Microemulsions as macroelectrolytes

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Water-in-oil microemulsions, composed of discrete aqueous droplets dispersed in a continuous oil medium, constitute a special class of electrolyte solutions. Such macroelectrolytes are analogous to conventional electrolyte solutions in most respects, with the notable difference that, in a microemulsion, the ionic (droplet) charge is not fixed but depends on the droplet interactions. Describing the microemulsion as a primitive-model electrolyte mixture with ions of variable charge and evaluating the statistical mechanics within the mean-spherical approximation (MSA), we construct a self-consistent theory of charge fluctuations and droplet interactions in ionic microemulsions. The droplet charge distribution is calculated as a function of the size, shape, polydispersity, and volume fraction of the droplets. We argue that the net droplet charges can have a decisive influence on microemulsion structure, especially at the higher volume fractions where clustering and spinodal decomposition are observed. At lower volume fractions, where the MSA treatment should be quantitatively accurate, the Coulomb interaction between charged droplets has no effect on the structure factor deduced from scattering data. © 1995 American Institute of Physics.

I. INTRODUCTION

Water-in-oil microemulsions are thermodynamically stable dispersions of water droplets in a continuous oil medium, stabilized by a monolayer of surfactant molecules at the droplet interface. By adjusting the composition of the microemulsion phase, one can independently vary the size and concentration of the droplets. In favorable cases, droplet diameters in the range 1–50 nm and concentrations from effectively infinite dilution to near close-packing can be achieved. These phases exhibit a rich variety of physical behavior, including clustering, percolation, and critical phenomena. While extensively studied by various experimental methods, these phenomena are still poorly understood. In particular, little is known about the interdroplet interactions that ultimately must govern all the observed microstructural phenomena. For the interpretation of scattering data, microemulsions are often regarded as macrofluids and the theoretical methods developed for simple fluids are used to calculate the structure factor for various empirical potential models. The general aim of the present work is to carry this analogy one step further by regarding microemulsions as macroelectrolytes.

The vast majority of water-in-oil microemulsions contain at least one strong electrolyte, such as an ionic surfactant plus counterion and/or inorganic salt. Due to the low dielectric permittivity of the oil medium, these ions are confined to the aqueous droplet cores. For the same reason, there is a strong driving force (the Born energy) for matching the ionic content so as to make each droplet electroneutral. A typical microemulsion droplet of radius 10 nm contains on the order of $10^3$ surfactant ions and an equal number of oppositely charged counterions. The entropic cost of precisely matching these two very large numbers is considerable; in fact, it is comparable to the Born energy. As a result, a substantial fraction of the droplets are charged in a typical microemulsion. Although the net droplet charge rarely exceeds one or two elementary charges, the resulting electric field is only weakly screened by the nonpolar oil medium. Consequently, the Coulomb interaction between charged droplets and the induction interaction between charged and neutral droplets may play important roles for the observed microstructural transformations.

While a net droplet charge may have important structural consequences, its most obvious, and most readily quantified, manifestation is the electrical conductivity resulting from the drift of charged droplets in an applied electric field. Charged droplets have occasionally been invoked to rationalize conductivity and diffusion data, but only recently have systematic conductivity measurements as a function of droplet size and concentration been presented, suitable for testing theoretical models of charge fluctuations in microemulsions. Following the thermodynamic fluctuation theory of Eicke et al., which accounts for the observed conductivity in the large-droplet regime, Halle and Hall independently proposed a more general theory, which includes the thermodynamic fluctuation theory as a limiting case and, in addition, accounts for the sharp conductivity drop for small droplets.

In the previous theoretical treatments of charge fluctuations in microemulsions, all interactions between the droplets were ignored. It is clear, however, that the Coulomb and induction interactions stabilize charged droplets, thus in-
increasing the mean-square droplet charge. By describing the microemulsion as a primitive-model electrolyte mixture and using the mean spherical approximation (MSA) integral-equation theory, originally devised for simple electrolyte solutions, we develop here a self-consistent theory of charge fluctuations in the presence of interactions. Furthermore, we investigate the effects of a nonspherical droplet shape and of droplet size polydispersity on the charge fluctuations.

This paper is organized as follows. Having defined the basic model and the associated free energy functional (Sec. II), we derive the contributions to the droplet chemical potential from Coulomb interactions (Sec. III) and from the self-energy (Sec. IV). The latter is shown to be dominated by the external part (Born energy), the internal self-energy being completely negligible under typical conditions (Appendix A). Regarding the microemulsion as a grand canonical ensemble of two-component droplet systems, we then establish the equilibrium droplet charge distribution by minimizing the free energy functional for the interacting macroelectrolyte (Sec. V and Appendix B). Since the droplet charge depends on the interactions between droplets, which in turn depends on the droplet charge, the equilibrium charge distribution is obtained by a self-consistent procedure rather than from a simple Boltzmann distribution, as in the infinite-dilution limit. Numerical results are then presented for the droplet charge distribution and the mean-square droplet charge as a function of the size and volume fraction of the droplets and the valency of the electrolyte in the core (Sec. V). Furthermore, we show that the net charge of small droplets can be drastically increased by a highly nonspherical droplet shape (Secs. IV and V) or by a modest droplet size polydispersity (Sec. IV). Finally, we discuss the consequences of a net droplet charge for the interactions, microstructure, and scattering behavior of water-in-oil microemulsions (Sec. VII).

II. MODEL

We consider a macroscopic amount of a water-in-oil microemulsion, consisting of a very large number of aqueous electrolyte droplets dispersed in a continuous oil medium and stabilized by the presence of surfactant molecules at the droplet interface. At the outset, we assume that the droplets are spherical in shape and monodisperse in size. The polar headgroups of the surfactant molecules belong to the hydrocarbon tails of the polar core, which also contains water and surfactant counterions and/or additional electrolyte. The hydrocarbon tails of the surfactant molecules extend into the surrounding oil medium, giving rise to a steric repulsion between the droplets. The equivalent hard-sphere diameter, \( \sigma_d \), of the droplet thus exceeds the diameter, \( \sigma_c \), of the polar core,

\[
\sigma_d = \sigma_c + 2 \delta,
\]

with \( \delta \) the effective length of the surfactant hydrocarbon tail.

Although the droplets are electroneutral on average, thermal fluctuations establish a distribution \( P(z_i) \) of net droplet charges \( z_i e \). The microemulsion can thus be regarded as a symmetric multicomponent macroelectrolyte with

\[
P(z_i) = P(-z_i),
\]

\[
\langle z \rangle = \sum_i P(z_i) z_i = 0,
\]

\[
\langle z^2 \rangle = \sum_i P(z_i) z_i^2 \neq 0.
\]

We assume that the Helmholtz free energy per unit volume of microemulsion can be decomposed according to

\[
A = A_F + A_I + A_S + A_0.
\]

\( A_F \) is the entropic driving force for the charge fluctuations. \( A_I \) is the contribution from interactions between the droplets. \( A_S \) is the self-energy of the droplets, i.e., the electrostatic work of charging the droplets. Finally, \( A_0 \) represents all contributions that are independent of the droplet charge distribution \( P(z_i) \). The equilibrium charge distribution is obtained by minimizing the free energy functional \( A[P(z_i)] \) in Eq. (2.5) with respect to \( P(z_i) \). The resulting functional derivatives, i.e., the chemical potentials \( \mu_i = \partial A/\partial \rho_i = \partial A/\partial \rho P(z_i) \) with \( \rho_i = \rho P(z_i) \) the number density of droplets with net charge \( z_i e \), are derived in the Secs. III and IV for the interaction and self-energy contributions, respectively. The free energy minimization is then carried out in Sec. V.

III. INTERACTION FREE ENERGY

A. Primitive model with effective permittivity

As discussed in Sec. VII, the interaction between microemulsion droplets is a sum of several contributions. Since we are concerned here with the effect of these interactions on the droplet charge distribution \( P(z_i) \), only those interactions that depend explicitly on the net droplet charge are relevant. We thus consider the Coulomb interaction between charged droplets and the induction interaction due to the polarization of the polar cores by charged droplets.

