

Auteur(s) Author(s)	Nom(s) Name(s)	Prénom(s) First Name(s)	Affiliation
1	<u>Kralchevsky</u>	<u>Peter A.</u>	LTPH, Faculty of Chemistry University of Sofia, Bulgaria
2	Denkov	Nikolai D.	
3	Danov	Krassimir D.	
4	Petsev	Dimiter N.	
<b>Adresse postale</b>		Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of	
<b>Mailing address</b>		Chemistry, University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria	

**RÉSUMÉ**

L'objectif général de cette étude consiste à étudier théoriquement l'impact des forces de surface et de la déformation des gouttelettes sur les processus de floculation et de coalescence des émulsions. En fait, les forces de surface attractives favorisent la formation de films fins dans la zone de contact de deux gouttelettes en collision, même lorsque leur taille est inférieure à 1  $\mu\text{m}$ . D'un autre côté, l'aplatissement dans la zone de contact augmente considérablement l'énergie d'interaction entre les deux gouttelettes, en raison des forces de surface (1).

Nous avons approché la forme des gouttelettes à l'aide de deux sphères tronquées, séparées par un film planar. Ce modèle géométrique nous a fourni des explications sur les contributions apportées par les diverses forces de surface (électrostatiques, van der Waals, stériques, etc.) à l'énergie d'interaction totale. L'énergie de dilatation de surface (due à une légère répulsion des gouttelettes) a également été prise en compte: sa contribution correspond à une légère répulsion entre les gouttelettes, et peut s'avérer considérable. Le couple de flexion d'interface peut également affecter l'interaction entre les gouttelettes ainsi que le type d'émulsion. Pour les émulsion huile dans l'eau, le couple de flexion empêche l'aplatissement de la surface des gouttelettes dans la zone de collision, tandis qu'il favorise ce même aplatissement dans les émulsions eau dans l'huile (2).

Nous avons également examiné le rôle joué par les diverses forces de surface sur la floculation: la répulsion d'hydratation (3), la force de corrélation ionique, les forces d'attraction déplétion et les forces structurelles oscillatoires.

**ABSTRACT**

The general aim of this study is to investigate theoretically the interplay of surface forces and droplet deformation in the processes of flocculation and coalescence in emulsions. In fact, the attractive surface forces favor the formation of thin films in the zone of contact of two colliding droplets, even when their size is smaller than 1  $\mu\text{m}$ . On the other hand, the flattening in the zone of contact considerably increases the energy of interaction between the two droplets due to the surface forces [1].

We approximated the shape of the droplets by two truncated spheres separated by a planar film. For this model geometry we obtained explicit expressions for the contributions of various surface forces (electrostatic, van der Waals, steric, etc.) to the total interaction energy. The surface extension energy (due to the drop deformation) was also accounted for; its contribution corresponds to a soft repulsion between the droplets and can be very significant. The interfacial bending moment can also affect the droplet-droplet interaction and the type of the emulsion. For O/W emulsions the bending moment usually opposes the flattening of the droplet surfaces in the zone of collision, but for W/O emulsions it favors the flattening [2].

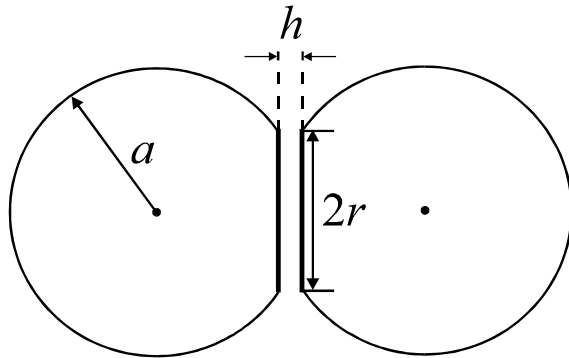
We examined also the role of various non-DLVO surface forces for the flocculation: the hydration repulsion [3], the ionic correlation force, the depletion attraction and the oscillatory structural forces.

