

Van der Waals Interaction between Two Truncated Spheres Covered by a Uniform Layer (Deformed Drops, Vesicles, or Bubbles)

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In this paper, we derive explicit expressions for the van der Waals interaction energy and force between two truncated spheres covered by a thin layer of uniform thickness. These expressions can be used for description of the interactions in dispersions of deformable particles (emulsions, vesicle suspensions, and foams). As an illustration of the applicability of these formulas to real systems, we consider the interaction between micrometer-sized oil drops, covered by a protein adsorption layer, in oil-in-water emulsions. The Hamaker constants for the interactions between protein, oil, and water are calculated from literature data. The equilibrium radius and thickness of the liquid film, which forms upon the collision of two emulsion drops, are determined as functions of the drop size and electrolyte concentration. From the parameters of the equilibrium films, we calculate the total interaction energy between the drops. The numerical results show that both factors, the presence of the protein layer and the drop deformation, have a significant effect on the pair interaction energy.

We consider the van der Waals interaction energy between two truncated spheres of radius a , whose surfaces are covered by uniform layers of thickness δ . The truncated spheres are placed with their foreheads against each other, so that a planar film of thickness h is formed (Figure 1). This configuration is often encountered when two deformable colloid particles (emulsion drops, lipid vesicles, or foam bubbles) are put in contact. The coat on the particle surface could be an adsorption layer (e.g., of protein, low-molecular mass surfactant, or solid particles), or it could be the lipid bilayer, which builds up the vesicle wall.

The description of the true *surface* forces (those acting between the surfaces of the particles), such as the electrostatic or steric repulsion, is practically the same as in the case of homogeneous truncated spheres, and one can use formulas obtained in previous studies.^{1–3} On the contrary, the van der Waals forces arise as an integral interaction between the volumes of the bodies, and they are substantially affected by the internal structure of the particles. Explicit expressions for the van der Waals interaction force and energy in the system shown in Figure 1 could be rather useful for solving various problems related to emulsion stability, vesicle adhesion, and many other areas. To the best of our knowledge, such expressions have not been published so far.⁴

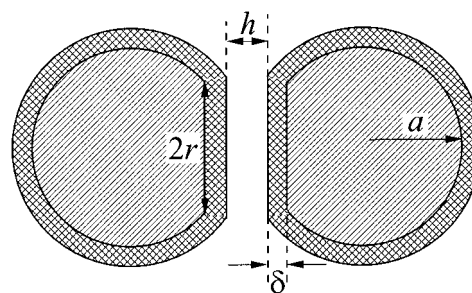


Figure 1. Geometry of the system under consideration: h is the film thickness, r is the film radius, a is the radius of the droplets, and δ is the thickness of the adsorbed layer.

1. Theoretical Background

The problem can be solved by using the general method for description of the van der Waals interaction between two bodies of multilayered structure, which was developed by Vold.⁵ According to this method, the general formula for the energy of van der Waals interaction of body L (on the left-hand side), which consists of N_L layers, with another body R (on the right-hand side), which consists of N_R layers, is (Figure 2)

$$W^{LW} = - \sum_{i=1}^{N_L} \sum_{j=1}^{N_R} A(i,j) H_{ij} \quad (1)$$

where the effective Hamaker constant for the interaction between layers i and j , $A(i,j)$, is given by the expression

$$A(i,j) = A_{ij} - A_{i,j-1} - A_{i-1,j} + A_{i-1,j-1} \quad (2)$$

$A_{i,j}$ is the Hamaker constant of interaction between the macrophases i and j across a vacuum. The indices $i = 1$

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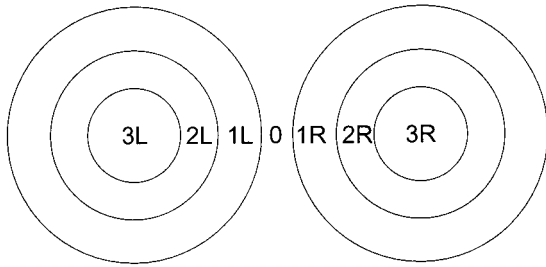


Figure 2. Notation used for description of the interaction between two multilayered bodies separated by medium 0, according to the approach in ref 5 (see eqs 1 and 2).

and $j = 1$ correspond to the layers, which are adjacent to the central film (phase 0, see Figure 2).

