Electrostatic attraction between neutral microdroplets by ion fluctuations

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The interaction between two aqueous droplets containing ions is investigated. The ion-fluctuation correlation gives rise to attraction between two neutral microdroplets, similar to the van der Waals interaction between neutral atoms. Electrostatic attraction consists of contributions from various induced multipole-multipole interactions, including dipole-dipole $\langle P_z^2 \rangle^2 r^{-6}$, dipole-quadrupole $\langle P_z^2 \rangle \langle Q_{zz}^2 \rangle r^{-8}$, dipole-octupole $\langle P_z^2 \rangle \langle O_{zzz}^2 \rangle r^{-10}$, and quadrupole-quadrupole interactions $\langle Q_{zz}^2 \rangle^2 r^{-10}$. The mean-square multipole moments are determined analytically by linear response theory. The fluctuation-driven attraction is so strong at short distance that it may dominate over the Coulomb repulsion between like-charged droplets. These theoretical results are confirmed by Monte Carlo simulations.

Aqueous microdroplets exist ubiquitously in water-in-oil (W/O) microemulsions and emulsions. Water droplets immersed in a continuous apolar medium are stabilized by a film of surfactants at the interface. Microemulsion droplets, sometimes also called swollen reversed micelles, are approximately spherical with sizes in the range 5–100 nm. The ability of microdroplets to host nanosized particles finds applications in biotechnology and materials development [1]. The fact that W/O microemulsions display significant electric conductivity indicates that there are ions within the aqueous core, and a substantial fraction of microdroplets acquire charges due to fluctuating exchange of ions between droplets[2]. Ions come from dissociation of the ionic surfactant shell or added inorganic salt.

The electric conductivity of a W/O microemulsion can be altered by several orders of magnitude as the temperature or the water content varies over a very narrow range. It is generally believed that the sharp change in conductivity, characterized as a percolation phenomenon, is attributed to the formation of clusters of water globules [3]. The interdroplet attraction is responsible for the cluster formation and has been elucidated by electrostatic interactions [4,5] and overlaps of the surfactant tail region [6]. For the former the mean-field theory, i.e., the Poisson-Boltzmann (PB) equation, predicts an induced attraction between a neutral and a charged droplet but no electrostatic interaction results between two neutral droplets [7]. However, by means of Monte Carlo (MC) simulations [4], it is found that correlated ion fluctuations give rise to attractive forces, which are of comparable magnitude to the van der Waals interactions between two neutral particles. The typical Hamaker constant for hydrocarbon/water dispersions was then used to depict the result. Nevertheless, this empirical analogy fails to predict the effects of ion concentrations, droplet sizes, and dielectric mismatch.

For a spherically symmetric atom such as neon there exists no permanent dipole or higher order moments and thus the induction forces are absent. Nonetheless, an instantaneous dipole in an atom can induce a dipole moment in a neighboring atom and lead to attraction, as in classical induction forces. It is well known that the van der Waals force between two nonpolar atoms arises from the correlation between charge fluctuations. The origin of the dispersion force is nonclassical. A rigorous derivation by London, considering the perturbation produced in the solution of the Schrödinger equation, results in an attraction and the attraction falls off with the separation as r^{-6}. A similar phenomenon with classical origin is anticipated for the interaction between two neutral salty microdroplets. In this Rapid Communication, we take into account the ion-fluctuation correlation and derive the attractive force, which consists of contributions from various induced multipole-multipole interactions, such as induced dipole-dipole and dipole-quadrupole interactions. Each interaction is proportional to the product of the mean-square multipole moments, which can be calculated by linear response theory (LRT) or MC simulation. The analytical expression for such an attraction is similar to that of the dispersion force. However, the former is statistical mechanical but the latter is quantum mechanical. The theoretical results are confirmed by MC simulations.

Consider two aqueous droplets with dielectric constant ε_1 (≈ 80) immersed in an apolar environment with dielectric constant ε_2. The center-to-center separation between the droplets A and B is $r = |\mathbf{A} - \mathbf{B}|$. There are N counterions enclosed in a spherical cavity of radius R with uniform surface charge density σ. These ions are located at position $\{\mathbf{x}_i^k\}$ with charge q (in units of the elementary charge e), where $i = 1, \ldots, N$ and $k = A$ and B. We assume that the counterions are point charges and consider only Coulomb interactions between ions. In the presence of dielectric jumps at the interface, the Coulomb interaction between ions, $q^2 \psi(\mathbf{x}_i, \mathbf{x}_j)$, is in general a complicated function and can be obtained by solving the Poisson equation, which relates the space charge distribution to the electric potential,

