

Analytical expression for the oscillatory structural surface force

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Abstract

A semiempirical expression is proposed to describe the dependence of the oscillatory surface force on both film thickness and particle volume fraction for a hard sphere fluid between hard walls. The expression is tested successfully against the predictions of integral equations, computer simulations and experimental data for liquid films containing ionic and nonionic surfactant micelles. The proposed expression can be used to interpret experimental data for stability of liquid films and colloidal dispersions, or can be incorporated in complex theoretical models of dynamics of liquid film drainage, or kinetics of flocculation in emulsions and suspensions.

1. Introduction

For the last 15 years a number of non-DLVO surface forces have been discovered experimentally [1]. One of them is the oscillatory structural force, which is the subject of the present Letter. It appears in two cases: (i) in thin liquid films between two smooth solid surfaces and (ii) in liquid films containing colloidal particles, e.g. surfactant micelles or macromolecules. In the first case the oscillatory forces are called the ‘solvation forces’ [2] as the period of oscillations is of the order of the diameter of a solvent molecule; they contribute to the short-range interaction between molecularly smooth solid surfaces. In the second case the structural forces affect the stability of foam and emulsion films as well as the flocculation processes in various colloids. At higher particle concentrations these colloid structural forces *stabilize* the liquid films and dispersions [3–5]. At lower particle concentrations the structural force degenerates into the so-called depletion force,

which is found to *destabilize* various dispersions [1,6].

It all cases the oscillatory structural forces appear when spherical particles are confined in the gap between two surfaces. As shown in many theoretical works, even one planar wall induces ordering among the neighbouring particles which propagates at some distance in the depth of the liquid. The oscillatory structural force is a result of the overlap of the structural zones at two approaching surfaces, see Refs. [1,7,8] and the literature quoted therein.

The oscillatory structural forces can be directly measured by means of the surface force apparatus [2]. This method is successfully applied to detect solvation oscillatory forces [1,2], depletion forces [9], and colloid structural forces due to surfactant micelles [10] or microemulsion droplets [11]. Another experimental tool for studying the colloid structural forces is provided by the phenomenon stratification, i.e. step-wise thinning of a foam or emulsion type liquid film containing colloidal particles. Nikolov et

al. [3–5,12,13] and Bergeron and Radke [14,15], demonstrated that the step-wise transitions represent a manifestation of structural forces. It is worthwhile noting the universality of stratification: it is observed with particle diameters varying between 5 nm and 2 μm [13]. This is an indication for size invariance of the volume exclusion effect due to particles involved in Brownian motion.

The oscillatory structural force can be accounted for by adding an extra term, Π_{os} , in the DLVO expression for the disjoining pressure [12,15],

$$\Pi(h) = \Pi_{\text{vw}}(h) + \Pi_{\text{el}}(h) + \Pi_{\text{os}}(h). \quad (1)$$

Here Π_{vw} is the van der Waals disjoining pressure [16,17],

$$\Pi_{\text{vw}} = -\frac{A_{\text{H}}}{6\pi h^3} \quad (2)$$

(h is film thickness, A_{H} is Hamaker constant) and Π_{el} is the electrostatic disjoining pressure [18]

$$\Pi_{\text{el}} = 64n_0kT \tanh^2 \frac{Ze\psi_s}{4kT} \exp(-\kappa h), \quad (3)$$

where k is Boltzmann constant, T is the temperature, n_0 and Ze are the bulk concentration and charge of the ions of a symmetrical $Z:Z$ electrolyte, κ is the Debye screening parameter, ψ_s is the surface electrostatic potential. Both Eqs. (2) and (3) have an approximative character, but nevertheless they have a wide range of validity and are very convenient for application; the reason is that Eqs. (2) and (3) give the zeroth-order effect and the more rigorous (and complicated) theories yield only higher-order corrections.

