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Long-range surface forces and their role in the progress of nanotechnology

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Abstract. Different theories of stability of liquid nanolayers, disperse and colloidal systems are considered. Limitations intrinsic in the classical Derjaguin – Landau – Verwey – Overbeek (DLVO) theory (in particular, calculations of the van der Waals forces acting between macroscopic bodies separated by a thin liquid interlayer) are briefly outlined. Studies devoted to the analysis and calculations of non-DLVO interactions of different nature are reviewed. Particular attention is paid to the forces caused by the inhomogeneity of liquid interlayers. The applicability of the known approaches for solving the nanotechnology challenges (namely, calculations of interaction forces acting through nanolayers and between nanoparticles) is discussed. The bibliography includes 174 references.

I. Introduction

Nanoscience and nanotechnology are two relatively young fields of science and technology. They are based on a theoretical assumption that reduction of the particle size to nanoscale leads to significant changes in the known properties of the corresponding materials and to the appearance of new properties that are not inherent in the bulk state. Later, this assumption was confirmed experimentally. Progress in these new fields of natural science concerns almost all avenues of human activity from biology and medicine to production of polymeric materials, metallurgy, microelectronics, space research, *etc.* Although formally nanoscience and nanotechnology emerged only 20 – 25 years ago, studies concerned with the dependence of the properties of nanosystems on their size date back to the 1940s. For instance, at that time Derjaguin repeatedly pointed to the dependence of the structure of water in thin liquid interlayers on the interlayer thickness. Manufacture of ultradisperse powders, a new production area established in the USSR in the 1950s, was based on the observed dependence of the properties of nanoparticles on the particle size.

A specific feature of small objects is that the smaller the particles the greater the percentage of the molecules (atoms) in the near-interface layer that strongly interact with the phases that bound the object under study. Therefore, reduction of the size of such an object leads to an increase in the surface-to-volume ratio and to a more pronounced effect of the surface phenomena on the properties of the object. Yet another feature of such systems is a stronger effect of the size of small particles on the character of collective phenomena and on the density of states of elementary excitations in the systems.

These features point to the key role of two-phase and three-phase surface phenomena in nanotechnological processes. A considerable proportion of physicochemical studies on these phenomena are carried out using the methods of physics of fluids and colloid chemistry. This is due to the fact that fluids are active participants of liquid-phase chemical synthesis of nanoparticles. The properties of fluids affect the size and stability of particles produced, the course of chemical reactions on the surface of such particles and the strength and character of adsorption at interfaces. In addition, solid nanoparticles prepared using all the known methods [1] were designed for operation under atmospheric conditions or in industry rather than laboratories with controllable gaseous medium. When nanomaterials are exposed to atmosphere, the small size of the objects made of them becomes of crucial importance, because it causes the formation of either capillary condensate in nanoporous media or wetting films on the surfaces of certain particles. As a result, a nanomaterial with well-studied (under laboratory conditions) properties is replaced by a composite nanosystem comprising the solid nanomaterial and a liquid interlayer or capillary bridges. The properties of the system as a whole are determined by the properties of not only the solid phase, but also the liquid interlayer, the character of the interaction between the liquid and the solid nanoparticles and, finally, the character of the interaction between nanoparticles separated by the liquid interlayer. The presence of liquid interlayers can play a decisive role in, *e.g.*, self-organisation of nanoparticles, their flowability, *etc.*

Even the examples given above point to particular importance of the studies on the properties of liquids in the nano state

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for further progress in nanotechnology. In spite of a variety of challenges in this field, here we will dwell on one problem, namely, stability of liquid nanofilms and disperse and colloidal systems. We believe that this problem is of paramount importance for the development of scientific foundations of nanotechnology; in addition, the author of this review was directly involved in research in this field.

II. The surface forces and stability of disperse systems

A modern physical theory that describes the state and stability of liquid films and the disperse and colloid systems is based on the analysis of the surface forces acting across thin liquid interlayers separating particles or macroscopic surfaces. Here, the surface forces play the same role as the intermolecular interaction forces in condensed systems. In the 1940s, Derjaguin showed [2] that consideration of the interactions between two surfaces approaching each other is equivalent to consideration of the dependence of the disjoining pressure on the interlayer thickness. The dependence of the disjoining pressure on the thickness of the liquid interlayer is the key thermodynamic characteristic of the thin interlayer that distinguishes it from the bulk liquid. In particular, if the interlayer thickness is such that its medium fragment retains the properties of the bulk phase and, therefore, there is no overlap of the boundary layers adjacent to the interfaces, the disjoining pressure in the interlayer is zero. On the contrary, overlap of the boundary layers leads to anisotropy of the pressure tensor in the interlayer and to appearance of the disjoining pressure [$\Pi(h)$] dependent on the thickness of the liquid interlayer,

$$\Pi(h) = P_{\mathrm{N}}(h) - P_0\,, \tag{1}$$

where $P_{\mathrm{N}}(h)$ is the normal component of the pressure tensor in the thin interlayer with thickness h and P_0 is the pressure in the bulk isotropic fluid that is in equilibrium with the interlayer. The character of the dependence of the disjoining pressure on the liquid film thickness characterises the physical nature of the forces that govern the interaction between two surfaces separated by the liquid interlayer. The nature of the interaction forces is naturally determined by three factors, namely, characteristics of the interacting bodies, properties of the fluid, constituting the interlayer and the character of the interaction between the fluid and the boundary phases and, as a consequence, by the dependence of the properties of fluid in the interlayer on the interlayer thickness.

Quantitative analysis of the surface forces is based on the Gouy–Chapman [3–5] theory of diffuse ionic atmospheres and the theory of molecular forces by London.[6] These two approaches underlie the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of stability of lyophobic colloids.[7,8] In the framework of the DLVO theory, the total interaction energy is determined by the dispersion (van der Waals) and electrostatic mechanisms. Now we will consider them in more detail.

III. Dispersion (van der Waals) forces

The dispersion forces are universal in character and act in all systems. In 1930, London reported a general quantitative theory of the van der Waals forces.[6] Since then the theory of dispersion interactions between macroscopic bodies separated by an interlayer was developed using two different approaches, a microscopic and a macroscopic one.

The former approach is associated with de Boer [9] and Hamaker.[10] Here, the force of molecular attraction between identical macroscopic bodies is treated as the resultant of the London attraction forces acting between all pairs of molecules in the body. Details of calculations are available from original studies and monographs.[2,8,11] This approach allowed one to derive analytical expressions for calculation of the force of the interaction between two spheres, a sphere and a plane and two planes separated by a vacuum interlayer for both thin and thick interlayers (in the non-retarded limit and with allowance for electromagnetic retardation).† Hamaker's interaction constant addition rule [10] makes it possible to extend the microscopic approach to the interactions of condensed bodies separated by a condensed-phase interlayer. However, the state-of-the-art in physics of condensed media is such that the additivity of the London forces in the calculaton of the interactions between macroscopic bodies separated by dense-phase interlayers is quite a rough approximation. Thus, the simplicity of the microscopic method of calculations does not compensate for quantitative (in the case of absorbing interlayers, also qualitative) errors in the results of interaction force calculations.

A rigorous macroscopic approach to calculations of dispersion interactions between two bodies separated by a vacuum interlayer or an absorbing condensed phase was reported by Lifshitz *et al.*[12,13] [Dzyaloshinskii–Lifshitz–Pitaevskii (DLP) theory]. The formalism treats the bodies separated by a thin interlayer as continuous media interacting through fluctuating electromagnetic field. The interlayer thickness is assumed to be much greater than the size of the molecules constituting the bodies. Dzyaloshinskii, Lifshitz and Pitaevskii [12] took into account that the force of the interaction between bodies in vacuum coincides with the zz-component of the averaged Maxwell stress tensor, which was calculated by solving the Maxwell equations with inclusion of fluctuation field sources. To perform the field averaging procedure, the fluctuation-dissipation theorem was applied to the field sources. Later,[14] it was shown that the problem of determination of the stress tensor in the case of two macroscopic bodies separated by vacuum and by an interlayer is reduced to calculations of corresponding Green functions. Since the DLP theory is based on exact Maxwell equations, the retardation effects are included by default. The expression for calculating the disjoining pressure $\Pi(h)$ equal to the specific force of the interaction between macroscopic bodies separated by a homogeneous plane-parallel liquid interlayer of thickness h has the form [13]

$$\Pi(h) = -\frac{kT}{\pi c^3}{\sum_{N=0}^{\infty}}' \xi_N^3 \varepsilon_3^{3/2} \int_1^{\infty} p^2 \left\{ \left[\frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)} \times \right.\right.$$
$$\left. \times \exp\left(\frac{2p\xi_N h \varepsilon_3^{1/2}}{c} \right) - 1 \right]^{-1} + \left[\frac{(s_1+ap)(s_2+bp)}{(s_1-ap)(s_2-bp)} \times \right. \tag{2}$$
$$\left.\left. \times \exp\left(\frac{2p\xi_N h \varepsilon_3^{1/2}}{c} \right) - 1 \right]^{-1} \right\} \mathrm{d}p.$$

Here k is the Boltzmann constant; T is temperature; c is the speed of light; p is the integration variable, $\xi_N = 2\pi kTN/\hbar$ (N is a natural number, $\hbar$ is the Planck constant); ε_1, ε_2 and ε_3 are the dielectric permittivities of the macroscopic bodies 1 and 2 and of the liquid interlayer 3 considered as functions of the imaginary field frequency ($\omega = \mathrm{i}\xi$), *i.e.*, $\varepsilon = \varepsilon_j(\mathrm{i}\xi_N)$; $s_1 = (a - 1 + p^2)^{1/2}$, $s_2 = (b - 1 + p^2)^{1/2}$, where $a = \varepsilon_1/\varepsilon_3$, $b = \varepsilon_2/\varepsilon_3$. The prime at the sum points that the first term in the sum corresponding to $N = 0$ is to be taken with a factor of 0.5. Note that direct substitution of $N = 0$ into Eqn (2) leads to uncertainty because ξ_N equals zero, whereas the integral with

† In principle, methods of numerical calculations in the framework of the microscopic approach allow one to calculate the interaction between bodies of arbitrary geometry.

respect to dp diverges. Once the uncertainty is disclosed,[13] the term with $N = 0$ takes a finite value.

From relation (2) it follows that calculations of the dispersion forces only require knowledge of the frequency dependence of the dielectric permittivities of the contacting media $\varepsilon_j(i\xi_N)$. These can be determined using the Kramers–Kronig relationships ‡ and the values of the imaginary part of dielectric permittivity measured for a broad spectral range.

Analysis of relation (2) shows that the dispersion interaction between identical bodies ($\varepsilon_1 = \varepsilon_2$) is always attractive. However, in the case of different bodies (*e.g.*, wetting films) both attractive and repulsive forces are possible depending on the behaviour of the functions $\varepsilon_j(i\xi_N)$. Moreover, since the behaviour of the functions $\varepsilon_1(i\xi_N)$, $\varepsilon_2(i\xi_N)$ and $\varepsilon_3(i\xi_N)$ in the frequency range important for these bodies is not related to the static dielectric permittivities of the contacting bodies, for certain systems the sign of the interaction force changes with variation of the liquid interlayer thickness (Fig. 1).

