



Depletion forces in thin liquid films due to nonionic and ionic surfactant micelles



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ARTICLE INFO

Article history:

Received 3 November 2014

Accepted 25 November 2014

Available online 4 December 2014

Keywords:

Depletion force

Oscillatory structural force

Nonionic micelles

Charged particles

Foam and emulsion films

Contact angles

ABSTRACT

The depletion force can be considered as a special (limiting) case of the oscillatory structural force at short distances between two surfaces. Here, we consider analytical expressions for the structural force in the depletion zone and compare their predictions with experimental data. In the case of particles that interact as hard spheres, an expression for the depth of the depletion minimum as a function of the particle volume fraction ϕ is available. This expression has been used to predict the rise of the contact angle α of plane-parallel foam films from nonionic surfactant solutions with the increase of surfactant concentration – a depletion effect due to the nonionic micelles, which can be treated as hard spheres. Further, knowing the theoretical α -vs.- ϕ dependence, from the experimental values of α the micelle aggregation number has been calculated, and the results agree well with data obtained by other methods. In the case of electrically charged particles, the depletion effect is strongly affected by the soft and long-range electrostatic repulsion. This interplay of electrostatic and depletion effects can be quantified by upgrading the Poisson–Boltzmann theory of electric double layer to take into account the presence of charged particles (macroions). The resulting theoretical model predicts the equilibrium thickness, h_0 , of plane-parallel films formed from micellar solutions of ionic surfactants in excellent agreement with the experiment.

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1. Introduction

One of the first observations of depletion effect was reported by Bondy [1], who detected coagulation of rubber latex in the presence of polymer molecules in the disperse medium. Asakura and Oosawa [2] explained the observed interparticle attraction by the overlap of depletion layers at the surfaces of two neighboring colloidal particles. de Hek and Vrij [3] studied systematically the flocculation of sterically stabilized silica suspensions in cyclohexane by polystyrene molecules. Patel and Russel [4] investigated the phase separation and rheology of aqueous polystyrene latex suspensions in the presence of polymer (Dextran T-500). It was found [5] that in some cases the stability of dispersions is due to the balance between electrostatic repulsion and depletion attraction. Interplay of steric repulsion and depletion attraction was studied theoretically by van Lent et al. [6] for the case of polymer solution between two surfaces coated with anchored polymer layers. Joanny et al. [7] and Russel et al. [8] re-examined the theory of depletion interaction by taking into account the internal degrees of freedom of the polymer molecules. Their analysis confirmed the earlier results of Asakura and Oosawa [2]. Evans and Needham [9] measured the depletion energy of two interacting bilayer surfaces in a concentrated Dextran solution and their results also confirmed the basic paper, Ref. [2]. The effect of polymer polydispersity on the depletion interaction

between two plates immersed in a nonadsorbing polymer solution was studied by the self-consistent-field theory [10]. The results showed that the range of the depletion potential increases, whereas the depth of the potential decreases with the rise of polydispersity. Synergistic effects of polymers and surfactants on the depletion forces have been also examined [11].

Depletion force in a bidisperse granular layer was investigated in experiments and simulations of mixtures of large and small steel spheres [12]. Sphere/wall and sphere/sphere interactions in a dilute suspension of infinitely thin rods were numerically calculated [13]. Shear-affected depletion interactions with disc-shaped particles were experimentally studied [14]. A detailed review on depletion surface forces can be found in the book by Lekkerkerker and Tuinier [15].

Foams and emulsions are often formed from solutions which contain colloidal particles. Such are the micellar solutions of nonionic and ionic surfactants, where the micelles play the role, respectively, of hard and charged spheres. In general, the confinement of colloid particles and surfactant micelles in liquid films gives rise to the oscillatory structural surface force [16,17]. The depletion interaction corresponds to the first minimum of the oscillatory force at small thicknesses, at which the particles are forced out of the film [18,19].

