. Difference charge density ($\sigma_1=-\sigma_2=\sigma_d$, $\overline{\sigma_1}=-\overline{\sigma_2}=\overline{\sigma_d}$)

For the case of difference charge density, the electric potentials around both droplets are identical but opposite in sign due to antisymmetry. The solution of the Laplace equation can be expressed as

$$\phi_o=\sum_{n=0}^{\infty}g_n\left[\left(\frac{a}{r_1}\right)^{n+1}P_n(\cos\theta_1)-\left(\frac{a}{r_2}\right)^{n+1}P_n(\cos\theta_2)\right], \tag{32}$$

where only one set of the coefficients g_n is used.

Like Eq. (17), the general solution of the linearized PB equation is given by

$$\phi_i^{(k)}(r_k,\theta_k)=(-1)^{k-1}\left[\sum_{n=0}^{\infty}b_n i_n(\kappa r_k)\times P_n(\cos\theta_k)+D+\lambda\right]\quad\text{for } k=1,2. \tag{33}$$

Utilizing Eqs. (32) and (33), a system of linear equations for the coefficients $\{g_n, b_n, D\}$ is obtained from Eqs. (8)–(12). With Eq. (12), the coefficient b_0 is readily decided,

$$b_0=\frac{\overline{\sigma_d}}{\kappa\varepsilon_1\varepsilon_0 i_0'(\kappa a)}. \tag{34}$$

The remainder of the coefficients will then be obtained by substituting Eqs. (32) and (33) into Eqs. (8) and (9),

$$b_n i_n(\kappa a)+(D+\lambda)\delta_{n0}=g_n-\sum_{m=0}^{\infty}g_m\binom{m+n}{n}\left(\frac{a}{R}\right)^{n+m+1}, \tag{35}$$

and

$$b_n i_n'(\kappa a)=\frac{\varepsilon_2}{\kappa a \varepsilon_1}\left[-(n+1)g_n-n\sum_{m=0}^{\infty} g_m\binom{m+n}{n}\times\left(\frac{a}{R}\right)^{m+n+1}\right]+\frac{\sigma_d}{\kappa\varepsilon_1\varepsilon_0}\delta_{n0}. \tag{36}$$

When $R\rightarrow\infty$, the results for the isolated droplet 1 are recovered,

$$g_0^*=\frac{\Delta\sigma_d a}{\varepsilon_2\varepsilon_0},\quad D^*=\frac{\Delta\sigma_d a}{\varepsilon_2\varepsilon_0}-\frac{\overline{\sigma}_d}{\kappa\varepsilon_1\varepsilon_0}\frac{i_0(\kappa a)}{i_0'(\kappa a)}-\lambda \tag{37}$$

and

$$g_n^*=b_n^*=0 \quad \text{for} \quad n\geqslant 1, \tag{38}$$

where $\Delta\sigma_d=\sigma_d-\overline{\sigma}_d$.

Again, b_n, g_n, and D can be expressed in terms of infinite series,

$$b_n=\sum_{i=0}^{\infty} b_n^{(i)},\quad g_n=\sum_{i=0}^{\infty} g_n^{(i)},\quad \text{and} \quad D=\sum_{i=0}^{\infty} D^{(i)}. \tag{39}$$

The leading terms $b_n^{(0)}$, $g_n^{(0)}$, and $D^{(0)}$ are selected as those for an isolated droplet,

$$b_n^{(0)}=b_n^*,\quad g_n^{(0)}=g_n^*,\quad \text{and} \quad D^{(0)}=D^*. \tag{40}$$

Inserting Eq. (39) into Eqs. (35) and (36) gives the following recurrence relations for $k\geqslant 1$:

$$b_n^{(k)} i_n(\kappa a)+D^{(k)}\delta_{n0}=g_n^{(k)}-\sum_{m=0}^{\infty} g_m^{(k-1)}\binom{n+m}{n}\left(\frac{a}{R}\right)^{m+n+1} \tag{41}$$

and

$$b_n^{(k)} i_n'(\kappa a)=\frac{\varepsilon_2}{\kappa a\varepsilon_1}\left[-(n+1)g_n^{(k)}-n\sum_{m=0}^{\infty} g_m^{(k-1)}\binom{n+m}{n}\times\left(\frac{a}{R}\right)^{m+n+1}\right]. \tag{42}$$

From Eqs. (34) and (42), one obtains

$$b_0^{(k)}=0 \quad \text{and} \quad g_0^{(k)}=0 \quad \text{for} \quad k\geqslant 1. \tag{43}$$