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$$\nabla \cdot [\varepsilon_r(\mathbf{r})\varepsilon_0 \nabla \psi(\mathbf{r})] = - \sum_{k=A,B} \left[\sum_{i=1}^{N} q \delta(\mathbf{r} - \mathbf{x}_i^k) + \int \sigma_k(\mathbf{x})d\mathbf{x} \right], \tag{1}$$

where ε_0 is the permittivity of a vacuum. Inside the droplet, the electric potential due to its surface charge is constant, $\sigma R/\varepsilon_0\varepsilon_2$, and thus is irrelevant in determining the ion distribution. When interacting with ions in droplet B, the surface charge of droplet A can be regarded as a point charge located at $\mathbf{A}$ with valency $Q=4\pi R^2\sigma$. The electrostatic interaction Hamiltonian can then be separated into three parts,

$$\mathcal{H} = \mathcal{H}_1^A + \mathcal{H}_1^B + \mathcal{H}_2, \tag{2}$$

with

$$\mathcal{H}_1^k = q^2\sum_{i>j} \psi(\mathbf{x}_i^k, \mathbf{x}_j^k), \tag{3}$$

and

$$\mathcal{H}_2 = q^2\sum_{i,j=1}^{N} \psi(\mathbf{x}_i^A, \mathbf{x}_j^B) + qQ\sum_{i=1}^{N} \psi(\mathbf{x}_i^A, \mathbf{B}) + qQ\sum_{i=1}^{N} \psi(\mathbf{x}_i^B, \mathbf{A}). \tag{4}$$

In Eq. (2) $\mathcal{H}_1^k$ represents the contribution due to ions within the same droplet k while $\mathcal{H}_2$ denotes the interaction between charges in different droplets.

The partition function is then given by

$$\mathcal{Z} = \frac{1}{(N!)^2} \int \int e^{-\beta\mathcal{H}}dC_N^A dC_N^B = \langle e^{-\beta\mathcal{H}_2(r)} \rangle, \tag{5}$$

where $\beta=1/k_BT$, $C_N^k=d\mathbf{x}_1^k\cdots d\mathbf{x}_N^k$, and $\langle\cdot\rangle=\int\int(e^{-\beta\mathcal{H}_1^A}dC_N^A)$ $\times(e^{-\beta\mathcal{H}_1^B}dC_N^B)$ denotes the average over realizations of counterion configurations. When the configuration of counterions within the droplet is only slightly disturbed by the neighboring droplet, $\mathcal{H}_1^k$ is essentially independent of interdroplet distance and can be determined from an isolated droplet. This statement is in general true because the mean ion-ion distance within a droplet is much smaller than that between two droplets. Consequently, the interaction between droplets is mainly decided by $\mathcal{H}_2$. To perform the average analytically, we expand the exponential of $\mathcal{H}_2$ in Eq. (5) in terms of Taylor series and retain only the terms up to order $(\beta\mathcal{H}_2)^3$, i.e., $\langle e^{-\beta\mathcal{H}_2(r)} \rangle \cong \langle 1 - \beta\mathcal{H}_2 + \frac{1}{2}(\beta\mathcal{H}_2)^2 - \frac{1}{6}(\beta\mathcal{H}_2)^3 \rangle$. When the interdroplet distance is large compared to the Bjerrum length, the thermal energy becomes greater than the electrostatic interaction, i.e., $\beta\mathcal{H}_2<1$, and the truncated series can give an accurate result. Owing to the spherical symmetry and electroneutrality $Q+Nq=0$ associated with an isolated droplet, there exists no permanent 2^n-pole $(n=0,1,2,\dots)$ and one has $\langle\beta\mathcal{H}_2\rangle=\langle(\beta\mathcal{H}_2)^3\rangle=0$. Since the interaction energy is given by $\mathcal{W}(r)=-k_BT[\ln\mathcal{Z}(r)-\ln\mathcal{Z}(r\to\infty)]$, one has

$$\mathcal{W}(r) = -\frac{\beta}{2}\langle(\mathcal{H}_2)^2\rangle. \tag{6}$$

The mean-field theory assumes $\langle(\mathcal{H}_2)^2\rangle=\langle\mathcal{H}_2\rangle^2$; therefore no interaction between two neutral droplets is obtained. However, if $\mathcal{H}_2\neq 0$ and its value fluctuates around the zero mean, one has $\langle(\beta\mathcal{H}_2)^2\rangle>0$, and an attraction will result.