In the restricted primitive model (RPM), a conventional electrolyte solution is treated as a collection of charged hard spheres of equal size immersed in a continuous dielectric medium. Since the charged droplets are much larger than the solvent molecules, the continuum solvent description should actually be more realistic for a microemulsion than for a conventional aqueous electrolyte solution. Since the RPM treats an ion as a point charge embedded in a hard sphere with the same permittivity as the solvent medium, it is desirable, for a microemulsion, to generalize the RPM by taking into account the much larger permittivity of the polar core as compared to the solvent. At a rigorous level, this is a difficult task since the droplet polarizability destroys the pairwise additivity of the potential energy. At a mean-field level of approximation, however, the effect of droplet polarizability is simply to renormalize the medium permittivity that is effective for the long-range Coulomb interaction.

We thus replace the bulk solvent permittivity \( \varepsilon_s \) by an effective-medium permittivity \( \varepsilon_m \). If the volume fraction \( \phi_c \) of droplet cores is sufficiently low that dipole–dipole interactions among the droplets can be ignored, \( \varepsilon_m \) can be obtained from the Clausius–Mossotti relation.

\[
\frac{2}{3} \varepsilon_m \left( \frac{1}{\varepsilon_m} - 1 \right) = \frac{1}{\varepsilon_s} - 1 = \frac{1}{\varepsilon_s} - 1.
\]
\[ \epsilon_m - \epsilon_s = \phi_s \frac{\epsilon_c - \epsilon_s}{\epsilon_c + 2 \epsilon_s}, \]  
(3.1)

which may be rearranged into
\[ \epsilon_n = \epsilon_s \left( 1 + \frac{\phi_s \Delta \epsilon}{\epsilon_c + (1 - \phi_s) \Delta \epsilon / 3} \right), \]  
(3.2)

where \( \Delta \epsilon = \epsilon_c - \epsilon_s \) is the difference between the permittivities of the polar core and the surrounding oil medium. (We neglect any permittivity difference between the surfactant tails and the oil solvent.) For water-in-oil microemulsions \( \epsilon_s \gg \epsilon_c \), so the core can be regarded as conducting and Eq. (3.2) reduces to
\[ \epsilon_n = \epsilon_s \left( 1 + \frac{3 \phi_s}{1 - \phi_s} \right). \]  
(3.3)

Within this slightly generalized RPM, the pair potential, \( u_{ij}(r) \), between two droplets with net charge \( z_i \) and \( z_j \) becomes
\[ \beta u_{ij}(r) = \begin{cases} \infty, & r < \sigma_d, \\ \frac{z_i z_j}{\lambda_B^2} \ln \left( \frac{1}{r} \right), & r > \sigma_d \end{cases} \]  
(3.4)

where \( r \) is the separation between droplet centers and \( \lambda_B \) is the effective-medium Bjerrum length,
\[ \lambda_B = \frac{e^2}{4 \pi \epsilon_0 \epsilon_m k_B T} = \lambda_s \left( 1 + \frac{3 \phi_c}{1 - \phi_c} \right)^{-1}, \]  
(3.5)

with \( \lambda_s \) the bulk solvent Bjerrum length.

**B. Mean spherical approximation**

The configurational averaging required to obtain the interaction free energy \( A_i \) will be carried out within the mean spherical approximation (MSA). Like the Debye–Hückel approximation (DHA), the MSA is a linear theory. In contrast to the DHA, however, the MSA accounts for excluded-volume effects in a consistent (albeit approximate) manner. As demonstrated in Sec. V, this is a necessary improvement for the present problem since the DHA leads to a divergent partition function even at low droplet volume fractions.

In the MSA, the exact (within the RPM) relations
\[ h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{r}' h_{ik}(r') c_{kj}(\mid \mathbf{r} - \mathbf{r}' \mid), \]  
(3.6)

and
\[ h_{ij}(r) = g_{ij}(r) - 1 = -1, \quad r < \sigma_d \]  
(3.7)

are supplemented with the approximate closure relation
\[ c_{ij}(r) = -\beta u_{ij}(r), \quad r > \sigma_d. \]  
(3.8)

The MSA has the great virtue of admitting analytical solutions for many potential models. For the general RPM, i.e., an arbitrary electroneutral mixture of equal-sized ions (possibly including an uncharged species), the direct correlation function has the simple form
\[ c_{ij}(r) = c_{py}(r) - z_i z_j \frac{\lambda_B}{\sigma_d} \frac{B}{2 - \frac{r}{\sigma_d}}, \quad r < \sigma_d, \]  
(3.9)

where \( c_{py}(r) \) is the direct correlation function for the reference hard-sphere system in the Percus–Yevick approximation.\(^{k,22}\) The dimensionless parameter \( B \) is defined as
\[ B = \frac{1}{x} \left[ 1 + x - (1 + 2x)^{1/2} \right], \]  
(3.10)

where
\[ x = \sigma_d/\lambda_D, \]  
(3.11)

and \( \lambda_D \) is the Debye screening length (sometimes denoted as \( \kappa^{-1} \)), given by
\[ \lambda_D^{-2} = 4 \pi \lambda_B \sum_i z_i^2 \rho_i = 4 \pi \lambda_B \rho(z^2), \]  
(3.12)

where \( \rho = 6 \phi \sigma^3 / (\pi \sigma^3) \) is the overall droplet number density, and the second equality follows from Eq. (2.4).

By inserting the direct correlation function, Eqs. (3.8) and (3.9), into the Ornstein–Zernike relation, Eq. (3.6), one can obtain the pair correlation function \( g_{ij}(r) \),\(^{23}\) from which all thermodynamics follows.\(^8\) Since \( g_{ij}(r) \) has a relatively complicated form (cf. Sec. VII), it is more convenient to rewrite the exact relations in terms of \( c_{ij}(r) \). One thus obtains for the excess (relative to a hard-sphere fluid) internal energy per particle of species \( i \),\(^{24}\)
\[ E_i^{ex} = \frac{1}{2} k_B T [ c_{ii}(0) - c_{py}(0) ] = -z_i^2 B \frac{\lambda_B}{\sigma_d} k_B T, \]  
(3.13)

where Eq. (3.9) was used in the second step.

The interaction part of the chemical potential per droplet of species \( i \) is given by \( \mu_{ii} = \partial \mu / \partial \rho_i \), with \( \mu_i \) obtained by integrating \( E^{ex} = \sum_i \rho_i E_i^{ex} \) over \( \rho \) at constant permittivity \( \epsilon_m \). In the MSA treatment of the conventional RPM, the thermodynamic relations depend on temperature and number density only in the combination \( \rho T \). In our mean-field treatment of droplet polarizability, featuring an effective, \( \rho \)-dependent permittivity \( \epsilon_m \), this is no longer the case. Since we are concerned with charge fluctuations at constant droplet volume fraction (and, hence, constant \( \epsilon_m \)), however, the required functional derivative \( \partial \epsilon / \partial \rho \) is equivalent to the excess chemical potential of the conventional RPM, the only difference being that the solvent permittivity \( \epsilon_s \) is replaced by the effective permittivity \( \epsilon_m \). Consequently,\(^{23,24}\)
\[ \mu_{ii} = E_i^{ex} = -z_i^2 B \frac{\lambda_B}{\sigma_d} k_B T. \]  
(3.14)

Since the hard-sphere and Coulomb interactions contribute additively in the MSA, cf. Eq. (3.9), the excess internal and free energies do not depend on the overall droplet density \( \rho \), but depends only on the densities \( \rho_i \) of charged droplets via the Debye length \( \lambda_D \) in Eq. (3.12).

To leading order in \( x = \sigma_d / \lambda_D \), Eq. (3.10) reduces to \( B = x/2 \). Inserting this into Eq. (3.14) we recover the well-known DHA limit
\[ \mu_{ii} = -z_i^2 \frac{\lambda_B}{2 \lambda_D} k_B T. \]  
(3.15)
IV. SELF-ENERGY

The self-energy part of the chemical potential, \( \mu_{Si} = \partial \phi_s / \partial \rho_s \), is simply half the free energy transformation of two electroneutral droplets into two droplets with net charge \( z_i e \) and \(-z_i e \). We decompose this contribution as

\[
\mu_{Si} = \mu_{Si}^{\text{int}} + \mu_{Si}^{\text{ext}} .
\]

(4.1)

The internal self-energy, \( \mu_{Si}^{\text{int}} \), accounts for changes in the configurational free energy of the charge distribution within the droplet core as ions are transferred between droplets to create a net charge. As previously asserted, \( \mu_{Si}^{\text{int}} \) is negligible compared to \( \mu_{Si}^{\text{ext}} \) if, as in virtually all cases of practical interest, the departure from electroneutrality is small in a relative sense, i.e., if \( |z_i| \ll N \), with \( N \) the total number of ions in the core. This is demonstrated explicitly in Appendix A.