The final results for $g_n^{(k)}$ and $D^{(k)}$ can then be written as

$$g_n^{(1)}=\Theta_n\left(\kappa a;\frac{\varepsilon_2}{\varepsilon_1}\right)g_0^{(0)}\left(\frac{a}{R}\right)^{n+1},\quad n\geqslant 1, \tag{44}$$

$$g_n^{(k)}=\Theta_n\left(\kappa a;\frac{\varepsilon_2}{\varepsilon_1}\right)\sum_{m=1}^{\infty} g_m^{(k-1)}\binom{n+m}{n}\left(\frac{a}{R}\right)^{n+m+1} \quad \text{for} \quad k\geqslant 2, \tag{45}$$

and

$$D^{(k)}=-\sum_{m=0}^{\infty} g_m^{(k-1)}\left(\frac{a}{R}\right)^{m+1} \quad \text{for} \quad k\geqslant 1. \tag{46}$$

We have solved two fundamental problems, Eqs. (15) and (17) for common charge density and Eqs. (32) and (33) for difference charge density. The coefficients are obtained analytically in Eq. (23) for the former and in Eq. (39) for the latter. For the arbitrary charge pairs, σ_1 ($\overline{\sigma_1}$) and σ_2 ($\overline{\sigma_2}$), one can readily prove that the governing equations and boundary conditions are satisfied by the linear superposition of the solutions of the common charge pair with $\sigma_c=(\sigma_1+\sigma_2)/2$ and the difference charge pair with $\sigma_d=(\sigma_1-\sigma_2)/2$. Note that the reference potential inside the droplet k, C_k, as defined in Eq. (2), is related to the reference potentials associated with two fundamental problems by $C_1=C+D$ and $C_2=C-D$.

IV. INTERNAL ENERGY

The electrostatic free energy F_{el} of the present system is evaluated by combining the electrostatic internal energy U_{el} and the entropy associated with mobile ions, $-TS_{el}$. The electrostatic energy contribution is

$$U_{el}=\int_{V_i}\rho\phi_i d\mathbf{r}^3+\int_A\sigma\phi d\mathbf{r}^2-\frac{\varepsilon_1\varepsilon_0}{2}\int_{V_i}|\boldsymbol{\nabla}\phi_i|^2 d\mathbf{r}^3-\frac{\varepsilon_2\varepsilon_0}{2}\int_{V_o}|\boldsymbol{\nabla}\phi_o|^2 d\mathbf{r}^3, \tag{47}$$

and the entropy contribution is given by

$$-TS_{el}=k_BT\int_{V_i}[n_+(\ln n_+-1)+n_-(\ln n_--1)]d\mathbf{r}^3. \tag{48}$$

The last two terms in U_{el} represent the self-energy of the electric field in the aqueous phase V_i and the oil phase V_o, respectively.

Using the divergence theorem and Eq. (9), the internal energy becomes

$$U_{el}=\frac{1}{2}\int_{V_i}\rho\phi_i d\mathbf{r}^3+\frac{1}{2}\int_A\sigma\phi d\mathbf{r}^2. \tag{49}$$

Substituting the Boltzmann distribution (2) into Eq. (48) for n_i, the entropy is expressed as

$$\begin{aligned}-TS_{el}&=-\sum_{k=1}^{2}\sum_{j=\pm}\left[\int_{V_{i,k}} n_j z_j e(\phi_i-C_k)d\mathbf{r}^3\right]+\text{const},\\&=\sum_{k=1}^{2}\left[C_k\int_{V_{i,k}}\rho d\mathbf{r}^3-\int_{V_i}\rho\phi_i d\mathbf{r}^3\right]+\text{const},\end{aligned} \tag{50}$$

where the constant denotes the terms independent of the separation R. The combination of Eqs. (49) and (50) yields the total free energy

$$F_{el}(R)=\frac{1}{2}\int_A \sigma\phi d\mathbf{r}^2-\frac{1}{2}\int_{V_i}\rho\phi_i d\mathbf{r}^3+\sum_{k=1}^{2} C_k(R)\times\int_{V_{i,k}}\rho d\mathbf{r}^3+\text{const.} \tag{51}$$

