

# Pair interaction energy between deformable drops and bubbles

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(Received 1 March 1993; accepted 12 July 1993)

The potential energy of interaction between two deformed particles, having the shape of spherical segments and separated by a planar film, is considered. An exact explicit expression for the van der Waals interaction energy between such deformed particles of arbitrary size and deformation is derived by using the microscopic approach of Hamaker [Physica 4, 1058 (1937)]. By means of Derjaguin's approximation [Kolloid Z. 69, 155 (1934)] explicit expressions for the electrostatic, steric, depletion, and other types of interaction are derived. The relative contributions of the interaction across the planar film and between the spherical surfaces surrounding the film, are analyzed for different cases. The surface deformation energy caused by an increase of the interfacial area during the particle deformation is also considered. The implication of the obtained formulas for treatment of the particle interactions in some particular systems like emulsions, microemulsions, and vesicles, as well as for the adhesion of such particles to a solid wall is briefly discussed.

## I. INTRODUCTION

The stability and behavior of disperse systems depend mostly on the interaction between the particles. The stability of dispersions consisting of solid particles is usually satisfactorily explained in the framework of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory,<sup>1-3</sup> which accounts for the electrostatic and van der Waals interactions between the particles. In the last two decades the experiments with surface force balance revealed that other types of interactions may also exist at small surface to surface separations—oscillatory structure forces, hydrophobic and hydration forces, etc.<sup>4</sup> The experiments proved also the important role of steric<sup>5,6</sup> and depletion<sup>7</sup> interactions in stabilizing (or destabilizing) the dispersions.

For deformable particles (drops and bubbles) the situation is more complex because they possess somewhat different properties than the solid ones. The most important are the drop deformability and surface fluidity.<sup>8</sup> These two effects have great impact on the intermolecular and hydrodynamic interactions between fluid particles, and have been the subject of numerous studies.<sup>9-14</sup> It is established that when two large macroemulsion drops or bubbles of millimeter or submillimeter size approach each other, they deform and a planar film forms between them.<sup>9-11</sup> The rate of thinning and the stability against rupture of this film determine the overall stability of emulsions or foams.<sup>8</sup> The role of different factors on the behavior of the liquid films is theoretically and experimentally investigated in details.<sup>8-14</sup> However, several important questions can be raised, which still have no definite answer. It is not clear whether such deformation takes place when smaller particles (of micron or submicron size) are considered: on the one hand the smaller drops possess higher capillary pressure which opposes their deformation, but on

the other hand they undergo intensive Brownian motion which gives rise to an additional force<sup>5,15</sup> enhancing the deformation. Another problem is how the energy of drop deformation, connected with the extension of the interfacial area, contributes to the pair interaction. It is not clear also how the presence of a planar film between the two particles will affect the other interactions with the appearance of the deformation.<sup>16-18</sup> Indeed, when a film with small radius is present, the interaction cannot be described by the existing theories neither for infinite planar films, nor for spheres,<sup>18</sup> because the contribution of the spherical parts to the interaction is comparable to that of the film.

The construction of an appropriate pair interaction potential, accounting for the specific features of the deformed particles (drops or bubbles), is the main aim of the present paper. Such potential enables one to define the radial distribution function for diluted systems and hence to calculate different thermodynamic quantities. This potential could be introduced into the Smoluchowski theory<sup>19</sup> for colloidal coagulation allowing to investigate Brownian flocculation and coalescence in emulsion systems. Such a study is published elsewhere.<sup>18</sup> In the present paper, we obtained *explicit* expressions for the van der Waals interaction between two deformed particles, by using the Hamaker approach.<sup>20</sup> The other types of interactions, which might be present in dispersions of deformable particles, are treated by applying the Derjaguin's method<sup>2,3,21</sup> to slightly deformed spheres.

The developed approach allows also the investigation of interactions between deformable particle and a solid wall, which is important for studying drop (or biological cell) attachment and adhesion to different surfaces.

The paper is organized as follows: In Sec. II the geometry of the system under consideration is specified. Section III A is devoted to the derivation of an exact formula for

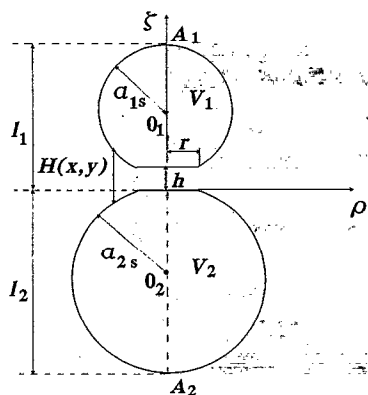


FIG. 1. Geometry of the system under consideration.  $h$  is the film thickness and  $r$  is the film radius.  $a_{ks}$  ( $k=1,2$ ) is the radius of the spherical part and  $V_k$  is the volume of the respective particle.  $\rho$  and  $\xi$  are the radial and axial coordinates, respectively.

the van der Waals interactions between two deformed particles. In Sec. III B the energy of deformation for emulsion drops is derived as a function of the interfacial tension and Gibbs elasticity; Sec. III C deals with application of the Derjaguin's method<sup>2,3,21</sup> to slightly deformed spherical particles; this approach is used for calculating the electrostatic interaction between two slightly deformed drops (bubbles, vesicles); the steric, depletion, and other types of interaction are also discussed; Sec. IV presents some numerical results and discussion and Sec. V contains the concluding remarks.

## II. GEOMETRY OF THE SYSTEM

We consider a system consisting of two deformed particles, having the shape of spherical segments with radii  $a_{1s}$  and  $a_{2s}$ , separated by a planar film of thickness  $h$  and radius  $r$  (see Fig. 1). When  $a_{1s} \rightarrow \infty$ , the case of interaction between a fluid particle and a solid wall is obtained. The radius and the thickness of the film are not necessarily the equilibrium ones—they may correspond to a given moment of the processes of particle deformation (variable  $r$ ) and film thinning (variable  $h$ ).

Two simplifying assumptions are imposed in our consideration (see Fig. 1). The first one is to consider the interaction between two spherical segments instead of accounting in details for the actual geometry of the deformed particles. As known, the local intermolecular interaction between surfaces 1 and 2 leads to a smooth transition from the flat film to the spherical surface far away from the film,<sup>2,3,22,23</sup> where this interaction is negligible. However, as a first approximation we will neglect the effect of the real shape in the transition zone and will integrate the interaction energy per unit area for the unperturbed (idealized) system shown in Fig. 1. This simplification allows one to obtain quite simple (although approximate) formulas which describe the main effects caused by the deformation. In principle, the inaccuracy involved by this assumption can be evaluated by solving the problem for the shape of

the surface in the transition zone,<sup>22,23</sup> which needs extensive numerical calculations.