Until now such a convenient zeroth-order expression for Π_{os} is missing. The integral equations of statistical mechanics lead to sophisticated computational procedures for Π_{os} [7,8,19,20]. Our aim in the present study is to construct a simpler expression for Π_{os} which is to represent correctly the dependence of Π_{os} on both film thickness (slit width), h , and particle volume fraction, φ . Being stimulated by the utilizability of such an expression, we pursue our goal even at the cost of some empiricism. Below we propose a formula for Π_{os} , which is further tested against the predictions of integral equations, computer simulations and experimental data for stratifying films.

2. Expression for the oscillatory structural force

2.1. Period and decay length

For the sake of estimates Israelachvili [1] used an approximated expression

$$\Pi_{\text{os}}(h) \approx -kT\rho_s(\infty) \cos\left(\frac{2\pi h}{d}\right) \exp\left(-\frac{h}{d}\right), \quad (4)$$

where $\rho_s(\infty)$ is the particle concentration in the sub-surface layer for $h \rightarrow \infty$; both the oscillatory period and the characteristic decay length are set equal to the particle diameter, d [21]. On the other hand, the works on stratifying films quoted above indicate that the period can depend on the particle volume fraction. To elucidate this point we examined the predictions of the theory by Henderson [20]. The latter theory is based on an inversion of the Laplace transforms of the radial correlation functions determined by Lebowitz [22] for a mixture of larger and smaller hard spheres in the framework of the Percus–Yevick closure. At a certain point of the derivation the radius of the larger spheres is set infinitely large and thus the interaction between two walls is determined.

By using Henderson theory [20] we calculated Π_{os} for various volume fractions of the (smaller) hard spheres, φ . The results confirm that in a first approximation Π_{os} is a periodical function of h with an exponential decay (for $h > d$). The oscillatory period, d_1 , and the decay length, d_2 , calculated by averaging over many consecutive maxima and minima, are listed in Table 1 for five different values of φ . The data show that $d_1 \approx d_2 \approx d$ only around $\varphi \approx 0.4$. For smaller volume fractions ($\varphi \approx 0.1$) d_1 increases with $\approx 20\%$, whereas d_2 decreases more than three times. The latter fact, coupled with the

Table 1
Period d_1 and decay length d_2 (scaled by the particle diameter d) for various hard sphere volume fractions, φ , as predicted by Henderson theory [20]

φ	d_1/d	d_2/d
0.1	1.234	0.317
0.2	1.124	0.476
0.3	1.040	0.696
0.4	0.973	1.053
0.5	0.910	1.583

circumstance that d_2 takes place under the sign of an exponent, implies a strong concentration dependence of Π_{os} . (Roughly speaking, for a given h the oscillatory disjoining pressure Π_{os} increases five times when φ is increased with 10% – see Fig. 3 below.)

We obtained interpolation formulas for the data in Table 1 by using the following heuristic considerations. When φ tends to the concentration of close packing, $\varphi_{max} = \Pi/(3\sqrt{2})$, the dimensionless period, d_1/d , should tend to $\sqrt{2/3}$, whereas the decay length d_2 should tend to infinity in so far as we deal with a densely packed fcc lattice. Then we seek d_1 and d_2 in the form of (truncated) series expansions with respect to $\Delta\varphi = \varphi_{max} - \varphi$,

$$\frac{d_1}{d} = \sqrt{\frac{2}{3}} + a_1\Delta\varphi + a_2(\Delta\varphi)^2, \quad (5)$$

$$\frac{d_2}{d} = \frac{b_1}{\Delta\varphi} - b_2, \quad \Delta\varphi \equiv \frac{\pi}{3\sqrt{2}} - \varphi. \quad (6)$$