Neglecting the internal contribution, we are left with the external self-energy or Born energy, \( \mu_{Si}^{\text{ext}} \), which is simply the electrostatic work of charging a conducting droplet in a dielectric medium. This contribution depends on the net droplet charge and on the shape of the droplet core. Since the charge distribution \( P(z_i) \) depends on droplet shape mainly via the self-energy, we evaluate \( \mu_{Si}^{\text{ext}} \) for a prolate-spheroidal core of axial ratio \( \gamma = \sigma_c / \sigma_d \), with \( \sigma_c \) and \( \sigma_d \) the minor and major axes of the core, but neglect the influence of droplet shape on the other free energy contributions. To a good approximation, the aqueous core can be modeled as a conducting spheroid with the excess charge distributed over the core surface. Then

\[
\mu_{Si}^{\text{ext}} = \frac{1}{2} z_i e \psi_0 ,
\]

(4.2)

with the surface potential \( \psi_0 \) given by

\[
\psi_0 = \frac{2 z_i e \arctanh (1 - y^2)^{1/2}}{4 \pi \varepsilon_0 \varepsilon_a \sigma_c (1 - y^2)^{1/2}}.
\]

(4.3)

We thus obtain

\[
\mu_{Si}^{\text{ext}} = z_i \left( \frac{\lambda_B}{\sigma_c} \right) f(y) \kappa_B T ,
\]

(4.4)

where \( \sigma_c = (\sigma_d^2 y^2)^{1/3} \) is the equivalent core diameter, and

\[
f(y) = \frac{y^{2/3}}{(1 - y^2)^{1/2}} \arctanh (1 - y^2)^{1/2}.
\]

(4.5)

The shape-dependent factor \( f(y) \) varies from 1 for a sphere to 0 in the limit \( y \to 0 \). The remaining factor in Eq. (4.4) is the traditional Born energy of a sphere.

V. DROPLET CHARGE DISTRIBUTION

A. Free energy minimization

To obtain the equilibrium distribution, \( P(z) \), of net droplet charge, we regard the microemulsion as a grand canonical ensemble of two-component droplet systems at fixed temperature, volume, and chemical potentials. (For notational convenience, we omit the droplet species subscript \( i \) here.) By minimizing the free energy density in Eq. (2.5) with respect to variations in the number densities of all possible droplet species, characterized by the numbers \( N_A \) and \( N_B \) of anions and cations in the core, we obtain the grand canonical equilibrium distribution \( P(N_A, N_B) \). This derivation is carried out in Appendix B, where we then proceed to show that fluctuations in the droplet charge, \( z \), and in the total ion occupancy, \( N = N_A + N_B \), are statistically independent provided that \( |z| \ll N \), i.e., \( P(N_A, N_B) = P(N) P(z) \) with

\[
P(z) = \frac{\exp[-\beta (\mu_c(z) + \mu_s(z))]}{\sum_{z = -z_{\text{max}}}^{z_{\text{max}}} \exp[-\beta (\mu_c(z) + \mu_s(z))]} ,
\]

(5.1)

where the sum runs over all droplet valencies \( z \) in increments of the “net charge quantum” \( \min (\nu_A, \nu_B) \), and with \( z_{\text{max}} = N_{\text{tot}}/(1/\nu_A + 1/\nu_B) \), \( N_{\text{tot}} \) being the total number of electrolyte ions in the microemulsion with ionic charges \( \nu_A e \) and \( -\nu_B e \). Substituting the interaction and self-energy contributions to the droplet chemical potential from Eqs. (3.14) and (4.4), we obtain

\[
P(z) = \frac{\exp(-z^2 \alpha)}{\sum_{z = -z_{\text{max}}}^{z_{\text{max}}} \exp(-z^2 \alpha)} ,
\]

(5.2)

with the dimensionless coupling parameter \( \alpha \) given by

\[
\alpha = \frac{\lambda_B}{\sigma_c} \left( \frac{f(y)}{\lambda_B} - \frac{B}{\sigma_d} \right).
\]

(5.3)

If the excluded volume of the droplets is neglected, as in the DHA chemical potential \( \mu_c \) in Eq. (3.15), Eq. (5.3) reduces to (for spherical droplets)

\[
\alpha = \frac{1}{\sigma_c} - \frac{1}{2 \lambda_B}.
\]

(5.4)

When this is substituted into Eq. (5.2), one finds that the partition function in the denominator diverges unless the Debye length \( \lambda_D \) is larger than the core radius \( \sigma_c / 2 \). This unphysical behavior renders the DHA inadequate for treating a fluctuating electrolyte. By introducing a hard-sphere droplet diameter \( \sigma_d \) (exceeding \( \sigma_c \)), as in the MSA treatment of Sec. III B, we ensure (at least in the case of spherical droplets) that \( \alpha \) remains positive even if the Debye length is small. Thus, in the limit \( \lambda_D \ll \sigma_d \), Eq. (5.3) reduces to (for spherical droplets)

\[
\alpha = \frac{1}{\sigma_c} - \frac{1}{2 \lambda_D} ,
\]

(5.5)

which, in view of Eq. (2.1), is always positive.

Due to the dependence of the coupling parameter \( \alpha \) in Eq. (5.3) on the charge distribution \( P(z) \) (more precisely, on its second moment, \( \langle z^2 \rangle \)) via the MSA parameter \( B \), Eq. (5.2) is not simply a Boltzmann distribution. It is thus necessary to use an iterative scheme to calculate a self-consistent distribution \( P(z) \). In the infinite-dilution limit, however, the Coulomb and polarization interactions may be neglected and Eq. (5.2) reduces to a Boltzmann distribution involving only the droplet self-energy, i.e.,

\[
\alpha_0 = \lambda_B \frac{f(y)}{\sigma_c} ,
\]

(5.6)

as previously obtained (for spherical droplets).

The protocol for the iterative computation of \( P(z) \) is as follows.
(1) Start with \( \langle z^2 \rangle_0 \) in the absence of Coulomb interactions, as obtained from Eqs. (2.4), (5.2), and (5.3) with \( B = 0 \).
(2) Calculate \( B \) from Eqs. (3.10)–(3.12).
(3) Calculate \( \alpha \) from Eq. (5.3) with \( f(y) \) from Eq. (4.5).
(4) Calculate \( P(z) \) from Eq. (5.2).
(5) Calculate a new value of \( \langle z^2 \rangle \) from Eq. (2.4).
(6) Repeat from step (2) until \( \langle z^2 \rangle \) converges to desired accuracy.

**B. Limiting cases**

The weak and strong coupling regimes, previously considered in the infinite-dilution limit, are relevant also in the presence of interactions. In the weak-coupling regime \( (\alpha \approx 1) \), where the charge fluctuations are large, the sum in Eq. (5.2) can be replaced by an integral, whereby

\[
\langle z^2 \rangle_{\text{wc}} = \frac{1}{2\alpha}. \tag{5.7}
\]

This regime corresponds to the continuum approach of Eicke et al. \(^{15}\) In the strong-coupling regime \( (\alpha \gg 1) \), where the charge fluctuations are small, the sum in Eq. (5.2) can be truncated to give

\[
\langle z^2 \rangle_{\text{sc}} = 2 \exp(-\nu^2 \alpha), \tag{5.8}
\]

where \( \nu = \min(\nu_A, \nu_B) \) is the smallest possible charge fluctuation. In the strong-coupling regime \( \langle z^2 \rangle \) thus depends sensitively on \( \nu \), whereas \( \langle z^2 \rangle \) is independent of \( \nu \) in the weak-coupling regime.\(^{12–14}\)

Since \( \alpha \) depends on \( \langle z^2 \rangle \) via \( B \), \( \langle z^2 \rangle \) must be computed iteratively also in the weak and strong coupling regimes. For the DHA in the weak-coupling regime, however, Eqs. (3.12), (5.4), and (5.7) can be combined to yield a cubic equation for \( \langle z^2 \rangle \), from which \( \langle z^2 \rangle \) can be obtained analytically. By examining the sign of the discriminant, one can show that a physically admissible solution exists only for \( \phi_e < 4/81 \approx 0.05 \). The DHA thus breaks down already at very low droplet concentrations.