To carry out the calculation for Eq. (6) with Eq. (4), we have to determine $\psi(\mathbf{x}_i^A, \mathbf{x}_j^B)$, which is complicated because of the inhomogeneous dielectric constant. The dielectric mismatch between the aqueous droplet and the apolar medium results in polarization at the interface and therefore leads to corrections to the Coulomb interaction, $k_BT\ell_B/|\mathbf{x}_i^A - \mathbf{x}_j^B|$, where the Bjerrum length $\ell_B\equiv e^2/4\pi\varepsilon_2\varepsilon_0 k_BT$ defines the length at which two unit charges interact with thermal energy k_BT. In a continuous medium, dielectric mismatch gives rise to polarization charges at the interface induced by point charges inside the droplet and external field. Equation (6) reveals that the attraction between neutral droplets can be caused only by ion fluctuations, which are manifested through the mean-square multipole moments. As a result, the effect of polarization is simply shown by modifying the mean-square multipole moments.

Without loss of generality, we consider $\varepsilon_2=\varepsilon_1$, for which there exists no polarization. The polarization effect will be taken into account later. On the basis of the multipole expansion, the Hamiltonian $\mathcal{H}_2$ can then be written as [8]

$$\mathcal{H}_2 = \frac{1}{4\pi\varepsilon_2\varepsilon_0}\left\{ -P_\alpha^A P_\beta^B \nabla_\alpha \nabla_\beta\left(\frac{1}{r}\right) - \frac{1}{3}(P_\alpha^A Q_{\beta\gamma}^B - Q_{\alpha\beta}^A P_\gamma^B) \right.$$
$$\times\nabla_\alpha\nabla_\beta\nabla_\gamma\left(\frac{1}{r}\right) - \left[\frac{1}{15}P_\alpha^A O_{\beta\gamma\delta}^B - \frac{1}{9}Q_{\alpha\beta}^A Q_{\beta\gamma}^B \right.$$
$$\left. + \frac{1}{15}O_{\alpha\beta\gamma}^A P_\delta^B \right]\nabla_\alpha\nabla_\beta\nabla_\gamma\nabla_\delta\left(\frac{1}{r}\right) + \cdots \left.\right\}, \tag{7}$$

where the instantaneous dipole, quadrupole, and octopole moments are defined as $\mathbf{P}=q\Sigma_i\mathbf{x}_i$, $\mathbf{Q}=(q/2)\Sigma_i(3\mathbf{x}_i\mathbf{x}_i-\mathbf{x}_i^2\mathbf{I})$, and $\mathbf{O}=(q/2)\Sigma_i(5\mathbf{x}_i\mathbf{x}_i\mathbf{x}_i-\mathbf{x}_i^2\mathbf{x}_i\mathbf{I})$, respectively. $\mathbf{I}$ is the unit tensor. Note that permanent multipoles do not exist, $\langle\mathbf{P}\rangle=\langle\mathbf{Q}\rangle=\langle\mathbf{O}\rangle=0$. Substituting Eq. (7) into Eq. (6) and performing the integration yields the interaction energy, which consists of contributions from various induced multipole-multipole interactions,

$$\mathcal{W}_{00} = \mathcal{W}_{PP} + \mathcal{W}_{PQ} + (\mathcal{W}_{PO} + \mathcal{W}_{QQ}) + O(r^{-12}), \tag{8}$$

where

$$\mathcal{W}_{PP} = -3\frac{\langle P_z^2\rangle^2}{(4\pi\varepsilon_2\varepsilon_0)^2 k_BT}r^{-6}, \quad \mathcal{W}_{PQ} = -15\frac{\langle P_z^2\rangle\langle Q_{zz}^2\rangle}{(4\pi\varepsilon_2\varepsilon_0)^2 k_BT}r^{-8}, \tag{9}$$

and

$$\mathcal{W}_{PO} = -28\frac{\langle P_z^2\rangle\langle O_{zzz}^2\rangle}{(4\pi\varepsilon_2\varepsilon_0)^2 k_BT}r^{-10}, \tag{10}$$

$$\mathcal{W}_{QQ} = -35\frac{\langle Q_{zz}^2\rangle^2}{(4\pi\varepsilon_2\varepsilon_0)^2 k_BT}r^{-10}.$$