# 1. INTRODUCTION

The experiment evidences that the deformability of the emulsion droplets may essentially affect their interactions and the overall equilibrium properties of emulsions. Aronson and Princen (1,2) investigated the coexistence of single drops with flocs, the latter being aggregated drops separated by thin liquid films. Hofman and Stein (3) studied experimentally the flocculation of emulsions containing droplets of micrometer size and interpreted some of the results with the droplet deformation at certain conditions (high ionic strength and low interfacial tension). Similar interpretation was proposed for experimental results obtained with microemulsions (4).

Our aim in this paper is to review our recent results about the effect of droplet deformability on the interactions in emulsions and to analyze the relative importance of the various factors connected with this effect. Indeed, a deformation of a droplet at fixed volume leads to an expansion of the droplet area. In addition, the flattening of the droplet surfaces in the zone of their contact (Fig. 1) is accompanied with a variation of the interfacial bending energy of the droplets. Last but not least, the formation of a thin liquid film between the two drops much enhances the role of the surface forces, such as the van der Waals attraction, electrostatic repulsion, hydration, ionic correlation, protrusion and oscillatory structural forces, steric interactions, etc. The deformation of two droplets upon collision affects also their hydrodynamic interactions, but these non-equilibrium effects (recently reviewed in ref. 5) are not a subject of the present article.

In ref. (6) it was demonstrated that the droplet-droplet interaction energy calculated for the model shape of truncated spheres (see Fig. 1) quantitatively agrees very well with the energy calculated by accounting for the gradual transition between the flat film and spherical portions of the drop surface. Therefore, below we will use the configuration depicted in Fig. 1.



**Figure 1.** Sketch of two deformed emulsion droplets of radius,  $a$ . The film thickness,  $h$ , and the film radius,  $r$ , are exaggerated.

It was shown in ref. (7) that the energy of interaction between two deformed emulsion droplets,  $W$ , depends on two geometrical parameters, the film thickness,  $h$ , and the film radius,  $r$ , i.e.  $W=W(h,r)$ , see Fig. 1. On the other hand, it is natural to present the interaction energy as a function of the distance  $z$  between the droplets' mass centers, i.e.  $W=W(z)$ . In the rigorous approach to this problem (8) the dependence of the interaction energy on the distance  $z$  is characterized by the potential of the mean force,  $w_f(z)=-kT\ln g(z)$ , where  $k$  is the Boltzmann constant,  $T$  is temperature, and  $g(z)$  is the pair (radial) correlation function. The latter function is determined by statistical averaging over all possible droplet configurations (of various  $h$  and  $r$ ) corresponding to a given  $z$ :

$$g(z) = 1.103 \left( \frac{\pi a^2 \gamma}{2kT} \right)^{1/4} \frac{1}{a} \int \exp\{-W[h(r),r] / kT\} dr \quad [1]$$

Here  $a$  and  $\gamma$  are the drop radius and the interfacial tension;  $h(r)$  represents the geometrical relation between  $h$  and  $r$  for fixed  $z$  and drop volume. To calculate  $w_f(z)$  one needs to know the function  $W=W(h,r)$ , which may contain contributions due to various effects considered below.

## 2. CONTRIBUTION OF THE INTERFACIAL DEFORMATION TO $W(h,r)$

**2.1 Effect of the interfacial dilatation.** It is assumed that before the collision the two droplets are spheres of radius  $a$ . When the distance between the droplets is small enough a flattening (a film of radius  $r$ , Fig. 1) appears in the zone of their contact. This deviation from the

spherical shape causes a dilatation of the droplet surface; the respective increase of the surface energy of the two drops follows from simple geometrical considerations (6,7):

$$W_{\text{dil}} = \gamma \frac{\pi r^4}{2a^2}, \quad \text{for} \quad \left(\frac{r}{a}\right)^2 \ll 1 \quad [2]$$

Our calculations show, that for typical emulsion systems the condition  $(r/a)^2 \ll 1$  is always satisfied and Eq. [2] holds with a good precision. One sees that  $W_{\text{dil}}$  strongly increases with the film radius  $r$ . In fact,  $W_{\text{dil}}$  is related to the interfacial tension  $\gamma$ . The contribution of the surface (Gibbs) elasticity to  $W_{\text{dil}}$  turns out to be a higher order effect and can be neglected. Note that  $W_{\text{dil}} > 0$ , i.e. the interfacial dilatation gives rise to an effective repulsion between the two droplets.