Equation (51) is derived without making the assumption of linearization of the Boltzmann distribution. The integrations in Eq. (51) can be carried out analytically under the Debye-Hückel approximation. To be consistent with the linearized PB equation (3), we consider the leading order contributions and discard higher order terms of $e\phi/k_BT$. Due to the orthogonality property associated with the Legendre polynomials, only the P_0 mode in $\phi_i^{(k)}$ gives contributions to the free energy. That is, the coefficients a_0 and C are required for the case of common charge density and b_0 and D for difference charge density. As a consequence, the total free energy of common charge density case becomes

$$\frac{F_{el}(R)}{k_BT}=\sum_{k=1}^{2}\left[\frac{1}{2}(4\pi a^2\sigma_k)+\frac{1}{2}\left(\int_{V_i}\rho_k d\mathbf{r}^3\right)\right]\frac{C(R)}{k_BT}+O\left(\frac{e\phi}{k_BT}\right)^2+\text{const.} \tag{52}$$

For the case of difference charge density, we have

$$\frac{F_{el}(R)}{k_BT}=\sum_{k=1}^{2}(-1)^{k-1}\left[\frac{1}{2}(4\pi a^2\sigma_k)+\frac{1}{2}\left(\int_{V_i}\rho_k d\mathbf{r}^3\right)\right]\frac{D(R)}{k_BT}+O\left(\frac{e\phi}{k_BT}\right)^2+\text{const.} \tag{53}$$

The interaction energy $W(R)$ is defined as the difference between the free energy F_{el} of the droplets at separation R and infinity,

$$W(R)=F_{el}(R)-F_{el}(\infty). \tag{54}$$

Since the interaction energy is related to the separation-dependent terms, one has

$$W_c(R)=4\pi a^2\Delta\sigma_c[C(R)-C^{(0)}], \tag{55}$$

for common charge density and

$$W_d(R)=4\pi a^2\Delta\sigma_d[D(R)-D^{(0)}], \tag{56}$$

for difference charge density. For the droplet k with net charge densities $\Delta\sigma_k=\sigma_k-\overline{\sigma_k}$, the two-droplet interaction energy can be expressed as

$$\begin{aligned}W(R)&=2\pi a^2\{\Delta\sigma_1[C_1(R)-C_1^{(0)}]+\Delta\sigma_2[C_2(R)-C_2^{(0)}]\}\\&=4\pi a^2\{\Delta\sigma_c[C(R)-C^{(0)}]+\Delta\sigma_d[D(R)-D^{(0)}]\},\end{aligned} \tag{57}$$

where $\Delta\sigma_c=(\Delta\sigma_1+\Delta\sigma_2)/2$ and $\Delta\sigma_d=(\Delta\sigma_1-\Delta\sigma_2)/2$. The linear superposition principle is still valid since only the linear terms are kept in the interaction energy calculation. The above result indicates that there are no interactions between two neutral droplets from the viewpoint of mean-field theory.

The dependence of the interaction energy on the separation is shown through the reference potentials C and D. According to Eqs. (27)–(30) and Eqs. (43)–(46), the potentials C and D are expanded in terms of infinite series of (a/R),

$$\begin{aligned}C(R)-C^{(0)}=f_0^{(0)}\Bigg\{&\left(\frac{a}{R}\right)-\Theta_1\left(\frac{a}{R}\right)^4-\Theta_2\left(\frac{a}{R}\right)^6+2\Theta_1^2\left(\frac{a}{R}\right)^7\\&-\Theta_3\left(\frac{a}{R}\right)^8+6\Theta_1\Theta_2\left(\frac{a}{R}\right)^9-(\Theta_4+4\Theta_1^3)\\&\times\left(\frac{a}{R}\right)^{10}+O\left(\frac{a}{R}\right)^{11}\Bigg\}\end{aligned} \tag{58}$$

and

$$\begin{aligned}D(R)-D^{(0)}=g_0^{(0)}\Bigg\{&-\left(\frac{a}{R}\right)-\Theta_1\left(\frac{a}{R}\right)^4-\Theta_2\left(\frac{a}{R}\right)^6-2\Theta_1^2\left(\frac{a}{R}\right)^7\\&-\Theta_3\left(\frac{a}{R}\right)^8-6\Theta_1\Theta_2\left(\frac{a}{R}\right)^9-(\Theta_4+4\Theta_1^3)\\&\times\left(\frac{a}{R}\right)^{10}+O\left(\frac{a}{R}\right)^{11}\Bigg\}.\end{aligned} \tag{59}$$

V. RESULTS AND DISCUSSION

The electrostatic interaction between two aqueous microdroplets immersed in an oil medium is investigated. Two fundamental problems, including two spherical droplets of common and difference charge densities, are considered. Under the Debye-Hückel approximation, the ion distributions inside the droplets and the electric field are evaluated analytically. The interaction energy can then be obtained based on the free energy calculations.

