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A Simple Calculation of Structural and Depletion Forces for Fluids/Suspensions Confined in a Film

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By use of the analytic result for the Laplace transform of the radial distribution function for two large hard spheres dispersed in a fluid of the smaller hard spheres, simple equations for the film interaction energy and film disjoining pressure, due to the structural and depletion forces, are derived. The proposed equations satisfy some known exact results and explicitly express the energy and pressure as a function of the film thickness and volume fraction of the small hard spheres. The predicted results for the film energy and film disjoining pressure are compared with existing computer simulation data. The proposed simple analytical expressions can be applied to understand the stability of liquid films containing colloidal particles and the stability of suspensions, foams, and emulsions.

1. Introduction

Numerous products, such as emulsions, foams, gels, polymer latexes, paints, inks, coatings, and so forth, have one important common feature, namely, their ingredients are characterized by the extremely different geometric sizes. These are air bubbles or liquid droplets that are large compared to the dispersed nanosized latex or micellar colloidal particles as well as nanosized colloids themselves that are large compared to the atoms or molecules of the liquid solvents in which they are dispersed. In all these cases, the surfaces of the large particles serve as a slitlike confinement for the subsystem of the small particles. It follows that the problems of the quality of the mentioned and similar products as well as the quality of processes such as coagulation, flocculation, sedimentation, lubrication, and paper making become relevant to the problem of the stability of films containing the small particles.

The stability of fluid films is determined to a large extent by the forces acting between film surfaces. The classical theory due to Derjaguin–Landau–Verwey–Overbeek (DLVO)¹ gives a qualitative interpretation of film stability and has been found to be very useful in guiding scientists, engineers, and practitioners in the development of industrial products and processes employing colloids, biocolloids, polymers, and surfactants. According to the DLVO theory, the interaction between the confining surfaces is the sum of effective electrostatic [when surfaces are charged] and dispersion interactions. However, in recent years, due to the advent of new instrumentation for the measurement of surface forces, new intersurface forces, which are not taken into account by the DLVO theory, have been found. These forces are of entropic origin and usually are referred to as the structural and depletion

forces [sometimes also as hydration or solvation forces]. They are mediated by the medium of the confined fluid and are weakly affected by temperature changes. Their physical origin comes from the difference between the normal stress acting on the inner [film] and outer [bulk] side of giant particles. When the film thickness [separation between the outer surfaces of the macroparticles] is sufficiently large, that is, of the order of tens of diameters of the confined fluid particles, the pressure in the bulk and in the film region is the same and the structural/depletion forces are negligible. But once the film has thinned to less than a few layers of the film particles, the normal component of the pressure in close confinement starts to vary, inducing an oscillatory change of the force acting between the confining surfaces. It follows that the predictions of the continuum DLVO theory break down for the treatment of small separations between large particles, that is, for thin fluid films. Accounting for the discrete nature of the confined fluid becomes essential for the description of the structural/depletion forces. Recent theoretical studies of the colloidal systems by means of computer simulations, integral equation theory, and density functional methods, with the molecular solvent treated explicitly, agree with the experimental observations that the profile of the force between macroparticles is not monotonic when the separation between confining surfaces is sufficiently small.

The oscillatory structural/depletion forces can be described by the evaluation of an extra hard-core-like excluded volume contribution known as the effect of the finite size of confined fluid particles. Some methods for adding a hard-core excluded volume contribution to the DLVO theory have been developed.^{2–7} It was shown that

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the origin of the oscillations in the resulting force acting between the surfaces of the large particles is the well-defined layering or stratification of the small particles near confinement.⁸ However, all of the existing theories of the structural/depletion forces use rather complicated expressions and one of the main advantages of the DLVO theory, that is, its simplicity, is lost. Recently, a few attempts to give simple empirical expressions for the structural/depletion forces contribution to the film disjoining pressure have been made by fitting the theoretical or experimental data.^{8–12}

The main goal of the present work is to obtain an expression for the structural/depletion forces contribution to the film properties that is as convenient for applications as the DLVO result and is based on a statistical mechanics treatment of both species, that is, solutes [macroparticles] and discrete solvent [suspensions or molecular fluids]. From experience, it is clear that this aim can be fulfilled even if the simplest nontrivial model and theory are employed. The starting point for this task is the assumption that the hard-sphere model is suitable for the confinement surfaces and the particles of the confined fluid. This assumption is quite reasonable and based on physical intuition and experience that we have learned from our research efforts in this area as well as from studies carried out by other authors. The simplest analytically solvable theory for a hard-sphere problem is the Percus–Yevick (PY) theory. It has been applied and examined by means of computer simulations for both bulk hard-sphere-like fluid as well as hard-sphere-like fluid under single wall and film confinements. The PY theory has been shown to be reliable in this respect for the majority of applications using hard-sphere modeling.

2. Model and Theory

Although we aim to study the structural/depletion forces that arise in planar [slitlike] film geometry [i.e., we are interested in the evaluation of the interaction free energy per unit area and disjoining pressure between flat surfaces], we start by considering a pair of giant spherical particles of the diameter $2R$, immersed in a discrete fluid formed by the spherical particles with significantly smaller diameter, d ; that is, we assume that $d \ll 2R$. The smaller particles occupied volume fraction $\phi = \pi \rho d^3/6$, where ρ corresponds to their number density, N/V . By use of the Ornstein–Zernike relation for the direct and total correlation functions of such a two-component [giant/small] hard-sphere mixture, the macroparticle radial distribution function, g , can be calculated.^{5,13} Statistical mechanics provides an exact expression¹⁴ which relates g to the potential of mean force between giants; that is, $w/kT = -\ln g$. By limiting ourselves to working within the PY theory for correlation functions, which is inherently a linear response theory, we can further approximate the relation between w and g . In particular, within the framework of PY theory, the excess [without pair interac-