**C. Numerical results**

Figure 1 shows how the net charge varies with droplet size in a typical water-in-oil microemulsion. Here, and in the following, we use a solvent Bjerrum length of \( \lambda_B = 28.60 \text{ nm} \), corresponding to isoctane at \( 30 \text{ °C} \), and a steric parameter of \( \delta = 0.6 \text{ nm} \), appropriate for the widely studied surfactant AOT.\(^{27}\) As the core radius reaches about 10 nm, we find comparable populations of monovalent and neutral droplets. The effect of droplet interactions is seen to be significant already at a volume fraction of 10%. This is also apparent from Fig. 2, showing the variation of the root-mean-square (rms) droplet charge, \( \langle z^2 \rangle^{1/2} \), with droplet size. The limiting forms, Eqs. (5.7) and (5.8), are seen to be useful approximations over a wide range of droplet sizes. Figure 2 also compares the predictions of our theory with Monte Carlo simulation data for an identical system (\( \lambda_B = 28.60 \text{ nm} \) and infinite dilution).\(^{28}\) Since the simulation explicitly accounts for all ionic interactions within the core, the excellent agreement seen in Fig. 2 justifies our neglect of the internal self-energy (cf. Sec. IV and Appendix A).
proximately taking into account the positional correlations among hard-core droplets. For $e_z \gg e_s$, this theory yields

$$e_n = e_s \frac{(1 + 4 \xi)^2 (1 + \xi)^4}{(1 - 2 \xi)^b},$$

with the parameter $\xi$ determined by the core volume fraction $\phi_c$ according to

$$\frac{(1 + 4 \xi)^2 (1 - 2 \xi)^3}{(1 + \xi)^2} = 3 \phi_c.$$  \hspace{1cm} (5.10)

For $\phi_c < 0.3$, this improved $e_n$ is virtually indistinguishable from the Clausius–Mossotti approximation, Eq. (3.3).

As noted in connection with Eq. (5.1), the net droplet charge $z$ is “quantized” in units of the smallest charge number $\nu$ of the electrolyte(s) contained in the core. In Fig. 4 we compare the cases $\nu = 1$ and $\nu = 2$. Since the partition function in the denominator of Eq. (5.2) has a smaller value in the divalent case (the sum is restricted to even $z$), $P(z)$ is larger for $\nu = 2$ than for $\nu = 1$ for all allowed valencies $z$. For large droplets, charge quantization has a negligible effect on $\langle z^2 \rangle$ ($z$ may be treated as a continuous variable), which then is independent of $\nu$ as predicted by Eq. (5.1). For small droplets, $\langle z^2 \rangle$ is smaller in the divalent case since the large Born energy ensures that very few droplets have a net charge $|z| > 1$.

A deformation of the spherical shape of the droplet core reduces the self-energy by distributing the net surface charge of the effectively conducting core over a larger area (cf. Sec. IV). Figure 5 shows the resulting effect on the rms droplet charge in the case of a prolate-spheroidal core. At an axial ratio $\sigma_c/\sigma_s = 0.5$, the self-energy is reduced by merely 4%, with a consequent small increase of $\langle z^2 \rangle$. For more extreme deformations, however, the relative increase of $\langle z^2 \rangle$ can be substantial, especially for small droplets.

VI. DROPLET SIZE POLYDISPERSITY

Throughout the preceding treatment we have assumed that the microemulsion droplets are monodisperse in size. However, scattering data typically suggest a polydispersity of 10%–30% in the core diameter $\sigma_c$ (assuming spherical shape). It is therefore of interest to examine the effect of size polydispersity on the charge fluctuations. For simplicity, we consider only the weak and strong coupling regimes. (As seen from Fig. 2, this is a minor limitation.) Furthermore, we ignore droplet interactions ($\phi_d = 0$). According to Eqs. (5.6)–(5.8), we have for a distribution $f(\sigma_c)$ of core diameters,

$$\langle z^2 \rangle_{sc} = 2 \int_0^{\infty} d\sigma_c f(\sigma_c) \exp\left(-\frac{\nu^2 \lambda_B^2}{\sigma_c} \right).$$

$\langle z^2 \rangle_{wc}$ is the case where $\sigma_c = 4$ nm. For $\sigma_c = 40$ nm, the effect is negligible.
A mathematically convenient distribution function, frequently applied to microemulsions,\textsuperscript{15,31} is the Schulz distribution
\begin{equation}
    f(\sigma_c) = \frac{s^{1/p^2} e^{-s}}{\sigma_c \Gamma(1/p^2)},
\end{equation}
where \( s = \sigma_c/(p^2 \langle \sigma_c \rangle) \), \( \Gamma(x) \) is the gamma function, and \( p \) is the relative polydispersity
\begin{equation}
    p = \frac{\langle (\sigma_c - \langle \sigma_c \rangle)^2 \rangle^{1/2}}{\langle \sigma_c \rangle}.
\end{equation}
As \( p \) increases from \( \approx 0 \) to 1, the Schulz distribution goes from a narrow Gaussian centered at \( \sigma_c = \langle \sigma_c \rangle \) to an exponential distribution. In general, the Schulz distribution is skewed towards larger values \( \langle \sigma_c \rangle > \langle \sigma_c \rangle \).

If all surfactant molecules reside at the interface of spherical droplets and if their headgroup area is independent of \( \sigma_c \), the mean core diameter \( \langle \sigma_c \rangle \) in a polydisperse droplet population is related to the nominal core diameter \( \sigma_0 \), which follows from geometrical considerations if one neglects polydispersity, as\textsuperscript{31}
\begin{equation}
    \langle \sigma_c \rangle = F(p) \sigma_0^p,
\end{equation}
with
\begin{equation}
    F(p) = \frac{\langle \sigma_c \rangle \langle \sigma_c^2 \rangle}{\langle \sigma_c \rangle} = \frac{1}{1 + 2p^2}.
\end{equation}
where the second equality holds for the Schulz distribution. In the weak-coupling regime, we obtain from Eqs. (6.1), (6.5), and (6.6),
\begin{equation}
    \langle z^2 \rangle_{\text{WC}} = \frac{(z^2)_{\text{p=0}}}{1 + 2p^2}.
\end{equation}
Since \( \langle z^2 \rangle \) only depends on the mean core diameter \( \langle \sigma_c \rangle \) in this regime, it is always reduced by polydispersity.

In the strong-coupling regime, we obtain from Eqs. (6.2)–(6.6),
\begin{equation}
    \langle z^2 \rangle_{\text{SC}} = \frac{4}{\Gamma(1/p^2)} A^{1/2} p^2 K_{1/p^2}(2 \sqrt{A}),
\end{equation}
where \( K_n(x) \) is the modified Bessel function of the second kind of order \( n \), and
\begin{equation}
    A = \frac{\nu^2 \lambda_B^3}{\sigma_c^3} \left[ 2 + \frac{1}{p^2} \right].
\end{equation}
Figure 6 shows the effect of polydispersity on \( \langle z^2 \rangle \) in the strong-coupling regime. (As seen from Fig. 2, the strong-coupling approximation is highly accurate for the \( \sigma_0^p \) values used in Fig. 6.) Although \( \langle \sigma_c \rangle \) decreases with \( p \), the distribution nevertheless contains droplets with \( \sigma_c > \sigma_0^p \). For small \( \sigma_0^p \), where the self-energy is large, the reduction of the self-energy for droplets in the large-\( \sigma_c \) tail of the distribution dominates over the \( \langle \sigma_c \rangle \) effect. Even a moderate polydispersity can thus produce a large relative increase of \( \langle z^2 \rangle \) for small droplets. This effect may explain the quantitative discrepancy between the theoretically predicted and experimentally measured microemulsion conductivity for small droplets.\textsuperscript{13,14}

![FIG. 6. Variation of the mean-square droplet charge, \( \langle z^2 \rangle \), in the strong-coupling regime, with the relative polydispersity, \( p \), for a Schulz distribution of core diameters. Parameter values as in Fig. 1, \( \phi_c=0 \), and nominal \( \langle p=0 \rangle \) core diameter, \( \sigma_0^p \), as indicated.](image-url)
events, however, the steric repulsion between surfactant tails prevents the droplet cores from coming into contact, i.e., \( r > \sigma_d + \sigma_s + 2 \Delta \). Since \( u_{ij}^{\text{ind}}(r) \) decays very rapidly within a fraction of the core diameter, the induction interaction is always small compared to the Coulomb interaction at physically realizable separations. At larger separations, \( r \gg \sigma_c \), Eqs. (7.2) and (7.3) reduce to the well-known asymptotic form

\[
\beta u_{ij}^{\text{ind}}(r) = -(z_i + z_j)^2 \frac{\lambda_p \sigma_c^3}{16 r^5}.
\]  

(7.4)

It should be noted that the induction interaction requires only that one of the droplets carries a net charge.