**2.2 Effect of the interfacial bending.** A work of interfacial flexural deformation is carried out in the process of flattening of the drop surfaces in the zone of contact (Fig. 1) due to the action of the *interfacial bending moment*,  $B_0$ :

$$W_{\text{bend}} = -2\pi r^2 B_0 / a, \quad (r/a)^2 \ll 1 \quad [3]$$

Note that  $B_0 = -4k_c H_0$ , where  $H_0$  is the so called spontaneous curvature and  $k_c$  is the interfacial curvature elastic modulus; typically  $B_0$  is of the order of  $5 \times 10^{-11}$  N (see ref. 10 for details). For oil-in-water (O/W) emulsions  $B_0$  usually opposes the flattening of the droplet surfaces in the zone of collision, but for water-in-oil (W/O) emulsions  $B_0$  favors the flattening (9). Therefore,  $W_{\text{bend}} > 0$  for two droplets in an O/W emulsion, while  $W_{\text{bend}} < 0$  for a couple of droplets in a W/O emulsion; consequently the interfacial bending moment stabilizes the O/W emulsions, but destabilizes the W/O ones. There are numerous experimental evidences (11) for droplet aggregation in W/O microemulsions, which can be attributed (at least in part) to the effect of  $W_{\text{bend}}$ . It is interesting to note, that the effect of the bending moment can be important even for droplets of  $\mu\text{m}$  size (9). Indeed, assuming  $a = 300$  nm,  $r \approx a/50$ ,  $|B_0| = 5 \times 10^{-11}$  N (see e.g. ref. 10), from Eq. [3] one calculates  $|W_{\text{bend}}| \approx 10 kT$ .

By means of similar considerations one can deduce (9) that an emulsion containing microemulsion droplets in the continuous phase should be more stable than an emulsion containing microemulsion droplets in the disperse phase, as it was observed experimentally (12).

### 3. CONTRIBUTION OF THE SURFACE FORCES TO $W(h,r)$

**3.1 Van der Waals interaction.** Based on the assumption for pair-wise additivity of the van der Waals interaction energy with respect to the couples of molecules, one may derive (see ref. 7) an exact (though rather long) expression for the energy,  $W_{\text{vw}}$ , of the van der Waals interactions between two deformed drops of equal size (Fig. 1). In most cases an approximate expression (for moderate deformations and separations) holds with a very good precision (9):

$$W_{\text{vw}}(h,r) = -\frac{A_H}{12} \left[ \frac{3}{4} + \frac{a}{h} + 2 \ln\left(\frac{h}{a}\right) + \frac{r^2}{h^2} - \frac{2r^2}{ah} \right], \quad \text{for} \quad \frac{h}{a} < 0.3, \quad \frac{r}{a} < 0.5, \quad [4]$$

$A_H$  is the Hamaker constant. More general expressions for arbitrarily deformed spheres of different size (as well as for a deformable sphere and a wall) are given in ref. (7).

**3.2 Electrostatic interaction.** The rigorous theory of the electrostatic (double layer) interaction yields rather complicated expressions for the respective interaction energy, even in the simpler case of a plane-parallel liquid film (13,14). Fortunately, some useful approximate expressions could be derived. By using the Derjaguin approximation (14) one can obtain (7):