tion] potential of mean force between two giant spheres, mediated by background of the small hard spheres, is given by

$$\beta w(r; R) = -g^{\text{PY}}(r; R) + 1 \quad (1)$$

where $\beta = 1/kT$, k is the Boltzmann constant, T is the temperature, and r is the distance between centers of the large spheres. It has been shown by Attard et al.^{13,15} that for infinitely large spheres [$R \rightarrow \infty$] there is the exact relation,

$$\lim_{R \rightarrow \infty} \frac{-\partial w(H + 2R; R)}{\pi R \partial H} = W(H) \quad (2)$$

where $W(H)$ is the excess interaction energy per unit area between planar surfaces and $H \equiv r - 2R$ is the separation between the surfaces. Equation 2 is of central importance, since it provides a bridge between the theoretical modeling and the property of primary practical interest, that is, the film interaction energy per unit area, W . This is just the Derjaguin approximation,¹⁶ which is routinely used in colloid science and in the surface force apparatus experiments to relate the measured force per radius between bodies with curved surfaces to the interaction free energy per unit area between planes.

Thus, within the PY approximation, the interaction energy per unit area between flat surfaces due to the film formed by fluid of the small hard spheres can be calculated as

$$\beta W^{\text{PY}}(H) = \frac{1}{\pi R} \frac{\partial g^{\text{PY}}(H + 2R; R)}{\partial H} \quad (3)$$

By differentiation of the energy with respect to film thickness, we obtain the pressure exerted by the hard-sphere fluid film on the confining plates,

$$\beta \Pi^{\text{PY}}(H) = -\frac{1}{kT} \frac{\partial W^{\text{PY}}(H)}{\partial H} = -\frac{1}{\pi R} \frac{\partial^2 g^{\text{PY}}(H + 2R; R)}{\partial H^2} \quad (4)$$

The pressure $\Pi(H)$ usually is referred to as the disjoining pressure of a film.

Equations 1–4 represent the rather commonly used approach to describe the fluid films by means of statistical mechanics. The key element of such a scheme is a macroparticle radial distribution function, $g^{\text{PY}}(r; R)$. Usually, an analytic PY result for the Laplace transform, $\mathcal{G}(t) = \mathcal{L}[g^{\text{PY}}(r; R)]$, rather than the radial distribution function, $g^{\text{PY}}(r; R)$ itself, is obtained:⁵

$$\mathcal{G}(s) = 3\phi \frac{[(s^2 - 2s + 2)e^s - 2] R}{S(s)e^s + L(s)} \frac{R}{d} \quad (5)$$

with ϕ being the volume fraction occupied by small particles and s being the dimensionless Laplace transform variable, that is, $s = td$.

Because differentiation in real space corresponds, apart from the initial value of the function, to multiplication by variable t in Laplace space, it is more convenient to obtain the Laplace transform of the energy, $\beta \mathcal{W}(t) = t \mathcal{G}(t)/\pi R$, and then invert this result rather than to invert first the Laplace transform, that is, to calculate $g^{\text{PY}}(r; R) = \mathcal{L}^{-1}[\mathcal{G}(t)]$ followed by differentiation (eq 3) to obtain the energy

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$W^{\text{PY}}(H)$. Thus, the Laplace transform of the film interaction free energy has the form

$$\beta \mathcal{W}(s) = \frac{3}{\pi} \frac{\phi}{d^2} \frac{s[(s^2 - 2s + 2)e^s - 2]}{S(s)e^s + L(s)} \quad (6)$$

where

$$\begin{aligned} S(s) &= (1 - \phi)s^3 + 6\phi(1 - \phi)s^2 + 18\phi^2s - 12\phi(1 + 2\phi) \\ L(s) &= 12\phi \left[\left(1 + \frac{1}{2}\phi\right)s + 1 + 2\phi \right] \end{aligned} \quad (7)$$

Using the definition of the inverse Laplace transform and taking into account eq 6, for the structural/depletion forces contribution to film interaction energy per unit area between planes in the PY approximation, we can write

$$\begin{aligned} \beta W^{\text{PY}}(H) &= \\ (2\pi i)^{-1} \int_{\delta - i\infty}^{\delta + i\infty} \frac{3}{\pi} \frac{\phi}{d^2} \frac{[(s^2 - 2s + 2)e^s - 2] \exp(sH/d)}{S(s)e^s + L(s)} s \, ds \end{aligned} \quad (8)$$

By repeating a similar manipulation for the differentiation of the film interaction energy, $\partial W^{\text{PY}}/\partial H$ [or equivalently for the second derivative of the radial distribution function, $\partial^2 g^{\text{PY}}/\partial H^2$], for the film disjoining pressure of a hard-sphere fluid film in the PY approximation, we have

$$\begin{aligned} \beta \Pi^{\text{PY}}(H) &= \\ -(2\pi i)^{-1} \int_{\delta - i\infty}^{\delta + i\infty} \frac{3}{\pi} \frac{\phi}{d^2} \frac{[(s^2 - 2s + 2)e^s - 2] \exp(sH/d)}{S(s)e^s + L(s)} s^2 \, ds \end{aligned} \quad (9)$$

To evaluate the above integrals, Henderson⁵ has used a zonal expansion technique providing a closed piece-wise form for $W^{\text{PY}}(H)$ and $\Pi^{\text{PY}}(H)$, for given H . The numerical calculations have shown the qualitative success of eqs 8 and 9 for both applications, that is, to reproduce the computer simulation data for the hard-sphere fluid in a hard-wall slit^{17,18} and to describe the measurement of the solvation force in molecular solvents.⁴⁻⁸ In particular, it has been found that $W^{\text{PY}}(H)$ and $\Pi^{\text{PY}}(H)$ correctly reproduce the periodicity, phase, and decay of the energy and pressure profiles for the range of solvent volume fractions of common practical interest and in a wide range of separations, except for a small film thickness that slightly exceeds one solvent layer. In particular, this failure of the PY theory is concerned with the smaller magnitudes of energy and pressure stabilizing barriers, that is, $W^{\text{PY}}(H)$ and $\Pi^{\text{PY}}(H)$ near the film thickness $H \approx d$. The underestimation of a small-separation [contact] magnitude for distance-dependent functions is a general feature of the PY theory for hard-sphere-type models. However, despite the discrepancy at small thicknesses, the main disadvantage of the expressions in (8) and (9) is that the inversion algebra⁵ is not simple and can become rather cumbersome with an increase of the separation H .