Another simplification is achieved by assuming that the film is flat. In fact this is possible only when the particles are identical:  $a_{1s} = a_{2s}$  and  $\gamma_1 = \gamma_2$  ( $\gamma_1$  and  $\gamma_2$  are the respective interfacial tensions), or when the interaction between a drop and solid wall is considered. In the case of two drops of different radii and interfacial tensions, the film has its own curvature with radius  $a_f$  determined by the capillary pressure drops across the different surfaces

$$\frac{2(\gamma_1 + \gamma_2)}{a_f} = \frac{2\gamma_1}{a_1} + \frac{2\gamma_2}{a_2} \quad (2.1)$$

It is assumed for simplicity in Eq. (2.1) that the film tension is the sum of the interfacial tensions of the two drops. If  $a_{1s} \approx a_{2s}$  and  $\gamma_1 \approx \gamma_2$ ,  $a_f \gg a_{ks}$  ( $k=1, 2$ ). As shown by Ivanov, Vasan, and Borwankar,<sup>24</sup> in this case the curvature of the film can be accounted by simply taking  $r = (A^f/\pi)^{1/2}$ , where  $A^f$  is the actual area of the curved film. Therefore, strictly speaking our consideration is restricted to drops of similar size and interfacial tension, or to the interaction between a fluid particle and a solid wall.

## III. INTERACTION ENERGY BETWEEN TWO DEFORMED DROPS

In this section the interaction energy between two deformed drops having the shape of spherical segments, like those shown in Fig. 1, is considered. Our aim is to formulate a procedure for calculation of this energy by taking into account all the effects, stemming from the drop deformation. As a reference thermodynamic state we chose the system of two nondeformed (spherical) drops of radius  $a_k$  ( $k=1, 2$ ) at infinite separation. The deformation is assumed to occur at constant volume of the drops, i.e., the radius of the spherical part of a deformed drop  $a_{ks} \geq a_k$  ( $k=1, 2$ ).

The total interaction potential energy for two deformed drops,  $W$ , is assumed to be the sum of several contributions:

$$W = W^S + W^{VW} + W^E + W^{St} + \Delta W \quad (3.1)$$

Here  $W^S$  is the contribution due to the change of the surface energy during the drop deformation,  $W^{VW}$  is due to van der Waals interaction,  $W^E$  is the electrostatic term,  $W^{St}$  accounts for the steric interaction if polymers are adsorbed at the drop surface and  $\Delta W$  stands for other possible interactions, e.g., those, mentioned above (depletion, structural, etc.). These contributions are considered below.

### A. Van der Waals interaction between two deformed particles

The Derjaguin's approach<sup>2,3,21</sup> is often applied for deriving the van der Waals energy of interaction between two spheres at small distances.<sup>2-5</sup> However, the obtained result is valid only for  $h/2a \ll 1$ .<sup>2,3</sup> In the case of deformed spheres, an additional restriction is  $r/a \ll 1$ . Therefore, it is preferable to derive an exact expression for the van der Waals energy of interaction between two deformed spheres as shown in Fig. 1. For this purpose the microscopic ap-

proach of Hamaker<sup>20</sup> is used. We should note that the electromagnetic retardation effects are neglected in the consideration, but they could be easily incorporated by introducing an effective Hamaker constant to account for them.<sup>5</sup>

It is convenient to introduce a cylindrical coordinate system where  $\rho$  is the radial coordinate,  $\Theta$  is the polar angle, and  $\xi$  is the vertical coordinate. The particles have the shape of spherical segments with radii  $a_{1s}$  and  $a_{2s}$  and centers  $O_1$  and  $O_2$ , respectively. The planar parts for both particles have identical radii  $r$ . The corresponding particle volumes are  $V_1$  and  $V_2$  (see Fig. 1). Other important geometrical points are the most remote points of the particle surfaces  $A_1$  and  $A_2$  with respect to the coordinate center  $O$ . The coordinates of these two points are  $A_1(0,0,l_1)$  and  $A_2(0,0,l_2)$  where

$$l_1 = h + a_{1s} + \sqrt{a_{1s}^2 - r^2}; \quad l_2 = a_{2s} + \sqrt{a_{2s}^2 - r^2}. \quad (3.2)$$

The energy of van der Waals interaction between two particles is defined by<sup>20</sup>

$$W = -\frac{1}{\pi^2} \int_{V_1} \int_{V_2} \frac{A_H dV_1 dV_2}{|\mathbf{r}_1 - \mathbf{r}_2|^6} \quad (3.3)$$

where  $dV_k$  is an element of the volume  $V_k$  ( $k=1,2$ );  $\mathbf{r}_k$  is the radius vector of a given point in the volume  $V_k$  with coordinates  $\mathbf{r}_k(\rho_k, \Theta_k, \xi_k)$ .  $A_H$  is the Hamaker constant. In the present coordinates we have<sup>16</sup>

$$|\mathbf{r}_1 - \mathbf{r}_2|^2 = \rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos(\Theta_1 - \Theta_2) + (\xi_1 - \xi_2)^2. \quad (3.4)$$

Hence, the general expression for the interaction energy  $W$  [see Eq. (3.3)] can be written in the following form (see Fig. 1)

$$W = -\frac{A_H}{4\pi^2} \int_h^{l_1} dz_1 \int_0^{l_2} dz_2 \int_0^{b_1} dx_1 \times \int_0^{b_2} dx_2 \int_0^{2\pi} d\Theta_1 \int_0^{2\pi} d\Theta_2 F_6, \quad (3.5)$$

where

$$\begin{aligned} x_1 &= \rho_1^2; \quad x_2 = \rho_2^2, \\ z_1 &= \xi_1; \quad z_2 = -\xi_2. \end{aligned} \quad (3.6)$$

The function  $F_6$  is given by

$$F_6 = [x_1 + x_2 - 2\sqrt{x_1 x_2} \cos(\Theta_1 - \Theta_2) + (z_1 + z_2)^2]^{-3}. \quad (3.7)$$

The integration limits  $b_k$  are defined as

$$b_k = a_k^2 - (l_k - a_k - z_k)^2, \quad k=1,2. \quad (3.8)$$

The sixfold integral can be calculated analytically. Integrating over  $\Theta_1$ ,  $\Theta_2$ ,  $x_1$ , and  $x_2$  leads to the following expression:

$$F_2 = \frac{b_1 + b_2 - \sqrt{Q}}{4(z_1 + z_2)^4} + \frac{b_1 + b_2 + (z_1 + z_2)^2}{4(z_1 + z_2)^2 \sqrt{Q}}, \quad (3.9)$$

where

$$Q = [b_1 + b_2 + (z_1 + z_2)^2]^2 - 4b_1 b_2. \quad (3.10)$$

From  $F_2$  we can derive

$$W_2 = -\frac{A_H}{4\pi^2} F_2 \quad (3.11)$$

which is the interaction energy of two discoidal cross-sections placed in particles 1 and 2 and parallel to the planar region (Fig. 1). Equation (3.11) is valid for axysymmetrical bodies with arbitrary profiles. The specific shape of the bodies is introduced in the next two integrations. Our consideration below is restricted to the case of two deformed spheres (see Fig. 1) where an analytical solution is possible. For other axysymmetrical geometries numerical integration of the energy  $W_2$  over the coordinates  $z_1$  and  $z_2$  might be needed (see Sec. IV D).