The function H_{ij} in eq 1 depends on the particular shape of the respective layers in the interacting bodies and on the distance between them. In our case, H_{22} is a geometrical function accounting for the interaction between the two cores of the droplets and H_{11} accounts for the interaction between the two adsorbed layers, whereas H_{12} and H_{21} account for the interaction between one of the adsorbed layers and the core of the other droplet. Therefore, if we know the Hamaker constants for the different phases, A_{ij} , and the functions H_{ij} , we can calculate the interaction energy by means of eqs 1 and 2. For simplicity, hereafter we will consider the system of two deformed particles of identical composition, size, and shape; the generalization to different particles is straightforward.

The geometrical functions H_{ij} can be derived in our case by using the expressions for the van der Waals interaction between two homogeneous truncated spheres, which were derived in ref 1. To simplify our consideration, we will use the approximations derived in the case when both the thickness and the radius of the planar film are smaller than the drop radius ($h/a < 0.3$ and $r/a < 0.5$). This approximation is justified in most of the practical systems, because (1) for thicker films, $h/a > 0.3$, the van der Waals interaction is almost always negligible and (2) for larger deformations, $r/a > 0.5$, one can use the well-known expressions for flat films, because the interaction across the planar film surfaces prevails over the interaction across the curved meniscus surrounding the film. There is no problem, however, in applying the same approach to the general case of arbitrary film thickness and particle deformation, by using the more general (and substantially longer) expression, eq 3.12 in ref 1.

In the case of thin films ($h/a < 0.3$) and small deformations ($r/a < 0.5$), one derives the following expression for H_{11} (cf. eq 3.17 in ref 1, where we substitute a by $a + \delta$):

$$H_{11} = \frac{1}{12} \left[\frac{3}{4} + \left(\frac{a + \delta}{h} \right) - 2 \ln \left(\frac{a + \delta}{h} \right) + \frac{r^2}{h^2} - \frac{2r^2}{(a + \delta)h} \right] \quad (3)$$

The Hamaker constant $A(1,1)$ can be expressed as

$$A(1,1) = A_{1,1} - 2A_{1,0} + A_{0,0} = A_{101} \quad (4)$$

that is, $A(1,1)$ coincides with the Hamaker constant, A_{101} , of interaction between two half-spaces of phase 1 across the continuous phase 0. Therefore, the contribution of the van der Waals interaction energy between the two adsorbed layers to the total interaction energy is

$$W_{\text{VW}}^{1-1} = -\frac{A_{101}}{12} \left[\frac{3}{4} + \left(\frac{a + \delta}{h} \right) - 2 \ln \left(\frac{a + \delta}{h} \right) + \frac{r^2}{h^2} - \frac{2r^2}{(a + \delta)h} \right] \quad (5)$$

In a similar way, one can derive equations for the van der Waals interaction energy between the cores of the droplets (in this case h is substituted by $h + 2\delta$ in eq 3.18 of ref 1):

$$W_{\text{VW}}^{2-2} = -A_{212} H_{22} \\ H_{22} = \frac{1}{12} \left[\frac{3}{4} + \left(\frac{a}{h + 2\delta} \right) - 2 \ln \left(\frac{a}{h + 2\delta} \right) + \frac{r^2}{(h + 2\delta)^2} - \frac{2r^2}{(h + 2\delta)a} \right] \quad (6)$$

It is less trivial to obtain an expression for the interaction energy between the core of one of the droplets and the adsorbed layer on the other droplet, because we are not allowed to use the formula for two particles equal in size. The correct procedure requires starting in this case with the complete formula, eq 3.12 in ref 1, for the interaction energy between two truncated spheres of different sizes; one should substitute there $a_1 = a$, $a_2 = a + \delta$, and $h_1 = h + \delta$. One can simplify the obtained long expression by expanding the geometrical function H_{12} in terms of three small parameters:

$$\epsilon_1 = (r/a)^2 \ll 1 \quad \epsilon_2 = h/2a \ll 1 \quad \epsilon_3 = \delta/2a \ll 1 \quad (7)$$

Such an expansion corresponds to a small film radius, a small film thickness, and a small thickness of the adsorption layer with respect to the radius of the spheres, respectively. As discussed above, these conditions are satisfied in most of the practical systems. After performing long algebraic calculations and ignoring all terms of order higher than ϵ_1 , ϵ_2 , and ϵ_3 , one obtains⁴

$$W_{\text{VW}}^{1-2} = -2(A_{102} - A_{101})H_{12} \\ H_{12} = \frac{1}{12} \left[\frac{3}{4} + \left(\frac{a}{h + \delta} \right) - 2 \ln \left(\frac{a}{h + \delta} \right) + \frac{r^2}{(h + \delta)^2} - \frac{r^2}{(h + \delta)a} \left(\frac{15}{8} + \frac{h + 3\delta}{8(h + \delta)} \right) + \frac{\delta}{2(h + \delta)} \right] \quad (8)$$