In spite of the fact that linearization of the PB (LPB) equation is a necessary step to make the problem analytically tractable, the validity of the Debye-Hückel (DH) approximation in the present study can be justified as follows. When the electric potential is small compared to the thermal energy, $e\phi/k_BT\ll 1$, the DH assumption (LPB) is an accurate approximation to the full PB equation. With a small amount of ionic additives such as salt and ionic surfactant, the microdroplets formed by nonionic surfactants such as C_iE_j possess low electrical conductivity and also show percolation phenomena [23]. These systems are not highly charged and certainly LPB can be applied.

When $e\phi/k_BT\sim 1$, LPB can also be valid. As discussed in Ref. [24] for the counterion distribution within a microdroplet, a comparison of the surface potential obtained from PB with that from LPB shows that LPB is valid if the dimensionless surface charge density $\Lambda=\sigma ea/(\varepsilon_1\varepsilon_0 k_BT)<10$. Here σ is the surface charge density and related to the number of counterions. This condition can be satisfied by a microdroplet of radius $a=2.8$ nm with 20 counterions, $\Lambda \sim 5.1$ (AOT w/o microemulsion) [18,25]. Addition of salt can increase the upper limit of Λ furthermore and therefore the validity range of the DH approximation. For highly charged systems for which Λ is as large as 20, we have performed Monte Carlo simulations based on a primitive model and the Poisson equation recently. The results show that the DH approximation can give a quite reasonable estimation of the polarizability, which is responsible for the induction interaction as will be shown in Eq. (65).

The formulation in the present work is, indeed, the inverse problem of two particles of low dielectric constant in an aqueous solution [26]. The potential is set to zero at infinity and thus the reference concentrations $n_\pm^0$ in the Boltzmann distribution, Eq. (2), are determined afterwards,

$$\int_{V_1} n_\pm^0 \left[1-\frac{z_\pm e(\phi_i - C)}{kT}\right] d\mathbf{r}^3 = N_\pm , \tag{60}$$

where $N_\pm$ is the total number of positive and negative ions inside the droplet, respectively. The reference concentrations are independent of the interdroplet distance and essentially the average concentrations within the droplet, i.e., $n_\pm^0 = N_\pm / V_1$. In the present work, we assume the Debye-Hückel parameters are the same for both droplets. This approximation is reasonable as long as $|\kappa_1 - \kappa_2| \ll \kappa_1$. When $\kappa_1 \neq \kappa_2$, one still can obtain the interaction by solving the linear equations of a_n and f_n, e.g., Eqs. (19) and (20), for both droplets numerically.

The electrostatic interactions between two aqueous microdroplets with mobile ions inside, immersed in a low dielectric solvent, are obtained in Eqs. (55) and (58) for common charge density and in Eqs. (56) and (59) for difference charge density. This interaction energy is similar to the intermolecular interactions involving the polarization of molecules. The leading term is simply the Coulomb interaction, $(4\pi a^2 \Delta\sigma)^2/(4\pi\varepsilon_2\varepsilon_0 R)$. The second term represents the charge-induced dipole interaction with Θ_1 being related to the polarizability, $-[(4\pi a^2\Delta\sigma)^2\Theta_1 a^3]/(4\pi\varepsilon_2\varepsilon_0 R^4)$. It will be explained later in detail.

The polarization due to the existence of net charge leads to extra contributions to the interaction energy in addition to the Coulomb interaction. The induction interaction for common charge density is given as $(4\pi a^2\Delta\sigma_c)^2/(4\pi\varepsilon_2\varepsilon_0 a)C_{ind}^*$ with $C_{ind}^* = [C - C^{(0)} - C^{(1)}]/f_0^{(0)}$. The dimensionless induced interaction energy C_{ind}^* against the interparticle distance is plotted in Fig. 2(a) at $\kappa a = 1$. The approximate solution by keeping terms up to $(a/R)^{10}$ in Eq. (58) agrees quite well with the exact solution, Eq. (30). Similarly, Fig. 2(b) shows the variation of the dimensionless induction interaction, $D_{ind}^* = [D - D^{(0)} - D^{(1)}]/g_0^{(0)}$, with R for difference charge density at $\kappa a = 1$. The deviation of the approximate solution, Eq. (59), from the exact solution, Eq. (46), becomes significant when two droplets are near contact. Both $C^{(1)}$ and $D^{(1)}$ denote the Coulomb contributions. The induced interactions are essentially attractive for both cases and the energy associated with difference charge density is larger than that associated with common charge density. The differences between the two fundamental cases can be illustrated by comparing the two approximate solutions. The two cases have opposite signs in the terms with odd powers, such as $\Theta_1^2(a/R)^7$, which reflects the polarization at the droplet 1 due to the induced charge at the droplet 2.