For two deformed spheres the final result reads

$$\begin{aligned} W = & -\frac{A_H}{12} \left[ \frac{2a_2(l_1-h)}{l_1(l_2+h)} + \frac{2a_2(l_1-h)}{h(l_1+l_2)} + 2 \ln \left[ \frac{h(l_1+l_2)}{l_1(h+l_2)} \right] + \frac{r^2}{h^2} - \frac{l_1-h}{l_2} \frac{2r^2}{hl_1} - \frac{l_1-a_1-(l_2-a_2)}{2l_1-2a_1-h} \frac{2r^2}{hl_1} - \frac{2(l_2-a_2)-h}{2l_1-2a_1-h} \frac{d-h}{2h} \right. \\ & + \frac{2a_2 l_2^2 (l_1-h)}{hl_1(l_1+l_2)(l_2+h)} - \frac{2a_2^2}{h(2l_1-2a_1-h)} \frac{l_1^2+r^2}{(l_1+l_2)(l_1+l_2-2a_2)} \\ & + \frac{2a_2^2 d}{(2l_1-2a_1-h)[(h+l_2)(h+l_2-2a_2)-(l_1-h)(l_1-2a_1-h)]} \\ & \left. - \frac{4a_2^3(l_1-h)}{(l_1+l_2)(l_1+l_2-2a_2)[(h+l_2)(h+l_2-2a_2)-(l_1-h)(l_1-2a_1-h)]} \right], \end{aligned} \quad (3.12)$$

where

$$d = \sqrt{h^2 + 4r^2}. \quad (3.13)$$

It can be shown that the general expression (3.12) transforms into the well known Hamaker expressions<sup>20</sup> for the interaction energy between two spheres ( $r=0$ ) and between two infinite half-spaces ( $a \rightarrow \infty, l \rightarrow \infty, r \rightarrow \infty$ ). The general result (3.12) can be simplified also in the following particular cases:

(i)  $a_1 = a_2 = a$ ;  $l_2 = l$ ;  $l_1 = l + h$ , i.e., the energy of interaction of two identical deformed spheres can be expressed as

$$W = -\frac{A_H}{12} \left\{ \frac{2al}{(l+h)^2} + \frac{2al}{h(2l+h)} + 2 \ln \left[ \frac{h(2l+h)}{(l+h)^2} \right] + \frac{r^2}{h^2} - \frac{2r^2}{h(l+h)} - \frac{2r^2}{(l+h)[2(l-a)+h]} + \frac{d^2(d-h)}{2h[2(l-a)+h]^2} - \frac{2r^2(2l^2+lh+2ah)}{h(l+h)^2[2(l-a)+h]^2} \right\}. \quad (3.14)$$

(ii)  $l_1 \rightarrow \infty, a_1 \rightarrow \infty$ ; this case corresponds to the interaction between deformed sphere and a semi-infinite slab

$$W = -\frac{A_H}{12} \left[ \frac{2a}{l+h} + \frac{2a}{h} + 2 \ln \left( \frac{h}{h+l} \right) + \frac{r^2}{h^2} - \frac{2r^2}{lh} \right], \quad (3.15)$$

where  $l = l_2$  and  $a = a_2$ , which are connected by the relationship

$$l = a + \sqrt{a^2 - r^2}. \quad (3.16)$$

(iii) For two identical spheres (i.e.,  $a_1 = a_2 = a$ ;  $l_2 = l$ ;  $l_1 = l + h$ ) which are weakly deformed,  $r^2/a^2$  is a small parameter and after neglecting the terms  $O[r^4/a^4]$  we derive

$$W = -\frac{A_H}{12} \left[ \frac{4a^2}{(2a+h)^2} + \frac{4a^2}{h(4a+h)} + 2 \ln \left[ \frac{h(4a+h)}{(2a+h)^2} \right] + \frac{128a^5r^2}{h^2(2a+h)^3(4a+h)^2} \right]. \quad (3.17)$$

The numerical comparison showed that Eq. (3.17) gives results coinciding with the numerical data presented by Denkov *et al.*<sup>16</sup>

(iv) Further simplification can be achieved by introducing the small parameters  $\varepsilon_1 = (r/2a)^2$ ,  $\varepsilon_2 = h/2a$ , and  $\varepsilon_3 = \sqrt{h/2a + 4(r/2a)^2}$  (i.e., small deformations at small interparticle distances). Ignoring all terms of higher order with respect to the above small parameters we obtain

$$W = -\frac{A_H}{12} \left[ \frac{3}{4} + \frac{a}{h} + 2 \ln \left( \frac{h}{a} \right) + \frac{r^2}{h^2} - \frac{2r^2}{ah} \right]. \quad (3.18)$$

The numerical calculations showed that this simple formula gives very accurate results for  $h/a < 0.3$  and  $r/a < 0.7$  (see Sec. IV below). We should note that Derjaguin's approximation (see Sec. III C below) does not provide the last term in the square braces in Eq. (3.18) when applied to van der Waals interaction. The numerical

comparison showed that Eq. (3.18) is more accurate and less restricted (it can be applied in larger regions of values for  $h$  and  $r$ ) than the result of Derjaguin's approach.

## B. Surface deformation energy

For simplicity in this subsection we consider two identical drops. The generalization of the derivation to drops, different in size and interfacial tension, is trivial.

Since the drop volume remains constant during deformation, any deviation of the drop shape from the spherical one leads to an increase of the interfacial area.<sup>16</sup> This corresponds to an increase of the free energy of the system

$$W^S = 2 \int_{\text{sphere}}^{\text{deformed drop}} \gamma(S) dS, \quad (3.19)$$

where  $S$  and  $\gamma$  are the area and the interfacial tension of a deformed drop. The dependence of  $\gamma$  on  $S$  can be expressed by the effective Gibbs elasticity  $E_G$  of the adsorbed surfactant monolayer (for small deformations  $E_G$  can be assumed constant)

$$\gamma(S) = \gamma_0 + E_G \ln(S/S_0); \quad E_G = \left( \frac{d\gamma}{d \ln S} \right)_{S=S_0}. \quad (3.20)$$

Then

$$W^S = 2(\gamma_0 - E_G)(S - S_0) + 2E_G S \ln(S/S_0), \quad (3.21)$$

where  $\gamma_0$  is the interfacial tension and  $S_0$  is the area of a nondeformed drop

$$S_0 = 4\pi a^2. \quad (3.22)$$

Usually, for small drops the capillary pressure is high and the deformation (the relative surface extension) is small,  $(S - S_0)/S_0 \ll 1$ . Hence with sufficient accuracy one can write<sup>16</sup>

$$W^S = 2\gamma_0(S - S_0) + E_G S_0 \left[ \frac{(S - S_0)}{S_0} \right]^2. \quad (3.23)$$

The first term on the right-hand side of Eq. (3.23) accounts for the drop surface extension at constant interfacial tension, while the second term is related to the possible increase of the interfacial tension during the deformation. It is convenient to express  $W^S$  as a function of the planar film radius  $r$ . From geometrical considerations (see Fig. 1) for small deformations, ( $r/a \ll 1$ ), one obtains

$$\frac{(S - S_0)}{S_0} = \left( \frac{\varepsilon}{2} \right)^4 + 0 \left[ \left( \frac{\varepsilon}{2} \right)^6 \right], \quad (3.24)$$

where  $\varepsilon = r/a$ . Then Eq. (3.23) can be transformed to read

$$W^S = \pi a^2 \left( \frac{\gamma_0}{2} \frac{r^4}{a^4} + \frac{E_G}{64} \frac{r^8}{a^8} \right); \quad \left( \frac{r}{a} \right)^2 \ll 1. \quad (3.25)$$

In emulsions containing soluble surfactants in the continuous phase and/or the drops, the adsorption surfactant flux may keep constant the interfacial tension of the extended surface during the deformation. In this case the effective Gibbs elasticity defined by Eq. (3.20) is zero and the surface deformation energy can be simply expressed as

$$W^S = 2\gamma_0 S_0 \left(\frac{\varepsilon}{2}\right)^4 = \frac{\pi\gamma_0 r^4}{2a^2}. \quad (3.26)$$

Even if  $E_G$  is not zero but of comparable magnitude with  $\gamma_0$  the second term in Eq. (3.25) still can be neglected and Eq. (3.26) remains a reasonable approximation. However, in *microemulsions*  $\gamma_0$  can be several orders of magnitude smaller than  $E_G$  and in this case Eq. (3.25) should be used.<sup>16</sup> Since  $W^S$  is positive, the contribution of the surface deformation energy corresponds to a soft repulsion between the drops.