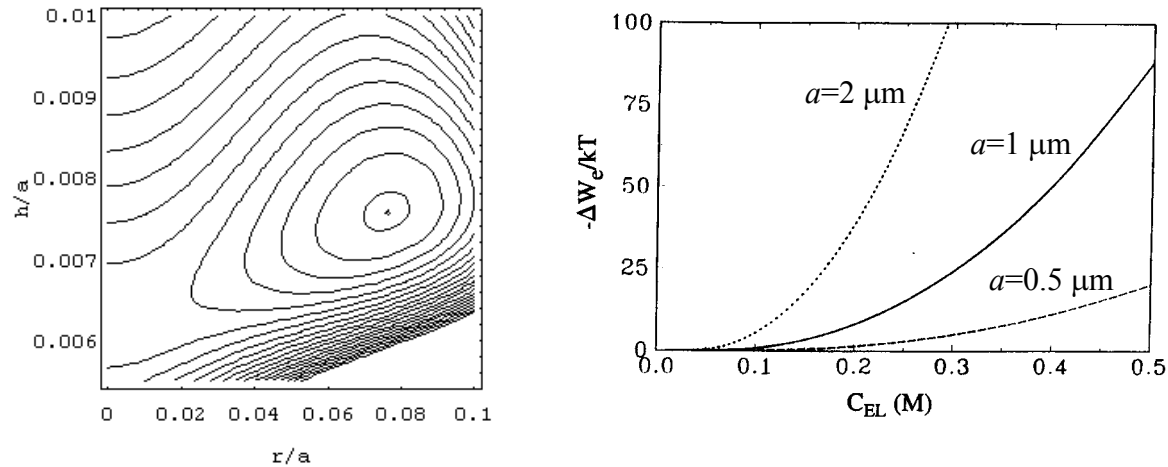
$$W(h,r) = \pi r^2 f(h) + \pi a \int_h^\infty f(H) dH \quad [5]$$

Here  $W$  is the energy of interaction of the two droplets,  $f(h)$  is the interaction energy per unit area in a plane-parallel film; the first term in the right-hand side of Eq. [5] expresses the interaction across the flat film of radius  $r$ , whereas the last term in Eq. [5] accounts for the interaction across the Plateau border encircling the flat film (Fig. 1). Eq. [5] can be applied to any type of surface force (irrespective of its physical origin) if only the range of action of this force is much smaller than the drop radius  $a$ . In the special case of electrostatic interaction and weak double layer overlap the substitution of the Verwey-Overbeek (13) expression for  $f_{el}(h)$  in Eq. [5] yields (6-9)

$$W_{el}(h,r) = \frac{64\pi C_{el} k T}{\kappa} \tanh^2\left(\frac{Ze\psi_0}{4kT}\right) \exp(-\kappa h) \left[r^2 + \frac{a}{\kappa}\right]; \quad \kappa^2 = \frac{2Z^2 e^2}{\epsilon_0 \epsilon k T} C_{el} \quad [6]$$

where  $\kappa^{-1}$  is the Debye screening length,  $C_{el}$  ( $\text{cm}^{-3}$ ) is the concentration of a symmetric  $Z:Z$  electrolyte,  $\epsilon$  denotes the dielectric permittivity;  $\psi_0$  is the droplet surface potential.

Fig. 2a shows a contour plot of  $W(h,r) \equiv W_{dil} + W_{vw} + W_{el}$  for  $a = 1 \mu\text{m}$ ,  $\psi_0 = 100 \text{ mV}$ ,  $\gamma = 1 \text{ mN/m}$ ,  $C_{el} = 0.1 \text{ M}$ ,  $A_H = 2 \times 10^{-20} \text{ J}$ . The minimum of the potential surface, corresponding to an equilibrium doublet of drops, has a depth  $W(h_e, r_e) = -60 kT$ . Hence, the equilibrium doublet should be rather stable. As shown in ref. (9), the radius of the equilibrium doublet,  $r_e$ , increases with the rise of both  $C_{el}$  and the drop radius  $a$ . Let us denote by  $W(h^*, 0)$  the minimum value of  $W$  along the ordinate axis in Fig. 2a, corresponding to two spherical (non-deformed) drops. Fig. 2b shows  $\Delta W_e \equiv W(h_e, r_e) - W(h^*, 0)$  vs.  $C_{el}$  for three values of the drop radius  $a$ . One sees that the effect of droplet deformation, expressed by  $\Delta W_e$ , strongly increases with the rise of  $C_{el}$  and  $a$ .