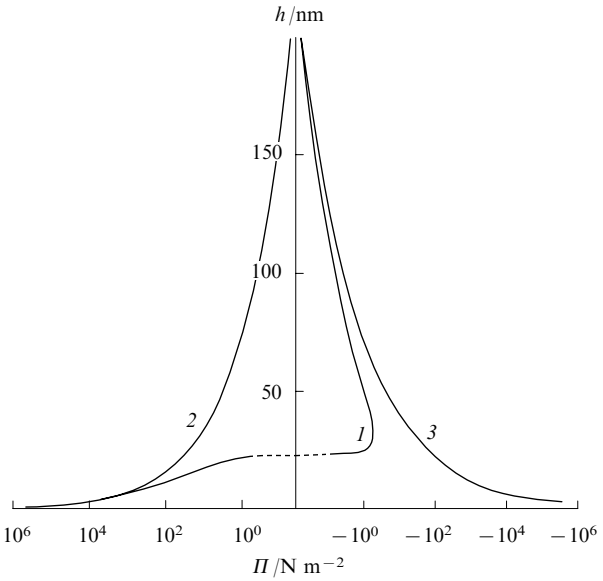


Figure 1. Change in sign of the molecular component of the disjoining pressure (dispersion forces) plotted *vs.* film thickness (curve *1*). Shown are the results of $\Pi(h)$ calculations using Eqn (2) for the air–water–fluorite system. Curves *2* and *3* are calculated using Eqns (3a) and (3b), respectively.

Expression (2) can be simplified using integration over $d\xi = (2\pi kT/\hbar)dN$ instead of summation. However, the force calculation error due to neglect of the contribution of the term with $N = 0$ to the net integral can be significant for the polar fluid interlayers that exhibit strong absorption in the low-frequency range of electromagnetic vibrations. If we compare the interlayer thickness to the main wavelength (λ_0) in the absorption spectra of the contacting media and consider two limiting cases, namely, the thin and thick interlayer limits ($h \ll \lambda_0/2\pi$ and $h \gg \lambda_0/2\pi$, respectively), expression (2) is reduced to asymptotic relationships (3a) and (3b) for the delayed and non-delayed dispersion forces, respectively.

$$\Pi(h) = -\frac{\hbar}{8\pi h^3}\int_0^\infty \frac{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}d\xi = -\frac{A_{132}}{6\pi h^3} \text{ at } h \ll \frac{\lambda_0}{2\pi}, \quad (3a)$$

$$\Pi(h) = -\frac{B(\varepsilon_{10},\varepsilon_{20},\varepsilon_{30})}{h^4} \qquad \text{at } h \gg \frac{\lambda_0}{2\pi}. \quad (3b)$$

Here ε_{10}, ε_{20} and ε_{30} are the electrostatic dielectric permittivities of the contacting media, A_{132} and $B(\varepsilon_{10},\varepsilon_{20},\varepsilon_{30})$ are the dispersion force constants in the non-retarded and retarded limits, respectively. The constant B is determined by the electrostatic dielectric permittivities of the contacting media in the low-frequency range. Analysis of the disjoining pressure values calculated using exact relation (2) shows that marked deviations of the $\Pi(h)$ dependence from the h^{-3} law [expression (3a)] begin at distances of 2–3 nm. As to the h^{-4} law [relationship (3b)], the correctness of the application of this expression to a wide variety of systems is doubtful.[15] In particular, if the systems are characterised by the same sign of the van der Waals forces and the contacting bodies show weak absorption in the radiofrequency and IR region, this law is reasonably obeyed at film thicknesses of 30–40 nm.[2] At the same time if the van der Waals forces change the sign as h increases, the h^{-4} law can be used as an asymptotic relation only at interlayer thicknesses of the order of hundreds of nanometres (see Fig. 1). From expression (3a) it follows that the dispersion force increases as the dielectric contrast (differences $\varepsilon_1 - \varepsilon_3$ and $\varepsilon_2 - \varepsilon_3$) between the contacting phases increases. As an example, Table 1 lists the Hamaker constants A_{132} of certain systems calculated using relations (2) and (3a).

An alternative approach to calculations of dispersion interactions was proposed by Van Kampen *et al.*[19] The method is based on calculations (in the harmonic approximation) of the excess energy of the normal modes of surface oscillators as function of the interlayer thickness. The approach is somewhat more simple and clear compared to that used in the DLP theory;[13] however, it proved itself as 'heuristic and intuitive'.[20]

‡ These are the integral relationships relating the real and imaginary parts of the complex dielectric permittivity $\varepsilon = \varepsilon'(\omega) + i\varepsilon''(\omega)$. A particular case of the Kramers–Kronig relations is the expression

$$\varepsilon(i\xi_N) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon''(\omega)}{\omega^2+\xi_N^2}d\omega,$$

which determines the values of the ε function of the imaginary argument $\omega = i\xi$. It is these $\varepsilon(i\xi_N)$ values that appear in relation (2).

Table 1. Hamaker constants of various systems.

System	Hamaker constant (A_{132}) /J	Ref.
Gold–water–gold	2.5×10^{-19}	16
Gold–KCl solution–gold	4.0×10^{-19}	17
Platinum–KCl solution–platinum	1.4×10^{-19}	17
Platinum–$MgSO_4$ solution–platinum	8.5×10^{-20}	17
Silicon–water–silicon	1.2×10^{-19}	17
Quartz–water–quartz	7.5×10^{-21}	16
Quartz–water–quartz	8.5×10^{-21}	18
Sapphire–water–sapphire	5.3×10^{-20}	18
Poly(vinyl chloride)–water–poly(vinyl chloride)	1.2×10^{-20}	16
Polystyrene–water–polystyrene	1.3×10^{-20}	16
Polyisoprene–water–polyisoprene	7.4×10^{-21}	18
Fluorite–water–fluorite	1.0×10^{-20}	18
Polytetrafluoroethylene–water–polytetrafluoroethylene	3.3×10^{-21}	18
Ice–water–gold	1.6×10^{-21}	16
Ice–water–silicon	-1.7×10^{-21}	16
Ice–water–quartz	3.0×10^{-23}	16
Ice–water–polystyrene	1.2×10^{-22}	16
Quartz–water–air	-1.0×10^{-20}	18
Fluorite–water–air	-1.2×10^{-20}	18

Later, Barash and Ginzburg [21] reported a substantiation of the Van Kampen approach and analysed its applicability to the solution of new problems with arbitrary media.

Experimental studies of dispersion interactions between bodies were carried out using various model systems containing both symmetrical liquid and gaseous interlayers and wetting films. Comprehensive analysis of these studies was done in a monograph.[2] Without dwelling on details, note that by and large the interactions between macroscopic bodies separated by vacuum or air and the dispersion interactions of neat non-polar fluids in wetting films can well be described using the macroscopic theory of the van der Waals forces with an error of 15% – 30%. Deviations in the behaviour of macroscopic bodies separated by vacuum or air interlayer from the theoretically predicted in the thin interlayer limit are associated [22–24] with both the effect of the roughness and heterogeneity of the surface of solids and with the formation of the adsorption or oxide layers on the surface (Fig. 2). Although in each case shown in Fig. 2 the experimental data are reasonably described by the inverse cube law, the calculated Hamaker constants differ appreciably and only for curve *3* the value of this constant ($A_{132} = -0.88 \times 10^{-20}$ J) is in good agreement with the theoretical estimates for a hexane wetting film immobilised on fused quartz. At the same time, in some cases the behaviour of solids separated by liquid interlayers strongly differs from that predicted by the theory of the van der Waals forces (Figs 3 and 4). The reasons for the deviation seem to be due to the assumptions underlying the theory in the case of liquid interlayers.

Detailed analysis of the key assumptions in the DLP theory was reported by Barash and Ginzburg.[21] They used the Green functions for the Maxwell equations to determine the contribution of the long-wavelength equilibrium electromagnetic fluctuations in matter to the free energy of a system comprising macroscopic bodies separated by a thin liquid interlayer. The solutions of the Maxwell equations were expanded over the eigenfunctions of an auxiliary system.[21] This made it possible to reduce an infinite series for free energy calculations to a rather simple expression suitable for further analysis and reveal limitations on the use of the equations [13] for calculating the interaction forces acting between two macroscopic bodies.

First, the DLP theory ignores the contribution of the interaction between the long-wavelength fluctuation field and matter to the dielectric permittivity (in essence, the spatial dispersion for an arbitrary system is ignored). Second, the expressions for the energy of the system and the interaction

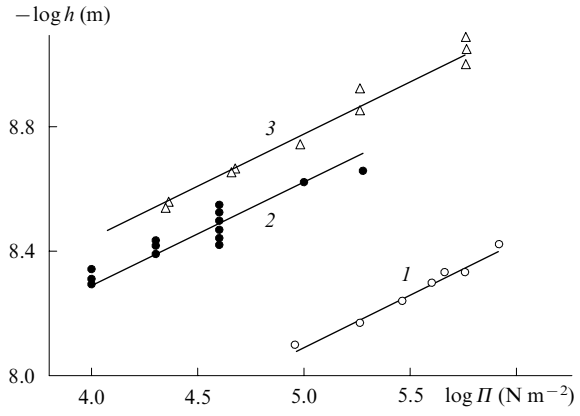


Figure 2. Disjoining pressure isotherms of hexane films on a polished substrate (roughness of about 5 nm) (*1*) and on molecularly smooth films-substrates (roughness at most 0.5 nm) in air in the presence of water vapour (*2*) and in anhydrous nitrogen atmosphere (*3*).

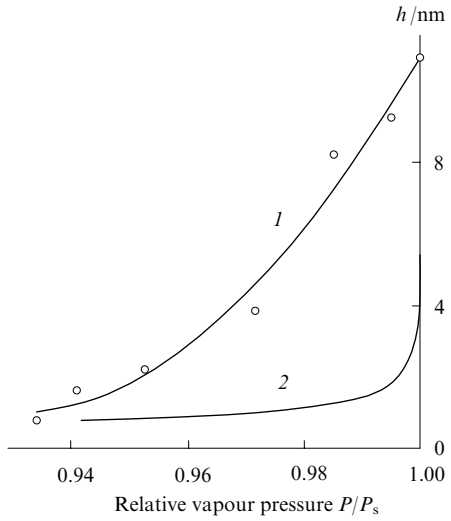


Figure 3. Adsorption isotherm of n-heptan-1-ol on an optical glass K-8. Experimental data by Derjaguin and Zorin [25] (*1*) and theoretical curve for the dispersion component of the disjoining pressure (*2*).

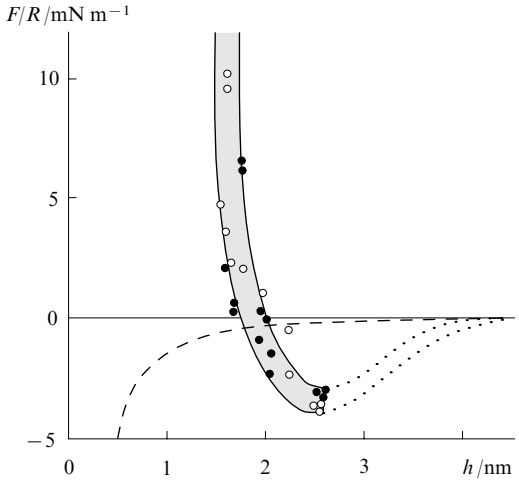


Figure 4. Reduced force (F/R) plotted *vs.* distance between two mica surfaces in white oil (mixture of branched alkanes) at 22 °C under different experimental conditions.[26]
Solid circles correspond to completely anhydrous liquid existing in equilibrium with air dried over P_2O_5, open circles correspond to completely anhydrous liquid in anhydrous nitrogen atmosphere, and the dashed line corresponds to the van der Waals forces.
Here and in Figs 5 and 9, the reduced force is the ratio of the measured force (F) of the interaction between cylindrical surfaces to the surface radius R. The shaded region between the solid lines denotes the limits of scatter of the measured values. The dotted lines denote the expected behaviour of the forces in the case of thick films.

forces derived by Dzyaloshinskii, Lifshitz and Pitaevskii assume that the volumes and dielectric permittivities of the bodies in the system do not change upon the change in the distances between the bodies. This limitation is valid for interacting macroscopic bodies, but in the case of a thin interlayer it is non-rigorous and leads to significant underestimation of the forces produced in the system. Thus, if the dielectric permittivity of the interlayer depends on the interlayer thickness and/or if the interlayer shows a spatial dispersion, the approach developed by Dzyaloshinskii, Lifshitz and Pitaevskii appears to be somewhat incorrect for the description of the interaction forces in a real system.