For low values of  $\gamma_0$  (like in microemulsions or bilayer lipid vesicles) the bending elasticity of the interface (or lipid membrane) may contribute to the deformation energy.<sup>4</sup> This contribution,  $W^C$ , can be evaluated from the Helfrich approach<sup>25</sup> to give

$$W^C = 4\pi K_C \left(\frac{r}{a}\right)^2 \left(1 - \frac{2a}{R_0}\right), \quad (3.27)$$

where  $K_C$  is the bending elasticity constant and  $R_0$  is the radius of spontaneous curvature. For microemulsions  $K_C$  was measured to be about the thermal energy  $kT$ , while for lipid bilayers it is 2 orders of magnitude larger.<sup>26</sup>

## C. Other interactions

### 1. Application of the Derjaguin's approximation to deformed particles

When the interparticle distance and the range of interaction are much smaller than the particle size one can use the approach proposed by Derjaguin.<sup>2,3,21</sup> Let  $f(h)$  be the free energy of interaction per unit area in an infinite planar film. Then following Derjaguin's approach we can express the energy of interaction of the two deformed drops as (see Fig. 1)

$$W(h, r) = \iint dx dy f[H(x, y)]. \quad (3.28)$$

The plane  $xy$  is chosen to coincide with the lower surface of the planar film and  $\rho$  is the radial coordinate in this plane

$$\rho^2 = x^2 + y^2. \quad (3.29)$$

The integral in Eq. (3.28) is taken over the whole plane  $xy$ . For small deformations the local thickness  $H(x, y)$  in the film and its vicinity can be represented as

$$H(x, y) = h \quad \text{for } \rho < r,$$

$$H(x, y) = h + \frac{1}{a_s} (x^2 + y^2 - r^2) \quad \text{for } \rho > r,$$

$$\text{where } a_s = \frac{2a_{1s}a_{2s}}{a_{1s} + a_{2s}}. \quad (3.30)$$

The substitution from Eq. (3.30) into Eq. (3.28) allows one to express  $F(h, r)$  as a sum of two terms

$$W(h, r) = \pi r^2 f(h) + \pi a_s \int_h^\infty f(H) dH. \quad (3.31)$$

The upper limit of the integral in Eq. (3.31) is assumed to be infinity, because the range of interaction is supposed to be smaller than the particle size. For small deformations,  $(r/a)^2 \ll 1$ , it can be shown that

$$a_s = a \left[ 1 + O\left(\frac{\varepsilon}{2}\right)^4 \right]. \quad (3.32)$$

Hence, with sufficient accuracy one can write

$$W(h, r) = \pi r^2 f(h) + \pi a \int_h^\infty f(H) dH \left[ 1 + O\left(\frac{\varepsilon}{2}\right)^4 \right], \quad (3.33)$$

where

$$a = \frac{2a_1 a_2}{a_1 + a_2}. \quad (3.34)$$

What is remarkable in Eq. (3.33) is that the interaction energy between the two *deformed* drops is represented as a sum of two terms: (i) the interaction energy of two *non-deformed* drops, situated at the same surface to surface distance,  $h$ , and (ii) the interaction energy of a portion with area  $\pi r^2$  of an infinite flat film of thickness  $h$ . This general result, we derived in the present paper, allows one to use the known expressions for the interaction energy between spheres and infinite planar films in order to describe the interaction between deformed drops if the restrictions of Derjaguin formula are satisfied. Similarly, an expression for the force  $F$  acting between two deformed drops can be derived:

$$F = -\frac{\partial W}{\partial h} = -\pi r^2 \frac{\partial f}{\partial h} + \pi a f(h). \quad (3.35)$$

### 2. Electrostatic interaction

In emulsions  $a$  is typically above  $10^{-5}$  cm. For bulk electrolyte concentrations,  $C_{el}$ , higher than  $10^{-3}$  M, the Debye screening length  $1/\kappa$  (defined below) is less than  $10^{-6}$  cm. Hence, the product  $\kappa a$  is much larger than unity and one can apply Derjaguin's approach. The two different cases, of large and of small surface potentials, are considered below.

*Small surface potentials.* Let us consider the case of two identical drops possessing small electrical surface potentials  $\Psi_s$  in the presence of z:z electrolyte

$$\frac{ze\Psi_s}{kT} \ll 1. \quad (3.36)$$

In this case the function  $f(h)$  is<sup>2</sup>

$$f_{el}^\Psi(h) = \frac{\epsilon\kappa}{4\pi} \Psi_s^2 \left[ 1 - \tanh\left(\frac{\kappa h}{2}\right) \right], \quad (3.37)$$

$$f_{el}^\sigma(h) = -\frac{4\pi}{\epsilon\kappa} \sigma^2 \left[ 1 - \coth\left(\frac{\kappa h}{2}\right) \right], \quad (3.38)$$

where  $\sigma$  is the surface charge density,  $\epsilon$  is the dielectric permittivity of the medium. The superscripts  $\Psi$  and  $\sigma$  in Eqs. (3.37) and (3.38) correspond to the cases of constant potential and constant charge, respectively.  $\kappa$  is defined as

$$\kappa^2 = \frac{8\pi e^2 z^2}{\epsilon kT} C_{el} \quad (3.39)$$

$e$  is the elementary charge and  $kT$  is the thermal energy. By substituting these expressions for  $f(h)$  in Eq. (3.33) we obtain

$$W^{E,\Psi}(h,r) = \frac{\epsilon\kappa}{4} \Psi_s^2 \left\{ \left[ 1 - \tanh\left(\frac{\kappa h}{2}\right) \right] r^2 + \frac{2a}{\kappa} \ln(1 + e^{-\kappa h}) \right\} \quad (3.40)$$

and

$$W^{E,\sigma}(h,r) = -\frac{4\pi^2}{\epsilon\kappa} \sigma^2 \left\{ \left[ 1 - \coth\left(\frac{\kappa h}{2}\right) \right] r^2 + \frac{2a}{\kappa} \ln(1 - e^{-\kappa h}) \right\}, \quad (3.41)$$

respectively. These two expressions can be generalized in a straightforward manner to include the case of two drops different in size and surface potential. The final results read

$$\begin{aligned} W^{E,\Psi}(h,r) = & \frac{\epsilon\kappa r^2}{8} \left[ 2\Psi_{s1}\Psi_{s2} \frac{1}{\sinh \kappa h} - (\Psi_{s1}^2 + \Psi_{s2}^2) \right. \\ & \times (\coth \kappa h - 1) \left. \right] + \frac{\epsilon a_1 a_2}{4(a_1 + a_2)} [(\Psi_{s1} + \Psi_{s2})^2 \\ & \times \ln(1 + e^{-\kappa h}) + (\Psi_{s1} - \Psi_{s2})^2 \ln(1 - e^{-\kappa h})], \end{aligned} \quad (3.42)$$

$$\begin{aligned} W^{E,\sigma}(h,r) = & \frac{2\pi^2 r^2}{\epsilon\kappa} \left[ 2\sigma_1\sigma_2 \frac{1}{\sinh \kappa h} + (\sigma_1^2 + \sigma_2^2) \right. \\ & \times (\coth \kappa h - 1) \left. \right] - \frac{4\pi^2 a_1 a_2}{\epsilon\kappa^2(a_1 + a_2)} [(\sigma_1 + \sigma_2)^2 \\ & \times \ln(1 - e^{-\kappa h}) + (\sigma_1 - \sigma_2)^2 \ln(1 + e^{-\kappa h})]. \end{aligned} \quad (3.43)$$