The remaining contributions to the pair potential in Eq. (7.1) do not depend on the net droplet charge and are included here merely for comparative purposes. The dispersion interaction, \( u_{\text{disp}}(r) \), due to correlated charge fluctuations within the two droplet cores, consists of two contributions that are usually treated at different levels of description,

\[
u_{\text{disp}}(r) = u_{\text{vdW}}(r) + u_{\text{corr}}(r).
\]

(7.5)

The traditional van der Waals interaction, \( u_{\text{vdW}}(r) \), between two spherical particles is given by

\[
u_{\text{vdW}}(r) = -\frac{A_H}{36} \left( \frac{\sigma_c}{r} \right)^6 F_{\text{vdW}}(r/\sigma_c),
\]

(7.6)

where \( A_H \) is the Hamaker constant, and

\[
F_{\text{vdW}}(x) = 3 x^4 \left[ 1 + \frac{x^2}{x^2 - 1} + 2 x^2 \ln \left( 1 - \frac{1}{x^2} \right) \right]
\]

(7.7)

represents a correction to the asymptotic \( r^{-6} \) distance dependence, i.e., \( F_{\text{vdW}}(x \rightarrow \infty) = 1 \). An artifact of the pairwise addition approximation underlying this result is that \( u_{\text{vdW}}(r) \) diverges when the cores come into contact. As noted above, however, this does not happen because of the steric repulsion.

The second term in Eq. (7.5) represents the zero-frequency (classical) contribution to the dispersion interaction. When this contribution is singled out as in Eq. (7.5), the Hamaker constant in Eq. (7.6) should not include the zero-frequency term in the mode sum of the Lifshitz theory.\(^{37}\)

Using tabulated dielectric data,\(^{38}\) we obtain \( A_H = 3.95 \times 10^{-21} \) J for a spherical water droplet in decane. The principal contribution to \( u_{\text{corr}}(r) \) comes from correlated fluctuations of the ion configurations within the two droplet cores. This contribution has been estimated for microemulsion droplets by Monte Carlo simulation\(^{39}\) as well as by a linear response approximation.\(^{28}\)

The last contribution, \( u_{\text{solv}}(r) \), in Eq. (7.1) represents an effective adhesion of two droplets near contact \((r = \sigma_d)\) due to the reduction of the osmotic pressure as solvent molecules are expelled from the interdroplet region.\(^{40,41}\) This interaction, sometimes called a depletion force, is of similarly short range as the steric repulsion incorporated in \( u_{\text{ind}}(r) \).

In Fig. 7 we compare the induction and van der Waals attractions for droplets in steric contact \((r = \sigma_d)\) with \( \delta = 0.6 \) nm. For relatively small droplets \((\sigma_c < 10 – 20 \) nm\), the induction is seen to be dominant even when one of the droplets is electroneutral. Furthermore, the induction is of longer range \((r^{-4}\) asymptotically\) than the van der Waals attraction \((r^{-6}\) asymptotically\). This is illustrated in Fig. 8. The correlation interaction was previously\(^{28}\) studied for a core diameter of \( \sigma_c = 13 \) nm and a (rather small) steric parameter of \( \delta = 0.25 \) nm, giving \( \beta u_{\text{corr}}(\sigma_d) = -0.09 \). For comparison, we obtain for the same parameter values \( \beta u_{\text{corr}}(\sigma_d) = -0.66 \), \( \beta u_{\text{ind}}^{\text{ind}}(\sigma_d) = -0.20 \), and \( \beta u_{\text{vdW}}^{\text{vdW}}(\sigma_d) = -0.56 \). Disregarding any short-range interactions related to the molecular nature of the solvent and surfactant tails, it appears that the dominant attraction between microemulsion droplets is provided by the traditional van der Waals interaction for a neutral pair, the induction interaction for a charged-neutral droplet pair (with \( \sigma_c < 10 – 20 \) nm\) and, of course, the Coulomb interaction for oppositely charged droplets.
B. Potential of mean force

To investigate how Coulomb screening and excluded volume influence the microstructure of a water-in-oil microemulsion, we examine the potential of mean force \( w_{ij}(r) \), defined by

\[
\beta w_{ij}(r) = -\ln g_{ij}(r).
\]  

(7.8)

Within the limitations of the MSA treatment of the RPM potential model, the pair correlation function \( g_{ij}(r) \) can be obtained by substituting the direct correlation function \( c_{ij}(r) \), Eqs. (3.8) and (3.9), into the Ornstein–Zernike relation, Eq. (3.6). The result is

\[
g_{ij}(r) = g_{PV}(r) - z_i z_j \frac{\lambda_B}{r} (1 - B)^2 G(r/\sigma_d),
\]  

(7.9)

where

\[
G(r/\sigma_d) = \sum_{n=1}^{\infty} \frac{\theta(r/\sigma_d - n)}{(n-1)!} r^n e^{-[\xi_n(t) - \xi_{n-1}(t)]},
\]  

(7.10)

with \( t = (r/\sigma_d - n)/(1/B - 1) \). Here \( \theta(x) \) is the unit step function and \( \xi_n(t) \) is a spherical Bessel function. Further, \( g_{PV}(r) \) is the well-known hard-sphere pair correlation function in the Percus–Yevick approximation. 8,45 For two droplets in steric contact, \( G(1) = 1 \) and

\[
g_{ij}(\sigma_d) = \frac{1 + \phi_d/2}{(1 - \phi_d)^2} - z_i z_j \frac{\lambda_B}{\sigma_d} (1 - B)^2.
\]  

(7.11)

On account of the linear closure approximation, Eq. (3.8), the MSA is not expected to yield quantitatively accurate results in the strong-coupling regime. That this is so in the infinite-dilution limit is immediately apparent from Eqs. (7.9) and (7.10), which reduce to \( g_{ij}(r) = 1 - z_i z_j \lambda_B / r \), rather than to the exact result \( g_{ij}(r) \propto \exp(-z_i z_j \lambda_B / r) \). At relatively high volume fractions, say \( \phi_d > 0.1 \), \( g_{ij}(r) \) is dominated by packing effects, accurately described by \( g_{PV}(r) \). Consequently, the MSA should be widely applicable under typical microemulsion conditions.

Figure 9 shows the potential of mean force, \( w_{ij}(r) \), between oppositely charged monovalent microemulsion droplets of core diameter \( \sigma_c = 20 \) nm and at several droplet volume fractions. While the MSA \( w_{ij}(r) \) at \( \phi_d = 0 \) deviates considerably from the exact \( u_{ij}(r) \) at small separations, the MSA results for finite \( \phi_d \) should be accurate at all separations. At \( \phi_d = 0.01 \), \( w_{ij}(r) \) describes a screened Coulomb attraction. The effective attraction due to hard-sphere correlations is significant for \( r < 2\sigma_d \) at \( \phi_d = 0.1 \), while, at \( \phi_d = 0.3 \), it dominates the effectively screened potential of mean force at all separations. The microemulsion system at \( \phi_d = 0.1 \), with an effective coupling parameter of \( \lambda_B/\sigma_d = 0.66 \), corresponds to a symmetric aqueous electrolyte (\( \sigma_c = 0.4 \) nm, \( \lambda_B = 0.715 \) nm) of valency 0.61 and concentration 2.5 mol dm\(^{-3}\). Under such conditions, the MSA yields highly accurate thermodynamics as well as structure.8,23

C. Structure factor

A large fraction of the experimental information about microemulsion structure derives from scattering studies. If size polydispersity is neglected, all droplets have the same scattering properties (irrespective of their net charge) and the measured scattering intensity is proportional to a static structure factor averaged over all pairs of droplets.

\[
S(k) = 1 + \rho \sum_i \sum_j P_i P_j \tilde{h}_{ij}(k),
\]  

(7.12)

where \( P_i = P(z_i) \) and \( \tilde{h}_{ij}(k) \) is the Fourier transform of \( h_{ij}(r) = g_{ij}(r) - 1 \). In a conventional electrolyte solution, of course, the ionic species scatter differently and this can be exploited to determine the more informative partial structure factors \( S_{ij}(k) \). For a microemulsion, however, only the average structure factor in Eq. (7.12) is accessible.