Both these factors act, as a rule, in complex molecular liquids, especially in the case of thin interlayers. This causes deviations of the experimental interaction curves from the dependences predicted by the DLP theory. In addition, interlayers a few Ångström thick violate one of the DLP theory conditions, according to which the film thickness much exceeds the size of the molecules. In this case, treatment of the liquid as a continuous medium is somewhat incorrect. Finally, calculations of dispersion interactions in the framework of the DLP theory ignore the existence of surface layers of the interacting bodies (dielectric permittivities of these layers can differ appreciably from the corresponding bulk characteristics used in calculations). Thus, theoretical calculations of dispersion interactions between bodies separated by a liquid or gaseous interlayer [13, 19] are reliable only for the interlayers tens of nanometres thick. In the case of thinner interlayers, such calculations are of limited use.

IV. Ionic electrostatic interactions

In the case of ionic fluids and particles having charged surfaces the stability of a liquid film is to a great extent governed by the electrostatic forces due to the overlap of the electric double layers in the liquid interlayer. The main difficulty in calculating these forces consists of the need of determining the spatial arrangement and concentration of ions in the interlayer with allowance for deformation of ionic atmospheres as the surfaces approach each other.

Rigorous calculations of the ionic electrostatic component of the disjoining pressure Π_e based on the solution of the Debye–Hückel equation for strong electrolytes were first reported by Derjaguin.[27] He derived equations for calculating the interactions between two identical spheres or two plates separated by a liquid interlayer. Derjaguin used the linearised Debye–Hückel equation, therefore the equations derived by him are only applicable to calculations of electrostatic forces in weakly charged sols.

The interaction of strongly charged particles in electrolyte solutions was studied by Derjaguin and Landau.[7, 28] Using the constant potential approximation for the surfaces brought closer together, they derived relationships for calculating the repulsive forces and the energy of the interaction between flat plates and convex macroscopic surfaces, formulated the coagulation criterion and substantiated the Schulze–Hardy rule according to which the coagulating concentration of electrolyte rapidly decreases as the valence of the counterion increases. Verwey and Overbeek reported an independent study [8] of the interaction between identical plates in potentials with arbitrary magnitudes, which was also carried out in the constant potential approximation. Additionally, they introduced the Stern correction, which allows for the dense component of the electric double layer.

It should be noted that in solving the problem of electrostatic interaction of charged surfaces separated by an ionic interlayer the boundary conditions are first of all determined by the charging mechanism. In particular, if the surface charging occurs by adsorption of ions from solution and the entropy contribution to the free energy of the system is independent of the amount of adsorbed ions, the charged surfaces will approach each other under the constant-potential boundary condition. If the charging occurs by complete dissociation of surface groups, the constant-charge boundary conditions are applied. In the case of incomplete dissociation of ionised groups or if the entropy depends on the concentration of adsorbed ions, the charge-regulation boundary condition is used.[29, 30] Yet another type of boundary conditions corresponds to the interaction of 'soft' ion-permeable particles or polyelectrolyte particles.[31] If the particle size much exceeds the Debye wavelength, the potential in the bulk of the particle is always equal to the Donnan potential.

The classical theory of ionic electrostatic interactions is restricted to consideration of the first two types of boundary conditions. Both analytical and numerical solutions to the problem of electrostatic interaction between charged identical surfaces (in symmetrical and non-symmetrical electrolytes, see Refs 2 and 31) were derived in the framework of this theory. There is a feature that permits essential simplification of the procedure for evaluation of the ionic electrostatic component of the disjoining pressure Π_e in the systems with unknown or interlayer-thickness-dependent surface charging mechanism. For instance, all possible dependences of Π_e on the interlayer thickness obtained under different boundary conditions lie between the curves corresponding to the constant potential of the diffuse layer boundaries and to the constant density of the surface charge and the charge of the dense Stern monolayer. The former and latter cases correspond to minimum and maximum repulsive forces, respectively.

Later, calculations of the ionic electrostatic component were generalised to electrostatic interactions between different-type particles, which are of particular value in the case of particle–electrode interaction and in electrofiltering and electrophoretic sedimentation. Derjaguin [2] proposed a graphical method of isodynamic curves, which allows one to estimate the magnitude and character of hetero-interactions at constant potentials of diffuse ionic layers. A feature of the case in point is that the ionic electrostatic forces acting between two likely charged particles bearing non-equal charges are repulsive in character at long distances. The repulsive forces increase as the interlayer thickness decreases, pass through a maximum and then change their character to attractive. The attractive forces increase without limit as the interlayer thickness tends to zero. Analysis showed that the maximum repulsion is determined by the surface potential of the particle bearing the smaller charge.

Considering weakly charged surfaces, an analytical solution to the problem was obtained using the linearised Poisson–Boltzmann equation for both flat interlayers (under constant potential [32] and constant charge [33] boundary conditions) and spherical particles of different radii. A simple equation for calculating the energy of the interaction between spherical particles at constant potentials on both surfaces was obtained by Hogg *et al.*[32] The problem with the constant charge boundary conditions was first solved by Usui.[34] Kar *et al.*[35] considered a complex case corresponding to a constant potential on one surface and a constant charge on the other surface for the case of thin (compared to the particle radii) double layers. It should be noted that the solutions were obtained for the problem of the interaction between spherical particles the radii of which much exceed the thicknesses of the liquid interlayers between them.

A general numerical method of solving the non-linear Poisson–Boltzmann equation developed by McCormack *et al.*[36] makes it possible to calculate electrostatic interactions between different-type surfaces in flat interlayers of symmetrical electrolytes at large surface charges not only for the abovementioned cases of constant potential and charge at both interfaces simultaneously, but also in the case where the surface of one particle has a constant charge while the other particle has a constant potential. However, it should be emphasised that a wide variety of the laws of variation of the ionic electrostatic component of the disjoining pressure with the interlayer thickness and the dependence of these changes on the boundary conditions [2, 31] can only be observed if the film thickness is smaller than or comparable to the Debye screening length.§ At long distances, the interaction between both flat and spherical particles exponentially decreases as the interlayer thickness increases irrespective of the surface charging mech-

§ The Debye screening length is the action range of the electric field of a single charge in electrolyte.

anism; this was confirmed by numerous experiments (see, *e.g.*, Ref. 37).

The mechanisms of the van der Waals forces and electrostatic interactions considered above underlie the theory of stability of lyophobic colloids. It is lyophobic surfaces and colloids (their particles are treated as weakly interacting with the dispersion medium) that usually permit a correct description of the stability of interlayers (Fig. 5), kinetics of coagulation and the destabilising effect of electrolyte additives using the two approaches to calculations of surface forces (see above). We believe that the last stage of the evolution of the DLVO theory in its classical form should be dated to the early 1960s; at that time, the macroscopic theory of the van der Waals forces was already elaborated and various theories of calculations of electrostatic interactions between same-type and different-type particles separated by uniform liquid or solvent interlayers were developed. However, the development of the DLVO theory was accompanied by accumulation of experimental data that not only showed poor quantitative agreement, but in some cases qualitatively contradicted the predictions of the classical DLVO theory. Examples are provided by recent studies on the stability of foam films,[38,39] wetting films and interlayers between solid surfaces.[40–44]

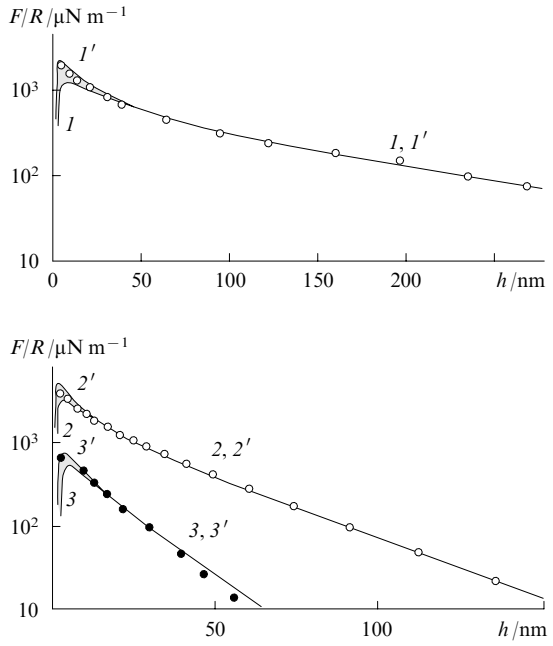


Figure 5. Reduced forces of interaction (F/R) between two crossed cylindrical mica surfaces of radius 1 cm in water (curves *1*, *1′*) and in dilute potassium nitrate solution (10^{-4} M KNO_3, curves *2*, *2′*) and calcium nitrate solution [10^{-4} M $Ca(NO_3)_2$, curves *3* and *3′*, respectively].[11]
The open and solid circles denote the experimental data, the solid lines correspond to the results of force calculations using the DLVO theory (the Hamaker constant $A_{132} = 2.2 \times 10^{-20}$ J) in the constant potential (Ψ_0, curves *1*–*3*) and constant surface charge (curves *1′*–*3′*) approximations. For thick interlayers, both approximations give the same results. $\Psi_0 \approx -150$ mV (*1*, *1′*), $\Psi_0 \approx -120$ mV (*2*, *2′*) and $\Psi_0 \approx -50$ mV (*3*, *3′*).

Attempts to attain agreement between the theory and experiments led, on the one hand, to allowance for specific features of real experimental systems in the framework of the evolution of the classical approaches and, on the other hand, to development of some new mechanisms of long-range surface forces that have a common name 'non-DLVO'-forces.

V. Progress in the theory of dispersion forces

Non-uniformity of a real liquid interlayer due to the change in the film density across the interlayer thickness and to monomolecular or diffuse adsorption of a solution component near the boundary media was included in calculations of the van der Waals interactions in the framework of the model layered systems. Calculations were carried out either assuming identical dielectric properties within each layer[20,45–48] or using different laws of the changes in the dielectric properties along the normal to the layers.[49,50] In all cases, the results obtained with allowance for non-uniformity were appreciably different from those obtained in the homogeneous interlayer approximation. For instance, the interaction energies calculated using these models for films a few nanometres thick differed by almost an order of magnitude from the values calculated using the DLP theory[13] with the bulk dielectric permittivities.

An alternative microscopic approach to evaluation of the non-uniformity of the liquid interlayer is based on the molecular statistics methods.[51,52] Here, the non-uniformity of the film can be taken into account by augmentation of the equations for interaction energy calculations with an additional term proportional to the inverse cube of the interlayer thickness. This term becomes of particular importance as the interlayer thickness decreases.

Eventually, Derjaguin and Churaev[2,53] developed a method of inclusion of the non-uniformity of the interlayer, which involves thermodynamic treatment of adsorption and evaluation of the interaction between components of non-polar solutions and the boundary phases in the framework of the macroscopic approach. Later, the method was extended to solutions of polar substances dissolved in a non-polar solvent.[54–58] Additional interactions due to non-uniform distribution of the solution components across the interlayer thickness were named 'adsorption component of the disjoining pressure'. Depending on the ratio of the dielectric permittivities of the solvent and solute and on the ratio of the dielectric permittivities of the solvent and boundary phases, these interactions can either stabilise or destabilise the liquid interlayer. It should be noted that the effect of these additional forces is significant only in the case of interlayers a few nanometres thick.

Calculations of dispersion interactions with allowance for the spatial dispersion of dielectric permittivity appeared in the electrolyte solution films were carried out by Gorelkin and Smilga[59,60] using either the Dzyaloshinskii–Lifshitz–Pitaevskii method (based on calculations of the temperature Green functions) or the Bogolyubov functions. An analytical solution was obtained for electrolytes modelled by the Debye plasma and collisionless plasma with mirror reflection from the boundaries assuming neutral film boundaries and diagonal dielectric permittivity tensor within the electrolyte interlayer.