Note that van der Waals attraction is not included in Eq. (8) and $\mathcal{W}_{00}=0$ if all charges are absent. When $\varepsilon_1\neq\varepsilon_2$, the polarization charge simply gives an extra contribution to the instantaneous multipole in Eq. (7). The interface polarization on droplet B due to A is equivalent to applying an external field on B [see Eq. (13) for an ion-free sphere]. Therefore, Eqs. (8)–(10) still hold and the effect of dielectric mismatch

is displayed through the mean-square multipole moments. The foregoing results show that the induced interaction between a 2^m-pole and a 2^n-pole is always attractive. It falls off as $r^{-2(m+n+1)}$ and is proportional to the product of the mean-square multipole moments of 2^m and 2^n. The analytical expression is very similar to the dispersion interaction between atoms, $U_{\mathrm{dis}} = C_6 r^{-6} + C_8 r^{-8} + C_{10} r^{-10} + \cdots$ [8]. At large separations, just like the coefficient C_6 [9], the leading term of $\mathcal{W}_{00}$, proportional to $\langle P_z^2 \rangle^2$, is also proportional to the square of the microdroplet's polarizability [7,10].

The mean-square multipole moments represent ion fluctuations inherent in a microdroplet and cannot be obtained from the mean-field theory directly. They can be obtained either from MC simulations or by LRT [10]. The latter simply applies an electric field externally and a field ϕ within the microdroplet results. The induced multipole moment M_i can then be calculated from the PB equation under the Debye-Hückel approximation [10]. For a weak external field, the response is governed by the same laws as are spontaneous ion fluctuations in an equilibrium system. Therefore,

$$M_i = \frac{1}{N!} \int M e^{-\beta[\Sigma_k \phi(\mathbf{x}_k) + \mathcal{H}_1]} dC_N / \mathcal{Z}$$

$$\cong \frac{1}{N!} \int M[1 - \beta \sum_k \phi(\mathbf{x}_k)] e^{-\beta \mathcal{H}_1} dC_N / \mathcal{Z}$$

$$= -\beta \langle M \sum_k \phi(\mathbf{x}_k) \rangle. \tag{11}$$

where $\langle M \rangle = 0$ and $\mathcal{Z} \cong (1/N!(\int e^{-\beta \mathcal{H}_1} dC_N$. In accodance with Eq. (11), the mean-square multipole moment $\langle M_{(n)z}^2 \rangle$, the $z \ldots z$ component associated with a 2^n-pole, can be evaluated analytically if one choose $\phi \propto M_{(n)z}$ [10]. For example, $\langle M_{(1)z}^2 \rangle = \langle P_z^2 \rangle$ is obtained if we choose $\phi \propto z$. This approach yields

$$\langle M_{(n)z}^2 \rangle = (4\pi \varepsilon_2 \varepsilon_0) \Theta_n R^{2n+1} k_B T, \tag{12}$$

where Θ_n is defined as

$$\Theta_n \left(\kappa R, \frac{\varepsilon_2}{\varepsilon_1} \right) = \left(1 - \frac{\varepsilon_2}{\varepsilon_1} \frac{n}{\kappa R} \frac{i_n(\kappa R)}{i_n'(\kappa R)} \right) \Big/ \left(1 + \frac{\varepsilon_2}{\varepsilon_1} \frac{n+1}{\kappa R} \frac{i_n(\kappa R)}{i_n'(\kappa R)} \right). \tag{13}$$

$i_n(x)$ is the modified spherical Bessel function of the first kind and $-1 < \Theta_n < 1$. κ denotes the inverse Debye length [10]. Note that, as $\kappa R \ll 1$, $\Theta_n \to n(\varepsilon_1 - \varepsilon_2)/[n\varepsilon_1 + (n+1)\varepsilon_2]$ corresponds to the induced multipole $M_{(n)z}$ associated with an ion-free dielectric sphere due to the external field.