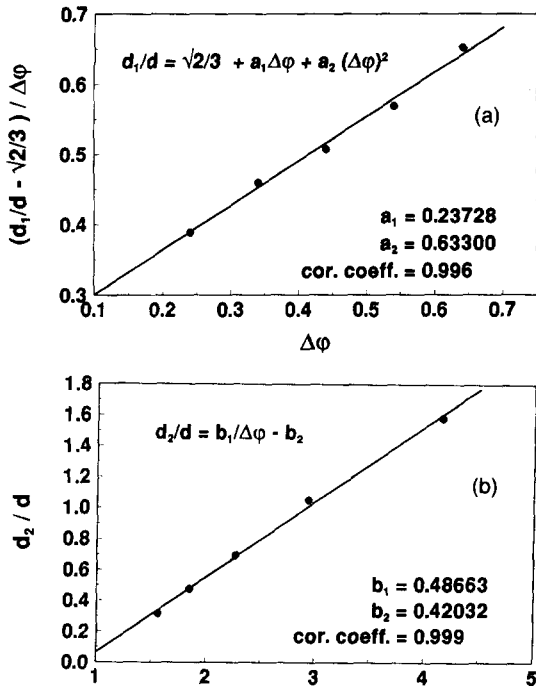


Fig. 1. Plots of the data for the period (a) and the decay length (b) from Table 1 (the circles) in accordance with Eqs. (5) and (6), respectively. The coefficients a_1 , a_2 , b_1 and b_2 are determined from the slopes and intercepts of the corresponding lines.

From the linear plots shown in Figs. 1a and 1b we determined

$$\begin{aligned} a_1 &= 0.23728, & a_2 &= 0.63300, \\ b_1 &= 0.48663, & b_2 &= 0.42032. \end{aligned} \quad (7)$$

The correlation coefficients 0.996 and 0.999 for the lines in Figs. 1a and 1b, respectively, show that the data are in a good agreement with Eqs. (5) and (6).

For volume fraction $\varphi = 0.419$ and $d = 0.74$ nm Attard and Parker [8] calculated theoretically $d_1 = 0.74$ nm and $d_2 = 0.78$ nm, which are to be compared with the predictions of Eqs. (5)–(7), viz. $d_1 = 0.71$ nm and $d_2 = 0.81$ nm. For volume fraction $\varphi = 0.357$ Kjellander and Sarman [7] determined $d_1/d = 1$, $d_2/d = 0.89$, which compares well with the outputs of Eqs. (5)–(7): $d_1/d = 1.00$ and $d_2/d = 0.85$. The lack of perfect numerical agreement between the different theories is not surprising in view of the different approximations and model assumptions used.

2.2. Disjoining pressure and interaction free energy

Next we analyzed numerical data for the positions and magnitudes of the minima and maxima of Π_{os} calculated by means of Henderson theory [20]. We concluded that the data for various h and φ are fitted well by means of the following formula:

$$\Pi_{os} = P_0 \cos\left(\frac{2\pi h}{d_1}\right) \exp\left(\frac{d^3}{d_1^2 d_2} - \frac{h}{d_2}\right),$$

for $h > d$,

$$\Pi_{os} = -P_0, \quad \text{for } 0 < h < d, \quad (8)$$

where d_1 and d_2 are given by Eqs. (5)–(7), and P_0 is the particle osmotic pressure determined by means of Carnahan–Starling formula [23],

$$P_0 = \rho kT \frac{1 + \varphi + \varphi^2 - \varphi^3}{(1 - \varphi)^3}. \quad (9)$$

Here

$$\rho = \frac{6\varphi}{\pi d^3} \quad (10)$$

is the particles number density. It is clear that for $h < d$, when the particles are expelled from the slit into the neighbouring bulk suspension, Eq. (8) de-

scribes the depletion attraction in accordance with the theory of Asakura and Oosawa [6]. On the other hand, for $h > d$ the structural disjoining pressure oscillates around P_0 as given by the Carnahan–Starling formula in agreement with the finding of Kjellander and Sarman [7]. The finite discontinuity of Π_{os} at $h = d$ is not surprising as at this point the interaction is switched over from oscillatory to depletion regime.