A comparison of the equations derived in Refs 59 and 60 with Eqn (2) derived using the DLP theory revealed significant difference only for the term with zero frequency. Therefore, the inclusion of spatial dispersion is of particular importance in studies of the systems where this term plays a significant role. In addition, the spatial dispersion also manifests itself in the appearance of specific effect of interfaces on the character of the frequency dependence of the dielectric permittivity of the interlayer. The effect is expected only for films a few nanometres thick in specific systems, such as metal solutions in ammonia. According to calculations, the presence of dilute electrolyte solution in the system leads to screening of the van der Waals forces at long distances (10^{-7}–10^{-6} m). At these distances, the molecular forces decrease exponentially rather than in proportion to $\Pi(h) \sim h^{-4}$, as follows from relationship (3b).

VI. Progress in the theory of ionic electrostatic interactions

The evolution of the classical theory of electrostatic interactions between surfaces immersed in electrolyte solutions has been accompanied by revision of its foundations, such as the continuity of charge distribution along the particle surfaces, constant surface potential or constant charge of the approaching surfaces, treatment of ions in solution as point changes and consideration of other (non-Poisson) potentials determining the ion distribution in solution, *etc*.

In particular, Muller showed (see Ref. 2) that drawing colloidal particles closer together is accompanied by rearrangement of not only the diffuse charge, but also the surface charge of the electric double layer except for the chemisorbed part of this layer. He derived an exact parametric equation relating the repulsive energy to the distance between flat plates assuming that the changes in the adsorption of ions as the plates approach each other are described by the Stern isotherm.

Healy and co-workers[61] reported the need of using a charge regulation model instead of the constant potential approximation in calculations of ionic electrostatic interactions at short distances between the charged surfaces.[29–31] Based on this model, a correction to the DLVO forces of the interaction between hydrophilic surfaces in water was calculated in the framework of constant dielectric permittivity of the solvent with inclusion of the Nernst layer of hydroxyl groups near the interface (this makes the position of the charge plane more distant from the surface).[62] This approach made it possible to explain the appearance of an additional minimum on the energy curve, which is located between the primary and secondary minima predicted by the DLVO theory.

A general thermodynamic consideration of changes in the charge of the interlayer in the course of approach of differently charged flat surfaces was reported by Lyklema and Duval[29] who assumed charge regulation in the Gouy–Stern layer. The approach was used for calculating the potential and charge distributions in plane-parallel interlayers and the forces and energy of the interaction between different-type surfaces in various model systems that simulate the behaviour of complex real systems, *e.g*., the interaction of clay and metal oxide particles. The constant charge or constant potential approximations of the diffuse double layer were shown to be correct only in the case of thick interlayers. Systems with thin interlayers exhibit deviations from both boundary conditions. To characterise the charge regulation processes occurring within the interlayer as the surfaces approach each other, it is appropriate to introduce the notion of the regulation capacity characterising the possibility of establishment of a new charge distribution in the interlayer without significant change in the potential. The higher the regulation capacity of the interlayer the more correct the description of the behaviour of the system in the constant potential approximation.

The next step in considering ionic electrostatic interactions between surfaces immersed in electrolyte solution is the inclusion of various factors determining the ion distribution in the liquid interlayer. For instance, the theory of the interaction of electric double layers, which is based on the classical Poisson–Boltzmann equation, assumes that ions obey the Boltzmann distribution with the interaction potential obeying the Poisson equation. This theory ignores the effects due to specific nature of the ions in solution. At the same time, experimental data on the stability of disperse systems in electrolyte solutions and on the forces of the interaction between such systems separated by electrolyte interlayers indicate that electrostatic forces depend not only on the valence of ions and the ionic force of the solution, but also on the type of the cations and anions present in the solution.[63–65]

To describe the specific order of ions with respect to the character of their effect on the interaction between the double layers, it was suggested to augment the Poisson–Boltzmann equation with additional potentials that include, in one way or another, the nature of the ion.[66–72] For instance, Ninham and Yaminsky[66] proposed to include the potential of the van der Waals forces acting between the ion and the remaining part of the system in the description of the ion distribution in the solution. In addition to the potential of ion-dispersion interaction including the potential of the van der Waals forces and the Poisson potential, Karraker and Radke[72] also proposed to take into account the potential of the interaction between ions and their 'images' in air, which causes additional repulsion of ions from the water/air interface. Manciu and Ruckenstein[70,71] considered not only the long-range ion-dispersion potential (see above), but also the short-range ion hydration potential, which describes the ion hydration free energy difference between the solution bulk and the near-interface region.

Thus, the ion redistribution in the solution interlayer in the potentials of ion-dispersion and ion hydration interactions depends on the type of ions. Such a redistribution causes changes in the surface charges and surface potentials and, therefore, affects the interaction between the double layers. Interestingly, the authors of all the approaches mentioned above get satisfactory descriptions for the experimentally observed dependence of the surface tension of electrolyte solutions on the ionic strength of the solutions in spite of different choice of the additional potentials.[68,70,72]

Correlations in mutual arrangement of ions in the electric double layers and the related additional forces were studied.[73–75] Additional contributions to the energy of ion–ion interactions in the liquid interlayer are due to correlations of charge density fluctuations in the double layers formed on the opposite surfaces of the liquid interlayer. Taking into account the ion size (passage from point ions presentation to the ions with finite sizes) also causes the energy to change due to additional repulsion between ion shells near the mid-plane of the film. The 'image' forces cause deformation of diffuse ionic atmospheres with the corresponding energy contribution. Finally, the ion concentration difference between the actual film and the value predicted using the conventional Poisson–Boltzmann approach leads to a change in the Debye screening length. Analysis showed[73–75] that the effect of ion–ion correlations mainly involves the appearance of additional attraction between the charged surfaces. This effect is most pronounced in di- and multivalent electrolyte solutions and leads to significant decrease in repulsion between the double layers or to the change in the sign of the interaction. The effect of ion size on the interaction force manifests itself to the greatest extent in the case of thin interlayers, large ionic radii and/or large surface charges. The influence of ion–ion correlations on stability of colloidal solutions with multivalent counterions was experimentally established[76] by direct measurements of interaction forces between mica surfaces in 0.15 M $CaCl_2$ solution.

Rejection of the uniformly 'smeared' surface charge model led to the development of a family of models[77–81] that allow for discrete structure of the dense part of the electric double layer at the interface.

For instance, Zhiguleva and Smilga[79] used the modified Evald method for two-dimensional geometry and analysed the electrostatic field and potential distributions in the electric double layer for various regular flat charge distribution lattices. According to calculations,[79] the inclusion of discrete structure of the double layer in many systems is necessary because the actual interaction force can be two orders of magnitude higher than the values obtained using the smeared charge model. Similar results were also reported by Kostoglou

and Karabelas [80] who considered the interaction of surfaces characterised by discrete distribution of round or square-planar potential-determining ions occupying regular lattice sites. They found that the interaction energy differences between the surfaces with discretely distributed and smeared charge are more pronounced (over a wider range of film thicknesses) at a constant potential of the approaching surfaces rather than in the constant charge approximation.

Derjaguin and Muller [2] established that in the case of delocalised adsorption of ions the discreteness of the surface charge distribution causes correlations in the arrangements of the ions on the opposite film surfaces. According to calculations, these correlations are responsible for the appearance of additional attraction forces that decrease as $\Pi(h) \sim h^{-4}$. In the case of thin interlayer, these correlation forces not only reduce the electrostatic repulsion, but in some cases cause a change in the sign of the interaction.

Analysis of the effect of discreteness of the surface charge distribution on the electrolyte/insulator interface showed [81] that the structure of the diffuse layer in counterions is determined by not only the exponential decay of the field due to the Debye screening, but also additional asymptotics with amplitudes depending on the dielectric permittivity of the insulator.

According to the results of theoretical studies,[82–84] the electric double layer near the surface bearing a non-uniformly distributed charge has a modified structure compared to the double layer near a uniformly charged surface. The deviation of the structure of the diffuse part of the counterion layer is particularly pronounced in the presence of multiply charged ions and at large average surface charges.

Basu and Sharma [85] found that repulsive forces additional to those given by the DLVO theory, acting between surfaces can also be due to changes in the static dielectric permittivity of the solvent near the charged interface. Henderson and Lozada-Cassou [86] attempted to take into account the structure of the thin solvent interlayer by analysing the preferred orientation of the dipole moments of the solvent molecules near the interface, which is interpreted in the framework of the continuum models as dielectric saturation. It was shown that this phenomenon, which manifests itself in a decrease in the static dielectric permittivity, causes an extra repulsion between surfaces (in addition to the DLVO forces) and can be used for explanation of the appearance of hydration forces in electrolyte solutions.

Paunov *et al.*[87–89] analysed the role of the size of hydrated ions in solution near the interface and showed that the ion size affects the ion distribution not only near the charged interface, but also outside the electric double layer. Redistribution of ions across the film thickness due to the ion size effect and to the changes in the static dielectric permittivity of the solvent near the charged interface requires introduction of a correction to the electrostatic component of the disjoining pressure. The correction describes the additional repulsive in thick and additional attraction in thin interlayers provided that the overlap of the double layers is small.[89]

Discrete dipole distributions along interfaces were studied by different authors.[54–58, 77, 90–93] For instance, Jönsson and Wennerström [90] analysed the contribution of image forces to the interaction between surfaces covered with surfactants having bipolar terminal groups using the continuum electrostatic model and pointed that these forces lead to appearance of repulsive forces that can be responsible for the swelling of phospholipid bilayers in aqueous solutions. Kjellander and Marcelja [91] restricted themselves to consideration of dipoles oriented normal to the surface in the hyperchain approximation and showed that the correlation attraction of dipoles located on different surfaces dominates over repulsion between the dipoles and their images. Similar results were obtained by Attard and Mitchell [92] and by Jönsson *et al.*[93] using methods of the perturbation theory and by Martynov and Smilga [77] who used the electrostatic approach. As was reasonably argued by Martynov and Smilga,[77] attraction between dipoles in a symmetrical system is a general result. Since the strength of the field created by the layer adsorbed on one dipole surface alternates in the plane of the second adsorption layer (this is a consequence of the Gauss theorem), at a constant interlayer thickness the dipole lattices on the opposite surfaces are displaced relative to each other in such a manner that the potential electric energy of their interaction be minimum. This in turn causes the appearance of attractive forces acting between the dipole lattices, *i.e.*, a negative disjoining pressure. Jönsson *et al.*[93] showed that the inclusion of orientation rotation of dipoles in the framework of perturbation theory (long-wavelength approximation) can cause either attraction or repulsion between the dipole layers. However, in a symmetrical system the repulsion forces are much weaker than the van der Waals attraction.[93] It should be noted that the authors of studies [77, 90–93] considered only symmetrical systems assuming that adsorption is independent of the interlayer thickness and ignoring specific features of the structure of dipole molecules.

VII. Electrostatic interactions in non-polar media

Specific features of ionic electrostatic interactions in non-polar media consist in that usually the bulk ion concentrations in such systems are low and, correspondingly, the Debye screening lengths are of the order of a few thousand nanometres,[94] which much exceeds the thickness of the interlayers under study. In this case, the interaction between charged surfaces can be treated as the Coulomb interaction ignoring screening. Analysis of the interaction between small charged particles, a polarisable particle and a charged electrode and between polarisable particles in a nonuniform electric field using this approach in the smeared surface charge approximation was reported in a recent review by Adamczyk.[95] Another approach is based on consideration of the interaction between electric double layers having diffuse parts comprising counterions only.[94, 96] If the source of counterions is the surface and no ion exchange with the bulk reservoir occurs, the energy of the interaction between two flat charged surfaces can be calculated using the total entropy maximisation approach [97] with the assumption of charge regulation or constant charge condition.[96] According to calculations, the long-range repulsion between surfaces separated by non-polar liquid interlayer is more than an order of magnitude weaker compared to ionic electrostatic interaction through a water interlayer. The repulsive forces asymptotically decrease with the interlayer thickness following a power law rather than exponential law predicted by the classical DLVO theory.