The validity of our analytical results for $\mathcal{W}_{00}$ can be verified by considering the dilute limit. For one counterion only, the interaction energy for $\varepsilon_2 = \varepsilon_1$ can be evaluated exactly. Its expansion is $\beta \mathcal{W}_{00} = -(\ell_B/R)^2 (\frac{3}{25} x^6 + \frac{9}{35} x^8 + \frac{11}{21} x^{10} + \cdots)$, where $x = R/r$. Equation (8) reduces to this asymptotic result as $\kappa R \ll 1$. The accuracy of the mean-square multipole moments calculated by LRT is further examined by comparing to those obtained from MC simulations for an isolated microdroplet. The simulation details are reported elsewhere [11]. The restricted primitive model is adopted with ion diameter $a = 0.4$ nm. Figures 1(a) and 1(b) show, respectively, the varia-
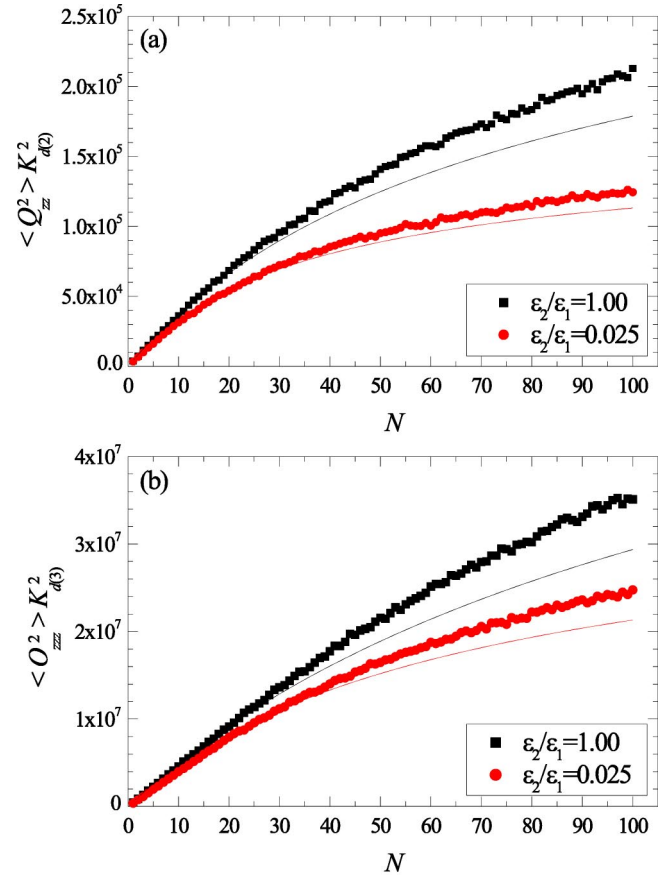

FIG. 1. The variation of scaled mean-square (a) quadrupole and (b) octopole with the number of counterions N for $R = 15a$. $K_{d(n)} = (2n+1)\varepsilon_2/[n\varepsilon_1 + (n+1)\varepsilon_2]$.

tion of scaled $\langle Q_{zz}^2 \rangle$ and $\langle O_{zzz}^2 \rangle$ with the number of counterions N for $R/a = 15$. Note that the contribution due to the external field disappears for an isolated droplet. Similar to $\langle P_z^2 \rangle$ [10], they grow rapidly at low ion concentrations but become saturated at high concentrations. The mean-square multipole moment of $\varepsilon_2 = \varepsilon_1$ is greater than that of $\varepsilon_2/\varepsilon_1 = 0.025$ because the counterion fluctuation is depressed by polarization charges at the interface. Those features are captured by LRT. The results of simulation and theory are in reasonable agreement.