It is interesting to note that in oscillatory regime the concentration dependence of Π_{os} is dominated by the decay length d_2 in the exponent. We established the presence of the term $d^3/d_1^2 d_2$ empirically, by fitting numerical data from the Henderson theory [20]; the physical origin of this term is still unclear.

The interaction free energy due to the oscillatory structural forces can be obtained by integrating Π_{os} [17],

$$f_{os}(h) = \int_h^\infty \Pi_{os}(h') dh'. \quad (11)$$

From Eqs. (8) and (11) one obtains

$$\begin{aligned} f_{os}(h) &= F(h), \quad \text{for } h \geq d, \\ f_{os}(h) &= F(d) - P_0(d-h), \quad \text{for } 0 \leq h \leq d, \end{aligned} \quad (12)$$

where

$$\begin{aligned} F(h) &\equiv \frac{P_0 d_1 \exp(d^3/d_1^2 d_2 - h/d_2)}{4\pi^2 + (d_1/d_2)^2} \\ &\times \left[\frac{d_1}{d_2} \cos\left(\frac{2\pi h}{d_1}\right) - 2\pi \sin\left(\frac{2\pi h}{d_1}\right) \right]. \end{aligned}$$

It should be noted that Eqs. (8) and (12) refer to hard spheres of diameter d . In practice, however, the interparticle potential can be ‘soft’ because of the action of some long range forces. If such is the case, one can obtain an estimate of the structural force by introducing an effective hard core diameter [5],

$$d(T) = \left(\frac{3}{2\pi} B_2(T) \right)^{1/3}, \quad (13)$$

where B_2 is the second virial coefficient in the virial expansion of the particle osmotic pressure,

$$\frac{P_{osm}}{\rho kT} = 1 + B_2 \rho + \dots \quad (14)$$

3. Numerical test and discussion

3.1. Comparison with the theoretical predictions

In Fig. 2 Eq. (12) is tested against the theories of Henderson [20] and Mitchell et al. [19]; in particular, the broken line in Fig. 2 is taken from Fig. 4 in Ref. [19], whereas the dotted line is calculated from the equations in Ref. [20] for the same volume fraction, $\varphi = 0.39$. It is seen that the three curves are in a very good quantitative agreement for $h \geq 1.5d$. We can be sure that Eq. (12) is correct for $h < d$ as it expresses the depletion interaction. The repulsive nonlinear branches exhibited by curves (2) and (3) in the region of depletion attraction, $0 < h < d$, where f_{os} should be a linear function of h , are most probably artefacts due to some used approximations. For instance, the approximation $\ln g_{cc} \approx g_{cc} - 1$ is used for the radial distribution function of a pair of larger spheres [20]; in fact the larger deviations of g_{cc} from unity are expected around $h = d$, where the linearization of the logarithm could fail. The HNC closure used in Ref. [19] might be also a source of some artefacts.

The inset in Fig. 2 compares Eq. (12) with the theory of Henderson [20] for a lower volume fraction, $\varphi = 0.15$. The two curves behave similarly, however the curve stemming from Ref. [20] again deviates from linearity in the depletion region, $0 < h < d$.

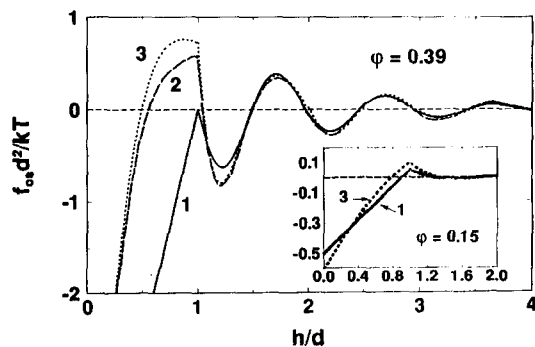


Fig. 2. Comparison of the oscillatory interaction energy calculated from Eq. (12), curve (1), with the results from Ref. [19], curve (2), and from Ref. [20], curve (3). The inset represents the shapes of curves (1) and (3) for lower volume fraction of the particles, $\varphi = 0.15$.