**Figure 2.** (a) Contour plot of the electrostatic, van der Waals, and surface extension energy  $W(h,r)/kT$  of two deformable drops:  $a=1 \mu\text{m}$ ,  $\psi_0=100 \text{ mV}$ ,  $\gamma=1 \text{ mN/m}$ ,  $C_{el}=0.1 \text{ M}$ ,  $A_H=2 \times 10^{-20} \text{ J}$ . The distance between two contours equals  $2 kT$ ; the minimum of the potential surface is equal to  $W(h,r)/kT = -60$ . (b) Difference between the minima in the energies for deformable and nondeformable drops,  $\Delta W_e$ , as a function of the electrolyte concentration,  $C_{EL}$ .

The double layer and van der Waals interactions are often termed "DLVO surface forces" since they were involved in the first version of the theory of colloid stability (13,14). Later, the existence of other surface forces was found out, which are called "Non-DLVO" surface forces (15). The contributions of some of these forces to  $W(h,r)$  are briefly considered below.

**3.3 Ionic correlation surface force.** As shown by Debye and Hückel the energy of formation of the counterion atmospheres of the ions in a solution gives a contribution to the free energy of the solution called "correlation energy". This correlation energy provides a contribution to the osmotic pressure of an electrolyte solution. Since the electrostatic disjoining pressure is a kind of excess osmotic pressure in a thin liquid film (13-15), it must include also a contribution from the correlation energy, which is not taken into account in the conventional DLVO theory. Both numerical and analytical methods have been developed for calculating the contribution of the ionic correlations,  $f_{\text{cor}}$ , to the interaction free energy  $f(h)$  - for review see ref. 16. Combining Eq. [5] with the asymptotic formula derived by Attard et al. (17) one obtains an expression for the contribution of the ionic correlations to the droplet-droplet interaction energy  $W(h,r)$  for the case when the electrolyte is symmetrical (Z:Z) and  $\exp(-\kappa h) \ll 1$ :

$$W_{\text{cor}} = W_{\text{el}} \frac{Z^2 e^2 \kappa}{16\pi\epsilon\epsilon_0 k T} (\ln 2 + 2I_C) \quad [7]$$

where  $W_{\text{el}}$  is the conventional DLVO electrostatic energy, Eq. [6],

$$I_C = \frac{2 - 2z^3 + z}{2z(2z^2 - 1)^2} - \frac{1}{2}(1 - J) \ln(z + z^2) - \frac{\sqrt{z^2 - 1}}{z} \left[ 1 + J + 4(2z^2 - 1)^{-3} \right] \arctan \sqrt{\frac{z-1}{z+1}} \\ + \frac{1}{2}(1 + J) \ln 2; \quad J \equiv \frac{2z^2 - 3}{(2z^2 - 1)^3}, \quad z \equiv \left[ 1 + \left( \frac{e\sigma_s}{2\epsilon\epsilon_0 k T \kappa} \right)^2 \right]^{1/2}$$

and  $\sigma_s$  is the surface charge density. As a rule,  $W_{\text{cor}}$  is negative and corresponds to attraction; its magnitude increases with the raise of  $C_{\text{el}}$  and  $\sigma_s$ . In the case of 1:1 electrolyte  $W_{\text{cor}}$  is usually small compared with  $W_{\text{el}}$ . In the case of 2:2 electrolyte, however, the situation can be quite different: the attractive forces,  $W_{\text{cor}} + W_{\text{vw}}$ , can prevail over  $W_{\text{el}}$  and the total energy,  $W$ , can become negative. In the presence of bivalent and multivalent counterions  $W_{\text{cor}}$  becomes the dominant surface force and should necessarily be taken into account.