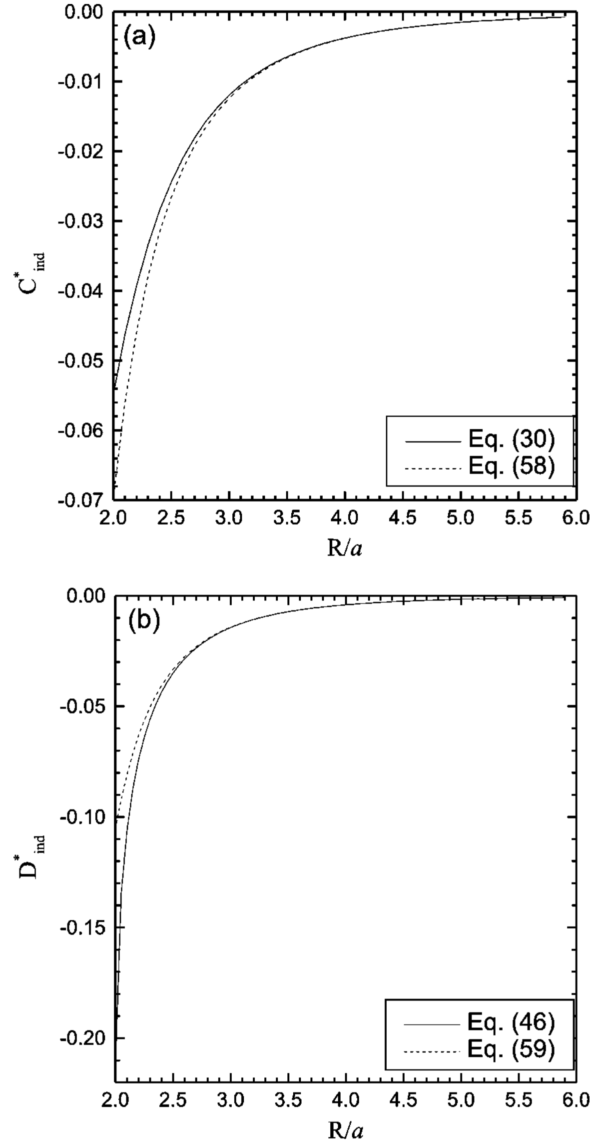

FIG. 2. The variation of the dimensionless induced interaction energy with the dimensionless interparticle distance R/a for two fundamental cases, (a) common charge density and (b) difference charge density.

The electrical interactions for two microdroplets with any charge densities can always be obtained by the linear superposition of two fundamental problems. For a droplet with net charge Q and a neutral one, the interaction energy can be calculated according to Eqs. (57)–(59),

$$W = -\frac{Q^2}{2(4\pi\varepsilon_2\varepsilon_0)a}\left[\Theta_1\left(\frac{a}{R}\right)^4 + \Theta_2\left(\frac{a}{R}\right)^6 + \Theta_3\left(\frac{a}{R}\right)^8 + (\Theta_4 + 4\Theta_1^3)\left(\frac{a}{R}\right)^{10} + O\left(\frac{a}{R}\right)^{12}\right]. \tag{61}$$

It is an attractive interaction. In other words, the droplet with net charge can polarize the neutral droplet and induce dipole, quadrupole, and multipoles, i.e., 2^n pole. Since the induced charge of opposite sign is located on the side near the charged droplet, the polarization yields an attraction.

The induction interaction has been considered in some detail in Refs. [17] and [27]. Since the dielectric constant of water is much larger than that of oil, the aqueous droplets are approximated as conducting spheres. Besides the assumption $\varepsilon_1/\varepsilon_2 \to \infty$, their analytical expression is obtained based on a point charge located at the center of the spheres. In our approach, the accuracy of the DH approximation has been justified. In addition, the effect of dielectric mismatch is correctly considered and can be applied to systems with finite ratio of dielectric constants. Moreover, our approach takes into account both the distribution of counterions and its contribution to the induction interaction due to the *entropy* associated with mobile ions. At large separation and $\varepsilon_1 \gg \varepsilon_2$, our result, Eq. (61) reduces to their asymptotic result. Note that there is a typographical error in Eq. (7.4) of Ref. [16]. For finite values of $\varepsilon_1/\varepsilon_2$, however, the induction interaction can vary significantly with the ratio of the Debye length and the droplet size, κa.