Therefore, the final formula for the van der Waals interaction energy between the bodies shown in Figure 1 is⁴

$$W^{\text{VW}}(h,r) = -\frac{A_{101}}{12} \left[\frac{3}{4} + \left(\frac{a + \delta}{h} \right) - 2 \ln \left(\frac{a + \delta}{h} \right) + \frac{r^2}{h^2} - \frac{2r^2}{(a + \delta)h} \right] - \frac{A_{212}}{12} \left[\frac{3}{4} + \left(\frac{a}{h + 2\delta} \right) - 2 \ln \left(\frac{a}{h + 2\delta} \right) + \frac{r^2}{(h + 2\delta)^2} - \frac{2r^2}{(h + 2\delta)a} \right] - \frac{(A_{102} - A_{101})}{6} \left[\frac{3}{4} + \left(\frac{a}{h + \delta} \right) - 2 \ln \left(\frac{a}{h + \delta} \right) + \frac{r^2}{(h + \delta)^2} - \frac{r^2}{(h + \delta)a} \left(\frac{15}{8} + \frac{h + 3\delta}{8(h + \delta)} \right) + \frac{\delta}{2(h + \delta)} \right] \quad (9)$$

The respective van der Waals force, F^{VW} , between the bodies can be derived by differentiating the interaction energy with respect to the film thickness:

$$F_r^{VW} = -\left(\frac{\partial W^{VW}}{\partial h}\right)_{a,r,\delta} = \frac{A_{101}}{12} \left[\frac{2}{h} + \frac{2r^2 - (a + \delta)^2}{h^2(a + \delta)} - \frac{2r^2}{h^3} \right] + \frac{A_{212}}{12} \left[\frac{2}{h + 2\delta} + \frac{2r^2 - a^2}{a(h + 2\delta)^2} - \frac{2r^2}{(h + 2\delta)^3} \right] + \frac{A_{102} - A_{101}}{6} \left[\frac{2}{h + \delta} - \frac{8a^2 - 15r^2 + 4a\delta}{8a(h + \delta)^2} - \frac{r^2(16a - h - 5\delta)}{8a(h + \delta)^3} \right] \quad (10)$$

The subscript r , for the force calculated by eq 10, denotes the particular procedure of differentiating at a fixed film radius. F_r^{VW} can be used to find the equilibrium configuration of a drop pair on the basis of a force balance. For instance, if two drops are pushed against each other by an external force, F^{EX} , the equilibrium film thickness, h , can be found by equilibrating the disjoining pressure in the film to the capillary pressure of the drop, whereas r is found by equilibrating F^{EX} to the total interparticle force, F_r^T , which comprises various components such as van der Waals, electrostatic, steric, and so forth. On the other side, both h and r can vary in an actual process of drop approach or detachment. In such a process, the external force must do some work for changing the drop area as well; that is, the actual applied force would be different from F_r^T . In the absence of external forces, $F^{EX} = F^T = 0$, the force balance is equivalent to the minimization of the total interaction energy, $W(h,r)$, which is used below for determination of the equilibrium film thickness and radius (see also ref 3).

Equations 9 and 10 can be further simplified if the interaction between lipid vesicles is considered; in this case, phase 2 is equivalent to phase 0, $A_{212} = A_{010} = A_{101}$, and $A_{102} = 0$. Thus, one obtains

$$W^{VW}(h,r) = -A_{101}(H_{11} - 2H_{12} + H_{22}) = -\frac{A_{101}}{12} \left[\frac{(a + \delta)^2 - 2r^2}{(a + \delta)h} - 2 \ln \left[\frac{(a + \delta)(h + \delta)^2}{ha(h + 2\delta)} \right] + \frac{a^2 - 2r^2}{a(h + 2\delta)} + \frac{15r^2 - 4a\delta - 8a^2}{4a(h + \delta)} + \frac{r^2}{h^2} + \frac{r^2}{(h + 2\delta)^2} + \frac{r^2(h + 3\delta - 8a)}{4a(h + \delta)^2} \right] \quad (11)$$

$$F_r^{VW} = \frac{A_{101}}{12} \left[\frac{2r^2 - (a + \delta)^2}{h^2(a + \delta)} + \frac{4\delta^2}{h(h + \delta)(h + 2\delta)} - \frac{a^2 - 2r^2}{a(h + 2\delta)^2} - \frac{15r^2 - 4a\delta - 8a^2}{4a(h + \delta)^2} - \frac{2r^2}{h^3} - \frac{2r^2}{(h + 2\delta)^3} + \frac{r^2(16a - 5\delta - h)}{4a(h + \delta)^3} \right] \quad (12)$$