In Figs. 3a–3d the effect of particle volume fraction, φ , on the oscillatory disjoining pressure is examined. The curves calculated from Eq. (8) compare well with the predictions of Henderson theory [20], except in the region around $h = d$, where the Henderson theory predicts about three times larger values of Π_{os} . The situation in the depletion region, $0 < h < d$, where one is to expect the trivial result $\Pi_{os} = -P_0 = \text{const.}$ (not shown in Fig. 3), is the same as discussed above. In Fig. 3c the theoretical curve calculated by Kjellander and Sarman [7] for $\varphi = 0.357$ and $h > 2$ by using the anisotropic Percus–Yevick approximation is also shown; the crosses represent grand canonical Monte Carlo simulation results due to Karlström [24]. (To avoid misunderstandings we note that the slit width used in Ref. [7] corresponds to $h - d$ in our notation.) One sees that the prediction of Eq. (8) is in good agreement with the results of the other authors.

A glance at Figs. 3a–3d shows that the oscillatory character is more pronounced for the higher volume fractions which is correlated with the increase of the decay length, cf. Eq. (6).

3.2. Comparison with experiment

In the experiments with stratifying liquid films [3–5,14,15] the plane-parallel film is encircled by a Plateau border. The capillary pressure, P_c , in the Plateau border can be controlled and measured. Equilibrium films can be formed only when the condition for mechanical equilibrium of the film surfaces [25],

$$\Pi(h) = P_c, \quad (15)$$

is satisfied. If P_c is kept constant during an experiment, the states of *stable* equilibrium (with $d\Pi/dh < 0$) are given by the intersection points of the disjoining pressure isotherm Π versus h with the horizontal line $\Pi = P_c = \text{const.}$, see Fig. 4. Below we compare the number of the metastable states observed experimentally with the number of the intersection points predicted by Eq. (15) in conjunction with Eqs. (1) and (8).

Table 2 contains data for stratifying films from aqueous solutions of an anionic surfactant, sodium dodecyl sulfate (SDS), studied in Refs. [4,12]. The diameter of the micelles is $d_0 = 4.8$ nm and the capillary pressure is $P_c \approx 50$ Pa. As suggested in