Based on the fact that the depletion force represents a special case of the oscillatory force, here we consider theoretical expressions for the oscillatory force in the depletion limit and compare their predictions with experimental data for the equilibrium thickness and contact angle of thin foam films formed from micellar surfactant solutions. In

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particular, Section 2 is dedicated to the case of particles that interact as hard spheres, which is an adequate model for uncharged colloidal beads and nonionic surfactant micelles. The cases of plane-parallel films (Fig. 1a) and two interacting larger particles (Fig. 1b) are considered. The available analytical expressions are compared with data for foam films from micellar solutions of nonionic surfactants. Likewise, in Section 3 we present analytical expressions describing electrostatic interactions influenced by the depletion force in the case of electrically charged particles. Next, the theoretical predictions are compared with the experimental equilibrium thicknesses of foam films formed from micellar solutions of ionic surfactants. The developed methodology can be applied to quantitatively interpret experimental data in many other systems affected by the depletion surface force.

2. Depletion attraction due to hard spheres and nonionic micelles

2.1. The depletion force as a special case of the oscillatory structural force

The stepwise thinning (stratification) of liquid films formed from solutions containing surfactant micelles or colloidal (e.g. latex) particles was interpreted as a layer-by-layer thinning of an ordered structure of micelles or particles inside the films [17,20,21], i.e. with the action of the oscillatory structural force [16,18,22–24]. At the final stage of film thinning, all micelles/particles are forced out of the film (Fig. 1a). Then, the two film surfaces experience a depletion attraction due to the osmotic pressure of the particles in the bulk liquid phase (Plateau border) around the film. In stable films, a repulsive force (electrostatic, steric, etc.) counterbalances the depletion attraction between the film

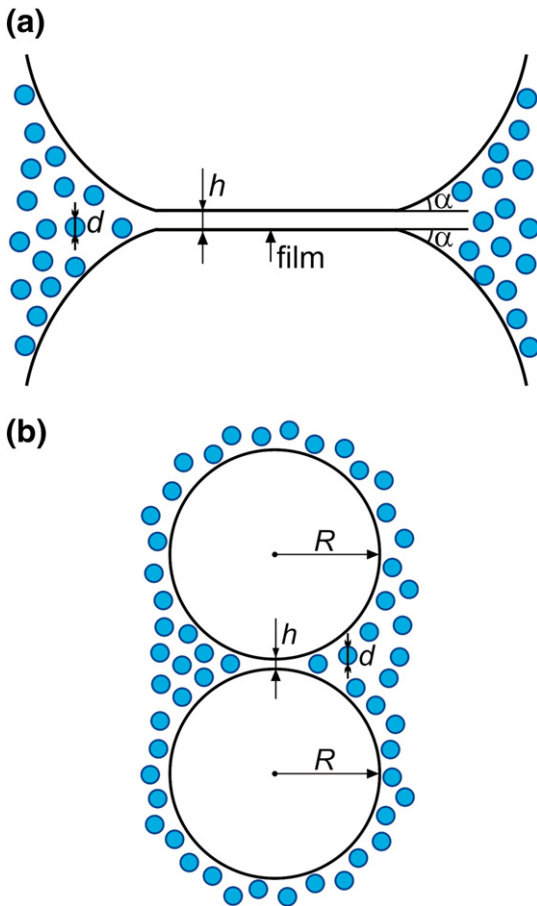


Fig. 1. (a) Sketch of a liquid film of thickness h , which is formed from a solution that contains uncharged colloidal spheres of diameter d ; at $h < d$ the film does not contain any particles. (b) The depletion zone between two larger particles of radius R is the region of contact, where the smaller colloidal spheres cannot penetrate.

surfaces. The depletion attraction affects the values of the final film thickness, h , and contact angle, α (Fig. 1a) – it tends to decrease h and increase α [25].