From eqs 9 and 10, one can obtain other particular cases. For instance, if the Hamaker constant of the layer, $A_{1,1}$, is equal to the Hamaker constant of the medium, $A_{0,0}$, one obtains

$$W^{VW} = -A_{202}H_{22} \quad (13)$$

which is equivalent to the interaction between two truncated spheres of radius a , separated at a distance $h + \delta$, that is, the layer does not contribute to the van der Waals interaction between the drops. Note that the

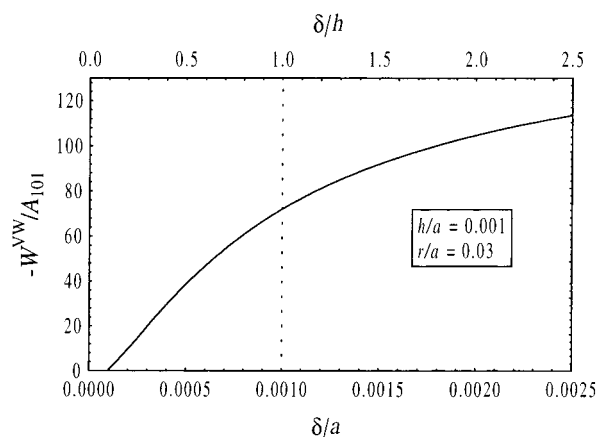


Figure 3. Plot of the geometrical function for vesicles, $H_{VES} = (H_{11} - 2H_{12} + H_{22}) = -W^{VW}/A_{101}$ (cf. eq 11), as a function of δ/h and δ/a at fixed values of $h/a = 0.001$ and $r/a = 0.03$. The vertical dashed line indicates $\delta/h = 1$.

electrostatic interaction, for example, could be affected in this system, because the surface charge might be located on the outer surface of the adsorption layer (or be distributed within the layer). Another particular case is derived when the Hamaker constant of the layer is equal to that of the drop core, $A_{1,1} = A_{2,2}$. In this case, one obtains

$$W^{VW} = -A_{101}H_{11} \quad (14)$$

which is equivalent to the interaction between two truncated spheres of radius $(a + \delta)$ separated at a distance h .

In the general case, however, the layer may contribute significantly to the van der Waals interaction, and the magnitude and sign of this contribution depend strongly on the Hamaker constants of the different phases. For a thin adsorption layer, $\delta/a \ll 1$, its relative contribution to the total van der Waals interaction energy depends primarily on the ratio δ/h . One should expect a significant contribution of the adsorption layer at $\delta/h \sim 1$, unless the layer's Hamaker constant is very close to that of the continuous phase.

To illustrate the importance of the ratio δ/h for the interaction energy, we plot in Figure 3 the geometrical function for vesicles, $H_{VES} = (H_{11} - 2H_{12} + H_{22}) = -W^{VW}/A_{101}$ (cf. eq 11), as a function of δ/h and δ/a at fixed values of $h/a = 0.001$ and $r/a = 0.03$. As seen from Figure 3, $H_{VES} \approx 70$ at $\delta/h = 1$ (the vertical dashed line). Taking into account⁹ that A_{101} is on the order of the thermal energy, $k_B T$, for lipid bilayers, one estimates $W^{VW} \approx 10^2 k_B T$ for $\delta \sim h$, despite the fact that the actual layer thickness is much smaller than the drop (vesicle) size, $\delta/a \sim 10^{-3}$. Additional numerical checks showed that the magnitude of H_{VES} , which characterizes the strength of the interaction, significantly increases with the film radius, r/a .