Recently,⁶ we have turned our attention to an alternative way to invert the Laplace transform into a real space. This is to use the integrals given by eqs 8 and 9 in the form

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$$\beta W^{\text{PY}}(H) = \frac{1}{\pi} \sum_{n=1} \gamma_n \exp\left(s_n \frac{H}{d}\right) \quad (10)$$

$$\beta \Pi^{\text{PY}}(H) = \frac{1}{\pi} \sum_{n=1} \tau_n \exp\left(s_n \frac{H}{d}\right) \quad (11)$$

where γ_n and τ_n are the residues of the right sides of eqs 8 and 9 at the pole s_n . Usually this procedure is not very popular since the integrands in eqs 8 and 9 have an infinite number of poles that are the roots of the transcendental equation

$$S(s)e^s + L(s) = 0 \quad (12)$$

However, the advantage of expressions such as (10) and (11) is that these equations permit one to obtain the asymptotic form at $H \rightarrow \infty$ and the decay of the functions $W^{\text{PY}}(H)$ and $\Pi^{\text{PY}}(H)$ in real space; these are determined only by the pair of complex conjugate nontrivial roots of eq 12, which are closest to the real axis. Thus, assuming that these poles are

$$s = [-\kappa \pm i\omega]d \quad (13)$$

the large thickness asymptotic and decay of the film interaction energy and film disjoining pressure, due to the structural/depletion forces, are given by

$$W^{\text{PY}}(H \rightarrow \infty) = W_0 \cos(\omega H + \varphi_1) e^{-\kappa H} \quad (14)$$

$$\Pi^{\text{PY}}(H \rightarrow \infty) = \Pi_0 \cos(\omega H + \varphi_2) e^{-\kappa H} \quad (15)$$

For the energy, the amplitude coefficient $W_0 = 2kT|\gamma|/\pi$ and the phase of oscillations $\varphi_1 = \arg\{\gamma\}$, where γ is the residue given by

$$\gamma = \frac{3}{\pi} \frac{\phi}{d^2} \frac{s[(s^2 - 2s + 2)e^s - 2]}{[(S'(s) + S(s))e^s + L'(s)]} \Big|_{s=-\kappa d + i\omega d} \quad (16)$$

and the prime in the denominator denotes differentiation. The similar coefficients, that is, Π_0 and φ_2 , for the disjoining pressure have the same meaning as W_0 and φ_1 , but with respect to the residue τ ,

$$\tau = -\frac{3}{\pi} \frac{\phi}{d^3} \frac{s^2[(s^2 - 2s + 2)e^s - 2]}{[(S'(s) + S(s))e^s + L'(s)]} \Big|_{s=-\kappa d + i\omega d} \quad (17)$$

The key quantities, which are decay parameters, κ and ω , determined by the poles in (13), can be evaluated numerically only. Fortunately, the denominator of the integrands in (8) and (9) is exactly the same as for the one-component hard-sphere model in the PY approximation, and the roots of eq 12 have been discussed already by Perry and Throop,¹⁹ nearly three decades ago, in their study of the decay of pair correlations in hard-sphere fluids. As for the explicit expressions for the rest of coefficients W_0 , Π_0 , φ_1 , and φ_2 , they are readily derived and need not be reproduced here. A set of numerical values for these coefficients supplemented by decay parameters, κ and ω [all being evaluated according to their definition given by eqs 13–17], are listed in Table 1 for several volume fractions.

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Table 1. Density [Volume Fraction] Dependence of the Parameters κ , ω , W_0 , Π_0 , φ_1 , and φ_2 for the Calculation of the Structural/Depletion Forces Contribution to the Energy and Disjoining Pressure between Two Macrosurfaces in a Hard-Sphere-Like Solvent

ρd^3	ϕ	κd	ωd	$\beta W_0 d^2$	$\beta \Pi_0 d^3$	φ_1	φ_2
0.2	0.1047	3.0934	5.1156	0.7531	4.5022	0.6141	-0.4128
0.3	0.1571	2.4865	5.3982	0.9317	5.5373	0.7366	-0.4025
0.4	0.2094	2.0338	5.6507	1.1419	6.8578	0.8470	-0.3783
0.5	0.2618	1.6674	5.8887	1.3910	8.5131	0.9529	-0.3420
0.6	0.3142	1.3576	6.1204	1.6868	10.5751	1.0588	-0.2937
0.7	0.3665	1.0894	6.3506	2.0385	13.1349	1.1681	-0.2328
0.8	0.4189	0.8549	6.5827	2.4555	16.2994	1.2838	-0.1579