**3.4. Hydration repulsion.** The hydration repulsion is a short-range monotonic repulsive force which appears as a deviation from the DLVO theory for short distances between two molecularly smooth electrically charged surfaces (15). Such a force may appear in foam or emulsion films stabilized by ionic surfactants. The physical importance of the hydration force is that it stabilizes thin films and emulsions preventing coagulation in the primary minimum of the DLVO disjoining pressure isotherm (13-15). It is believed that the hydration force is connected with the binding of strongly hydrated ions (such as  $\text{Mg}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ) to the interface. Empirically, this force, called the hydration repulsion, follows an exponential law (15). The substitution of this exponential law in Eq. [5] yields an expression for estimating the contribution of the hydration repulsion to the droplet-droplet interaction energy,  $W(h,r)$ :

$$W_{\text{hydr}}(h,r) = \pi f_0 \exp(-h/\lambda_0) [r^2 + a\lambda_0] \quad [8]$$

where, as usual,  $h$  is the film thickness; the decay length  $\lambda_0 \approx 0.6-1.1$  nm for 1:1 electrolytes; the pre-exponential factor,  $f_0$ , depends on the hydration of the surfaces but is usually about 3-30 mJ/m<sup>2</sup> (15). It seems that the main contribution to the hydration repulsion between two charged interfaces originates from the *finite size* of the hydrated counterions (18), an effect which is not taken into account in the DLVO theory (the latter deals with *point* ions). For more accurate calculation of  $W_{\text{hydr}}$  we recommend the theory from ref. (18) to be used.

**3.5 Protrusion and steric interaction.** Due to the thermal motion the protrusion of an amphiphilic molecule from an adsorption monolayer (or micelle) may fluctuate about the equilibrium position of the molecule. The configurational confinement of the protruding molecules within the narrow space between two approaching interfaces gives rise to short-range repulsive

surface force, called the protrusion force (19). The effect can be important for the stability of very thin emulsion films. The energy of molecular protrusion can be presented in the form  $u(z) = \alpha z$ , where  $z$  is the distance out of the oil-water interface ( $z > 0$ ) with  $\alpha \approx 3 \times 10^{-11}$  J/m for single-chained surfactants (20). By using a mean-field approach Israelachvili and Wennerström (19) derived an expression for the protrusion disjoining pressure which can be combined with our Eq. [5] to yield:

$$W_{\text{protr}}(h,r) \approx -\pi r^2 \Gamma kT \ln[1 - (1 + h/\lambda) \exp(-h/\lambda)], \quad \lambda \equiv \frac{kT}{\alpha}. \quad [9]$$

$\lambda$  has the meaning of protrusion decay length;  $\lambda = 0.14$  nm at 25°C;  $\Gamma$  denotes the number of protrusion sites per unit area. Note that  $W_{\text{protr}}$  decays exponentially for  $h \gg \lambda$ , but  $W_{\text{protr}} \propto -\ln(h/\lambda)$  for  $h \ll \lambda$ , i.e.  $W_{\text{protr}}$  is divergent for  $h \rightarrow 0$ .

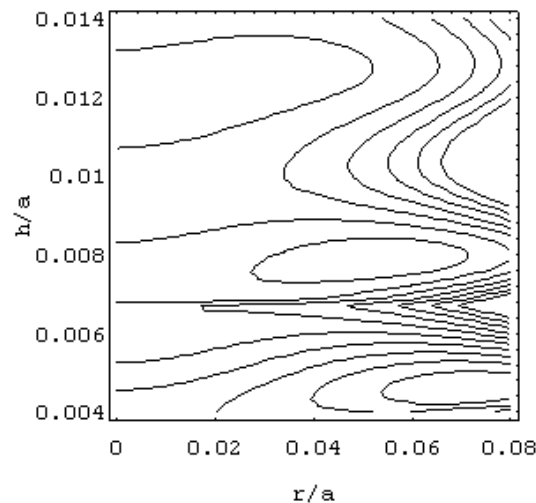
In fact, the protrusion force is a kind of *steric* interaction due to the overlap of spatially "diffuse" and thermally mobile interfacial zones. In the case of adsorption monolayers of nonionic surfactants, the steric repulsion originates from the overlap of the "brushes" of poly-oxyethylene chains at the surfaces of two approaching emulsion droplets. Expressions appropriate for calculating  $W(h,r)$  in this case can be found in ref. (9).

