

Interaction between Deformable Brownian Droplets

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The interaction energy between emulsion droplets of micron and submicron size is theoretically studied. The role of the droplet deformability is considered in detail and the equilibrium configuration of a doublet of droplets is determined. It is shown that the attractive interactions may lead to formation of a planar film between two colliding droplets. This deformation is particularly important at high electrolyte concentration and low interfacial tension. The radial distribution function, which can be used for determination of thermodynamic properties of emulsions, is calculated taking into account the droplet deformability.

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Emulsions (dispersions of liquid in liquid) are widespread in technological applications but their properties and stability are still not very well understood. The main problems in understanding emulsions, in comparison with dispersions of solid particles, are related to the deformability and the surface fluidity of the emulsion drops [1]. When two drops of millimeter size collide under the action of some outer force, one usually observes the formation of planar film between them. The lifetime of such film is the most important factor determining the overall stability of an emulsion [1]. However, for emulsions containing Brownian droplets of micrometer size (mini-emulsions) it is not clear in advance whether such a deformation will occur. That is why when interpreting experimental results the miniemulsion droplets are often considered as being nondeformable spheres [2,3]. Only a few studies [4,5] were published where some experimental observations (stability against flocculation and obtaining of emulsions with very high concentration of disperse phase) were explained by means of the droplet deformability.

Recently, a method for producing miniemulsions consisting of fairly monodisperse droplets was proposed [2]. This method allows quantitative experimental investigation of the interdroplet interaction and its role for the properties of miniemulsions—phase diagrams, structure factor, kinetics of flocculation, etc. The condensed-phase-diluted-phase phase transition, with monodisperse miniemulsion droplets, was explained in Ref. [2] by the joint action of attractive van der Waals and depletion forces between nondeformable spheres.

The possibility for deformation of small (micron and submicron) droplets and the impact of the deformability on the equilibrium miniemulsion properties are investigated in this theoretical study. In the following we show (i) that when attractive forces exist between the droplets, the interaction energy between two (even very small) deformed droplets in equilibrium can be lower than that between the same nondeformed spheres, i.e., the deformation is often a spontaneous process; (ii) how the equilibrium radius and thickness of the formed planar film can

be calculated; and (iii) how the droplet deformability can be taken into account when calculating the equilibrium properties (radial distribution function, osmotic virial coefficient, phase diagram, structure factor) of emulsions.

A recent theoretical study [6] shows that the interaction energy between two deformed drops, having the shape of spherical segments (see Fig. 1), can be expressed as

$$W(h, r, a) = W^{vw} + W^S + \Delta W, \quad (1)$$

where a is the drop radius (prior to the deformation) and h and r are the film thickness and radius, respectively. The different contributions are the van der Waals energy [6]

$$W^{vw} = -\frac{A}{12} \left[\frac{3}{4} + \frac{a}{h} + 2 \ln \left(\frac{h}{a} \right) + \frac{r^2}{h^2} - \frac{2r^2}{ah} \right], \quad (2)$$

$$h/a < 0.5, \quad r/a < 0.5,$$

where A is the Hamaker constant; the surface dilational energy, W^S , which accounts for the increase of the interfacial area due to the deformation [6]

$$W^S = \gamma \frac{\pi}{2} \frac{r^4}{a^2}, \quad (r/a)^2 \ll 1, \quad (3)$$

with γ being the interfacial tension. For systems with very low interfacial tension, like microemulsions or lipid vesicles, the bending elasticity of the surface may contribute to the deformation energy. In miniemulsion systems

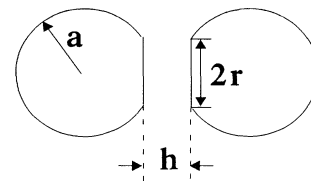


FIG. 1. Sketch of two deformed droplets (the film thickness and radius are exaggerated).