The terms, proportional to the film area,  $\pi r^2$ , in Eqs. (3.40)–(3.43) are connected with the interaction across the film. The other terms correspond to the interaction between the spherical parts of the particles and are equal to the respective interaction energy between nondeformed spheres.

**High surface potentials.** In this case analytical expressions can be derived only if the electric double layers around the two drops are weakly overlapping ( $\kappa h \gg 1$ , but still  $h/a \ll 1$ ), i.e., if the superposition approximation is valid.<sup>2,3,5</sup> For two different particles the result reads [cf. Eq. (3.33)]

$$f_{el}(h) = \frac{64}{\kappa} C_{el} kT \tanh\left(\frac{e\Psi_{s1}}{4kT}\right) \tanh\left(\frac{e\Psi_{s2}}{4kT}\right) e^{-\kappa h}, \quad (3.44)$$

$$\begin{aligned} W^E(h,r) = & \frac{64\pi}{\kappa} C_{el} kT \tanh\left(\frac{e\Psi_{s1}}{4kT}\right) \tanh\left(\frac{e\Psi_{s2}}{4kT}\right) \\ & \times e^{-\kappa h} \left[ r^2 + \frac{2a_1 a_2}{\kappa(a_1 + a_2)} \right]. \end{aligned} \quad (3.45)$$

The result for two equal in size and potential particles, can be obtained by supposing  $a_1 = a_2$  and  $\Psi_{s1} = \Psi_{s2}$  in Eq.

(3.45). The first term in the square braces corresponds to the interaction across the planar film, while the second term is for the interaction between the spherical parts of the drops.

If we are interested in the interaction at high surface potentials and small gaps between the drops ( $\kappa h \ll 1$ ) one can proceed numerically by substituting in Eq. (3.33) the exact complex dependence of  $f(h)$  derived by Muller<sup>27</sup> (for details see the review by Derjaguin, Churaev, and Muller<sup>2</sup>).

### 3. Steric interaction

Another type of interaction which often plays role in stabilizing emulsions is the steric interaction if polymers are adsorbed at the drop surfaces. Several theoretical approaches for calculation of the interaction energy between two parallel flat surfaces are available.<sup>5,28–31</sup> For *theta-solvent* the theory of Dolan and Edwards<sup>29</sup> can be used. If the thickness of the adsorbed polymer layer is much smaller than the drop radius, one can apply Derjaguin's approximation, Eq. (3.33) (cf. Chap. 6 in the monograph of Russel, Saville, and Schowalter<sup>5</sup>). The result for two identical drops of radius  $a$  reads

$$\begin{aligned} W^{St} = & 4\pi\Gamma kT \left[ r^2 e^{-(3/2)\tilde{h}^2} + \sqrt{\frac{\pi}{6}} a L_0 \operatorname{erfc}\left(\sqrt{\frac{3}{2}} \tilde{h}\right) \right] \\ & \text{for } h > L_0\sqrt{3}, \end{aligned} \quad (3.46)$$

$$\begin{aligned} W^{St} = & \pi r^2 \Gamma kT \left[ \frac{\pi^2}{3\tilde{h}^2} + \ln\left(\frac{3\tilde{h}^2}{8\pi}\right) \right] \\ & + \pi a \Gamma kT L_0 \left[ \frac{\pi^2}{3\tilde{h}^2} \left(1 - \frac{\tilde{h}}{\sqrt{3}}\right) \right. \\ & \left. + 2\tilde{h} \left(1 - \ln\sqrt{\frac{3}{8\pi}} \tilde{h}\right) - 8.84 \right], \quad \text{for } h < L_0\sqrt{3}, \end{aligned} \quad (3.47)$$

where  $L_0 = l\sqrt{N}$  is the mean-square thickness of the adsorbed polymer layer with  $l$  and  $N$  being the length and the number of segments in a polymer chain, respectively.  $\Gamma$  is the surface concentration of the adsorbed chains and  $\tilde{h} = h/L_0$  is the dimensionless film thickness. Similarly, for *good solvent* the theory of Alexander–de Gennes<sup>30</sup> predicts the following expression:

$$f(h) = 2kT\Gamma^{3/2} L_g \left[ \frac{4}{5} \tilde{h}_g^{-5/4} + \frac{4}{7} \tilde{h}_g^{7/4} - \frac{4}{5} - \frac{4}{7} \right] \quad \text{for } h < 2L_g. \quad (3.48)$$

Introducing Eq. (3.48) into Eq. (3.33) we obtain

$$\begin{aligned} W^{St} = & \pi r^2 f(h) + 4\pi a kT \Gamma^{3/2} L_g^2 \quad \text{for } h < 2L_g \\ & \times [1.37\tilde{h}_g - 0.21\tilde{h}_g^{11/4} + 3.20\tilde{h}_g^{-1/4} - 4.36], \end{aligned} \quad (3.49)$$

where

$$\tilde{h}_g = \frac{h}{2L_g}, \quad L_g = N(\Gamma\tilde{f})^{1/3}. \quad (3.50)$$

TABLE I. Summary of the approximate expressions for the interaction energy between two deformed drops.

Type of interaction	Equation
1. Van der Waals	(3.18)
2. Surface extension	(3.25)
3. Electrostatic	
(a) nonlinear superposition	(3.45)
(b) constant potential	(3.40)
(c) constant charge	(3.41)
4. Steric	
(a) theta-solvent	(3.46), (3.47)
(b) good solvent	(3.49)
5. Depletion	(3.51)

The more complex theory developed by Ploehn and Russel<sup>31</sup> both for good and poor solvents, can be also applied by performing numerical calculation of the function  $f(h)$ .

#### 4. Depletion interactions

The modified Derjaguin's approximation allows considering other types of interaction if the restrictions inherent to it are fulfilled. For example, a very simple expression can be obtained for the depletion interaction<sup>4,28,32</sup> caused by the presence of soluble polymers or micelles. The depletion energy, for small polymer molecules or micelles, is proportional to the volume, excluded from the gap between the colloidal particles. By incorporating the theory of Asakura and Oosawa<sup>32</sup> into the Derjaguin approximation one obtains

$$\frac{W^{\text{dep}}(h)}{kT} = -\frac{6\Phi}{d^3} \left[ \frac{a}{2} (d-h)^2 + r^2 h \right] \quad \text{for } h < d,$$

$$W^{\text{dep}} = 0 \quad \text{for } h \geq d, \quad (3.51)$$

where  $d$  is the diameter of the small colloidal species (polymer molecules or micelles) and  $\Phi$  is their volume fraction. It can be seen from Eq. (3.51) that the relative contribution of the film (the second term) increases with the film thickness  $h$ .