As already mentioned, the depletion force is a special case of the oscillatory structural force for $0 < h/d < 1$, where h is the thickness of the film's liquid core and d is the diameter of the particles that create the osmotic pressure. In superposition with the van der Waals and electrostatic surface forces, the depletion force gives rise to a minimum in the total interaction energy per unit area W at $h/d < 1$, which can be directly detected by colloidal probe atomic force microscopy (CP-AFM) [26], as well as by a surface-force apparatus [27]. In experiments with stratifying films, the effect of depletion interaction on the final film thickness, contact angle and disjoining pressure can be registered by using the capillary cell of Scheludko and Exerowa (SE cell) [28] and the porous-plate cell by Mysels and Jones (MJ cell) [29]; for examples, see Refs. [25,30]. At low values of the particle volume fraction ϕ , the oscillatory maxima and minima disappear, and the oscillatory structural force completely degenerates into the depletion force; see Fig. 2a.

2.2. Quantitative theoretical description for hard spheres

In the case of particles and micelles that can be treated as hard spheres, the oscillatory structural force (and the depletion force as its special case) has been calculated by using the equations of statistical mechanics [24,31–33] and numerical simulations [19,34,35]. Simpler, but quantitative semiempirical expressions have been proposed [18,36] on the basis of analytical and numerical results for hard sphere fluids. Here, following Ref. [25] we will present the predictions and application of the model from Ref. [36], which has been successfully tested against data from Monte Carlo simulations, CP-AFM measurements [37] and data for stratifying films [25]. This model yields the following expressions for the interaction energy per unit area of a plane-parallel film due to the oscillatory force, W_{osc} [36]:

$$\frac{W_{\text{osc}}d^2}{kT} = -\frac{p_{\text{hs}}d^3}{kT}(1-\hat{h}) - \frac{2\sigma_{\text{hs}}d^2}{kT}, \text{ for } 0 \leq \hat{h} < 1 \quad (1)$$

$$\frac{W_{\text{osc}}d^2}{kT} = w_0 \cos(\omega\hat{h} + \varphi_1) e^{-q\hat{h}} + w_1 e^{\delta(1-\hat{h})}, \text{ for } \hat{h} \geq 1. \quad (2)$$

Here, $\hat{h} = h/d$ is the dimensionless surface-to-surface distance; d is the micelle diameter; k is the Boltzmann constant and T is the absolute temperature; p_{hs} is the pressure of a hard-sphere fluid expressed through the Carnahan–Starling formula [38], and σ_{hs} is the scaled-particle-theory [39] expression for the excess surface free energy of a hard-sphere fluid:

$$\frac{p_{\text{hs}}d^3}{kT} = \frac{6}{\pi} \phi \frac{1 + \phi + \phi^2 - \phi^3}{(1-\phi)^3} \quad (3)$$

$$\frac{\sigma_{\text{hs}}d^2}{kT} = -\frac{9}{2\pi} \phi^2 \frac{1 + \phi}{(1-\phi)^3}. \quad (4)$$

The parameters w_0 , ω , φ_1 , q , w_1 and δ in Eq. (2) are known functions of the hard-sphere (micelle) volume fraction, ϕ ; see, e.g., Eqs. (8)–(16) in Ref. [37]. In particular, the parameters w_0 , ω , and q characterize, respectively, the amplitude, period and decay length of the oscillations.

Fig. 2a shows the dependence of the dimensionless energy $W_{\text{osc}}d^2 / (kT)$ on h/d calculated from Eqs. (1)–(4) for three different particle volume fractions, $\phi = 0.15, 0.26$ and 0.38 . At the lowest volume fraction, $\phi = 0.15$, the amplitude of the oscillatory maxima and minima is rather small and the interaction energy is dominated by the depletion minimum at $h/d < 1$. At the greater values of ϕ , the amplitude of decaying oscillations at $h/d > 1$ increases considerably, and the depletion minimum of W_{osc} becomes deeper.

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