The mechanisms of appearance of additional forces of the interaction between surfaces separated by a non-polar liquid interlayer in the presence of polar molecules were considered.[54–58] This case is of particular importance in the analysis of stability of suspensions in dispersion media represented by solutions of polar components in non-polar solvents. Discrete distributions of the dipoles simulating polar molecules across the interfaces and interlayer thickness cause the appearance of various types of image forces and to dipole–dipole interactions within the interlayer. Both symmetrical and asymmetrical systems characterised by different magnitude and, in some cases, type of adsorption at different interfaces were considered.[54–58] Equilibrium adsorption calculations were carried out with allowance for not only the specific potential of the interaction between polar adsorbable molecules and active sites at the interface, but also the potentials of the image forces and dispersion interaction of these molecules with the boundary phases. The last two potentials cause a significant dependence of the equilibrium adsorption on the thickness of the liquid interlayer.

The contribution of electrostatic interaction between layers of adsorbed dipole molecules and their images in the confining phases to the disjoining pressure can be rather large even in highly dilute solutions of polar substances in non-polar solvents. Generally, this contribution is a non-monotonic function of the concentration of polar molecules (Fig. 6) and decreases in a $\Pi(h) \sim h^{-4}$ mode as the film thickness decreases. It can cause either attraction or repulsion between film boundaries depending on the character of the changes in the adsorption of the solute across the interlayer thickness, on the ratio of the static dielectric permittivities of the contacting media and on the magnitude of dispersion interaction between the dipole molecules and the confining phases.

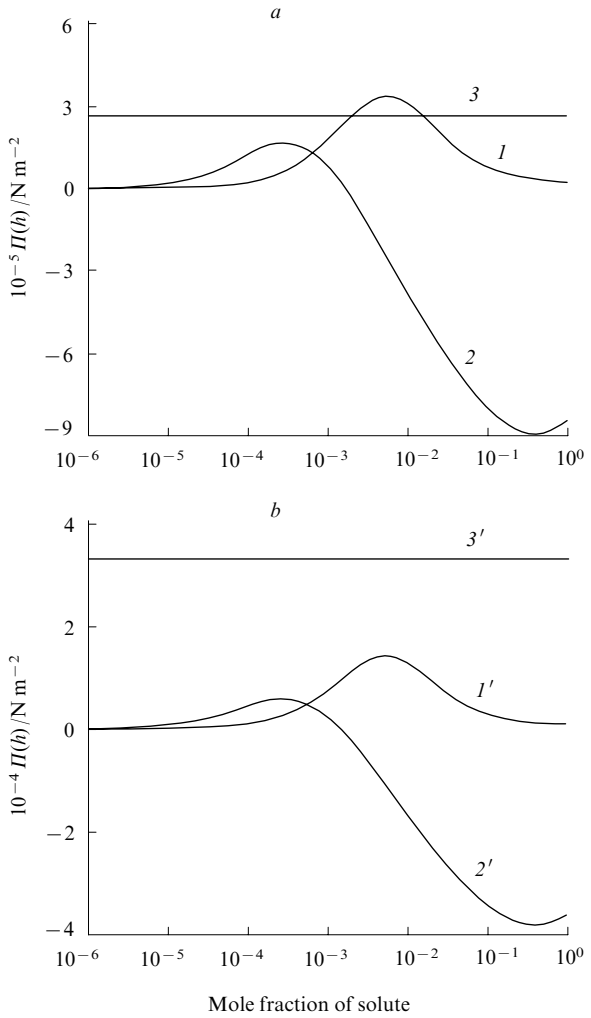


Figure 6. Contribution to the disjoining pressure related to the interaction between the adsorbed monolayer and its images plotted *vs.* mole fraction of polar solute for films 1 (*a*) and 2 nm (*b*) thick. Curves (*1*, *1′*) correspond to in-plane and curves (*2*, *2′*) correspond to normal orientation of dipoles in the monolayer. Curves (*3*, *3′*) correspond to dispersion interaction of bodies (the Hamaker constant $A_{132} = 5 \times 10^{-21}$ J) taken with the opposite sign. Disjoining pressure calculations were carried out for wetting films of solutions of alcohols in oil on the water surface.[57, 58]

Analysis of the expressions derived and numerical calculations carried out for monolayers of adsorbed molecules using different magnitudes and orientations of the dipole moments relative to the interfaces showed [54–58] that in non-symmetrical thin interlayers (*e.g.*, wetting films) at both in-plane and normal orientations of the dipoles in the monolayer the forces of the interaction between the monolayer and its images can

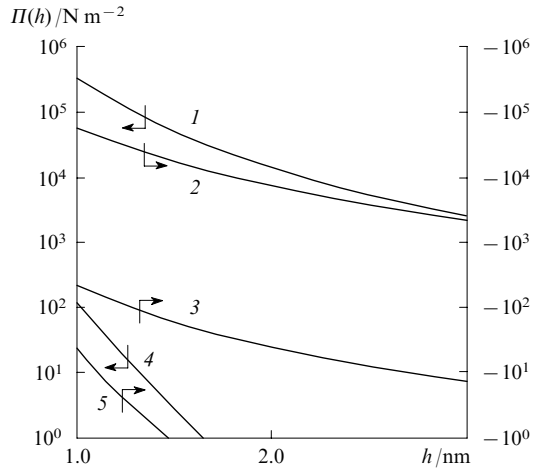


Figure 7. Various components of the disjoining pressure acting in the wetting films of pentanol solution in pentane on water surface plotted *vs.* film thickness.
Contribution related to the interaction between the adsorbed monolayer of dipole molecules and its images (*1*); molecular component calculated using published data [45] (*2*); adsorption component calculated using the constants of the interaction between pentanol molecules and the boundary phases (taken from Ref. 55) (*3*); contribution related to excess electrostatic energy of diffusely distributed alcohol molecules (*4*); and contribution of the correlation attraction of adsorption monolayers (*5*).

much exceed other types of interaction forces including the forces of the interaction between the diffuse adsorption layers, correlation attraction forces acting between the monolayers adsorbed on the opposite sides of the interlayer and the dispersion forces (Fig. 7). However, the force of dispersion interaction dominates over the image forces in 2–3 nm and thicker films because it decreases in proportion to $\Pi(h) \sim h^{-3}$ as the film thickness decreases.

VIII. Interaction forces caused by mofidied structure of liquid interlayer

1. Treatment of liquid in a continuum approximation

The assumptions of structural differences between the liquid in the thin interlayer and in the bulk phase and of the existence of long-range surface forces due to this difference were first made by Derjaguin.[2] Later, these assumptions were repeatedly (and fruitfully) used in discussing the nature of hydration, solvation and structural repulsive forces and hydrophobic attractive forces due to deviations of various structural parameters from the corresponding values in the bulk. One of the first theoretical studies of the processes occurring in a polar solvent as a result of decrease in the thickness of the liquid interlayer was reported by Marcelja and Radic.[98] They calculated the free energy density using the Landau expansion in the order parameter and showed that the inclusion of only quadratic expansion terms (with respect to the order parameter and its gradient) permits a correct description of the exponentially decreasing repulsive forces acting between the surfaces confining the liquid interlayer provided that variations of the order parameter are small. Later, other authors interpreted the order parameter as a characteristic of the local polarisation of water.[99–102]

The idea of surface-induced polarisation of water molecules as the source of hydration forces was used by different authors.[103–106] For instance, Kornyshev and Leikin [105, 106] proposed two different mechanisms of polarisation of water molecules near the interface. One mechanism is based on consideration of the contribution of the interaction between

oppositely charged groups of one electrically neutral surface of a lipid membrane and their images in a non-polar medium separated from the membrane surface by a water interlayer.[105] Spatial correlations of water polarisation fluctuations were included using the methods of non-local elecrostatics. It was shown that lateral ordering of polar groups on the membrane surfaces plays the key role in determining the character of the interaction forces between them (Fig. 8). The other, 'chemical', mechanism of ordering of water molecules is based on the use of the Landau free energy functional and introduction of a phenomenological order parameter and inhomogeneous boundary conditions. This approach allowed differences between the states of water near the polar surface and in the bulk phase to be analysed.[106] Both mechanisms predict an exponential decrease in repulsive forces with an increase in the thickness of the water interlayer. These forces are related to the character of ordering of the polar groups on the surface of lipid membranes. Both pre-exponents and correlation lengths depend on the nature and structure of the surfaces confining the interlayer.

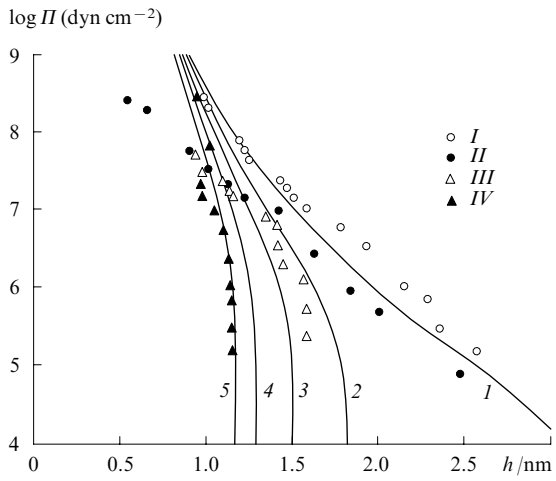


Figure 8. Comparison of theoretically predicted disjoining pressure (solid lines) calculated taking into account the forces of dispersion attraction between membranes[105] with experimental data for various lipids: POPE (*I*), egg PEt (*II*), egg PEt – Me (*III*) and SOPC (*IV*). Calculated using the following parameters: 8×10^{-21} J for Hamaker constant; 0.5 nm correlation length of water polarisation fluctuations; 0.4 nm for the distance between positively and negatively charged centres in the polar group; 0.5 nm for the distance between the dipole plane and interface; and 0.65 nm^2 for the average surface area per polar group. Theoretical curves were calculated at the following lateral correlation lengths of the polar groups: 0 (*1*), 0.2 (*2*), 0.3 (*3*), 0.5 (*4*), and 2 nm (*5*).

Mitlin and Sharma[107] studied the interaction between flat plates separated by a liquid interlayer. They combined, in the framework of the gradient theory, the Cahn approach proposed for analysing wetting transitions at an interface between two media[108] and the approach used by Marcelja and Radic.[98] The new analytical method[107] made it possible to derive asymptotically exact dependences of the disjoining pressure, free energy and order parameter profile on the interlayer thickness for an arbitrary dependence of the free energy density on the order parameter. It was found that in the general case the disjoining pressure can be described by a sum of exponents with the characteristic lengths proportional to the correlation radius in bulk liquid, the pre-exponent being dependent on both the deviation of the free energy density from the quadratic form in the expansion and on the parameters of the interaction between the liquid in the interlayer and both surfaces confining the interlayer. The interaction forces between the plates can be either attractive or repulsive. In addition, the sign of the forces changes as the interlayer becomes thinner.

A new approach to account for the interaction between the liquid and the confining surfaces in calculations of forces additional to DLVO was made by Kuklin.[109] The free energy of the system was modelled by the harmonic approximation of the Landau – Ginzburg functional, which depends on the order parameter. In addition to the free energy density expansion terms considered by Marcelja and Radic[98] and by Kornyshev and Leikin,[106] Kuklin proposed to augment the functional with functions characterising the contribution of direct short-range interaction between the near-surface layers of the liquid and the surface of the solid phase. It was shown[109] that the forces acting between surfaces of different nature can be either attractive or repulsive depending on the interlayer thickness. These forces depend on four scaling parameters, namely, two extrapolation lengths characterising the depth to which the field produced by each surface penetrates into the liquid phase and two field parameters that describe the effect of the solid surface on the properties of the nearest molecular layer in the liquid. When these parameters and the interlayer thickness are chosen appropriately, the forces show a nearly exponential dependence on the thickness of the liquid interlayer.