In a similar manner other types of interactions like structure, hydration, hydrophobic, etc., can be treated. A summary of the contribution of the different types of interaction into the total energy and force acting between two deformed drops is presented in Table I.

#### IV. DISCUSSION OF THE RESULTS AND APPLICATIONS

We start with numerical investigation of the role of deformation on the interaction energy between the two particles. In Fig. 2, the ratio  $W^{VW}/W_0^{VW}$  calculated from Eq. (3.14) and Hamaker result for two nondeformed spheres<sup>20</sup> is plotted. With  $W_0^{VW}$ , the van der Waals energy of interaction between two nondeformed particles separated by the same distance  $h$  is denoted.<sup>20</sup> The lines in Fig. 2 correspond to  $h/a=0.01$  (line 1),  $h/a=0.02$  (line 2),  $h/a=0.1$  (line 3) and  $h/a=1$  (line 4). One sees that the effect of deformation strongly depends on the separation

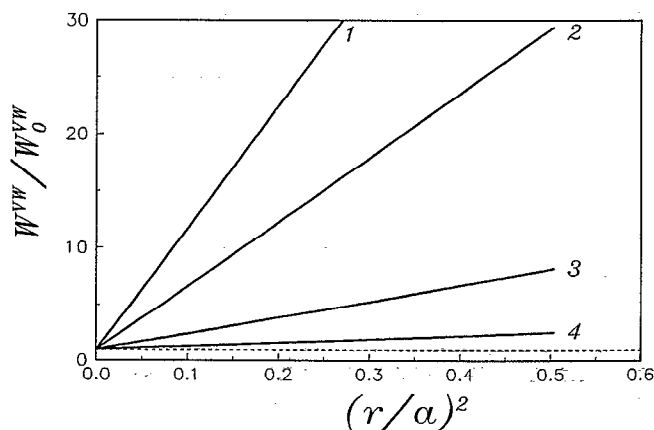


FIG. 2. Plot of the ratio of the van der Waals interaction energy,  $W^{VW}$ , of two deformed drops of radius  $a$ , and of two nondeformed drops of the same volume,  $W_0^{VW}$ .  $r$  is the film radius. The dimensionless film thickness is  $h/a=0.01$  (curve 1),  $h/a=0.02$  (curve 2),  $h/a=0.1$  (curve 3), and  $h/a=1$  (curve 4).

between the particles. For small separations,  $h/a=10^{-2}$  (line 1), even at small deformation,  $r/a \sim 0.3$ , the interaction across the planar film dominates the entire interaction energy. On the contrary, for large separation,  $h/a=1$  (line 4), the deformation practically does not affect the interaction energy. At intermediate gap width, both interactions, i.e., across the film and between the spherical parts, must be taken into account. The trend for the interaction energy between a deformed drop and a semi-infinite slab is similar (Fig. 3).

The same qualitative conclusions follow from Eqs. (3.15) and (3.18). One sees that in case of van der Waals interaction the contributions of the interaction across the planar film and of the interaction between the spherical surfaces surrounding the film are comparable if

$$r \sim \sqrt{ah}. \quad (4.1)$$

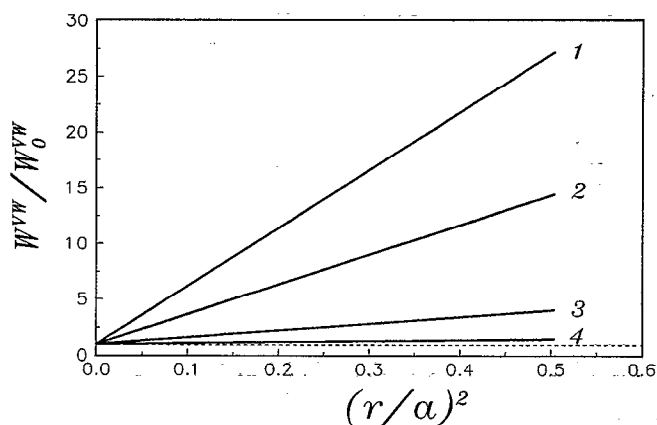


FIG. 3. Plot of the ratio of the van der Waals interaction energy,  $W^{VW}$ , between a deformed drop of radius  $a$  and an infinite slab, and of a nondeformed drop of the same volume and a slab,  $W_0^{VW}$ .  $r$  is the film radius. The dimensionless film thickness is  $h/a=0.01$  (curve 1),  $h/a=0.02$  (curve 2),  $h/a=0.1$  (curve 3), and  $h/a=1$  (curve 4).

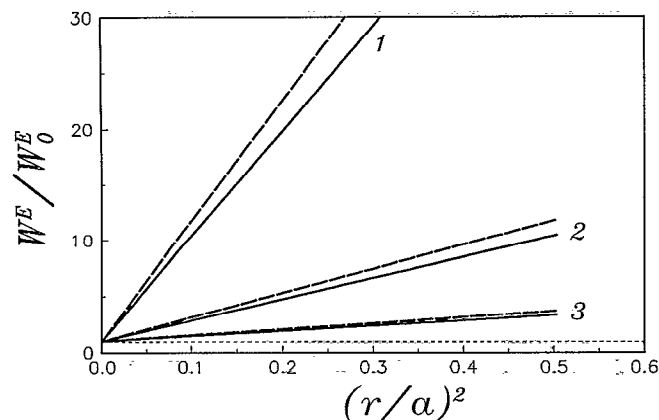


FIG. 4. Plot of the ratio of the electrostatic interaction energy,  $W^E$ , between two deformed drops, and the electrostatic energy of two nondeformed drops.  $r$  is the film radius.  $\kappa a = 100$  (curve 1),  $\kappa a = 20$  (curve 2), and  $\kappa a = 5$  (curve 3). The dashed curves correspond to constant charge regulation, while the solid curves are for constant potential.  $\kappa h = 2$  for all curves.

If  $r \gg \sqrt{ah}$  and  $h/a \ll 1$  the interaction is dominated by the contribution of the planar film. On the contrary, if  $r \ll \sqrt{ah}$  the interaction is approximately the same as the one between two spheres at the same surface to surface distance. Equation (4.1) reflects a situation which is often realized in the case of collision between emulsion and microemulsion drops<sup>16,18</sup> when bubbles (drops) of submillimeter size are attached to a surface, as well as in the surface force balance measurements.<sup>33</sup>

It is important to note that the results from the simplified expression, Eq. (3.18), practically coincide with the exact results presented in Fig. 2, except for the case of large separations,  $h/a \sim 1$ . The numerical comparison showed that Eq. (3.18) is very accurate and can be used without introducing substantial error (the error is less than a few percent) for  $h/a < 0.3$  and  $r/a < 0.7$ .