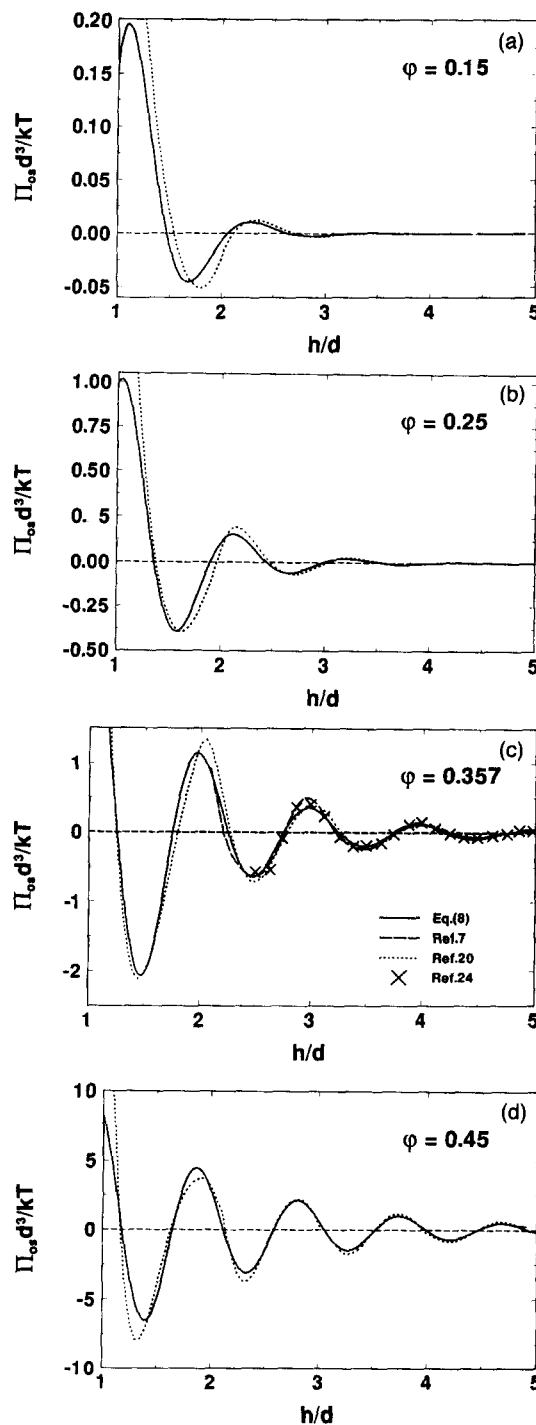


Fig. 3. Comparison of the oscillatory disjoining pressure, Eq. (8), the solid curves, with the results from Henderson theory [20], the dotted curves, for different particle volume fractions, φ . Numerical results from Refs. [7,24] are shown in Fig. 3c with a dashed curve and crosses, respectively.

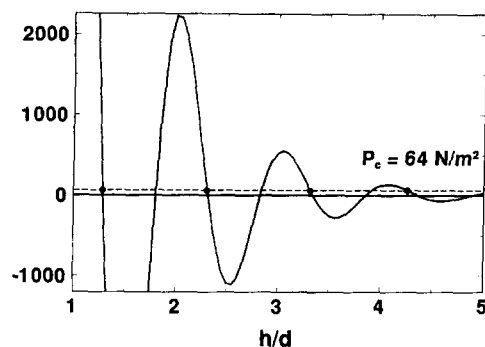


Fig. 4. Plot of the oscillatory disjoining pressure versus film thickness for stratifying foam film from 0.06 M aqueous solution of SDS (see also Table 2).

Ref. [4] we used $d = d_0 + 2/\kappa$ as an effective diameter of the micelles taking into account the thickness of the counterion atmosphere. The first column in Table 2 presents the total surfactant concentration, C ; the second column gives the volume fraction of the micelles calculated by using the effective diameter, d , listed in the third column. The next two columns compare the experimentally measured period characterised by the magnitude of the step-wise changes in the film thickness, Δh (see Table III in Ref. [4]), with the period of oscillations d_1 calculated from Eq. (5). In spite of the fact that d_1 is slightly smaller than Δh , these two quantities exhibit the same tendency of decreasing with the increase of φ . The last two columns in Table 2 compare the observed and predicted numbers of the film metastable states, n_{obs} and n_{pred} , the final stable state being excluded. The agreement between n_{obs} and n_{pred} is satisfactory in view of the fact that the softness of the double layer repulsion between the micelles and the possible role of dynamic factors are not accounted for when calculating n_{pred} . Fig. 4 illustrates the $\Pi(h)$ isotherm calculated with the

Table 2

Test of the predictions of Eq. (8) against data from Refs. [4,12] for stratifying films from aqueous solutions of SDS

C (M)	φ	$d_0 + 2/\kappa$ (nm)	Δh (nm)	d_1 (nm)	n_{obs}	n_{pred}
0.03	0.20	11.2	15.3	12.7	3	2
0.06	0.32	10.4	11.8	10.8	4	4
0.08	0.39	10.1	10.8	9.9	4	6
0.10	0.43	9.7	10.4	9.2	5	8

Table 3

Test of the predictions of Eq. (8) against data from Ref. [5] for stratifying films from aqueous solutions of Enordet AE 1215-30

C (M)	φ	Δh (nm)	d_1 (nm)	n_{obs}	n_{pred}
0.026	0.11	11.2	9.9	1	1
0.052	0.22	10.8	9.0	5	3
0.100	0.41	9.9	7.8	6	8

data for $C = 0.06$ M SDS in Table 2 by using Eq. (8).