The importance of the induction interaction depends on how close two microdroplets can approach each other. It has already been clearly demonstrated by experiments that temporary merge (fusion) of microemulsion droplets occurs very often and is responsible for material exchange between microdroplets [7–9,28]. Thus, we believe that the short-range steric repulsion due to the surfactant tail is unable to prevent the contact of two aqueous cores. For two charged microdroplets, the Coulomb interaction dominates as $R \gg a$. At near contact condition, however, the induction attraction can be as large as about 40% of the Coulomb interaction. When one of the droplets is neutral, the induction attraction at $R = 2a$ is about 0.7, 2.7, and $6.1 k_B T$ at 298 K for the charged droplet of $Q = 1, 2$, and $3e$, respectively. Consequently, the induction interaction may play an important role in determining the equilibrium structure of the microemulsion.

The physical meaning of Θ_1 can be comprehended by considering the polarization of a microdroplet under an externally applied electric field $\mathbf{E}_\infty$. The electric potentials inside and outside a microdroplet are given, respectively, by

$$\phi_i = \left(\frac{\sigma - \overline{\sigma}}{\varepsilon_0 \varepsilon_2} \right) a + \frac{\overline{\sigma}}{\kappa \varepsilon_0 \varepsilon_1} \frac{i_0(\kappa r) - i_0(\kappa a)}{i_0'(\kappa a)} + (\Theta_1 - 1) \frac{i_1(\kappa r)}{i_1(\kappa a)} \frac{a}{r} \mathbf{E}_\infty \cdot \mathbf{r} \tag{62}$$

and

$$\phi_o = \left(\frac{\sigma - \overline{\sigma}}{\varepsilon_0 \varepsilon_2} \right) \frac{a^2}{r} + \left[\Theta_1 \left(\frac{a}{r} \right)^2 - \frac{r}{a} \right] a \frac{\mathbf{E}_\infty \cdot \mathbf{r}}{r}. \tag{63}$$

The induced dipole moment $\mathbf{p}$ is related to polarizability α by [29]

$$\mathbf{p} = \alpha \mathbf{E}_\infty, \tag{64}$$

with

$$\alpha = 3 \varepsilon_0 \varepsilon_2 V_1 \Theta_1 \left(\kappa a, \frac{\varepsilon_2}{\varepsilon_1} \right). \tag{65}$$

TABLE I. The effect of ion concentrations, κa, on the electrostatic interactions of two microdroplets at contact, $R = 2a$, for two fundamental cases.

κa	$C - C^{(0)} - C^{(1)}$	$D - D^{(0)} - D^{(1)}$
0.1	−0.0544	−0.2083
1.0	−0.0549	−0.2125
10	−0.0570	−0.2539
100	−0.0575	−0.2890

For $\kappa a \ll 1$, we recover the classical result for a dielectric sphere of ε_1 immersed in a medium of ε_2, $\Theta_1 \simeq (\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + 2\varepsilon_2)$ [29]. On the other hand, for $\kappa a \gg 1$, $\Theta_1 \simeq 1 - 3\varepsilon_2/\kappa a \varepsilon_1$. As a consequence, $\Theta_1 \simeq 1$ for $\varepsilon_2 \ll \varepsilon_1$ and the polarizability associated with an aqueous microdroplet is essentially determined by the volume of the droplet and the dielectric constant of the oil medium. Note that the charge (Q)–nonpolar (α) intermolecular interaction is given by $-Q^2\alpha/[2(4\pi\varepsilon_2\varepsilon_0)^2 R^4]$ [30]. Using the polarizability associated with the microdroplet and accounting for two such interactions, one can obtain the next order, $1/R^4$, interdroplet contribution.

The physical explanation of Θ_n with $n > 1$ can be illustrated by considering the interaction of a point charge Q with a neutral microdroplet. The electric potential around the neutral droplet due to the polarization is given by

$$\phi_o = -\frac{Q}{4\pi\varepsilon_2\varepsilon_0 a} \left(\frac{a}{R} \right)^{n+1} \sum_{n=1}^{\infty} \Theta_n \left(\frac{a}{r} \right)^{n+1} P_n(\cos\theta) \quad \text{for } a \leq r \leq R. \tag{66}$$

The interaction energy is then obtained as

$$W(R) = -\frac{1}{2} \frac{Q^2}{4\pi\varepsilon_2\varepsilon_0 a} \sum_{n=1}^{\infty} \Theta_n \left(\frac{a}{R} \right)^{2n+2}. \tag{67}$$

Under an externally applied field by a point charge, the neutral droplet is polarized and multipoles are then induced. Evidently, Θ_n is related to the polarizability associated with the 2^n pole. The corresponding contribution to the interaction energy is attractive for $\Theta_n > 0$ and decays like $1/R^{2n+2}$. Equation (67) also points out that the primary contributions to the attraction between a charged and a neutral droplets are caused by the polarization due to the net charge.