2. Illustrative Example: Interaction between Emulsion Droplets Covered by Layers of Adsorbed Globular Protein

This section illustrates how the obtained expressions can be applied to real systems. We consider the interaction between two emulsion droplets of micrometer size, whose surfaces are covered by a compact adsorption layer of protein. To make our calculations more concrete and closer to a real system, we consider the interaction between two xylene droplets, covered by adsorbed layers of the protein bovine serum albumin (BSA) and immersed in an aqueous electrolyte solution of concentration varying between 0.1

and 0.4 M. The application of the above formulas to another interesting system (lipid vesicles) has been recently analyzed by Petsev.⁶

2.1. Total Interaction Energy. Following the approach from refs 1–3, we investigate how the interaction energy between two emulsion droplets depends on the governing parameters, such as the drop size and electrolyte concentration. We will take into account three contributions to the total interaction energy between the emulsion drops: (i) van der Waals interaction, (ii) electrostatic repulsion between the charged surfaces of the adsorbed layers, and (iii) interfacial energy accounting for the expansion of the drop surface upon deformation. These three contributions are always present in oil-in-water emulsions. The introduction of other types of interaction, such as colloid structural forces (due to the presence of micelles or protein molecules in the continuous phase), depletion forces, steric repulsion, and so forth, can be conducted in a straightforward manner.^{1,3}

The energy of electrostatic interaction, W^{EL} , can be calculated from the expression¹

$$W^{\text{EL}}(h,r) = \frac{64\pi}{\kappa} C_{\text{EL}} k_{\text{B}} T \left[\tanh\left(\frac{e\Psi_0}{4k_{\text{B}}T}\right) \right]^2 e^{-\kappa h} \left[r^2 + \frac{a}{\kappa} \right] \quad (15)$$

where C_{EL} is the electrolyte concentration, k_{B} is the Boltzmann constant, T is the temperature, e is the elementary charge, Ψ_0 is the electrical potential at the outer surface of the adsorbed layer, and κ^{-1} is the Debye screening length defined as

$$\kappa^2 = \frac{2e^2}{\epsilon\epsilon_0 k_{\text{B}} T} C_{\text{EL}}$$

Equation 15 is valid when the electric double layers around the two drops weakly overlap with each other ($\kappa h > 1$); that is, the superposition approximation is valid (the application of other possible expressions for the electrostatic interaction are discussed in ref 1).

The energy of surface extension, W^{S} , can be expressed as¹

$$W^{\text{S}}(r) = \frac{\pi}{2} \gamma \frac{r^4}{a^2} \quad (16)$$

where γ is the interfacial tension. Following the approach from refs 2 and 3, we minimize the total interaction energy

$$W(h,r) = W^{\text{W}}(h,r) + W^{\text{EL}}(h,r) + W^{\text{S}}(r) \quad (17)$$

with respect to the variables h and r , to determine the equilibrium thickness and radius of the planar film (i.e., the equilibrium configuration of the doublet of droplets), as well as the corresponding interaction energy between the two droplets.

The formulas for the different contributions into the total interaction energy do not predict, strictly speaking, pairwise summation of the interaction energy in a many-body system (e.g., in a floc of drops). However, if (a) the range of the interdroplet interactions and the film thickness are much smaller than the drop radius and (b) the drop deformation is also small, $r/a \ll 1$, the interactions between each two drops in the floc are concentrated in the contact zone (viz., in the film and the closest meniscus region). Then, the different contact zones for a given drop

can be considered as independent of each other, and the expressions derived for a single pair of drops can be used for description of the interaction between any two contacting drops in the floc. Thus, the total interaction energy of a drop with its neighbors can be found through multiplication of the interaction energy per one contact by the number of contacts. In fact, this is quite often the case, because conditions a and b are satisfied in most systems, so the above formulas can be used to describe many-body interactions as well.⁷

2.2. Choice of the Parameters. There are two types of input parameters for the calculations: (i) those that can be varied by the experimentalist within a certain range (e.g., the drop radius and electrolyte concentration) and (ii) those that are determined by the used substances (Hamaker constants, thickness of adsorbed layer, interfacial tension, electrical surface potential). In the following calculations, we consider the first type as free parameters and vary their values within certain ranges: the drop radius is varied between 0.5 and 10 μm and the electrolyte concentration is varied between 0.1 and 0.4 M NaCl. The values of the remaining parameters were taken from the literature or calculated by using literature data.