The approach proposed by Eriksson *et al.*[110] is conceptually similar to that developed by Marcelja and Radic. Here, the order parameter characterises the relative local increase in the number of hydrogen bonds per water molecule in the thin interlayer compared to the corresponding characteristic of the bulk phase. Eriksson *et al.*[110] considered a system comprising the water interlayer and hydrophobic surfaces confining it and expanded the free energy of the system in terms of the order parameter, minimised it and concluded that an increase in the order parameter near the hydrophobic wall causes the appearance of long-range attractive forces. The action range of such forces is much shorter than that of hydrophobic attraction reported in the literature.

Yushchenko *et al.*[111] suggested another mechanism of the appearance of hydrophobic attraction forces acting at longer distances. This involves the formation of a cavity filled with vapour of the liquid under study (or with gas) between the interacting lyophobic particles. The hydrophobic attraction forces appeared in this case are in essence capillary forces. This mechanism is possible if the wetting angle exceeds 90° and the cavity is formed only after the interacting bodies are brought into contact. According to calculations,[111] the cavity is also thermodynamically stable even in the initial appearance of a gap between the plates; however, the energy barrier to cavity formation is as high as tens of kT before the bodies are brought into contact. We believe that this is responsible for the fact that the cavity formed only after the hydrophobic surfaces have preliminarily been brought into contact in water.[112]

It should be noted that hydrophobic attraction in the case of thick interlayers was also observed without explicit cavity formation.[113] The cavity formation mechanism proposed to explain the experimental data was based on the hypothesis that the formation of a vapour-filled cavity is preceded by nucleation in the liquid interlayer. Forsman *et al.*[114] also reported a decrease in the density of the liquid near the lyophobic wall, which was associated with the presence of gaseous nuclei. Analysis of the density functional of the liquid in the thin interlayer showed that non-uniform decrease in the density across film thickness causes the appearance of attractive forces which can be much stronger than the van der Waals forces for thin films. It is noteworthy that these forces increase rather than decrease (as is traditionally accepted in the literature) in absolute value as the temperature increases.

Other mechanisms leading to appearance of long-range hydrophobic forces related to formation of cavities and microbubbles between the interacting surfaces were also proposed.[115–118]

2. The accounting for discrete structure of liquid

The studies analysed in the preceding Section treated the solvent or the liquid (*i.e.*, the liquid interlayer) in the continuum approximation. However, extensive literature is also available (see, *e.g.*, Refs 119–129) in which the discrete structure of the liquid in the interlayer is included in the framework of the model of the Lennard-Jones fluid or the model of hard spheres. Here, irrespective of the model employed, both analytical methods and computer-aided calculations allow one to reproduce the oscillating character of the interaction forces (Fig. 9) observed in experiments with the liquid interlayers of different nature (see, *e.g.*, Refs 11 and 130).

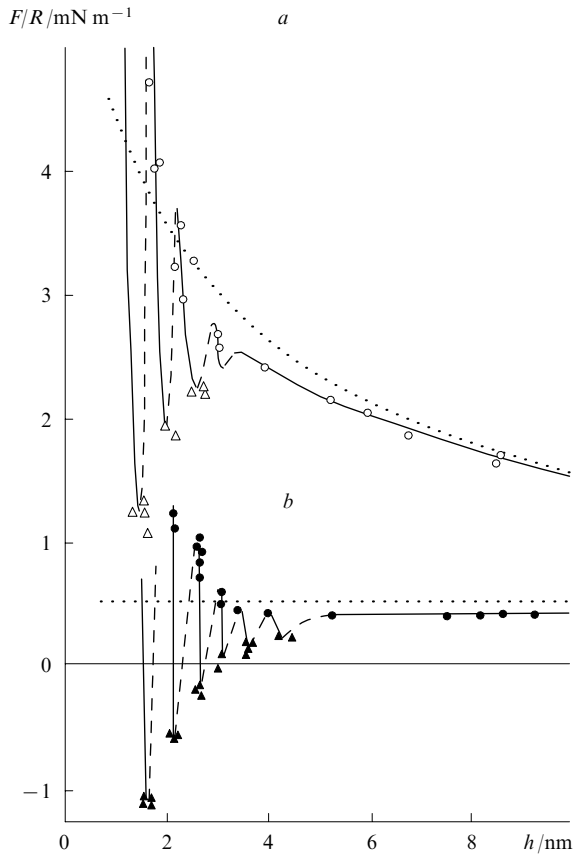


Figure 9. Oscillating forces of the interaction between mica surfaces separated by a propylene carbonate interlayer without electrolyte (*a*) and upon adding 10^{-4} mol of tetraethylammonium bromide (*b*).[130]
The circles and triangles denote the results of measurements obtained as the surfaces move away from or approach each other, respectively. The solid and dashed lines connect the experimental points. The dotted lines correspond to theoretically predicted DLVO forces with the Hamaker constant $A_{132} = 10^{-20}$ J.

The main problem in theoretical calculations of the interaction between two solid walls separated by a liquid interlayer consists of maintaining a constant chemical potential of the liquid as the interlayer thickness varies. If for Monte Carlo simulations this condition is explicitly met in the framework of the grand canonical ensemble,[119] it is hardly possible in the case of calculations based on analytical theories. There are also some exceptions, namely, approximate theories (*e.g.*, various versions of the mean field theory [120] and simple theories of integral equations for inhomogeneous systems [121]) in which the closure of the unary distribution functions is attained using the pair distribution functions of the bulk phase. However, the pair distribution functions characteristic of liquid interlayers are anisotropic in nature and therefore the results of corresponding calculations can be incorrect.[122] In this connection, a number of approaches were proposed, which permit a more correct inclusion of the anisotropy of the liquid in the thin layer.

Kjellander and Sarman [123] did their research in the framework of the theory of integral equations based on the solution of the exact Ornstein–Zernicke equation for anisotropic pair correlation function and proposed to use the Percus–Yewick anisotropic closure. Attard [124] showed that the use of a hyperchain approximation and its versions in solving the Ornstein–Zernicke equation permits a correct reproduction of the oscillating character of the forces using the model of hard spheres and the Lennard-Jones model of fluid. It should be noted that some authors (see, *e.g.*, Ref. 122) cast doubt on the correctness of the use of the hyperchain approximation for calculations of interaction forces in dense fluids with short-range potentials.

To study molecular liquids having non-spherical molecules, Chandler and Andersen [125] developed the reference interaction site model (RISM), which is a molecular analogue of the Percus–Yewick approximation of hard spheres for a simple fluid. According to the RISM model, the equilibrium correlations between molecules in the dense fluid are determined by the short-range repulsive component of the intermolecular potential. This model was used for calculating the solvation forces for liquid interlayers comprised of diatomic molecules based on the theory of integral equations.[126] The results of calculations revealed a high damping of oscillations on going from the model of hard spheres to the RISM model (Fig. 10), which allows for asymmetry of molecules of the liquid.

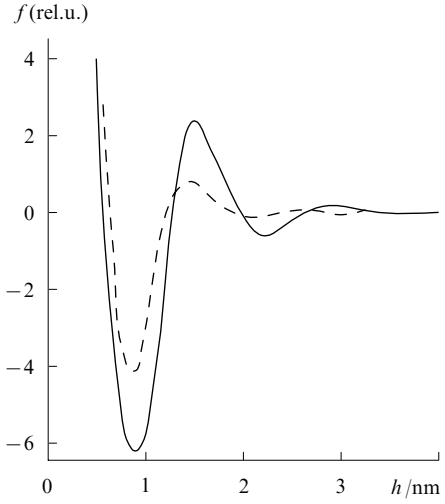


Figure 10. Reduced force of the interaction between two interfaces plotted *vs.* reduced distance between them for fluids with a reduced density of 0.3584:[126] the dashed line corresponds to a diatomic fluid with an interatomic distance of 0.6σ (σ is the atom diameter) and the solid line corresponds to the fluid of hard spheres (sphere diameter $1.2146\,\sigma$).

3. Phonon mechanism of surface forces

As mentioned above, Derjaguin, Churaev and their scientific school (see, *e.g.*, a monograph [2] and articles [131, 132] and references cited therein) repeatedly used the idea of the structural

difference between the liquid in the thin interlayer and in the bulk phase in discussing the stability of certain colloidal systems. However, in these studies the structural differences meant static deviations of the local polarisation, intermolecular distances and orientations of molecules relative to interfaces in the interlayer from the corresponding bulk characteristics. Thus, additional surface forces appeared in the system were associated with the overlap of the structure-modified boundary layers in the film.

Another approach to the problem of structuring of the liquid in a system of restricted dimension is based on consideration of the dynamic structure of the liquid.[133–138] Here, the dynamic structure of the liquid is treated as the set of vibrational and rotational motions of all atoms and molecules in the liquid confined within a thin interlayer. The dynamic structure of liquid strongly depends on both the interlayer thickness and the surface-induced changes in the intermolecular interactions. The dynamic structure differences between bulk liquid and the liquid in the state of restricted dimension manifest themselves in, *e.g.*, the absorption spectra of the liquid in the corresponding state (Fig. 11).

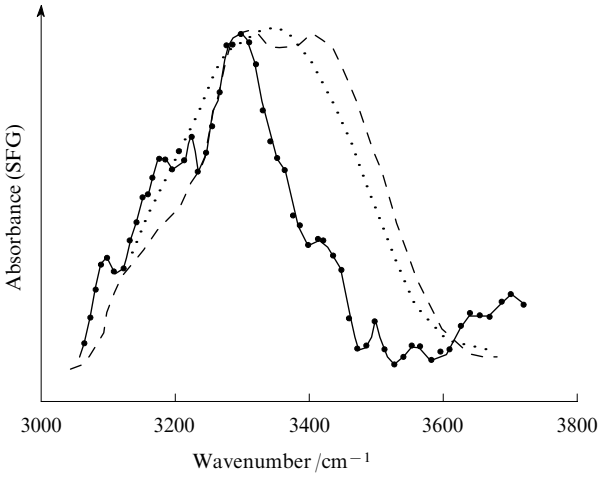


Figure 11. IR spectra of ethanol in the region of OH stretching vibrations.[136] The dotted curve is the spectrum of the bulk liquid and the dashed line is the spectrum of ethanol interlayer (25 nm thick) separating two fluorite plates. The points connected by the solid line are the sum-frequency generation (SFG) spectrum of ethanol–air interface.

Clearly, these two types of structuring in the thin liquid interlayer complement rather than exclude each other. Therefore, understanding of the character of molecular motions in thin layers of molecular liquids is important for the description of various properties of liquid films and the development of detailed mechanism of structure-induced surface forces.

Generally, molecular motions in bulk liquid are anharmonic. However, if the observation time is short compared to the characteristic relaxation times of the corresponding type of motion [139, 140] or the region under consideration is small,[141] the complex picture of intra- and intermolecular motions in the liquid can quite correctly be represented by a set of collective vibrational states, or normal modes, associated with acoustic waves in the liquid medium. The fruitfulness of this approach to the description of many phenomena in liquids has been well documented. The most important studies are based on the normal-mode approach, *e.g.*, the description of solvation dynamics,[142] calculations of diffusion constants [143] and absorption spectra [144] and the description of the nature of the glassy state.[145]

The approach developed in our studies [133–138] also treats the intra- and intermolecular motions in liquids as harmonic processes characterised by corresponding characteristic times and normal-mode spectra. Each normal mode is determined by the parameters of an oscillator involved in a vibrational (rotational) motion and by its interaction with neighbouring oscillators. The probability of realisation of a normal mode of an arbitrary oscillator depends on the ratio of the liquid interlayer thickness (h) to the free path length (L) of phonon corresponding to the normal mode in question, being equal to $\exp(-h/L)$. Because of the normalisation condition for the total number of degrees of freedom at each time instant any oscillator in the film is either involved in collective vibration of the entire ensemble of oscillators propagating normal to the interface or oscillates at a frequency characteristic of the bulk liquid and determined by both the internal force field of the whole molecule and the effective average field produced by the surrounding molecules.