this contribution is usually negligible as shown in Ref. [6]. ΔW stands for some other possible interactions, which can be evaluated in the framework of Derjaguin approximation [6,7]

$$\Delta W = \pi r^2 f(h) + \pi a \int_h^\infty f(H) dH, \quad (4)$$

$$h/a \ll 1, \quad (r/a)^2 \ll 1.$$

Here $f(h)$ is the interaction free energy per unit area in an infinite flat film of thickness h . One should note that the terms proportional to r^2 in Eqs. (2) and (4) correspond to the interaction across the planar film, while the other terms account for the interaction between the spherical surfaces surrounding the film [6]. The following particular cases present special interest due to their universality and practical importance: (i) exponential function

$$f(h) = B \exp(-h/d), \quad (5)$$

which can describe electrostatic, steric, hydrophobic, or hydration interactions [8]. B is positive for repulsive interactions and negative for attractive ones. The parameter d is positive and determines the range of the interaction. For electrostatic interactions d equals the Debye screening length κ^{-1} (which is defined below). The explicit expressions for B and d depend on the specific interaction under consideration and can be found in the literature [8]; (ii) depletion interaction

$$f(h) = -kTC_m(\sigma + 2b - h), \quad h \leq \sigma + 2b, \quad (6)$$

and $f(h) = 0$ (at $h > \sigma + 2b$) when much smaller colloid particles (micelles or polymer molecules) of concentration C_m with an effective diameter σ are present in the disperse medium [2,3,8-10]. The distance b accounts for the repulsion between the droplets and micelles, or polymer molecules. Richetti and Kekicheff [9] have directly measured the depletion interaction in solutions of charged micelles and found that in their system $b \approx 2.5\kappa^{-1}$ and $\sigma \approx 2(R_m + \kappa^{-1})$, where R_m is the actual micellar radius.

We study below the dependence of the interaction energy $W(h,r)$ between deformable droplets on the interdroplet separation h and the deformation expressed by the film radius r ; see Fig. 1. In Fig. 2 the contour plot of $W(h,r)$ is presented for two charged deformable droplets of radius $a = 1 \mu\text{m}$, $A = 2 \times 10^{-20} \text{ J}$, $\gamma = 1 \text{ mN/m}$, and surface potential $\Psi_0 = 100 \text{ mV}$, as calculated from Eqs. (1)-(5). The electrostatic repulsion between the drop surfaces is calculated by means of the nonlinear superposition approximation [8]:

$$B = 64kTC_{\text{EC}}\kappa^{-1} \tanh^2(e\Psi_0/4kT)$$

and $d = \kappa^{-1}$ (C_{EC} is the electrolyte concentration which in our case corresponds to 0.1 M NaCl , e is the elementary charge, and kT is the thermal energy). One sees from the plot that the minimum of the interaction energy corresponds to a deformed state with equilibrium values

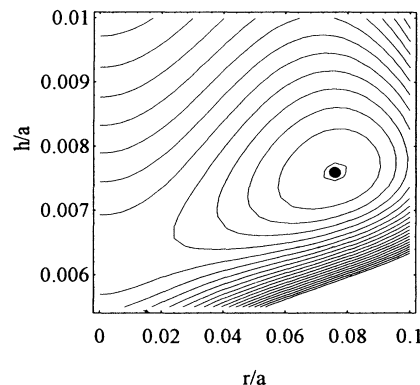


FIG. 2. Contour plot of the interaction energy, $W(h,r)/kT$, between two deformable charged droplets (the parameters are given in the text). The distance between two neighboring contours is equal to $2kT$. The minimum $W/kT = -60.1$ is shown with a full circle.

$r_E/a = 0.076$ and $h_E/a = 0.0076$. The magnitude of the interaction energy $W(h_E, r_E)/kT = -60.1$ is greater than the one for two nondeformable spheres with the same parameters, $W(h_E, r=0)/kT = -51.3$ ($h_E/a = 0.0062$ in this case). The deformation is even more pronounced for higher electrolyte concentration and lower interfacial tension. However, for lower electrolyte concentrations, smaller Hamaker constant, and/or larger interfacial tension the minimum of the interaction energy appears at $r_E = 0$; i.e., the nondeformed state is most probable. Although the interaction energy strongly depends on the droplet size a , the conditions at which the deformation occurs are slightly sensitive to a .