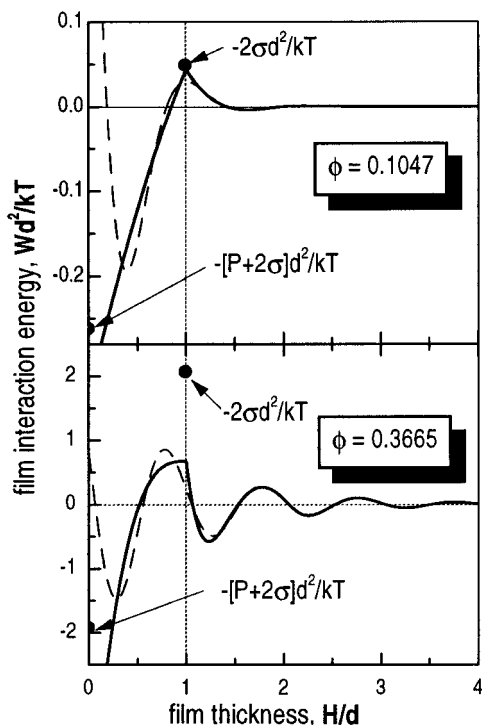


Figure 1. Film interaction energy per unit area between two macrosurfaces due to the structural/depletion forces that arise in a confined fluid of the small hard-sphere particles. The solid curve corresponds to the numerical results obtained from eq 8, while the dashed line is calculated from the asymptotic expression given by eq 14. The symbols correspond to the “exact” results with σ and P calculated from eq 29. The volume fraction of small hard-sphere particles is written on the figure.

3. Results and Discussion

To be precise, the idea to obtain simple explicit equations for the structural/depletion forces contribution to the film interaction energy and film disjoining pressure occurred after a comparison of the results for $W^{PY}(H)$ and $\Pi^{PY}(H)$, obtained from the exact numerical evaluation of the integrals in eqs 8 and 9, and those calculated according to the asymptotic forms in eqs 14 and 15, respectively. It was expected that the asymptotic expressions should reproduce complete results only for thick films but would fail at intermediate and small thicknesses. Some typical comparisons at two volume fractions of the small particles, $\phi = 0.1047$ and 0.3665 , are shown in Figures 1 and 2. Surprisingly, we found that for the film interaction energy as well as for the film disjoining pressure, the results from asymptotic expressions reproduce the complete PY results for the majority of the separations. Discrepancies arise only when the thickness gap is about one layer of the small particle or less. When the computed curves are compared with known statistical mechanics results¹³ and limiting law¹⁷ [see filled circles on Figures 1 and 2], we

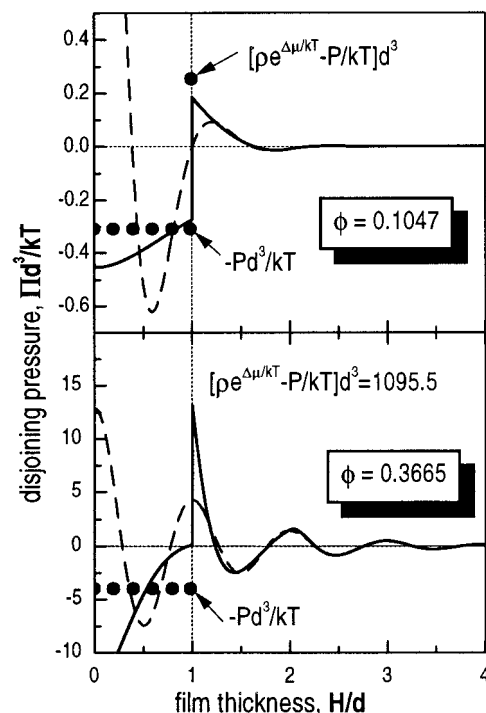


Figure 2. Film disjoining pressure between two macrosurfaces due to the structural/depletion forces that arise in a confined fluid of the small hard-sphere particles. The solid curve corresponds to the numerical results obtained from eq 9, while the dashed line is calculated from the asymptotic expression given by eq 15. The symbols correspond to the “exact” results with $\Delta\mu/kT$ and P calculated from eq 29. The volume fraction of small hard-sphere particles is written on the figure.

conclude that the PY prediction itself should be corrected in this region. Similar conclusions are valid for the whole region of the volume fractions of the small particles. Summarizing this important finding, what we need are simple correction terms to the expressions in (14) and (15) for the film surface separations, H , that include $0 < H < d$ and $d \leq H < 2d$.

The first portion of these separations, $0 < H < d$, corresponds to the film thickness free of fluid particles. This special region of film surface separations attracts attention of the theoreticians starting from the work of Asakura and Oosawa²⁰ and has been studied by many authors, and various approximations have been introduced.^{13,21,22} In particular, for the film interaction energy for these separations, Attard et al.¹³ used the equation

$$W(H) = -P[d - H] - 2\sigma \quad 0 < H < d \quad (18)$$

which leads to the constant film disjoining pressure in this region, that is,

$$\Pi(H) = -P \quad 0 < H < d \quad (19)$$

Equations 18 and 19 reflect the exact functional form for the wall–wall interaction in the slitlike geometry and also are given by Henderson²¹ and Gotzelmann et al.²² In the above expressions, P is the bulk [osmotic] pressure of the fluid of small hard-sphere particles, and σ is the wall–fluid interfacial tension of a single surface.