The effect of ion concentrations within the aqueous core on the electrostatic interactions is demonstrated in Table I. We consider a few values of κa from $\kappa a \ll 1$ to $\kappa a \gg 1$. Although the induced contribution does increase with increasing κa, the interaction energy is quite insensitive to κa. This result is indicative of the weak influence of the ion concentrations on the interactions between aqueous droplets in an apolar medium, i.e., $\varepsilon_2 \ll \varepsilon_1$. One can analyze this con-

TABLE II. The rate constants k_{ij} for collisions of two microdroplets with net charges *i* and *j*. k_{00} and k_{ij}^C are the rate constants for hard sphere and Coulomb interactions, respectively.

i	j	k_{ij}^C/k_{00}	k_{ij}/k_{00}
$+1$	$+1$	1.25×10^{-2}	2.02×10^{-2}
$+1$	-1	14.06	14.16
$+1$	0	1	2.40

sequence furthermore by considering the value of Θ_n in the asymptotic limits of κa. For $\kappa a \ll 1$,

$$\Theta_n \simeq \frac{1-\dfrac{\varepsilon_2}{\varepsilon_1}}{1+\dfrac{\varepsilon_2}{\varepsilon_1}\dfrac{n+1}{n}},$$

where the asymptotic expression, $i_{n-1}(z)/i_n(z) \simeq (2n+1)/z$ for $z \ll 1$, is used. In this limit, Θ_n is independent of κa. As $\varepsilon_2=\varepsilon_1$, $\Theta_n \simeq 0$ for $n \geq 1$ and therefore the interaction energy reduces to the Coulomb interaction. When $\varepsilon_2 \neq \varepsilon_1$, there is an $O(R^{-4})$ leading contribution due to the charge-induced dipole interaction and our result becomes the interaction between two dielectric spheres in a medium. On the other hand, for $\kappa a \gg 1$,

$$\Theta_n \simeq \frac{1-\dfrac{\varepsilon_2}{\varepsilon_1}\dfrac{n}{\kappa a}}{1+\dfrac{\varepsilon_2}{\varepsilon_1}\dfrac{n+1}{\kappa a}}.$$

Here the asymptotic expression, $i_n'(z)/i_n(z) \simeq 1-z^{-1}$ for $z \gg 1$, is employed. When $n \ll \kappa a(\varepsilon_1/\varepsilon_2)$, $\Theta_n \simeq 1$. Since the interaction is dominated by the first few 2^n poles, the dependence upon κa is insignificant as long as $\varepsilon_2 \ll \varepsilon_1$.

Because of Brownian motion, two microdroplets approach one another very frequently. During these Brownian collisions, the electrostatic interactions may have a profound effect on the rate of encounter. For a diffusion-limited process, the rate of collision is kn_d^2, where n_d is the number concentration of the droplet. The rate constant k for two-droplet collisions is related to the interaction energy by [31]

$$k=8\pi Da\left[\int_{R=2a}^{\infty}\frac{\exp[W(R)/k_BT]}{R^2}\right]^{-1}, \tag{68}$$

where D is the Brownian diffusivity. The ratio of the rate constant for two droplets with net charges *i* and *j*, k_{ij}, to that of hard spheres, k_{00}, is given in Table II. In addition to the contribution associated with hard spheres, the rate constant k_{ij}^C includes the Coulomb term only but k_{ij} takes into account the complete electrostatic interactions. The result points out that the induced attraction between a charged and a neutral droplet enhances their collision rates more than two times. The polarization effect on the rate constant is more significant for the attraction than the repulsion.

Since our approach is based on the mean-field theory, it predicts no interaction between uncharged microdroplets according to Eq. (57). However, just analogous to the dispersion force between neutral atoms, ion fluctuations inside a microdroplet can generate an instantaneous dipole moment and result in attraction [18,32]. In addition, van der Waals attraction also provide an interaction energy of $-Aa/12(R-2a)$ as $(R-2a) \ll a$. The Hamaker constant is $A \simeq k_BT$ for water/hydrocarbon system. When the separation is $(R-2a) \approx a/12$, the magnitude of the van der Waals interaction energy is about $1k_BT$, which is less than the induction interaction for $Q \geq 2e$. Though the van der Waals interaction diverges as $R \to 2a$, steric repulsions due to surfactant tails and shape fluctuations of microdroplets will most likely prevent the aqueous cores from making very close approach to one another.