Table 3 contains data for stratifying films from aqueous solutions of the nonionic surfactant Enordet AE 1215-30 (Shell Co.) reported in Ref. [5]. We carried out additional light-scattering experiments to determine the aggregation number and to characterise the interaction between the micelles of this surfactant. We conducted both static and dynamic laser light scattering measurements with the apparatus Malvern 4700 C (Malvern Instruments, Ltd.). The *static* light scattering yielded B_2 and then from Eq. (13) we calculated the *thermodynamical* diameter of a micelle, $d = 8.2 \pm 0.4$ nm. The aggregation number was determined to be 42 ± 3 surfactant molecules per micelle. In addition, the *dynamic* light scattering yielded the micellar diffusion coefficient from which we calculated the *hydrodynamical* diameter of a micelle, $d = 8.4 \pm 0.2$ nm. As the two methods give close values for d , one can conclude that these nonionic micelles can be really treated as hard spheres. They would be an ideal system for experimental tests of the theories of hard sphere fluids, if they were perfectly monodisperse; however the dynamic light scattering measurements show a polydispersity of about 15%.

As in the case of anionic micelles the measured Δh and the calculated d_1 decrease with the increase of the micellar concentration, with d_1 being slightly less than Δh . In addition, n_{obs} and n_{pred} are in satisfactory agreement; better agreement should not be expected in view of the polydispersity of the micelles and the dynamic character of the step-wise thinning.

A general conclusion is that the observed step-wise changes in the film thinning are really transitions between metastable states, rather than temporary deceleration in the film thinning due to the decreased driving pressure. In other words, the oscillatory maxima are high enough to intersect the line $\Pi = P_c =$

const (Fig. 4) and to satisfy the mechanical equilibrium condition, Eq. (15). Two alternative mechanisms have been proposed for explanation of the transitions between the consecutive metastable states. The *diffusion* mechanism [26] attributes the appearance and growth of spots of less thickness to the condensation and diffusion of vacancies in the particle structure inside the film. The *convection* mechanism [15] interprets the spots as instabilities engendered by the deep minima of Π_{os} . The former mechanism seems appropriate when the maxima are much higher than P_c , the latter mechanism is applicable when the maxima are not too high, and both mechanisms could be operative in the intermediate region.

4. Concluding remarks

In the present Letter, we propose an analytical semiempirical expression for the dependence of the oscillatory structural force, Π_{os} , on the film thickness, h , and particle volume fraction, φ , see Eq. (8). This expression is tested against the numerical predictions of the theories by Mitchell et al. [19], Henderson [20], Kjellander and Sarman [7] and the Monte Carlo simulations by Karlström [24]. In all cases a good numerical agreement is established except in a vicinity of the point $h = d$, where some of the theories based on integral equations disagree with the law of the depletion attraction.

The predictions of the proposed formula are compared also with the experimental data for stratifying films containing anionic [4,12] and nonionic [5] micelles. We carried out some auxiliary light scattering experiments to determine the aggregation number, the diameter and the polydispersity of the nonionic micelles. A satisfactory agreement between the predicted and observed values is established.

Finally, we point out to two problems for further investigation. The first one concerns the behaviour of Π_{os} around $h = d$ (see above). The second one is related to the possible effect of the bulk Kirkwood–Alder phase transition on the appearance of the oscillatory forces, which is not accounted for in Eq. (9).

We hope the proposed expression for the oscillatory structural force will be useful for interpretation

of experimental data for thin liquid films and stability of dispersions and will be utilised as an ingredient of theoretical models of dynamics of film drainage, kinetics of flocculation in dispersions of nondeformable and deformable colloidal particles, etc.

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