To correct the PY results for the film energy and film pressure at the separations $d \leq H < 2d$, extra terms,

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$\Delta W(H)$ and $\Delta \Pi(H)$, must be introduced. These correction terms should be of the same functional form as the main contributions (14) and (15), as follows from eqs 10 and 11. We chose them as follows:

$$\Delta W(H) = W_1 e^{-\delta_1(H-d)} \quad (20)$$

and

$$\Delta \Pi(H) = \Pi_1 e^{-\delta_2(H-d)} \quad (21)$$

The correction amplitude coefficients, W_1 and Π_1 , are chosen so that at thickness $H = d$, the film energy and film pressure have magnitudes

$$W(H=d) = -2\sigma \quad (22)$$

$$\Pi(H=d) = \rho kTZ - P \quad (23)$$

predicted by exact results^{13,22} and limiting law,¹⁷ respectively, with $Z = \exp(\beta\Delta\mu)$. These lead to

$$W_1 = -2\sigma - W_0 c_1 \quad (24)$$

$$\Pi_1 = \rho kTZ - P - \Pi_0 c_2 \quad (25)$$

where notations $c_1 = e^{-\kappa d} \cos(\omega d + \varphi_1)$ and $c_2 = e^{-\kappa d} \cos(\omega d + \varphi_2)$ are used. The set of short-range decay parameters, δ_1 and δ_2 , are designed to force $W(H)$ and $\Pi(H)$ to be self-consistent through the relation in (4), particularly at the film thickness $H = d$. Using these conditions in the form

$$-\frac{\partial W(H)}{\partial H} \Big|_{H=d} = \rho kTZ - P \quad (26)$$

$$\int_d^\infty \Pi(H) dH = -2\sigma \quad (27)$$

leads to

$$\delta_1 = \delta_2 \equiv \delta = \frac{\Pi_1}{W_1} \quad (28)$$

The usefulness of the expressions in eqs 20–28 lies in the fact that for hard-sphere fluid accurate simple formulas for the bulk [osmotic] pressure, P , the surface–fluid interfacial tension, σ , and the excess chemical potential, $\Delta\mu$, are known. In the following, we use the Carnahan–Starling²³ relation for the pressure and chemical potential and the scaled particle theory²⁴ result for the surface tension,

$$P = \rho kT \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3} \quad \beta\Delta\mu = \phi \frac{8 - 9\phi + 3\phi^2}{(1 - \phi)^3} \quad \sigma = -\frac{9}{2\pi} kT \frac{\phi^2}{d^2} \frac{1 + \phi}{(1 - \phi)^3} \quad (29)$$

Combining the results of eqs 18–21 with the basic expressions in eqs 14 and 15, the equations for the film interaction energy per unit area and film disjoining pressure for all film separations can be written in the form

$$W(H) = -P[d - H] - 2\sigma \quad 0 < H < d \\ = W_0 \cos(\omega H + \varphi_1) e^{-\kappa H} + W_1 e^{-\delta(H-d)} \quad H \geq d \quad (30)$$

and

$$\Pi(H) = -P \quad 0 < H < d \\ = \Pi_0 \cos(\omega H + \varphi_2) e^{-\kappa H} + \Pi_1 e^{-\delta(H-d)} \quad H \geq d \quad (31)$$

It follows that with respect to the distances between film surfaces, the film energy and film disjoining pressure exhibit two rather distinct forms of behavior: (i) monotonic changes for particle-free films, that is, $0 < H < d$, and (ii) oscillatory changes for film surface separations which permit particles to enter and fill the space between them, that is, for $H > d$. The physical reason for these different behaviors can be explained as follows. If particles are excluded from the space between surfaces, then only attractive depletion forces are acting between the film surfaces. Otherwise, if the space between surfaces is filled by one, two, and more layers of fluid particles, then both structural and depletion forces are present and the total force acting between film surfaces is the superposition of the attractive and repulsive interactions that give rise to the oscillatory changes in the film energy and film disjoining pressure profiles.

By analysis of the measured data for two macrosurfaces immersed into a molecular solvent, it has been already observed that the film disjoining pressure is a decaying oscillatory function and that the period of the oscillations is determined solely by the properties of the confined fluid. For the sake of making an estimate, Israelachvili⁸ intuitively suggested the approximate expression for the measured film disjoining pressure,

$$\Pi^{\text{EXP}}(H) \approx -kT\rho_s(\infty) \cos\left(\frac{2\pi}{D}H\right) e^{-H/D} \quad (32)$$

which is quite similar to the first term in the right-hand side of eq 31. The periodicity of the oscillations and decay length in eq 32 are set equal to the unique parameter, D , which usually is identified with the geometrical size of the film fluid particles and is called the “effective” diameter, and $\rho_s(\infty)$ is the film particle concentration in the subsurface layer for the thick film, that is, at $H \rightarrow \infty$. With respect to this, we note that according to eqs 30 and 31, both the film disjoining pressure and the film interaction energy, when the film thickness exceeds one particle layer, exhibit an exponentially decaying cosine-function dependence on the separation, with the same periodicity of the oscillations, $2\pi/\omega$, and the same decay length, $1/\kappa$, but with different phase and amplitude coefficients. Both κ and ω are explicitly determined by the pole in (13) and, indeed, depend exclusively on the fluid bulk properties, that is, its bulk volume fraction, ϕ , and particle hard-core diameter, d . These two key parameters, κ and ω , are shown in Figure 3 as functions of the volume fraction, ϕ . Figure 3 also shows the results of polynomial parametrization for the volume fraction dependence of the dimensionless inverse decay length, κd , and dimensionless frequency of oscillation, ωd , in the form

$$\kappa d = 4.78366 - 19.64378\phi + 37.37944\phi^2 - 30.59647\phi^3 \quad (33)$$

$$\omega d = 4.45160 + 7.10586\phi - 8.30671\phi^2 + 8.29751\phi^3 \quad (34)$$

(23) Carnahan N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.

(24) Reiss, H.; Frisch, H. L.; Helfand, E.; Lebowitz, J. L. *J. Chem. Phys.* **1960**, *32*, 119.