In Fig. 4 are shown the results for electrostatic interaction energy between two identical in size and electrical potential deformed particles [see Eqs. (3.40) and (3.41)]. All lines are calculated for  $\kappa h = 2$ , while the product  $\kappa a$  is varied:  $\kappa a = 100$  (line 1),  $\kappa a = 20$  (line 2) and  $\kappa a = 5$  (line 3). The solid lines correspond to constant potential upon approach, while the dashed lines are for constant charge. One can conclude from Fig. 4 that again the effect of the deformation (the relative contribution of the interaction across the planar film) strongly depends on the parameters like particle size, ionic strength and film thickness.

It is known<sup>2</sup> that when two flat (or spherical) surfaces are of different surface potentials, the electrostatic interaction between them can change from repulsive to attractive ( $\Psi_{s1}\Psi_{s2} > 0$ , constant potential<sup>34</sup>) or from attractive to repulsive ( $\sigma_1\sigma_2 < 0$ , constant charge<sup>35</sup>) at small distances. This suggests that when deformable particles (drops, bubbles, vesicles) are considered, the interaction can change from repulsive to attractive or vice versa during the deformation even at constant separation  $h$ . Such a possibility is illustrated in Fig. 5, where the interaction energy  $W^E$  is

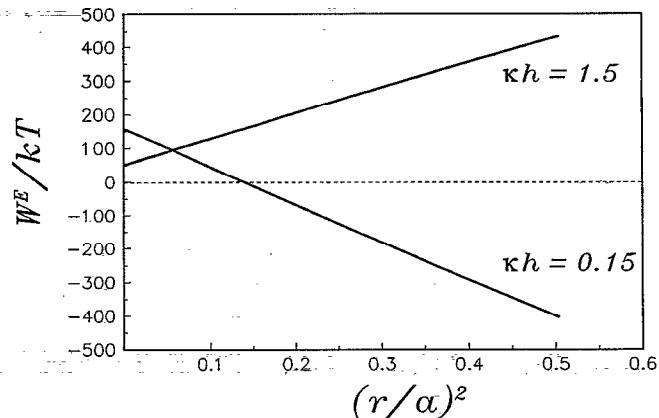


FIG. 5. Electrostatic interaction energy between two drops of different surface potential as a function of the film radius.  $\Psi_{s1} = 20$  mV and  $\Psi_{s2} = 10$  mV. The drop radius  $a = 1 \mu\text{m}$  and  $\kappa a = 20$ .

plotted as a function of the film radius  $r$ , for drops equal in size ( $a = 1 \mu\text{m}$ ) but having different surface potentials:  $\Psi_{s1} = 20$  mV and  $\Psi_{s2} = 10$  mV. Equation (3.42) with  $\kappa a = 20$  was used for calculation of these lines. One sees that at large distances ( $\kappa h = 1.5$ ), the repulsion between the particles increases with the deformation  $r/a$ . At small separations ( $\kappa h = 0.15$ ), however, opposite effect takes place. One can then conclude that in a certain range of deformations, as the film thins, the repulsion between the drops can change to attraction. This behavior can be understood if one remembers that for flat surfaces at constant potential, the force changes from repulsive to attractive at a film thickness<sup>2,3,34</sup>

$$h = \frac{1}{\kappa} \ln(\Psi_{s1}/\Psi_{s2}) \quad \Psi_{s1} > \Psi_{s2}. \quad (4.2)$$

For the quoted potentials this condition corresponds to  $\kappa h = 0.69$ . Hence, for  $\kappa h = 1.5$  the drops are in the repulsive region and the deformation only increases the repulsion. For spherical particles with  $\kappa h = 0.15$ , the caps of the spheres are attracting each other. The interaction energy between nondeformed spheres is still repulsive. With the deformation and the increase of the film radius, larger part of the drop surfaces will come closer in the attractive region. As a result the attractive interaction becomes prevailing.

Below we discuss briefly the application of the obtained results to some particular areas.

### A. Coalescence and flocculation in emulsions

As mentioned in Sec. I when two *macroemulsion* drops of millimeter and submillimeter size approach each other they deform and planar film between them is formed. Much less is known about the dynamics of mutual approach of smaller emulsion drops of micron and submicron size. Recently it was demonstrated theoretically<sup>18,36</sup> that due to the combination of Brownian and intermolecular forces acting between the small drops, the latter can also deform. For the case of coalescing droplets, when the sys-



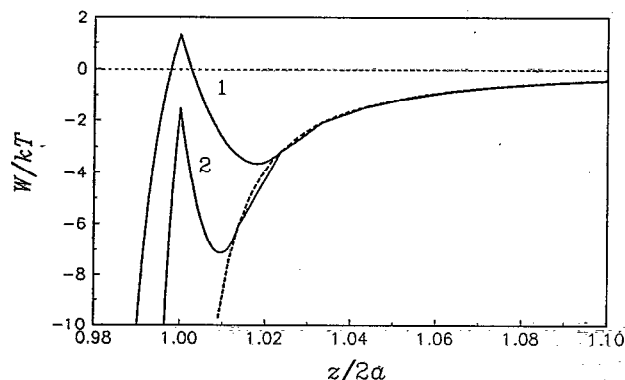


FIG. 6. Interaction energy between two deformable drops of radius  $a$  vs the distance between their mass centers,  $z$ . Curve 1 is for  $a=100$  nm, and curve 2 is for  $a=200$  nm.  $\sigma=1$  mN/m and  $A_H=10^{-20}$  J. The onset of drop deformation is calculated by using the theory of Danov *et al.* (Ref. 18). The dashed curve represents the interaction energy of two nondeformable spheres of radius 100 nm and the same Hamaker constant.

tem is not in equilibrium, the separation  $h_i$ , at which the deformation starts, was calculated using the expression<sup>9,10,18</sup>

$$h_i = \frac{F}{2\pi\gamma_0}. \quad (4.3)$$

$F$  is the total force acting between the two droplets.<sup>18</sup> The theory predicts that the radius of the film formed between two colliding drops should be  $0 \leq r \leq \sqrt{ah_i}$ . Hence, the calculations need expressions for the interaction energy, accounting both for the interaction across the film and the interaction between the spherical surfaces around the film. In Fig. 6 we show the calculated interaction energy,  $W$ , between two deformable emulsion drops as a function of the distance between their mass centers,  $z$ . Only the surface deformation energy, Eq. (3.26) and the van der Waals energy, Eq. (3.12), are taken into account. The parameters are  $\gamma=1$  mN/m,  $A_H=1 \times 10^{-20}$  J.

At  $z > z_i = 2a + h_i$ , the drops are considered to be spherical in shape and the interaction curve coincide with that for hard spheres. At separation  $h_i$  planar film is formed which radius  $r$  gradually changes from zero to  $\sqrt{ah_i}$ . It is assumed that the film thickness remains constant during this process. By following the theoretical approach of Danov *et al.*<sup>18</sup> [see Eqs. (3.20)–(3.23) in this reference] we calculated  $h_i=4.7$  nm (for  $a=100$  nm—curve 1) and  $h_i=5.5$  nm (for  $a=200$  nm—curve 2). For comparison the interaction energy between two nondeformable spheres with  $a=100$  nm is shown with the dashed curve. The positive surface deformation energy contributes during this process and leads to soft repulsion between the drops—note the increase of the total interaction energy. After that the film starts thinning at constant radius  $r = \sqrt{ah_i}$ . In Fig. 6 this corresponds to a sharp decrease of the interaction energy at small separations. At some critical thickness,  $h_{cr}$  (not shown in the figure) the film ruptures and the two drops coalesce. It is obvious from the figure that the interaction between deformable drops and nondeformable hard spheres is very different.