(a) *Hamaker Constants.* Roth et al.⁸ calculated the Hamaker constants protein–water–protein, $A_{\text{pr-w-pr}} = 1.275 \times 10^{-20} \text{ J} = 3.10 k_{\text{B}} T$, protein–vacuum–protein, $A_{\text{pr-pr}} = 23.42 k_{\text{B}} T$, and protein–water–polystyrene, $A_{\text{pr-w-ps}} = 1.54 k_{\text{B}} T$, for BSA. One can assume that the Hamaker constant of polystyrene is close to that of xylene, $A_{\text{pr-w-ps}} = A_{\text{pr-w-oil}}$, because both substances are aromatic hydrocarbons of similar structure. Under this assumption, one obtains

$$A_{\text{pr-w-oil}} - A_{\text{pr-w-pr}} = -0.64 \times 10^{-20} \text{ J} = -1.56 k_{\text{B}} T \quad (18)$$

The Hamaker constant $A_{\text{oil-pr-oil}}$, which is also needed for the computations, can be found from the so-called combining relations,⁹

$$A_{132} = A_{12} - A_{13} - A_{23} + A_{33} \quad (19)$$

which relates the Hamaker constant for the interaction of phase 1 with phase 2 across phase 3 with the respective constants for the interaction of these phases across a vacuum. After some algebraic calculations, one derives

$$A_{\text{oil-pr-oil}} = A_{\text{oil-oil}} - 2A_{\text{oil-pr}} + A_{\text{pr-pr}} = A_{\text{pr-w-pr}} - 2A_{\text{pr-oil}} + A_{\text{oil-w-oil}} \quad (20)$$

Taking the values of $A_{\text{pr-w-pr}}$ and $A_{\text{pr-w-oil}}$ quoted above and the value of $A_{\text{oil-w-oil}} = 2.31 k_{\text{B}} T$ from ref 9, we obtain $A_{\text{oil-pr-oil}} = 0.96 \times 10^{-20} \text{ J} = 2.33 k_{\text{B}} T$.

The above calculations do not account for the effect of screening of the “zero-frequency” contributions to the Hamaker constants, $A_{\nu=0}$, by the electrolyte.^{9,10} Because we consider systems containing electrolytes of high concentration, this effect could be rather significant. It can be properly taken into account by using the formulas¹⁰

$$A = A_{\nu=0} + A_{\nu>0} \quad (21)$$

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$$A_{\text{screened}}(\kappa h) = A_{v=0}(1 + 2\kappa h) \exp(-2\kappa h) + A_{v>0} \quad (22)$$

We calculated $A_{v=0}$ from eq 11.8 in ref 9:

$$A_{132,v=0} = \frac{3}{4} k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) \quad (23)$$

where ϵ_k is the static dielectric permittivity of phase k ($k = 1, 2, 3$). In the calculation, we used $\epsilon_W = 80$, $\epsilon_{pr} = 3$, and $\epsilon_{oil} = 2.55$.^{8,9} From eqs 21–23, we obtained the following values for the two counterparts of the respective Hamaker constants:

$$\begin{aligned} A_{v=0}^{\text{pr-w-pr}} &= 0.645 k_B T & A_{v>0}^{\text{pr-w-pr}} &= 2.455 k_B T \\ A_{v=0}^{\text{oil-pr-oil}} &= 0.005 k_B T & A_{v>0}^{\text{oil-pr-oil}} &= 2.325 k_B T \quad (24) \\ A_{v=0}^{\text{pr-w-oil}} - A_{v=0}^{\text{pr-w-pr}} &= 0.01 k_B T \\ A_{v>0}^{\text{pr-w-oil}} - A_{v>0}^{\text{pr-w-pr}} &= -1.57 k_B T \end{aligned}$$

which are used below in the calculations.

(b) *Thickness of the Protein Layer.* The thickness of the adsorbed protein layer was chosen as $\delta = 2.8$ nm. Such a value was determined by atomic force microscopy for the adsorption layer of BSA on a hexadecane/water interface.¹¹

(c) *Interfacial Tension.* The interfacial tension of the protein solutions was directly measured by de Nouy ring method using a platinized ring (Kruss tensiometer K10T, Germany). A value of $\gamma = 12.6$ mN/m was determined,⁴ which slightly depended on the electrolyte concentration.

(d) *Electrical Surface Potential of the Drops.* Bowen and Williams¹² obtained $\Psi_0 = -29.5$ mV for the surface potential of BSA molecules at pH = 7.4. The ionic strength in their experiments was 0.15 M NaCl, and the concentration of BSA was 0.4 wt %. In the following calculations, we use this value.

2.3. Numerical Results. Figure 4 shows the calculated dimensionless equilibrium film radius, r/a , as a function of the drop radius, a , at several electrolyte concentrations (0.1–0.4 M NaCl). The film radius is virtually zero for very small drops. However, at fixed other parameters, the film radius sharply increases around a certain threshold value of the drop radius (which depends on the electrolyte concentration) and reaches a plateau for large drops. The height of the plateau is related to the contact angle of film–meniscus, which can be measured in experiments with model emulsion films (e.g., in the capillary cell^{13,14}):

$$\alpha = \arcsin(r/a) \quad (25)$$

One should note that except in the case of the lowest concentration (0.1 M), where the deformation starts at $a \approx 4 \mu\text{m}$, in all other cases the micrometer-sized drops are deformed.