The dynamic structure differences between bulk liquid and the liquid in the thin film are due to the fact that the free path lengths of phonons, orientations of molecules relative to one another and to interfaces and intermolecular distances in the thin interlayer are changed due to the interaction between the molecules and the surface. In addition, the surfaces that bound the thin liquid interlayer induce changes in the conformational states of molecules. All these factors affect the normal-mode spectrum and give rise to an additional contribution to the film free energy, which depends on the interlayer thickness and is given by

$$F^E = \sum_j \int_0^\infty kT \ln \frac{\mathrm{sh}(\hbar\omega/2kT)}{\mathrm{sh}(\hbar\omega_{j0}/2kT)} Z_j(\omega) \exp\left(-\frac{h}{L_j(\omega)}\right) \mathrm{d}\omega \,, \qquad (4)$$

where ω_{j0} are the eigenfrequencies of corresponding molecular vibrations in the bulk liquid, $Z_j(\omega)$ is the thermodynamically averaged density of vibrational states determined from the dynamic matrices of instantaneous film states and L_j is the free path length of photons for the jth type of oscillators. Summation is carried out over all types of oscillators (j) associated with branches of the dispersion curve for the liquid interlayer. The product $Z_j(\omega)\exp(-h/L_j(\omega))\,\mathrm{d}\omega$ is the number of vibrational modes of the jth type per unit surface area of the liquid interlayer with allowance for finite relaxation time of the vibrational mode. For linear waves the free path lengths of phonons are given by the following transcendent relationship

$$L_j(\omega) = v_j(\omega)\tau_0 \left[\int_{L_j(\omega)} \rho(z) \exp\left(\frac{U(z)}{kT}\right) \mathrm{d}z \right]^{-1}, \qquad (5)$$

where $v_j(\omega)$ is the absolute value of the group velocity of collective vibration at the frequency ω, τ_0 is the average lifetime of oscillators between thermal jumps in the bulk liquid, $\rho(z)$ is the linear density of oscillators along the normal to the film boundaries and $U(z)$ is the excess (compared to bulk liquid) potential barrier to thermal jumps due to the interaction between the oscillators and the boundary phases. Integration is carried out along the chain of oscillators. In the harmonic approximation we neglected the phonon–phonon interaction. In this case the contribution of collective vibrational excitations to the disjoining pressure in the film is given by [133, 135]

$$\Pi(h) = \sum_j \int_0^\infty \left(-\frac{\mathrm{d}K_j}{\mathrm{d}h} - \frac{K_j h}{L_j^2(\omega)} \frac{\mathrm{d}L_j(\omega)}{\mathrm{d}h} + \frac{K_j}{L_j(\omega)} \right) \times \exp\left(-\frac{h}{L_j(\omega)} \right) \mathrm{d}\omega \,, \quad (6)$$

where

$$K_j = Z_j(\omega)\, kT \ln \frac{\mathrm{sh}(\hbar\omega/2kT)}{\mathrm{sh}(\hbar\omega_{j0}/2kT)} .$$

The contribution to the disjoining pressure described by expression (6) is due to collective vibrational excitations (phonons) in the film; therefore, it was called the phonon component of the disjoining pressure.

From relations (4) and (6) it follows that the excess free energy and the disjoining pressure are calculated as the sums of the contributions of different types of phonons. The signs of the summands are determined by the ratio of the mode frequencies in the film to the corresponding frequencies in the bulk liquid. The magnitudes of the summands are determined by not only the frequency difference, but also the density of phonon states in the nanofilm, the latter contribution being decisive.

Numerical analysis revealed great differences (several orders of magnitude) between the contributions of different types of oscillators. Usually, only a few less localised optical modes essentially contribute to the total disjoining pressure. According to relation (5), the contribution of a certain type of oscillators will first of all be determined by the coupling between these oscillators (both within the same molecule and within neighbouring molecules), which affect the group velocity of phonons. Calculations using the model of coupled oscillators [135–137] and the force constants of intermolecular interaction characteristic of associated liquids showed that in some cases the contribution of the phonon component of the disjoining pressure to stability of the liquid interlayer can be much larger than that of molecular forces.

From expressions (4) and (6) it follows that the contributions of different oscillators to the disjoining pressure and to the free energy of the film depend exponentially on the film thickness and also implicitly depend on the thickness (this is expressed through the dependence on the free path length of phonons and on the density of vibrational states).

Three terms in square brackets in Eqn (6) describe three different types of the disjoining pressure – film thickness interrelations. The third term dominates in the case of thick films.¶ Here, the phonon mechanism provides an exponential decrease in the disjoining pressure as the film thickness increases. In a broad range of thicknesses the phonon component of the disjoining pressure is usually described by the sum of several exponentially decreasing terms. This theoretically predicted type of dependence is in good agreement with numerous experimental data (see, *e.g.*, a monograph [2] and references cited therein).

The first term plays the decisive role for thin films where the discrete structure of the liquid should be taken into account. This discreteness leads to inhomogeneous distribution of molecules across the interlayer due to both the interaction of the liquid with the confining phases and the excluded-volume effect. The last-mentioned factor causes oscillations of the local density across the film thickness. This leads to oscillations of the force constants in the dynamic matrix, which in turn initiates oscillations of the density of vibrational states and, as a result, oscillations of the excess free energy and disjoining pressure. The use of the phonon mechanism for analysis and description of solvation forces in thin films [138] made it possible to explain many details of experimental observations, such as anharmonicity of oscillations, changes in the oscillation period with variation of the film thickness and similar oscillations periods for different liquids. Calculations [138] also clarified the mechanism of disappearance of such oscillations near rough surfaces and in wetting films.

However, it should be emphasised again that the approach under consideration predicts oscillations of forces in thin films with respect to some exponentially decaying function of the film thickness rather than zero. The role of the decaying function is played by the third term in square brackets in Eqn (6).

Eventually, at intermediate thickness of the liquid interlayer the contribution of the oscillations of the density of collective vibrational states can be neglected, but the changes in the mean free path of phonons with variation of the film thickness cannot be ignored. Here, a significant role is played by the second term in square brackets in Eqn (6). The magnitude and sign of this term are determined by the derivative, $\mathrm{d}L/\mathrm{d}h$, which mainly depends on the character of the interaction between the oscillators and the phases confining the film.

The effect of the character of the interaction between the liquid and the confining phases on the magnitude and sign of the phonon component of the disjoining pressure deserves particular attention. This effect is first of all due to significant changes in localisation of normal modes near interfaces owing to the interaction between the oscillators and the confining phases. For instance, the free path of phonons increases near the lyophilic surface due to an increase in the energy barrier to thermal jumps and, hence, a significant increase in the relaxation time of the entire ensemble of the oscillators involved in collective vibrations. On the contrary, the energy barrier to thermal jumps decreases near the lyophobic surface, which leads to higher mobility of the molecules near corresponding interface.

Figure 12 shows the normalised relaxation times of a linear ensemble of oscillators in a liquid film plotted *vs.* film thickness for different constants of the van der Waals interaction between the molecules and the phases confining the film. As can be seen, the effect of the lyophobic substrate manifests itself at much longer distances provided equal, in absolute value, interaction constants. However, the effect of the hydrophobic substrate is not restricted to shortening of the relaxation time of the ensemble of oscillators, but also manifests itself in significant strengthening of intermolecular interactions (*e.g.*, marked strengthening of hydrogen bonds in aqueous media near the hydrophobic surface [146]). In turn, the latter factor causes an increase in the group velocity of phonons associated with the O–H vibrations in water molecules. Therefore, for not too thick films the $L_j(\omega)$ parameter, which is sensitive to the interaction of oscillators with the film-confining phases, can vary over a rather wide range as the properties of the confining phases vary only slightly. This was found experimentally for water interlayers separating various lipid membranes.[147, 148] In the case of inhomogeneous boundary conditions, the free path lengths should fluctuate along the interface; however, these variations of $L_j(\omega)$ can hardly be measured experimentally because in actual experiments we usually measure the integrated characteristics.

Yet another factor affecting the magnitude and sign of the phonon component of the disjoining pressure is the orientation effect of substrate on the molecules in the near-wall layers of the liquid. As a result, the frequency distribution of the density of vibrational states changes significantly. Apparently, this distribution is a consequence of configuraton averaging over

¶ Thick films are the films for which the dependence of L and K on the film thickness can be ignored.

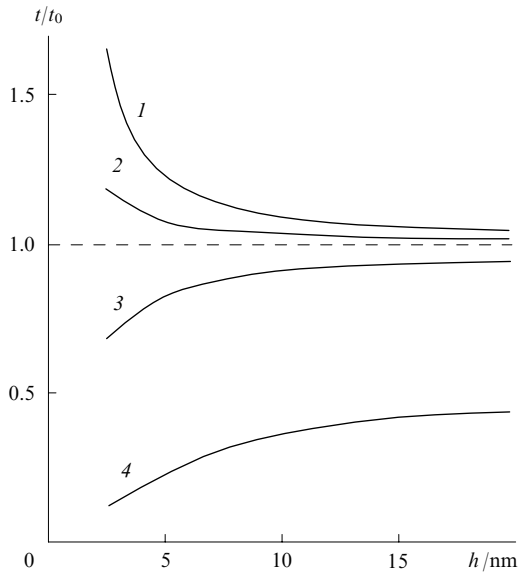


Figure 12. Relaxation time ratio of a linear molecular chain in symmetrical liquid film (t) and in bulk liquid (t_0) plotted *vs.* film thickness at different constants of dispersion interaction between the liquid molecules and the boundary phases: 1×10^{-49} (*1*), 2×10^{-50} (*2*), -2×10^{-50} (*3*) and -5×10^{-50} J m^{-3} (*4*).

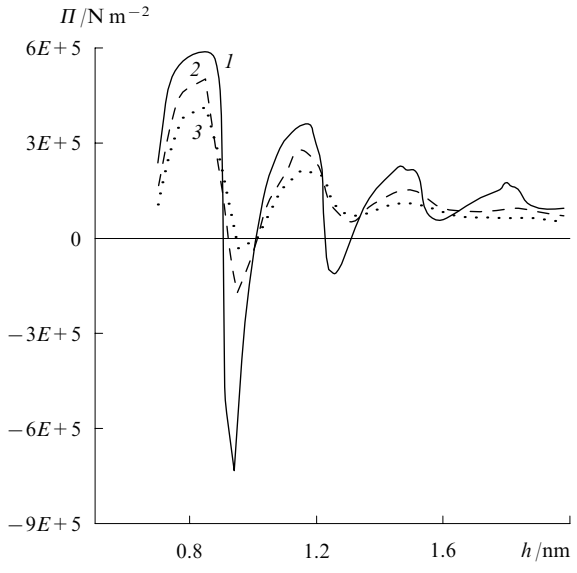


Figure 13. Damping of oscillations of the disjoining pressure with an increase in temperature: T = 20 (*1*), 50 (*2*), 70 °C (*3*). Calculated using the coupled oscillator model.[137]

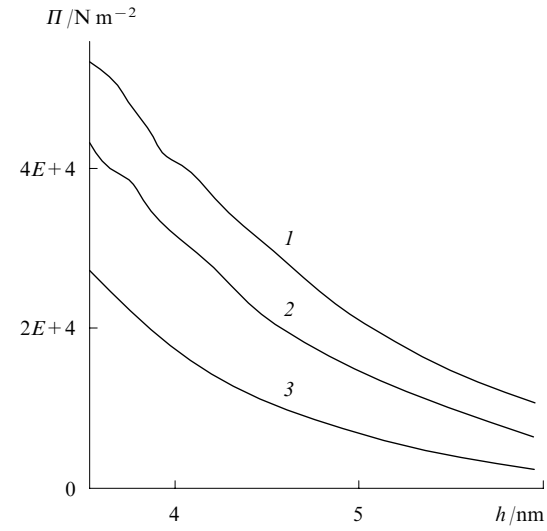


Figure 14. Changes in the non-oscillating portion of the disjoining pressure isotherm with temperature: T = 20 (*1*), 30 (2), 50 °C (*3*). Calculated using the coupled oscillator model.[137]

all possible orientations of the molecules in chains (corresponding to instantaneous static structure) with allowance for the statistical weight of each state. For instance, the orientations of molecules and their fragments (oscillators) relative to one another in bulk liquid are only determined by intermolecular interactions. In a liquid film, the field of surface forces of the substrate superimposes the field of intermolecular forces and thus causes redistribution of the statistical weights of different orientations.