Inserting the MSA pair correlation function, Eq. (7.9), into Eq. (7.12), we find

\[
S(k) = 1 + \rho \tilde{h}_{PV}(k),
\]  

(7.13)

which is simply the hard-sphere structure factor. As long as the MSA is valid, the Coulomb interaction between charged microemulsion droplets thus has no effect on the observed scattering profile. This is a consequence of the linear screening inherent in the MSA; near a given charged droplet, droplets of the same charge are depleted as much as droplets of opposite charge are accumulated.

It follows from Eq. (7.12) that scattering experiments probe a charge-averaged potential of mean force, \( \tilde{w}(r) \), which can be expressed in terms of the partial potentials of mean force, \( w_{ij}(r) \), as

\[
\beta \tilde{w}(r) = -\ln \left[ \sum_i \sum_j P_i P_j \exp(-\beta w_{ij}(r)) \right].
\]  

(7.14)

As noted earlier, Eq. (7.14) reduces to the hard-sphere result, \( \tilde{w}(r) = w_{PV}(r) \), within the MSA. However, if a nonlinear theory is used to evaluate \( w_{ij}(r) \) or \( g_{ij}(r) \), then electrostatic correlations will render \( \tilde{w}(r) \) more attractive. Since the MSA should be quite accurate for microemulsion systems, any such effects should be small.
In the infinite-dilution limit, where \( w_{ij}(r) \) can be replaced by the pair potential \( u_{ij}(r) \), Eq. (7.14) becomes (for \( r > \sigma_d \))

\[
\beta \tilde{w}(r) = -\ln \left[ \sum_i \left( \sum_j P_i P_j \exp(-z_i z_j \lambda B r) \right) \right],
\]

(7.15)

with \( P_i \) given by Eqs. (5.2) and (5.6). Figure 10 shows the predictions of Eq. (7.15) for two droplet sizes. The charge-averaged attraction is seen to be very weak, although of longer range than the van der Waals attraction (see, however, the following).

In the weak-coupling regime, we can convert the sums in Eq. (7.15) to integrals. We thus obtain the remarkably simple result

\[
\beta \tilde{w}(r) = \frac{1}{2} \ln \left[ 1 - \frac{\sigma_i^2}{2r} \right].
\]

(7.16)

In this regime, the maximum attraction is \( \beta \tilde{w}(\sigma_d) = \ln(\sqrt{3}/2) = -0.144 \) for \( \sigma_c \rightarrow \infty \). For given values of \( \lambda B \), \( \delta \), and \( \nu \), \( |\tilde{w}(\sigma_d)| \), as given by Eq. (7.15), increases monotonically with \( \sigma_c \). Since the weak-coupling approximation is valid for sufficiently large \( \sigma_c \), \( \tilde{w}(r) \) is thus never more attractive than \( -0.144k_B T \). With increasing droplet volume fraction \( \phi_f \), this weak attraction will rapidly be screened out and \( \tilde{w}(r) \) will be dominated by hard-sphere correlations (as in the MSA).

For \( r \gg \sigma_d \), the weak-coupling limit, Eq. (7.16), of the general result, Eq. (7.15), may be expanded to give

\[
\beta \tilde{w}(r) = -\frac{\sigma_i^2}{8r},
\]

(7.17)

a result previously obtained by a different (and perhaps less transparent) method.\(^{28}\) It has been suggested that this “correlated charge fluctuation interaction” is the dominant contribution to the long-ranged interaction between microemulsion droplets.\(^{28}\) In this regard, several comments are in order. First, the charge-averaged potential of mean force, \( \tilde{w}(r) \), does not reduce to a mechanical interaction at infinite dilution and, hence, is not directly comparable to the various contributions to the pair potential in Eq. (7.1). Rather, \( \tilde{w}(r) \) is an apparent potential of mean force, derivable from the structure factor of a pseudo-one-component fluid. While \( \tilde{w}(r) \) is a useful quantity for analyzing scattering data from microemulsions, it must not (even at infinite dilution) be regarded as one of the interactions that determine microemulsion structure. Second, \( \tilde{w}(r) \) is not related to the fact that the net droplet charge is a thermally fluctuating quantity. For a conventional \( \bar{z} z \) electrolyte, Eq. (7.15) yields \( \beta \tilde{w}(r) = -\ln(\cosh(\bar{z} \lambda B r)) \), giving a contact value of \(-1.12 \) for an aqueous \( 1:1 \) electrolyte solution (\( \sigma_f = 0.4 \) nm, \( \lambda B = 0.715 \) nm). Third, at finite droplet concentrations, \( \tilde{w}(r) \) becomes short-ranged due to electrostatic screening.

**VIII. CONCLUDING REMARKS**

By regarding a water-in-oil microemulsion as a primitive-model macroelectrolyte and applying conventional electrolyte theory, we have extended the previous treatments of charge fluctuations\(^{12–14} \) from infinite dilution into the experimentally relevant range of droplet concentrations. The analogy with simple electrolyte solutions is far-reaching, including hard-core, Coulomb, induction, dispersion, and solvation interactions.

A wealth of experimental data indicate a strong effective attraction between microemulsion droplets, which, under certain conditions, can lead to droplet aggregation, percolation, and critical phenomena.\(^{1–7} \) Our results suggest that, in a typical microemulsion, the dominant attraction is provided by (i) the traditional van der Waals interaction between two neutral droplets, (ii) the induction interaction between a charged and a neutral droplet, and (iii) the Coulomb interaction between two oppositely charged droplets. The former two interactions depend strongly on the range \( (2 \bar{d}) \) of the steric repulsion and, hence, may be sensitive to the molecular details of the surfactant and oil.

In our self-consistent MSA treatment of charge fluctuations in a primitive-model macroelectrolyte, only the excluded volume and Coulomb interactions were explicitly included, the induction interaction being incorporated rather crudely via an effective-medium permittivity. Since polarization effects were seen to be important, a more rigorous treatment that incorporates the induction interaction directly in the potential model would be of interest. To circumvent the complications with an induction energy that is not pairwise additive, one might treat the core polarizability as an autonomous, harmonically fluctuating, internal degree of freedom,\(^{48} \) in which case pairwise additivity is restored and the MSA equations can be solved.\(^{30} \)

The numerical results presented here show that droplet interactions significantly increase the mean-square droplet charge \( \langle z^2 \rangle \), even at droplet volume fractions well below the percolation regime. For small droplets, \( \langle z^2 \rangle \) also increases if the spherical droplet shape is deformed or if the droplet size is polydisperse. In view of the significant effects of droplet interactions on \( \langle z^2 \rangle \), the quantitative agreement between experiment (at \( \phi_f = 0.1 \)) (Ref. 12) and the previous infinite-dilution theories (Refs. 12–14) for the conductivity in the
large-droplet regime must be partly fortuitous. To obtain the conductivity at a finite droplet concentration, however, one must take into account, not only the enhancement of \( \langle z^2 \rangle \), but also the conductivity reduction due to the relaxation and electrophoretic effects.\(^{49–51}\) Our preliminary calculations indicate that, for large droplets, the equilibrium effect on \( \langle z^2 \rangle \) is essentially canceled out by these dynamic effects.