The calculated equilibrium film thickness, h , gradually decreases from 6 to 2.3 nm with the increase of the electrolyte concentration from 0.1 to 0.4 M (h depends very slightly on the drop radius^{3,4}). In all cases, the equilibrium of the film was ensured by electrostatic repulsion between the charged surfaces of the drops; that

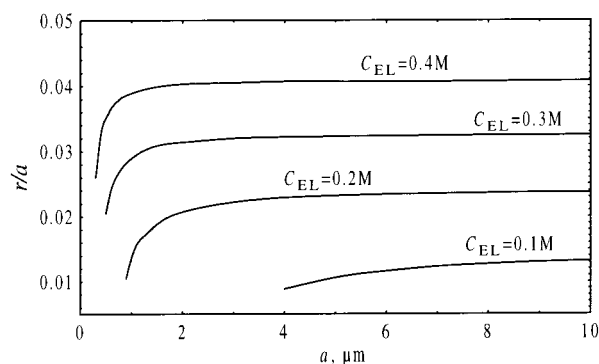


Figure 4. Variation of the dimensionless film radius as a function of the drop radius at four different electrolyte concentrations. Other parameters used in the calculations are $\delta = 2.8$ nm, $\Psi_0 = -29.5$ mV, $\gamma = 12.6$ mN/m, and $T = 298$ K.

is, a common black type of film is formed between the droplets. For comparison, by using the microinterferometric method^{13,14} we have measured⁴ $\alpha_{\text{EXP}} = 0.65 \pm 0.1^\circ$ ($\alpha_{\text{THEOR}} = 0.74$, see Figure 4) and $h_{\text{EXP}} = 6 \pm 2$ nm ($h_{\text{THEOR}} = 6$ nm) with millimeter-sized emulsion films xylene–water–xylene, formed from 0.02 wt % BSA solution containing 0.1 M NaCl ($T = 298$ K). A three-layer optical model was used to determine h , which accounts for the influence of the adsorbed protein layers on the intensity of the light reflected from the emulsion films. Very similar experimental results were obtained by Marinova et al.¹⁵ at slightly different conditions ($C_{\text{EL}} = 0.15$ M, 0.015 wt % BSA). The agreement between the calculated and the measured values of α and h evidences that the parameters used in the calculations are reasonably chosen.

The calculated pair interaction energy between deformable drops, W , is plotted in Figure 5A as a function of the droplet radius at several electrolyte concentrations. The interaction energy is negative in sign, which corresponds to attraction between the drops. As expected, the magnitude of the attractive energy increases with the increase of the drop size and the ionic strength. The numerical results indicate a rather strong attraction for drops of micrometer size, which would result in a pronounced tendency for flocculation under such conditions.

The effect of droplet deformation on the interaction energy is illustrated in Figure 5B, where the difference between the energy for two deformable drops, W , and that for two nondeformed spheres, W_0 , is plotted as a function of the drop radius and the electrolyte concentration. The parameters of the spheres (Hamaker constants and thickness of the protein layer) used for the calculation of W_0 are taken to be exactly the same as those of the deformable droplets. Therefore, the difference between W and W_0 is due entirely to the drop deformation. As seen from the figure, the attraction between deformable droplets is much stronger as compared to the interaction between solid spheres.

To illustrate the importance of the protein layer for the interaction energy, we show in Figure 5A,B the results for two other related systems (see curves 1 and 2). The electrolyte concentration in these calculations is 0.2 M NaCl, and the remaining parameters are the same as for all other curves ($\delta = 2.8$ nm, $\Psi_0 = -29.5$ mV, and $\gamma = 12.6$ mN/m). In the first system (curve 1), we assume that the adsorption layer has the same Hamaker constant as the aqueous phase. Not surprisingly, the magnitude of the