We have shown that static structuring even in the first layer of a liquid film strongly affects the dynamic structuring of liquid in the whole film. Therefore, changes in the wettability of the interface resulting in redistribution of the density of vibrational states over frequencies can induce changes in not only the magnitude, but also the sign of the phonon component of the disjoining pressure. In the framework of the phonon mechanism we explained the experimentally observed effect of temperature on the oscillating and exponentially decreasing forces (to a first glance the effect is somewhat contradictory). For instance, theoretical analysis showed [134] that if the parameters of the dynamic matrix are independent of temperature (neglect of thermal expansion and changes in the state of the surface), the increase in the temperature causes damping of oscillations (Fig. 13) and a decrease in the magnitude and correlation lengths for the exponentially decreasing forces (Fig. 14).

The results of molecular dynamics calculations [149] and measurements of oscillating forces reported by Christenson and Israelachvili [150] (they studied the interaction between mica cylinders separated by an octamethylcyclotetrasiloxane interlayer in the temperature interval 14–40 °C) and by Nakada *et al.*[151] (for the interaction between the Si_3N_4 and highly oriented pyrolytic graphite surfaces separated by interlayers of normal alcohols in the temperature range 25–60 °C) are in agreement with the results of theoretical studies indicating a slight damping of oscillations with an increase in temperature.

It is important that the decrease in the disjoining pressure with an increase in temperature, which is theoretically predicted for thick films in the framework of the approach we have developed (see Fig. 14), was repeatedly observed in experiments. Moreover, weakening of the surface forces in water interlayers with an increase in temperature was for long treated as a characteristic property of structural forces and interpreted as a result of partial breakdown of the structure (*e.g.*, disruption of the network of hydrogen bonds).[2]

The mechanism we have proposed does not contradict this interpretation and provides a better insight into the physical sense of the structural changes occurring in the liquid with an increase in temperature. In particular, an increase in temperature is accompanied by a decrease in the ratio of the energy of hydrogen bonds to kT; therefore, an increase in the frequency of thermal jumps is accompanied by redistribution of the density of vibrational states over frequencies.

However, the approximation of constant boundary conditions under temperature variation is not always valid. For instance, changes in the boundary conditions with an increase

in temperature can cause significant changes in the density of vibrational states for the interlayers bounded by bilayers, surfactant-coated surfaces, *etc*. This effect is most pronounced near the phase transition temperature in the surface layers. Calculations and theoretical analysis revealed [134] the possibility of strengthening rather than weakening of exponentially damping forces. Apparently, it is changes in the density of vibrational states that are responsible for the experimentally observed swelling of dipalmitoylphosphatidylcholine [147] and egg phosphatidylcholine [152] bilayers on heating above the melting point.

Thus, the phonon mechanism of surface forces is based on consideration of changes in the frequency spectrum of the liquid upon restriction of its dimension, which was repeatedly observed in the model and real experiments (see, *e.g.*, Refs 146 and 153–155). This mechanism provides better insight into the dynamic processes occurring under limitation of the characteristic sizes of the liquid medium and makes it possible to assess the role of the interaction between the liquid interlayer and the confining phases in the formation of the dynamic structure of the liquid. It should be noted that this mechanism allows one to describe the oscillating (solvation) forces and various manifestations of the exponentially decreasing forces, such as the hydration-induced repulsion between hydrophilic surfaces and hydrophobic attraction.

4. Forces associated with the presence of long-chain surfactants and high-molecular-mass polymers in a liquid interlayer

There is yet another type of forces, which is ignored by the DLVO theory but has a great practical value for colloidal and disperse systems. These are forces associated with the presence of high-molecular-mass polymers and long-chain surfactants in a thin liquid interlayer. In this case the non-DLVO forces are mainly determined by the character of the interaction between polymers (long-chain surfactants) and the surfaces of particles separated by the liquid interlayers. Theoretical analysis of the forces arising in such systems involves consideration of three different cases, namely, reversible and irreversible adsorption of polymers on particles and the 'no adsorption' case.

Determination of the magnitude, sign and action range of forces requires the inclusion of (i) character of the polymer–solvent interaction, which is determined by the Flory–Huggins interaction parameter; (ii) degree of surface coverage with the polymer, (iii) evaluation of the proportion of polymer segments contacting the surface and the adsorption energy per segment and (iv) estimation of the thickness of the adsorption layer and the concentration of the polymer in solution. Finally, the size ratio of colloidal particles to polymer molecules should also be taken into account.

De Gennes [156] and Fleer *et al.*[157] proposed models that describe the interaction between large particles coated with a polymer irreversibly adsorbed from solution. The approach by de Gennes is based on scaling theory methods, being restricted to the case where the polymer occupies a fraction of the available adsorption sites on the surface of a particle and the adsorption energy of each polymer chain is high. The second approach uses the self-consistent field theory and is not restricted to low adsorptions. Both methods are applicable to the case where the phases confining the interlayer approach each other rapidly compared to the rate of establishment of the adsorption equilibrium on the surface but slowly compared to the rate of establishment of the conformational equilibrium in the adlayer. Various types of forces can appear in this case. At low polymer concentrations in a good solvent, bringing the surfaces closer together at constant surface coverages with the polymer causes the appearance of repulsive forces that decrease in proportion to the inverse cube of the separation between the surfaces (the interlayer thickness should be comparable with the doubled thickness of the adsorption layer).[158] At high polymer concentrations or under chemisorption conditions, the interaction between surfaces will have another character. An increase in the polymer concentration in solution leads to an increase in the interface coverage and to formation of brush structures (polymer molecules are arranged normal to the interface) under chemisorption conditions. In the latter case the elastic energy of the initially stretched chains in the brush structures decreases as the interlayer thickness decreases. This provides a negative contribution to the disjoining pressure in the film (attraction), which decreases in proportion to $h^{3/4}$. In addition, the osmosis contribution, which includes the change in the entropy of mixing and solvation energy of the polymer segments, and steric effects due to limitation of the number of possible conformations of the polymer molecules confined within the thin interlayer cause the appearance of repulsive forces that increase in proportion to $h^{-9/4}$ as the interlayer thickness decreases. Thus, the sign of the resultant force is determined by competition of the factors mentioned above and the interlayer thickness normalised to the thickness of the adlayer.[158] Numerous experimental data (see, *e.g.*, Refs 159–161) revealed the key role of the steric factor.

It should be noted that the idea of elastic repulsion between the surfactant and polymer adsorption layers was proposed by Rehbinder [162] in discussion of the effect of surfactants and polymers on the stability of colloids long before elaboration of theories of steric stabilisation. Recently, Huang and Ruckenstein [163] showed that changes in the polymer concentration over a wide range can induce a sequence of (re)stabilisation–destabilisation processes. For instance, on the one hand, a considerable increase in the polymer concentration causes an increase in adsorption of the polymer on the surface of particles and thus increases steric repulsion between them. On the other hand, it induces aggregation of the polymer in solution resulting in the appearance of attractive forces due to depletion forces (see below).

As to reversibly adsorbable polymers (usually, homopolymers), both theories, by Fleer [157] and by de Gennes,[156] predict attraction of the surfaces owing to bridging bonding through polymer molecules under equilibrium approach and free desorption of the polymer from the interface.

The effect of non-adsorbable polymers on the interaction between flat plates and spherical particles has been a subject of extensive research (see, *e.g.*, Refs 164–174). In this case, the sign and magnitude of the interaction depend on the thickness of the liquid interlayer, the shape of particles, the charge state of polymer molecules and the ratio of the gyration radius of the polymer to the radius of the colloidal particle. For instance, if macroscopic surfaces immersed in a liquid approach each other and the interlayer thickness is smaller than the length of a free polymer molecule, the concentration of the polymer in the interlayer decreases compared to its concentration in the bulk phase.[165–168] The osmotic pressure produced in this case causes the appearance of attractive forces (the so-called 'depletion forces'). These forces considerably increase (i) as the polymer concentration increases,[165, 167–168] (ii) on going from spherical polymer molecules to polymer chains or asymmetrical molecules,[165, 166] (iii) in the case of charged polymer molecules [166, 168] and (iv) if the particle–solution interface is covered with an adlayer of a polymer having a higher molecular mass compared to that of the free polymer.[167] Contrary to this, for thick interlayers bringing the surfaces closer together leads to an increase in the concentration of free polymer in the interlayer due to displacement of the solvent, which in turn causes the appearance of repulsive forces.[167, 168] It should be noted that the repulsive forces at thick interlayers are always weaker than attractive forces at thin interlayers. Nevertheless, an increase in long-range repulsion with an increase in the concentration of a charged polymer at polymer

concentrations >1 vol.% favours stabilisation of suspensions.[168]

The methods and approaches mentioned above are applicable to macroscopic colloidal particles. The interaction of small (compared to the gyration radius of the polymer) particles was also studied.[169–171] The polymer was treated as an ensemble of monomer units involved in manybody interactions. If the particle size is comparable with the gyration radius of the polymer, the theoretical analysis of the interactions in question is much more complicated.[172–174] For instance, Tuinier and Fleer[173] used the notion 'depletion thickness' in the framework of the mean-field theory and derived an analytical expression for calculating the potential of depletion forces acting between two disperse particles. This method was also used[174] in a study of the effect of the polymer chain length, bulk concentration and solubility on the polymer segment distribution density across the liquid interlayer and on the magnitude of the depletion forces. It was pointed out that if the disperse particles, polymer molecules and the correlation length in the polymer solution are comparable, the actual magnitudes of depletion forces much exceed those reported in the literature.[165–168] Thus, for nanodispersions the destabilising role of depletion forces is much more significant than for microdisperse systems.

Summing up, it should be noted that poor understanding of all specific features of the interactions between disperse particles in solutions of polymers or long-chain molecules is to a great extent due to a non-equilibrium character of the approach of the surfaces of particles in polymer solutions.

IX. Conclusion

Usually, the classical DLVO theory permits reliable calculations of the destabilising effects of electrolytes in classical colloidal and disperse systems characterised by a particle size of 100 nm and more and weak particle–dispersion medium interaction.

However, modern nanotechnology deals with much more complex objects. The use of nanocolloidal and nanodisperse systems comprising solid (or liquid) particles comparable in size with not only the Debye screening length, but also the thickness of the liquid interlayer between them requires the introduction of significant corrections for the curvature of the particle surfaces in calculations of the van of der Waals and ionic electrostatic interactions and simultaneous inclusion of the specific features of the charge distributions along the surface of particles and across the interlayer separating them.

One of the key problems in nanotechnology is reliable manipulation of the size and properties of the surface of nanoparticles. This involves the use of multicomponent dispersion media characterised by strong interaction between particles and the medium (when it possesses lyophilic or lyophobic properties). This significantly reduces the efficiency of the classical theory in prediction and control of the stability of complex nanocolloidal and nanodisperse systems.

The author hopes that this review of modern theoretical approaches to calculations of surface forces of different nature acting in nanoscale liquid interlayers will help researchers and nanotechnologists to reasonably choose procedures for, and regimes of, treatment of systems containing nanoobjects in order to attain the desired results.

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