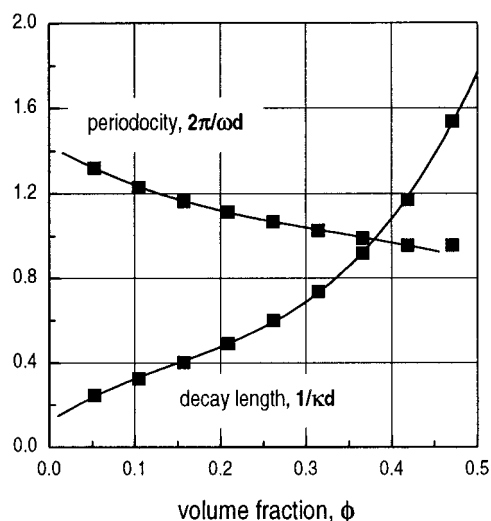


Figure 3. Dimensionless decay length, $1/\kappa d$, and dimensionless periodicity of oscillations, $2\pi/\omega d$, of the structural/depletion forces that arise between two macrosurfaces immersed in a fluid of the small hard-sphere particles as a function of the volume fraction of the small particles.

Table 2. Coefficients of the Polynomial Fit of the Form $a_0 + a_1\phi + a_2\phi^2 + a_3\phi^3$ for the Parameters κ , ω , W_0 , Π_0 , φ_1 , and φ_2 for the Calculation of the Structural/Depletion Forces Contribution to the Energy and Disjoining Pressure between Two Plane Macrosurfaces in a Hard-Sphere-Like Solvent

parameter	a_0	a_1	a_2	a_3
κd	4.78366	-19.64378	37.37944	-30.59647
ωd	4.45160	7.10586	-8.30671	8.29751
$\beta W_0 d^2$	0.57909	0.83439	8.65315	
$\beta \Pi_0 d^3$	4.06281	-3.10572	76.67381	
φ_1	0.40095	2.10336		
φ_2	-0.39687	-0.3948	2.3027	

and a comparison with the numerical solution of eq 12. The polynomial parametrization, similar to that for κ and ω , has been made for the rest of the parameters listed in Table 1. The coefficients of the corresponding polynomials are collected in Table 2. The results for the energy and pressure, presented and discussed below, have been evaluated by using for κ , ω , W_0 , Π_0 , φ_1 , and φ_2 the values calculated from eqs 31 and 32 and Table 2.

From Figure 3, we can see that the dimensionless decay length of the structural/depletion forces, $1/\kappa d$, increases with rising of the particle volume fraction, while the dimensionless periodicity of the oscillations, $2\pi/\omega d$, has the opposite trend. This means that when the small particles become more packed, the structural/depletion forces become more long-ranged and show increased frequency of their oscillations. There is a unique value of the bulk fluid volume fraction where the decay length is equal to the periodicity of oscillations. It is quite interesting

that at this crossline both quantities are equal to unity [$1/\kappa d = 2\pi/\omega d = 1$], that is, periodicity and decay length are set to be equal to the particle hard-core diameter, $1/\kappa = 2\pi/\omega = d$. This is the case of the approximate expression in (32). This particular volume fraction value is near $\phi \approx 0.35$ – 0.4 , which is a typical volume fraction for the commonly used molecular solvents [e.g., volume fraction of water with diameter $d = 0.28$ nm corresponds to $\phi = 0.38$]. This also is in agreement with the experimental observations of the oscillatory structural/depletion [Israelachvili⁸ calls this the solvation or hydration] force and explains the success of an empirical expression of the form of eq 32. This is illustrated by the data collected in Table 3, where the values of the decay length, $1/\kappa$, and the periodicity of oscillation, $2\pi/\omega$, for some commonly used molecular solvents, predicted by eqs 33 and 34, respectively, are presented. Each solvent is characterized by the hard-core diameter d and volume fraction ϕ , that correspond to the experimental values. The differences between the predicted decay length and periodicity of oscillation of the structural/depletion forces in different solvents are caused by differences in their number densities, ρ , and estimates for their hard-core diameters, d . We see that the observations for the periodicity of oscillations correlate and agree well with present predictions.

Approximate forms for the film disjoining pressure that are similar to eq 32 have been introduced and used by other authors also.^{9–12} We would like to draw attention to the fact that according to Figure 3, such expressions will fail for lower and higher [than $\phi \approx 0.35$ – 0.4] bulk fluid volume fractions, where the decay length and periodicity of the oscillations will differ from the particle hard-core diameter d . These are illustrated in Figure 4, where the film energy is plotted for three different volume fractions, $\phi = 0.25$, 0.35 , and 0.45 . Indeed, we see that for smaller volume fractions decay of oscillations is faster while periodicity of oscillations is slightly larger than particle diameter d ; upon increasing the volume fraction, the structural/depletion forces extend to larger separations while periodicity of their oscillations shrinks.

Variations of the volume fractions, similar to that used in Figure 4, can be observed in the case of molecular solvents under some extreme conditions [high/low pressure, temperature] or in the case of colloidal suspensions where volume fraction of colloidal particles is the initial parameter. Moreover, even in the case of molecular solvents under normal conditions, expressions similar to eq 32 can be applicable for the thick films only, since the strength, decay length, and periodicity of oscillations of the structural/depletion forces also depend on the film thickness. Namely, as we can observe from the computer simulation data for the film disjoining pressure,¹⁷ at small thicknesses [from one to two particle layers] the structural forces become significantly stronger, their decay is faster, and they oscillate more frequently, that is, their periodicity

Table 3. Predicted Values of Decay Length, $1/\kappa$, and Periodicity of Oscillations, $2\pi/\omega$, for the Energy per Unit Area and Disjoining Pressure Acting between Two Parallel Plates Immersed in Some Commonly Used Molecular Solvents

solvent		density ρ [gm/cm ³]	diameter estimates ^a [nm]	volume fraction ϕ	decay $1/\kappa$ [nm]	periodicity $2\pi/\omega$ [nm]	expt periodicity ^b [nm]
benzene	C ₆ H ₆	0.879	0.51	0.4702	0.81	0.47	0.52 ± 0.02
cyclohexane	C ₆ H ₁₂	0.779	0.55	0.4854	0.99	0.55	0.56 ± 0.02
tetrachloromethane	CCl ₄	1.590	0.52	0.4581	0.76	0.48	0.55 ± 0.02
OMCTS	[(CH ₃) ₂ SiO] ₄	0.956	0.79	0.5009	1.65	0.71	0.89 ± 0.03
isooctane	C ₈ H ₁₈	0.692	0.65	0.5163	1.65	0.58	0.5–0.8
water	H ₂ O	1.000	0.28	0.3793	0.27	0.27	0.26
methanol	CH ₃ OH	0.792	0.38	0.4365	0.48	0.36	

^a Reference 26. ^b References 25 and 27.