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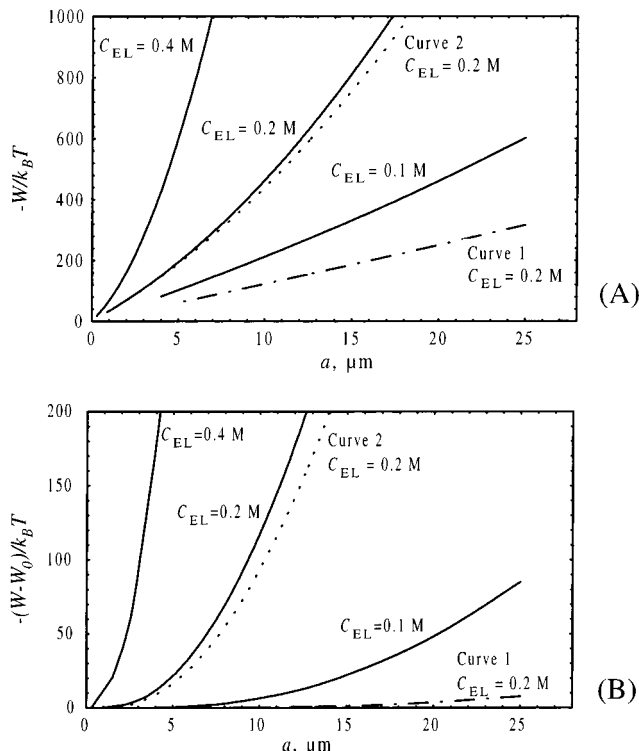


Figure 5. (A) Calculated pair interaction energy between two deformable drops as a function of the drop radius at three different electrolyte concentrations. (B) The difference between the calculated pair interaction energy for two deformable drops, W , and the interaction energy between two nondeformable spheres, W_0 , as a function of the drop radius. The solid curves in (A) and (B) present the results for oil drops covered by a protein layer ($\delta = 2.8 \text{ nm}$, $\Psi_0 = -29.5 \text{ mV}$, $\gamma = 12.6 \text{ mN/m}$, and $T = 298 \text{ K}$). For comparison, the interaction energy between oil drops covered by a layer having a Hamaker constant equivalent either to that of the aqueous phase (curve 1) or to that of the oil phase (curve 2) is shown for a 0.2 M electrolyte (the remaining parameters being the same).

total interaction energy in this system is strongly reduced; in fact, this assumption corresponds to a complete elimination of the layer contribution to the van der Waals interaction energy. In the second system (curve 2), we assume that the adsorption layer has the same Hamaker constant as the *drop core* (the oil phase). In this case, the total interaction energy is reduced by only 10%, as compared to the curve for protein-covered drops. However, further numerical checks showed that the contribution of the layer can be much more significant for other Hamaker constants of the phases. Thus, if we take $A_{101} = 1.65 k_B T$,

$A_{212} = 1.685 k_B T$, and $A_{102} = 0.89 k_B T$ (these Hamaker constants are calculated if one fictitiously replaces the oil and protein phases in our emulsion system), a total interaction energy, $W = -347 k_B T$, is calculated for $a = 10 \mu\text{m}$ and $C_{EL} = 0.2 \text{ M}$. For this system, the assumption that the layer has the same Hamaker constant as the *drop core* leads to almost a 3-fold increase of the magnitude of the interaction energy, $W = -950 k_B T$; that is, the layer has a very significant contribution. In conclusion, the relative contribution of the layer to the total interaction energy depends strongly not only on geometrical factors but on the values of the various Hamaker constants as well.

3. Conclusions

The main results of this study are the derived explicit expressions for the van der Waals interaction energy and force between two truncated spheres covered by a thin layer of uniform thickness (eqs 9 and 10). These expressions can be used for description of the interactions in emulsions, vesicular suspensions, or foams of fine bubbles.

As an illustration of the applicability of the formulas to real systems, we consider the interaction between micrometer-sized drops of an oil-in-water emulsion, covered by a protein layer. The relevant Hamaker constants for the interactions between the protein, oil, and water are calculated from literature data (eq 24). The equilibrium radius and thickness of the liquid film, which forms upon the collision of the emulsion drops, are determined as functions of the drop size and electrolyte concentration. From the parameters of the equilibrium films, we calculate the total energy of interaction between the drops. The numerical results show that the drops of micrometer size are deformed if the electrolyte concentration is above 0.1 M (Figure 4). The higher electrolyte concentration leads to more pronounced deformation. The latter has a noticeable effect on the pair interaction energy between the emulsion droplets; the attraction between deformable droplets is stronger in comparison with the interaction between two nondeformable spheres with the remaining parameters being the same (Figure 5). The relative contribution of the adsorption layer to the total interaction energy depends strongly not only on geometrical factors, such as the layer thickness, but on the values of the various Hamaker constants as well.

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