In order to demonstrate the role of the depletion interaction, we calculate $W(h,r)$ between the same droplets but in the presence of micelles. The micellar volume fraction is $\Phi = 1\%$. The other parameters are $R_m = 2.4 \text{ nm}$, aggregation number $\nu = 80$, micellar charge number 20 (degree of dissociation $\alpha = 0.25$), and critical micellar concentration $C_{\text{MC}} = 10^{-3} \text{ M}$. These values are typical for ionic surfactants like sodium dodecylsulfate [8] (and are used also when plotting curve 3 in Fig. 3 below). When defining Debye length κ^{-1} we took into account both the neutral electrolyte (0.1 M NaCl) and the ions due to surfactant dissociation [see Eq. (3) in Ref. [9]]

$$\kappa^2 = \frac{8\pi e^2}{\epsilon kT} \left[C_{\text{EC}} + C_{\text{MC}} + \frac{3a\nu\Phi}{8\pi R_m^3} \right].$$

The quantities b and σ are calculated as described above. As a result we obtain that the depletion interaction leads to much larger deformation and stronger attraction: $r_E/a = 0.093$, $h_E/a = 0.0072$, $W(h_E, r_E)/kT = -83.3$. The increase in the micellar concentration enhances the deformation and the attraction.

The equilibrium configuration of the pair of two droplets can be determined from the general expressions, Eqs. (1)-(4). The extremum of the function $W(h,r)$ can be

found from the conditions

$$(\partial W/\partial h)_r = 0, \quad (\partial W/\partial r)_h = 0. \quad (7)$$

From Eqs. (1)–(4) and (7) one can obtain a system of two equations for determination of the equilibrium film thickness h_E and radius r_E ,

$$\frac{A}{12\pi h^2} \left[1 + \frac{2r^2}{ha} \right] - f(h) + \frac{r^2}{a} \frac{df}{dh} = 0, \quad (8)$$

$$r \left[\frac{A}{12\pi h^2} - f(h) - \gamma \frac{r^2}{a^2} \right] = 0, \quad (9)$$

which can be solved numerically. The terms proportional to h/a are neglected in Eqs. (8) and (9) because the equilibrium thickness is always much smaller than the droplet radius. In general, Eqs. (8) and (9) may have one, several, or no solutions. By using standard mathematical procedures one can recognize among them the local minima and the global minimum of $W(h, r)$. The latter may correspond to a deformed or nondeformed state depending on the parameters of the system and type of interaction $f(h)$.

The energy plot presented in Fig. 2 suggests a way for considering the thermodynamic properties of emulsions consisting of deformable Brownian droplets. These properties can be presented by means of the radial distribution function $g(z)$,

$$g(z) = \exp[-w_f(z)/kT]. \quad (10)$$

z is the separation between the mass centers of the drops (it depends on both h and r); $w_f(z)$ is the potential of mean force. For diluted dispersions of hard spheres $w_f(z)$ coincides with the pair interaction energy. However, in our case we should account for the fact that a given z can be realized within a range of different values of h and r . This variety of configurations can be accounted for by applying the potential distribution theorem [8,11]. It states that the potential of mean force, $w_f(z)$, can be determined by averaging over all possible configurations which correspond to a given z . In our case this can be written in the form

$$g(z) = \text{const} \times \int \exp\{-W[h(r), r]/kT\} dr, \quad (11)$$

where $h(r)$ represents the connection between h and r at fixed z . The value of the normalizing constant in Eq. (11), which is equal to $4(\pi a^2 \gamma / 2kT)^{1/4} / \Gamma(\frac{1}{4})$, we found from the requirement $w_f(z \rightarrow \infty) = 0$ [or $g(z \rightarrow \infty) = 1$] and Eqs. (1)–(6) where $\Gamma(x)$ is the gamma function. In the calculations below we neglect all configurations corresponding to large deformations ($r/a > \frac{1}{2}$) and very small thicknesses ($h/a < 0.003$) because, as seen from Fig. 2, these correspond to high energy of the system and are quite improbable. Hence they can be omitted when calculating $w_f(z)$ without a substantial error. Besides, Eqs. (2)–(4) are correct for small deformations. Equation (4) is restricted to small separations ($h/a \ll 1$) but typically