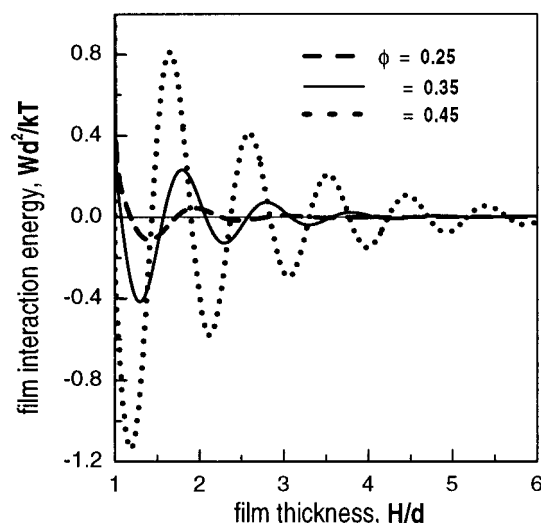


Figure 4. Film interaction energy per unit area between macrosurfaces immersed in a fluid of the small hard-sphere particles at three different volume fractions, $\phi = 0.25$ [dashed line], 0.35 [solid line], and 0.45 [dotted line].

decreases compared to the thick [three and more particle layers] films. In the present work, these thin film features of the structural/depletion forces are accounted for in an effective way through the second [correction] terms on the right-hand sides of eqs 30 and 31.

Shrinking of the periodicity of oscillations of the structural forces at film thickness between one and two particle layers is consistent with our earlier experimental findings²⁸ regarding the self-organization of colloidal particles in the monolayers parallel to the film surfaces. In particular, from the geometric arguments it is easy to show that smaller than particle diameter, d , distance between two neighboring repulsive maxima in the film energy profile at film thicknesses $d \leq H < 2d$, which we can see from Figure 4 at higher volume fractions, can be explained by two-dimensional hexagonal in-layer ordering of the monodisperse particles in both surface layers. Such predominantly two-dimensional hexagonal in-layer packing structure has been observed in diffraction patterns obtained from a vertical macroscopic latex film formed from a 44 vol % aqueous latex suspension. This hexagonal structure has been found to appear only at film thicknesses corresponding to two and one particle layers.²⁹ No such in-layer hexagonal structuring was observed for films corresponding to three particle layers thick.

Figure 5 shows the comparison of the film disjoining pressure predicted by eq 31 with those simulated by Wertheim et al.¹⁷ between two parallel hard plates immersed in a fluid of hard spheres with diameter d and at two volume fractions, $\phi = 0.1503$ and 0.3142 . As we can see, the agreement between both sets of results is almost perfect, including the highest bulk fluid volume fraction and for all separations.

Recently, Kralchovsky and Denkov (KD)⁹ using an equation of the form in (32) have proposed a semiempirical expression for film disjoining pressure. These results also are shown in Figure 5. The amplitude and decay param-

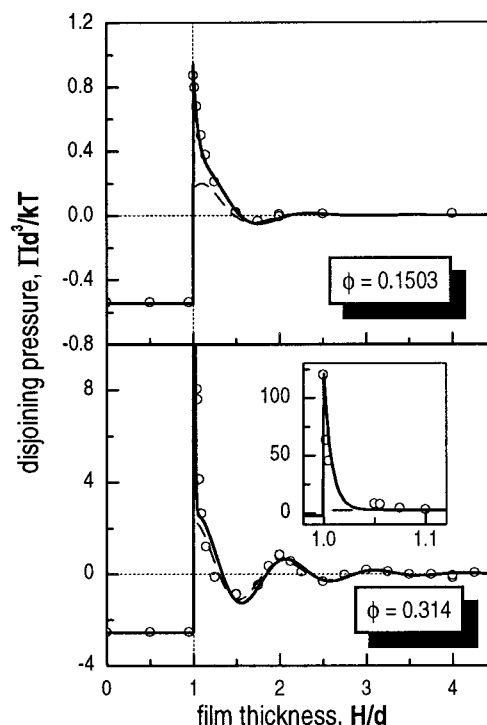


Figure 5. Film disjoining pressure between macrosurfaces immersed in a fluid of the small hard-sphere particles. The solid curves result from eq 31, while the dashed curves have been calculated according to ref 9. The symbols give the Monte Carlo simulation data.¹⁷

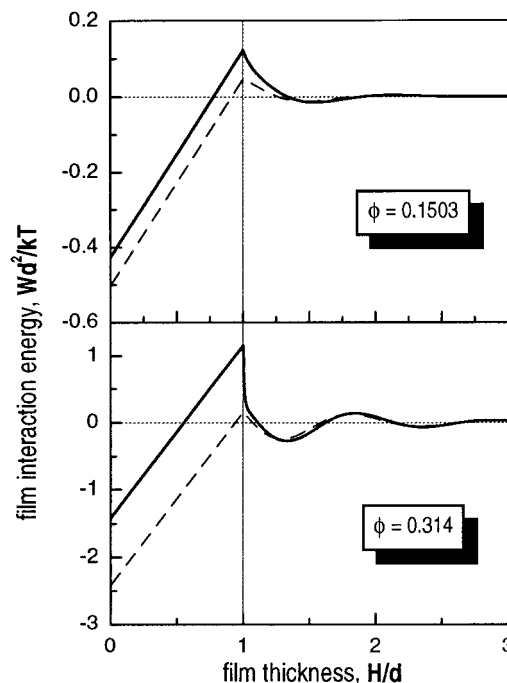


Figure 6. Film interaction energy per unit area between macrosurfaces immersed in a fluid of the small hard-sphere particles. The solid curve results from eq 30, while the dashed curves have been calculated according to ref 9.