The equilibrium droplet charge distribution is established and maintained by a fusion-fission mechanism, enabling diffusive exchange of the contents of two transiently coalesced droplet cores. The kinetics of this process have been amply studied by various experimental methods.\(^{3,36,52–54}\) The second-order rate constant for core exchange is typically 3 orders of magnitude below diffusion control (assuming hard spheres), implying a substantial fusion barrier.\(^{36}\) The existence of strongly interacting charged droplets clearly has implications for the mechanism of core exchange. In particular, the Coulomb and induction attractions should reduce the lifetime (with respect to coalescence) of charged droplets as compared to neutral droplets.

Finally, we note that charge fluctuations may provide a mechanism for the observed spinodal decomposition, whereby a microemulsion phase separates into two phases of unequal droplet concentration (but equal droplet size).\(^{6,31,55}\) Just as for conventional electrolytes in nonpolar solvents, oppositely charged droplets should form transient zwitterionic dimers when the droplet concentration is sufficiently high. (The fact that the fusion-fission mechanism limits the lifetime of these dimers is irrelevant for the thermodynamics.) Due to their large dipole moment, the zwitterionic dimers should dramatically enhance the effective permittivity of the microemulsion, as indeed observed\(^{56,57}\) (but attributed to a different effect).\(^{2,19}\) This would lower the Born energy, thus increasing \( \langle z^2 \rangle \) and, hence, the mean-square dipole moment. We are currently investigating quantitatively whether this could lead to an instability. A similar mechanism has been proposed to explain spinodal decomposition in simple electrolyte solutions.\(^{58,59}\)

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**APPENDIX A: INTERNAL SELF-ENERGY**

In this Appendix we justify the neglect of the internal contribution, \( \mu_{\text{int}} \), to the self-energy of a charged microemulsion droplet. Without loss of generality, we consider the transfer of monovalent ions between two, originally electro-neutral droplets (\( N_+ = N_- = N_0 \)). The internal self-energy \( \mu_{\text{int}} \) does not depend on the net droplet charge per se, but rather on the variation in the ion occupation numbers per droplet, \( N_+ \) and \( N_- \), which affect the configurational free energy of the core. It is thus clear that \( \mu_{\text{int}} \) may be estimated as one half of the work of transferring \( z_i \) neutral electrolyte molecules between the droplets, i.e.,

\[
\mu_{\text{int}} = \frac{\Delta A(z_i, N_0)}{2} = \frac{1}{2} \left[ A(N_0 + z_i) + A(N_0 - z_i) - 2A(N_0) \right],
\]

where \( A(N) \) is the free energy of an electroneutral droplet containing \( N \) (dissociated) electrolyte molecules. There are three cases to consider, depending on whether both, one, or none of the electrolyte ions are surfactant ions, residing at the interface of the spherical core.

The case of a surfactant-surfactant electrolyte is easily handled. If the surfactant charge is modeled as a uniform surface charge density \( \sigma \), then \( \sigma = 0 \) for all \( N \) in this case and, hence, \( \mu_{\text{int}} = \Delta A = 0 \) (ignoring nonelectrostatic contributions).

On the other hand, if the net charge is created by the transfer of \( z_i \) surfactant ions, the concomitant change in core diameter \( \sigma \) will give rise to a small correction to \( \mu_{\text{int}} \) in Eq. (4.4).

Since the number of surfactant ions is proportional to \( \sigma_i \), we have in place of Eq. (4.4) (for a spherical core)

\[
\mu_{\text{int}} = \frac{1}{2} z_i^2 \frac{\lambda_B}{\sigma_c} \left[ (1 + \xi)^{-1/2} + (1 - \xi)^{-1/2} \right]
\]

\[
= z_i^2 \frac{\lambda_B}{\sigma_c} \left[ 1 + \frac{1}{2} \xi^2 + O(\xi^4) \right],
\]

where \( \xi = z_i / N_0 \). Since \( z_i \ll N_0 \) in all cases of interest, we recover Eq. (4.4).

In the cases where the electrolyte contains at least one mobile ion species, it is convenient (since \( z_i \ll N_0 \)) to expand \( A(N) \) around \( N = N_0 \) as

\[
A(N) = A(N_0) + (N - N_0) \frac{\partial A}{\partial N} \bigg|_{N_0} + \frac{1}{2} \frac{\partial^2 A}{\partial N^2} \bigg|_{N_0} + \cdots.
\]

Substitution into Eq. (A1) yields to leading order (all odd orders vanish by symmetry)

\[
\mu_{\text{int}} = -\frac{z_i^2}{2} \frac{\partial^2 A}{\partial N^2} \bigg|_{N_0} = \frac{z_i^2}{2} \frac{\partial \mu}{\partial N} \bigg|_{N_0},
\]

where \( \mu(N) \) is the chemical potential of a neutral electrolyte molecule.

If both electrolyte species are mobile (monovalent) ions, we have in the DHA (Ref. 60)

\[
\mu = \mu^0 - \frac{\epsilon^2}{4 \pi \epsilon_0 \epsilon \lambda_{Dc}},
\]

where \( \epsilon \) is the permittivity of the water in the core and \( \lambda_{Dc} \) is the Debye length inside the core, given by

\[
\lambda_{Dc} = \frac{\epsilon^2}{\epsilon_0 \epsilon \kappa B T} V_c,
\]

where \( V_c = \pi \sigma_i^3 / 6 \) is the core volume. Combination of Eqs. (A4)–(A6) now yields

\[
\mu_{\text{int}} = -\frac{(z_i \epsilon)^2}{16 \pi \epsilon_0 \epsilon \lambda_{Dc} \epsilon N_0}.
\]

Comparing this with the Born energy in Eq. (4.4), we find

\[
- \mu_{\text{int}} / \mu_{\text{ext}} = (\epsilon_m / \epsilon) \frac{3 z_i}{5 \epsilon} (3 \lambda_B / \sigma_c)^{1/2} N_0^{-1/2} \ll N_0^{-1/2}.
\]
where \( \lambda_B \) is the Bjerrum length associated with the nonpolar solvent, as given by Eq. (3.5). The strong inequality in Eq. (A8) follows since \( \varepsilon_m \ll \varepsilon_w \), while \( \lambda_B \) does not exceed \( \sigma_c \) by more than an order of magnitude in the cases of interest here. Since always \( N_0 \gg 1 \), it is clear that \( \mu^\text{int}_{Si} \) may be neglected in comparison with \( \mu^\text{ext}_{Si} \). The result, Eq. (A8), is in accordance with recent Monte Carlo simulations,28 showing that \( (z^2) \) is significantly affected by salt addition \((N_0 \) was varied from 20 to 240) only in the (experimentally irrelevant) case that \( \varepsilon_m \) is comparable to \( \varepsilon_w \).

Finally, we consider the case where the electrolyte consists of a surfactant ion and a mobile counterion. Regarding the microemulsion droplet as a two-component macroscopic phase, we can make use of the Gibbs–Duhem relation61

\[
Nd \mu + N_w \, d \mu_w = 0,
\]

where \( \mu_w \) is the chemical potential of water. Combination of Eqs. (A4) and (A9) yields

\[
\mu^\text{int}_{Si} = -z^2 \frac{N_w}{2N_0} \frac{\partial \mu_w}{\partial N} \bigg|_{N_0}.
\]

In a mean-field approximation, with the counterions modeled as point charges, one has62

\[
\mu_w = \mu_w^0 + \frac{E_{el}}{N} (N + N_w) k_B T / N_w,
\]

where \( E_{el} \) is the electrostatic energy associated with the internal counterion distribution. Substitution into Eq. (A10) yields

\[
\mu^\text{int}_{Si} = -z^2 \frac{N_w}{2N_0} \frac{\partial E_{el}}{\partial N} \bigg|_{N_0}.
\]

Since, by definition, \( N_0 \) is the equilibrium surfactant aggregation number of the droplet, it follows that \( \mu^\text{int}_{Si} = \Delta A > 0 \). Furthermore, it can be shown63 that \( \partial E_{el} / \partial N > 0 \), whereby

\[
\mu^\text{int}_{Si} = -z^2 \frac{N_w}{2N_0} k_B T.
\]

In all cases of interest, \( z \) is of order 1 and \( N_0 \gg 1 \). We can, therefore, safely neglect \( \mu^\text{int}_{Si} \) in comparison with \( \mu^\text{ext}_{Si} \) also in this case. A similar conclusion was recently reached from a rather elaborate treatment, based on an approximate solution of the Poisson–Boltzmann equation for the mobile counterions within the core.64 It is reassuring that the same conclusion emerges from the relatively simple arguments presented here.