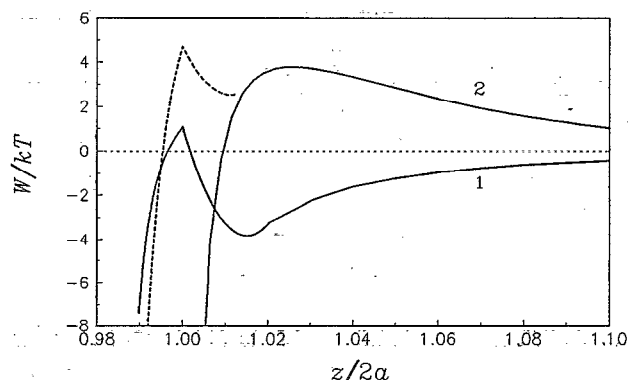


FIG. 7. Interaction energy between two charged deformable emulsion drops.  $a=100$  nm,  $\sigma=1$  mN/m,  $\Psi_s=10$  mV and  $A_H=10^{-20}$  J. Curve 1 is for electrolyte concentration  $C_{el}=10^{-1}$  mol/dm<sup>3</sup> and curve 2 is for  $C_{el}=10^{-3}$  mol/dm<sup>3</sup>. At lower electrolyte concentration the drops do not deform (curve 2). The dashed curve illustrates what would be the interaction energy if the drops deform even at this ionic strength.

It is worthwhile mentioning that the maximum in the curve 1 is above  $W/kT=1$ , i.e., we have barrier coalescence of the drops. On the contrary, in curve 2 the van der Waals attraction prevails at any  $z$  and we have barrierless coalescence.

As it was shown by Danov *et al.*,<sup>18</sup> for strong repulsion the deformation becomes impossible and the drops behave as charged hard spheres. Such situation is illustrated in Fig. 7 with the plot of the interaction energy between two charged deformable drops. The parameters of the drops are  $a=100$  nm,  $\gamma=1$  mN/m,  $A_H=10^{-20}$  J,  $\Psi_s=10$  mV. Curve 1 is for  $10^{-1}$  M NaCl solution ( $\kappa a=10$ ) and curve 2 for  $10^{-3}$  M NaCl ( $\kappa a=1$ ). The calculations show that at the higher electrolyte concentration the deformation starts at  $h_i=4.0$  nm (see curve 1). The electrostatics slightly affects the interaction in this case and the shape of curve 1 is similar to that shown in Fig. 6. At lower electrolyte concentration (curve 2) the electrostatic repulsion is large and the drops do not deform. The dashed curve shows what would be the interaction energy between these drops if they will deform at  $h_i=4.0$  nm. One sees that the energy barrier for deformation and coalescence is several times larger than  $kT$  in this case.

A possible alternative is the case of flocculating droplets in equilibrium where  $h_i$  can be determined by minimization of the free energy of a pair of drops (with respect to the film radius) at fixed distance between their mass centers  $z$ . A detailed study of this case is performed elsewhere.<sup>36</sup>

The overall conclusion from this consideration is that the change in the behavior of the drops from nondeformable to deformable and vice versa will strongly affect the stability of emulsions against coalescence and flocculation.

## B. Adhesion of vesicles, drops, and bubbles to solid surfaces

The problem of adhesion of deformable particles like drops or vesicles is of great practical importance. The kinetics of this process, as well as the equilibrium configura-

tion of the system strongly depend on the interaction between the particle and the substrate. The formulas obtained in the present paper can find application in studying this phenomena. Since more detailed investigation needs additional considerations concerning the hydrodynamic interaction, bending energy, etc., we postpone it for a separate study.

### C. Interaction and fusion of microemulsion drops

It is known that in microemulsions exchange of material between the microemulsion drop cores takes place. Although this phenomenon is extensively studied by fluorescence techniques during the last few years,<sup>37–39</sup> its mechanism is not understood. Recently, we proposed that the microemulsion drops can deform when colliding.<sup>16</sup> The intermolecular and hydrodynamic interaction between two deformed drops is quite different from that between non-deformable spheres.<sup>16,18,36</sup> The obtained formulas can help one to investigate the interaction between microemulsion drops in more details and to calculate the rate of reversible coalescence and flocculation in such system.

### D. Surface force balance

In the last 20 years the surface force balance found considerable application for direct measurement of the intermolecular and adhesion forces between solid surfaces, eventually covered with amphiphilic substances.<sup>2,4,40–42</sup> In some cases a deformation of the surfaces under the applied loads and formation of flat portions is observed.<sup>33</sup> For quantitative interpretation of the experimental data, the intermolecular interaction between the two surfaces should be known, along with the external load. Typical parameters are  $a \sim 2$  cm,  $h \sim 5$  nm,  $r \sim 10$   $\mu$ m.<sup>33</sup> Hence,  $r \sim \sqrt{ah}$  and the interaction across the film is comparable in magnitude with that between the curved surfaces surrounding the film. Exact calculation of the interaction energy can be performed in this case if we put in the Derjaguin approach more accurate expression than parabola for the shape of the curved surfaces. For example, Horn, Israelachvili, and Pribac<sup>33</sup> showed that for contactless adhesion of two solid spheres, the Hertz theory<sup>43</sup> predicts correctly the deformation and can be used in such calculations

$$H(x) = h + \frac{1}{\pi a} \left\{ r(x^2 - r^2)^{1/2} + (x^2 - 2r^2) \times \arctan \left[ \left( \frac{x}{r} \right)^2 - 1 \right]^{1/2} \right\}, \quad \text{for } x > r \quad (4.4)$$

$$H(x) = h, \quad \text{for } x \leq r.$$

Then, one can use Eq. (4.4) instead of Eq. (3.30) and to calculate numerically the integral in Eq. (3.28).

### V. CONCLUDING REMARKS

In the present paper, the interaction between two deformed particles is considered (see Fig. 1). The most important result of this study is the obtained explicit expression for the van der Waals interaction energy between two

deformed particles, having the shape of spherical segments [see Eq. (3.12)]. It gives the well known Hamaker expressions<sup>20</sup> for interaction between spheres and for semi-infinite slabs as particular cases. The contribution of the surface deformation energy is incorporated in the total interaction potential [see Eqs. (3.1), (3.25), and (3.26)]. The electrostatic (and other) interactions are treated by means of Derjaguin's approach<sup>21</sup> [see Eqs. (3.40)–(3.45)]. Simple asymptotic formulas for different types of interaction between deformed spheres are suggested (see Table I). It is shown that very often the contributions of the planar and spherical parts of the particles in the interaction are of similar order of magnitude. Also the particle deformation can change dramatically given type of interaction, thus leading in some cases to a qualitatively different picture. For example, the particle interaction between two nondeformed equal in size particles (having different surface potentials, however) can be repulsive, while for deformed ones it could be attractive for the same interparticle spacing (see Fig. 5).

The present consideration could be useful in studying many different systems and phenomena as interdroplet interactions and coalescence in emulsions, microemulsions and vesicles, drop and/or cell adhesion on solid surfaces and many others.

### ACKNOWLEDGMENTS

We are indebted to Professor I. B. Ivanov for the most helpful discussions. This work was supported financially by Kraft General Foods.

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