eters have been determined by these authors from the fit of numerical PY results and qualitatively are correct. However, for both considered bulk volume fractions the KD predictions are too low at the film thicknesses of the order of one particle layer, that is, $d \leq H < 1.5d$, which are important from the view of the film stability. These discrepancies in the film disjoining pressure produce more drastic inaccuracies for the film interaction energy that

(25) Israelachvili, J. N.; Pashley, R. M. *Nature* **1983**, *306*, 243.

(26) Size estimates have been obtained from diffusion data presented in ref 27.

(27) Christenson, H. K. *J. Chem. Phys.* **1983**, *78*, 6906.

(28) Nikolov, A. D.; Wasan, D. T. *Langmuir* **1992**, *8*, 2985.

(29) Wasan, D. T.; Nikolov, A. D. In *Supramolecular Structure in Confined Geometries*; Manne, S., Warr, G., Eds; ACS Symposium Series No. 736; American Chemical Society: Washington, DC, **1999**; pp 40–53.

usually is obtained by integration of the pressure curve. The results predicted by eqs 30 and 31 avoid this problem since they have been developed in a way that satisfies the self-consistency relations between energy and pressure for all separations and, particularly, at the film thickness $H = d$ [see eqs 26 and 27]. Thus, even in the absence of computer simulation data for the interaction energy per unit area between two hard plates, we can suggest that the results of eq 30 are of high accuracy because they are consistent with the pressure from eq 31 which reproduces the computer experiments of Wertheim et al.¹⁷ The film interaction energy per unit area calculated from eq 30 for the same conditions as the film disjoining pressure [Figure 5] is shown in Figure 6 in comparison with KD results. The underestimation of the pressure at a film thickness of about one solvent particle layer in the expressions like eq 32 results in an overestimation of the attractive interactions for a film thickness near one particle layer. This always will predict a lower film stability of the slitlike films formed by hard-sphere-like fluids.

4. Conclusions

Summarizing, we have presented simple equations to calculate the structural and depletion forces contribution to the interaction free energy (eq 30) and disjoining pressure (eq 31) between plane surfaces immersed in a hard-sphere-like fluid. Depending on the reader's practical interests, these equations can be successfully applied to investigate the problems of the stability of the bulk [colloids dispersed in molecular solvents] or confined [foam lamella or films] suspensions. These equations have been derived from the asymptotic solution of the Ornstein–Zernike equation for a binary mixture of large and small hard spheres and, to the best of our knowledge, are the first expressions of such a simple form that are mathematically and physically well-grounded. These proposed equations are developed to satisfy known exact statistical mechanics results and limiting laws, and their predictions are tested by comparison with computer simulation data.

In the case of thick films, our equations are quite similar to the semiempirical expressions that have been already published in the literature and very often are used to analyze experimental data. In contrast to the semiempirical expressions, where the basic parameters of the film energy and film disjoining pressure profiles, that is, decay length and periodicity of oscillations, are used as adjustable parameters, we have determined them as the pole of the Laplace transforms of the pair correlation function between film surfaces. We found that indeed they are the unique functions of the particle bulk volume fraction and particle hard-core diameter. The analytical

expressions of the simple polynomial form to evaluate decay length and periodicity of oscillations and other necessary quantities to calculate film energy and film disjoining pressure are given.

We found that for any film thickness exceeding one film particle layer, structural/depletion forces contribute to the film energy and film disjoining pressure in the same thickness-dependent functional form, that is, they are decaying oscillatory functions with parameters [decay length and periodicity] completely determined by the bulk properties [particle volume fraction and particle hard-core diameter] of the confined fluid. However, there are two sets of such parameters, corresponding to thick [more than two particle layers] and thin [from one to two particle layers] films. The nature of the difference between thick and thin films lies in the different influence of the film confinement on the in-layer structuring for particles belonging to the first [surface] layer and to the next [second, third, etc.] layers. This results in two types of contributions of the structural/depletion forces produced by the film particles. These two types of contributions are characterized by different decay lengths [κ and δ in our notations] and have to be treated separately. This was the main weak point of semiempirical attempts to apply expressions like eq 32 to analyze structural forces which suggest unique decay lengths for thick and thin films. Since thick films cover the main part of the measured thickness range, the decay length practically always has been adjusted to fit the thick film data.

We hope that experimentalists will find our equations in (30) and (31) suitable and useful. To help this, we provide a brief guide for their use:

(1) For a fixed bulk solvent volume fraction, ϕ , calculate bulk properties, that is, osmotic pressure, P , chemical potential, $\Delta\mu$, and interfacial tension, σ , by using eq 29.

(2) Calculate the parameters κ and ω by using eqs 33 and 34 and calculate the parameters W_0 , Π_0 , φ_1 , and φ_2 by using coefficients collected in Table 2.

(3) Calculate the correction amplitude coefficients, W_1 and Π_1 , from eqs 24 and 25 and the thin film inverse decay length, δ , from eq 28.

(4) Calculate interaction energy and disjoining pressure, $W(H)$ and $\Pi(H)$, from eqs 30 and 31.

An advantage of the proposed equations is that the computer programming is rather simple. The FORTRAN program also is available from the authors upon request.

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