all interactions (except the van der Waals one) are negligible at separations comparable to the drop size. An expression for the van der Waals interaction energy between deformed droplets at arbitrary separations, which can be used for determination of $w_f(z)$ at larger distances, is given elsewhere [6]. To illustrate the importance of the deformation we plot in Fig. 3 $w_f(z)$ for deformable and nondeformable particles with parameter values being the same as in Fig. 2. One sees that the deformation leads to a greater attractive energy and a much broader minimum of the interaction curve; cf. curves 1 and 2. The presence of micelles (depletion effect) causes stronger attraction and more pronounced droplet deformation (curve 3). The broadening of the minima of curves 2 and 3 is due to the droplet deformability which allows configurations with $z/a < 2$. At large separations all the curves coincide.

Having $g(z)$ one can proceed with the calculation of other properties like the second osmotic virial coefficient and the static structure factor which can be directly measured by light scattering techniques [2]. Also, a phase diagram condensed-diluted phase can be constructed; see, e.g., Ref. [2]. Taking into account the deeper and the wider minima (curves 2 and 3 compared to curve 1 in Fig. 3) one may expect a strong influence of the droplet deformability on these properties.

The detailed quantitative comparison of the proposed model with experimental results is beyond the scope of this Letter. However, we can point out several experimental observations which are most probably closely related to the droplet deformability. Bibette and co-workers [2] observed a strong increase of the interdroplet attraction at electrolyte concentrations above 0.2M NaCl. The analysis performed above shows that in this region of electrolyte concentrations a spontaneous droplet deformation, accompanied with considerably greater interdroplet attraction, can be expected. At higher electrolyte concen-

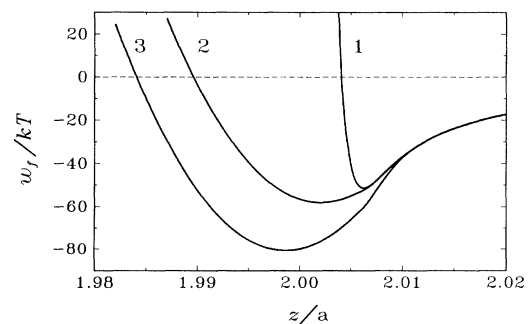


FIG. 3. Interaction energy, $w_f(z)$, averaged over the possible configurations [see Eqs. (10) and (11)] as a function of the distance between the mass centers of the droplets. Curve 1 is for nondeformable spheres; curves 2 and 3 are for deformable droplets. Curve 3 corresponds to the presence of 1 vol% of charged micelles when depletion interaction between the droplets is present.

tration (0.5M NaCl) Bibette and co-workers [2] observed gelation of the studied emulsion even at very small volume fraction of the droplets (0.5 vol%). As pointed out by the authors this effect is due to very strong inter-droplet attraction which is probably connected with the deformability of the droplets. Experimentally such deformation, at electrolyte concentrations above 0.3M, was observed years ago [4] with much larger drops of diameter between 50 and 100 μm for a set of ionic surfactants. In another study [5] the rate of flocculation in emulsions stabilized with several ionic surfactants was measured as a function of the ionic strength. The difference in stability was explained by deformation of the droplets in the less stable emulsion (possessing much lower interfacial tension).

We believe that the theoretical analysis performed above convincingly shows that the droplet deformability is an important factor for the properties of miniemulsions. The attractive interactions between the droplets may lead to planar film formation even for very small droplets, thus changing significantly the magnitude of the interaction energy. The deformation is particularly important at high electrolyte concentrations (above 0.2M NaCl) and in emulsions stabilized by nonionic surfactants where there is no long-range repulsion between the droplets. The lower the interfacial tension and the stronger the attractive forces, the greater the deformation. The deformation certainly also affects the viscous resistance of the relative approach of the droplets. Hence, the droplet deformability should be accounted for when interpreting experimental results or when calculating the miniemulsion properties.

After certain modifications this approach can be applied to other important problems and systems, like the adhesion of deformable drops or vesicles to solid surfaces and the interaction between deformable gel particles. In the present study we consider only equilibrium properties

and the effect of surface fluidity (which is important for dynamic properties, e.g., diffusion coefficient) is not investigated. The film rupture and the coalescence of deformable drops are studied elsewhere [12].

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