We also perform MC simulations to calculate the interaction force between two neutral microdroplets for $\varepsilon_2 = \varepsilon_1 = 80$ at 298 K. The forces are plotted against the interdroplet distance as shown in Fig. 2(a) for different radii and in Fig. 2(b) for different numbers of counterions. The interaction is always attractive. At a given separation, the attraction $-\mathcal{F}$ increases with N for a specified R and grows with R for a fixed N. The MC results are compared to the theoretical prediction by $\mathcal{F} = -d\mathcal{W}_{00}/dr$. The agreement is quite good and confirms the validity of Eq. (8). At large separation, the leading terms dominate the attractive force. Nevertheless, the higher order terms may contribute as much as 20% of the total fluctuation-driven attraction at shorter separations, $r \to 2R$, in Fig. 2(b). In our analysis *weak* electrostatic interaction is assumed because of the Taylor expansion and small perturbation to the counterion configuration. As the counterion
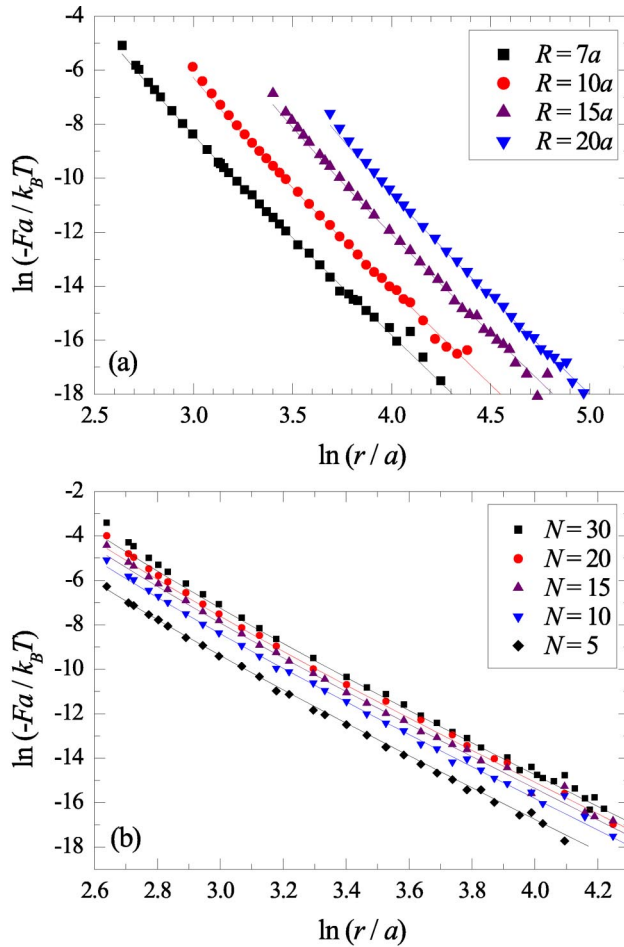
FIG. 2. The attractive forces $-\mathcal{F}$ plotted against the interdroplet distance r (a) for different radii with $N=10$ and (b) for different number of counterions with $R=7a$.
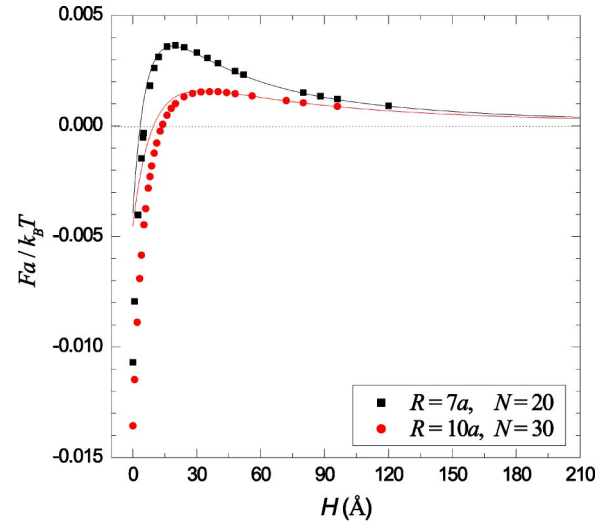

FIG. 3. The variation of the forces with the minimum separation between two like-charged droplets H. The microdroplet carries a unit net charge with $\varepsilon_2/\varepsilon_1=1$ and $\kappa R=20$.

concentration is increased, the deviation becomes significant as shown in Fig. 1. In fact, the attraction can be at least $0.2k_BT$ for $N>100$ in Fig. 2(b). Such attraction is significant enough to be measured [12].

The interaction between two like-charged droplets is dominated by the Coulomb repulsion. The ratio of Coulomb repulsion between two unit charges to $\mathcal{W}_{PP}$ at $r=2R$ is $(16/9\Theta_1^2)(\ell_B/R)$. This result reveals that at on near contact the Coulomb repulsion may be overcome by the fluctuation-driven attraction. In fact, the interaction energy between two droplets with unit charge is given by $\mathcal{W}_{11}=(\ell_B/r)k_BT+2\mathcal{W}_{10}+\mathcal{W}_{00}$, where $\mathcal{W}_{10}$ denotes the charge-induced multipole interaction, $\mathcal{W}_{10}=-\frac{1}{2}(\ell_B/R)k_BT\Sigma_{n=1}^{\infty}\Theta_n(R/\tau)^{2n+2}$ [7]. Figure 3 plots the forces against the minimum separation, $H=r-2R$, for $\varepsilon_2=\varepsilon_1$. The theory agrees quite well with the MC results. As $H\to0$, however, the theory underestimates the attraction $\mathcal{W}_{00}$ substantially, due to the absence of higher order moment contributions. This outcome reveals that, if two like-charged droplets are able to overcome the Coulomb barrier, they will fall into the attractive well caused by ion fluctuations. This is similar to the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential in colloidal suspensions stabilized kinetically by electrostatic repulsions [1].

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