**3.6 Oscillatory structural force.** Very often the emulsions contain small colloidal particles (such as surfactant micelles or protein globules) in the continuous phase. The presence of these small particles gives rise to the oscillatory structural force, which affects the stability of foam and emulsion films as well as the flocculation processes in various colloids (21). At higher particle concentrations (volume fractions above 15%) the structural forces stabilize the liquid films and emulsions. At lower particle concentrations the structural forces degenerate into the so called *depletion attraction*, which is found to destabilize the dispersions (9,15). To quantify the contribution of the oscillatory forces,  $W_{\text{osc}}$ , to  $W(h,r)$  one can combine Eq. [5] with the following semiempirical formula for the oscillatory structural component of disjoining pressure (22)

$$f_{\text{osc}} = \int_h^{\infty} \Pi_{\text{osc}} dh; \quad \Pi_{\text{osc}}(h) = P_0 \cos\left(\frac{2\pi h}{d_1}\right) \exp\left(\frac{d^3}{d_1^2 d_2} - \frac{h}{d_2}\right) \quad \text{for } h > d \quad [10]$$

$$= -P_0 \quad \text{for } 0 < h < d$$

Here  $d$  is the diameter of the small particles (micelles),  $d_1$  and  $d_2$  are the period and the decay length of the oscillations;  $P_0$  is the particle osmotic pressure.  $P_0$ ,  $d_1$  and  $d_2$  do not depend on  $h$ , but depend on the particle volume fraction - the respective expressions can be found in ref. (22). The contour plot of  $W_{\text{osc}}(h,r)$ , similar to Fig. 2a, exhibits several local minima separated by "mountain ranges" - see Figure 3. When the particle volume fraction is smaller than c.a. 10% in the continuous phase, the height of the taller "range" is smaller than  $kT$ , and it cannot prevent the flocculation of the two droplets in the deep "depletion" minimum.



**Figure 3.** Contour plot of the energy,  $W(h,r) = W_{\text{dil}} + W_{\text{vw}} + W_{\text{el}} + W_{\text{osc}}$ , between two drops of radius  $a = 2 \mu\text{m}$  in the presence of ionic micelles. The parameters are the same as in Ref. (23): sodium nonylphenol polyoxyethylene-25 sulfate micelles of  $d=9.8$  nm, aggregation number 26,  $\gamma = 7.5$  mN/m,  $A_H = 5 \times 10^{-21}$  J,  $\psi_0 = -135$  mV,  $C_{\text{el}} = 25$  mM,  $\kappa^{-1} = 1.91$  nm. The electrostatic repulsion between the micelles and the drop surfaces is also taken into account (see Eqs. [3.9]-[3.11] in Ref. (9)). The points on the contour plot correspond to three local minima:  $W/kT = -406$ ,  $-140$ , and  $-37$ .

However, at higher micellar volume fraction these "ranges" act like barriers (Fig. 3) against the closer approach and flocculation (or coalescence) of the droplets in emulsions (9).

**Conclusion.** In this paper we demonstrate, that even very small emulsion droplets behave as deformable particles and thin film might be formed between them (Fig. 1). Many effects can contribute to the energy of interaction between two deformable emulsion droplets, which can be presented in the form:

$$W = W_{\text{dil}} + W_{\text{ben}} + W_{\text{vw}} + W_{\text{el}} + W_{\text{cor}} + W_{\text{hydr}} + W_{\text{protr}} + W_{\text{osc}} + \dots \quad [11]$$

where the various contributions can be calculated from Eqs. [2-10]. For each specified system an estimate may reveal which of the terms in Eq. [11] are predominant, and which of them can be neglected. The analysis shows that the same approach can be applied to describe the multidroplet interactions in flocs, because in most cases the interaction energy is pairwise additive.

The droplet deformability is important also for the process of *coalescence* in emulsions; a theoretical study is presented in Ref. (24).

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