We have dealt with a two-body problem by the method of twin-spherical harmonic expansion. When current results are applied to a many-body problem, one must be careful about polarization near the oil/water interface and the boundary effect of the system since electrostatic interactions are long ranged, $\sim 1/R$. In principle, a rigorous approach based on similar multipole expansion can be applied to a many-body system. Because the induction interaction is relatively short ranged, $1/R^4$, we believe that the current results are usable in a many-body problem by the assumption of pairwise additivity.

In the present work, the size of the droplet is assumed the same. It is obviously an atypical situation. For two microdroplets of unequal sizes, nevertheless, one can still estimate the interaction approximately based on current results. As two droplets are slightly different in size, one can adopt an arithmetic mean of radii in Eq. (57). On the other hand, for large size ratio, the interaction can be approximated by Eq. (61) for the interaction between a point charge and a microdroplet. The effect of externally applied electric field is not considered here. The interaction of two microdroplets may be substantially influenced in such a circumstance. Moreover, the interactions may be significantly altered for microdroplets containing nanoparticles [33,34].

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APPENDIX

The solutions of $f_n^{(k)}$ and $C^{(k)}$ can be solved by the iteration method as shown in Eqs. (27)–(30). Here we perform the process and obtain the analytical form. Inserting Eq. (24) into Eq. (30), one has

$$C^{(1)}=f_0^{(0)}\left(\frac{a}{R}\right)^1. \tag{A1}$$

Using Eq. (28), $C^{(2)}$ is obtained,

$$C^{(2)}=-f_0^{(0)}\sum_{n=1}^{\infty}\Theta_n\left(\frac{a}{R}\right)^{2n+2}. \tag{A2}$$

According to Eqs. (28) and (29), we have

$$f_n^{(2)}=f_0^{(0)}\Theta_n\sum_{m=1}^{\infty}\Theta_m\binom{n+m}{m}\left(\frac{a}{R}\right)^{n+2m+2}. \tag{A3}$$

Substituting the above result into Eq. (30), $C^{(3)}$ is obtained,

$$C^{(3)}=f_0^{(0)}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\Theta_n\Theta_m\binom{n+m}{m}\left(\frac{a}{R}\right)^{2(n+m)+3}. \tag{A4}$$

Repeating the same procedure yields

$$f_n^{(3)}=-f_0^{(0)}\Theta_n\sum_{m=1}^{\infty}\sum_{p=1}^{\infty}\Theta_m\Theta_p\binom{n+m}{m}\binom{m+p}{p}\times\left(\frac{a}{R}\right)^{n+2m+2p+3} \tag{A5}$$

and

$$C^{(4)}=-f_0^{(0)}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sum_{p=1}^{\infty}\Theta_n\Theta_m\Theta_p\binom{n+m}{m}\binom{m+p}{p}\times\left(\frac{a}{R}\right)^{2(n+m+p)+4}. \tag{A6}$$

As a consequence, one can deduce that

$$f_n^{(k)}=(-1)^k f_0^{(0)}\Theta_n\sum_{n_1=1}^{\infty}\cdots\sum_{n_{k-1}=1}^{\infty}\Theta_{n_1}\cdots\Theta_{n_{k-1}}\times\binom{n+n_1}{n_1}\cdots\binom{n_{k-2}+n_{k-1}}{n_{k-1}}\left(\frac{a}{R}\right)^{n+2(n_1+\cdots+n_{k-1})+k}, \tag{A7}$$

$$C^{(k)}=(-1)^{k-1}f_0^{(0)}\sum_{n_1=1}^{\infty}\cdots\sum_{n_{k-1}=1}^{\infty}\Theta_{n_1}\cdots\Theta_{n_{k-1}}\times\binom{n_1+n_2}{n_2}\cdots\binom{n_{k-2}+n_{k-1}}{n_{k-1}}\left(\frac{a}{R}\right)^{2(n_1+\cdots+n_{k-1})+k}. \tag{A8}$$

Similarly, for the case of difference charge density, the reference potential $D^{(k)}$ is given by

$$D^{(k)}=-g_0^{(0)}\sum_{n_1=1}^{\infty}\cdots\sum_{n_{k-1}=1}^{\infty}\Theta_{n_1}\cdots\Theta_{n_{k-1}}\times\binom{n_1+n_2}{n_2}\cdots\binom{n_{k-2}+n_{k-1}}{n_{k-1}}\left(\frac{a}{R}\right)^{2(n_1+\cdots+n_{k-1})+k}. \tag{A9}$$

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