### APPENDIX B: FREE ENERGY MINIMIZATION

In this Appendix we derive the most probable distribution, i.e., the equilibrium distribution, of \( N_{0A} \) anions and \( N_{0B} \) cations among \( M \) identical microemulsion droplets. A generic configuration of the system may be specified by giving the numbers, \( m(N_A, N_B) \), of droplets with ion occupation numbers \( N_A \) and \( N_B \). The statistical weight of such a generic configuration, i.e., the number of distinct ways that it can be realized, is given by

\[
\Omega = \frac{M!}{\left( \prod_{N_A=0}^{N_{0A}} \prod_{N_B=0}^{N_{0B}} m(N_A, N_B)! \right)} \times \frac{\left( N_{0A} + N_{0B} \right)!}{\left( \prod_{N_A=0}^{N_{0A}} \prod_{N_B=0}^{N_{0B}} (N_A + N_B)! \right)^{m(N_A, N_B)}}.
\]

The first factor gives the number of distinct ways of forming this particular distribution of droplets (the droplets being distinguished by their occupation numbers), while the second factor gives the number of distinct ways of forming the individual droplets.

In terms of the probability, \( P(N_A, N_B) = m(N_A, N_B) / M \), of finding in the distribution a droplet with occupation numbers \( N_A \) and \( N_B \), we can express the three conservation relations, that must be satisfied by all distributions, as

\[
\sum_{N_A=0}^{N_{0A}} \sum_{N_B=0}^{N_{0B}} M P(N_A, N_B) = M,
\]

\[
\sum_{N_A=0}^{N_{0A}} \sum_{N_B=0}^{N_{0B}} M P(N_A, N_B) N_A = N_{0A},
\]

\[
\sum_{N_A=0}^{N_{0A}} \sum_{N_B=0}^{N_{0B}} M P(N_A, N_B) N_B = N_{0B}.
\]

The entropic contribution, \( A_F \), to the free energy functional in Eq. (2.5) can now be obtained as

\[
\beta A_F = -\frac{\ln \Omega}{V} = \rho \sum_{N_A=0}^{N_{0A}} \sum_{N_B=0}^{N_{0B}} P(N_A, N_B) [\ln P(N_A, N_B) + N_A \ln (N_A + N_{0A}) + N_B \ln (N_B + N_{0B})],
\]

with \( \rho = M/V \) and \( N_{tot} = N_{0A} + N_{0B} \). In deriving Eq. (B5) we have made use of the conservation relations (B2)–(B4) and assumed that \( N_A \), \( N_B \), and \( M \) are sufficiently large that Stirling’s approximation, \( \ln x! = x \ln x - x \), is accurate.

The equilibrium distribution, \( P_{eq}(N_A, N_B) \), is obtained by minimizing the free energy functional in Eq. (2.5) with respect to \( P(N_A, N_B) \). Evaluating the derivative \( \partial \delta(A) / [\rho \delta P(N_A, N_B)] \) and introducing the Lagrange multipliers \( \lambda, \alpha, \) and \( \gamma \), associated with the constraints (B2)–(B4), we obtain

\[
P_{eq}(N_A, N_B) = \exp \left[ -\beta \mu^\text{ex}(N_A, N_B) - N_A \ln (N_A + N_{0A}) - N_B \ln (N_B + N_{0B}) - 1 + \lambda + \alpha N_A + \gamma N_B \right],
\]

where \( \mu^\text{ex}(N_A, N_B) \) is the excess (nonideal) chemical potential of a droplet with occupation numbers \( N_A \) and \( N_B \), i.e.,

\[
\mu^\text{ex}(N_A, N_B) = \frac{\partial (A - A_F)}{\partial \rho P(N_A, N_B)} = \mu_1 + \mu_S + \mu_0.
\]

The constant \( -1 \) is eliminated by the constraint (B2), while the other two multipliers are associated with the chemical potentials of the two ionic species through \( \alpha = \beta \mu_A \) and \( \gamma = \beta \mu_B \).65 We thus obtain the grand canonical distribution function.
\[ P_{eq}(N_A, N_B) = \frac{Q(p, N_A, N_B, T) \exp(\beta N_A \mu_A) \exp(\beta N_B \mu_B)}{\sum_{N_A=0}^{\infty} \sum_{N_B=0}^{\infty} Q(p, N_A, N_B, T) \exp(\beta N_A \mu_A) \exp(\beta N_B \mu_B)}, \]  

(B8)

with

\[ Q(p, N_A, N_B, T) = \exp\left[-\beta \mu^n(N_A, N_B) - N_A \ln(N_A/N_{tot}) - N_B \ln(N_B/N_{tot})\right]. \]  

(B9)

Equations (B8) and (B9) are easily generalized to an arbitrary number of ion species.

Changing variables from \( N_A \) and \( N_B \) to \( N = N_A + N_B \) and \( z = N_A \nu_A - N_B \nu_B \), where \( \nu_A \) and \( -\nu_B \) are the ionic charges of the ions, we obtain

\[ P_{eq}(N, z, T) = \frac{Q(p, N, z, T) \exp(\beta \mu_A(N \nu_A + z)/(\nu_A + \nu_B)) \exp(\beta \mu_B(N \nu_A - z)/(\nu_A + \nu_B))}{\sum_{z = -\nu_A}^{\nu_A} \sum_{N = 0}^{\nu_A} Q(p, N, z, T) \exp(\beta \mu_A(N \nu_A + z)/(\nu_A + \nu_B)) \exp(\beta \mu_B(N \nu_A - z)/(\nu_A + \nu_B))}, \]  

(B10)

where, due to electroneutrality \( (N_{tot} \nu_A = N_{tot} \nu_B) \), \( z = N_{tot}/(1/\nu_A + 1/\nu_B) \), and

\[ Q(p, N, z, T) = \exp\left[-\beta \mu^n(N_A, N_B) - \frac{N \nu_A + z}{\nu_A + \nu_B} \ln\left(\frac{N \nu_A + z}{N_{tot}(\nu_A + \nu_B)}\right) - \frac{N \nu_A - z}{\nu_A + \nu_B} \ln\left(\frac{N \nu_A - z}{N_{tot}(\nu_A + \nu_B)}\right)\right]. \]  

(B11)

with a corresponding redefinition of the chemical potential. It is important to note that the net droplet charge \( z \) can only vary in increments of \( \min(\nu_A, \nu_B) \).

The results in Eqs. (B10) and (B11) can be further simplified by noting that, due to the large Born energy (cf. Sec. IV), only configurations with \( |z| \ll N \) contribute significantly to the equilibrium distribution \( P_{eq}(N_A, N_B) \). Expanding the logarithmic terms in Eq. (B11) and neglecting terms of order \( z/N \) and higher in Eqs. (B10) and (B11), we obtain

\[ P_{eq}(N, z) = \exp\left[-\beta [\mu(z) + \mu_S(z) + \mu_0(N) - \bar{\mu}]\right], \]  

(B12)

where we have exhibited the fact that the individual terms in the excess chemical potential in Eq. (B7) depend on \( z \) or \( N \), but not on both (cf. Secs. III and IV). Furthermore, we have introduced the mean chemical potential \( \bar{\mu} = (\nu_A \mu_A + \nu_B \mu_B)/(\nu_A + \nu_B) \) and a redefined \( \mu_0(N) \) which includes the \( N \)-dependent contribution from the logarithmic terms in Eq. (B11).

Equation (B12) shows that fluctuations in \( z \) and \( N \) are thus statistically independent (provided that \( |z| \ll N \)), i.e.,

\[ P_{eq}(N, z) = P_{eq}(N) P_{eq}(z), \]  

(B13)

with the equilibrium distribution of net droplet charge given by

\[ P_{eq}(z) = \frac{\exp\left[-\beta [\mu(z) + \mu_S(z)]\right]}{\sum_{z = -\nu_A}^{\nu_A} \exp\left[-\beta [\mu(z) + \mu_S(z)]\right]}. \]  

(B14)