

Structure of Water in Thin Layers[†]

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This paper considers the physical behavior of the boundary layers of water near the hydrophilic and hydrophobic surfaces. The overlapping of these layers leads to the generation of structural forces of repulsion, in the first case, and those of attraction, in the second. Inclusion of structural forces in the DLVO theory and the theory of heterocoagulation allows one to explain the results of measurements of contact angles for water solutions at different concentrations, pH values, and temperatures. The maximum influence of structural effects on colloid stability, wetting phenomena, and liquid flow in thin pores is to be expected in two extreme cases—that of a highly lyophobic system and that of a highly lyophilic one.

The successes achieved by the DLVO stability theory and the heterocoagulation theory, based on taking into account only the electrostatic and the molecular components of disjoining pressure, have to a considerable extent detracted attention from the effects caused by the structural peculiarities of the polymolecular liquid layers adjacent to lyophilic surfaces. Without considering and taking into account the arising "structural" forces, it would be impossible to explain not only the stability of lyophilic colloids and wetting films but also such phenomena as a reduced dissolving power of boundary layers, playing a fundamental part in the reverse-osmosis separation of solutions and the swelling of clays, as well as the existence of nonfreezing water in porous bodies.

The overlapping of structurally modified boundary layers, when an interlayer becomes thinner and the surfaces approach one another, gives rise to the appearance of the third component of disjoining pressure—structural forces.¹

The structural component of the disjoining pressure of water interlayers had been discovered for the first time in the 1930s by Derjaguin and Kussakov in their experiments on wetting films.² Still more definite results were obtained by Derjaguin and Zorin in 1950s in the course of determination of the isotherms of polymolecular adsorption of water vapor and the vapor of other polar liquids.³ A later analysis has shown⁴ that these isotherms, as those obtained subsequently by Kitchener and Pashley,⁵ cannot be explained by the joint effect of molecular and electrostatic forces.

The existence of the boundary layers of water possessing modified properties was indicated by the experiments carried out by Zachavaeva and Derjaguin, who had detected an enhanced viscosity of thin interlayers;⁶ by the experiments of Derjaguin and Krylov, who had established their reduced dielectric permittivity;⁷ and by the experiments on detection and investigation of thermosmosis.^{8,9} The birefringence of water interlayers in Na montmorillonite, detected by Green-Kelly and Derjaguin,¹⁰ is the most direct proof of a special, ordered structure of water. All these results enabled one to estimate the thickness of the boundary layers of water with a peculiar structure to be close to 100 Å.

In spite of the phenomenon being physically obvious, analytical expressions for the dependence of structural forces on the interlayer thickness were obtained only for very simplified models of liquid. This is associated with the difficulties inherent to the theory of the liquid state in general and the theory of liquid boundary layers in

particular. Therefore, it has so far been impossible to predict theoretically the peculiarities of the structural state of the boundary layers and the radius of action of structural forces, depending on the properties of the liquid and the state of the surface which it interacts with. This would be especially difficult to do for water, whose molecules interact simultaneously with dispersion forces and dipole forces and through the hydrogen bonds. The numerical calculations carried out by the Monte Carlo method and molecular dynamics¹¹⁻¹⁸ pretend to be some approximation of these properties. In view of technical difficulties, these calculations are, as a rule, more reliable for the layers having a thickness of a few molecular diameters. Yet just in this case, not the surface long-range forces but the short-range forces depending on the discrete structure of liquid prevail. As a result, the calculations give the forces oscillating as distance varies, with a period equal to the diameter of molecules. These forces correspond to the short-range, one-dimensional order of the arrangement of the molecules of liquid near the surface of an adjacent phase. In distinction from the long-range structural forces, those forces should be called microstructural. In the case

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of contact with microrough solid bodies or gases, the oscillations corresponding to those forces must decay rapidly with distance.

Much larger successes have been achieved in the direct experimental investigation of the structural long-range forces.¹⁹⁻²³ The arising difficulties are associated with the necessity of extraction of the isotherm of structural forces from the experimental isotherm of disjoining pressure, which contains also the molecular and electrostatic components. The accuracy of the determination of the isotherm of structural forces is limited mainly by the accuracy of calculation of electrostatic forces in the range of small interlayer thicknesses. As is known, these calculations require not only accounting for changes in the charge and potential of surfaces when these approach one another but also accounting for modified dielectric and dissolving properties of thin boundary layers²⁴ as well as for image forces and the discreteness of charges distribution.²⁵

In this connection, the analysis of the properties of the boundary layers examined by independent methods would be of interest. The nature of the solid substrate must substantially influence the formation of a special structure of the boundary layers of water. The interaction of water with the surface may be enhanced by the presence of atoms that are able to form hydrogen bonds and charged sites. Hence a correlation between the hydrophilicity of the surface and variation in the structure of the boundary layers should exist. Thus, for example, in the case of a hydrophilic surface the structure of the boundary layer should be essentially different from that on a hydrophobic substrate, because of the absence of hydrogen bonds between water and the surface in the later case.

Let us examine such a correlation between the surface hydrophilicity and the structural forces by using, on one hand, the results of measurement of contact angles and, on the other, their theoretical estimation on the basis of Frumkin-Derjaguin's theory of wetting.^{26,27} As is known, this theory establishes a relationship between the values of an equilibrium contact angle, θ_0 , and the isotherm of the disjoining pressure of wetting films, $\Pi(h)$:

$$\cos \theta_0 = 1 + (1/\sigma) \left[\int_{h_0}^{\infty} \Pi(h) dh + \Pi_0 h_0 \right] \quad (1)$$

where σ is the surface tension of liquids, h_0 is the thickness of a wetting film in equilibrium with the bulk liquid, and Π_0 is the disjoining pressure corresponding to that thickness. For instance, Hough and White had formerly applied this equation to calculating, on the basis of the macroscopic theory of molecular forces, the contact angles of liquid alkanes on a Teflon surface.²⁸

In the case of water, aside from the molecular forces, the effect of the electrostatic and the structural component will have to be taken into account. We have already

Table I. Influence of the Concentration of KCl Solution on the Contact Angles on Quartz

C, mol/l.	$-\Psi_1$, mV	$-\Psi_2$, mV	params of the $\Pi_s(h)$ isotherm, dyn/cm ²		contact angle, θ_0
			K	K_0	
10^{-5}	150	55	2×10^7	3×10^9	$4^\circ 30'$
10^{-4}	125	25	2×10^7	3×10^9	5°
10^{-3}	100	25	0	3×10^9	8°
10^{-2}	75	20	0	0	12°
10^{-1}	35	0	-2×10^7	2×10^9	12°
1	25	0	-2×10^7	0	16°

Table II. Influence of the pH Value of the HCl-KCl-KOH Solution^a on the Contact Angle on Quartz

pH	$-\Psi_1$, mV	$-\Psi_2$, mV	params of the $\Pi_s(h)$ isotherm, dyn/cm ²		contact angle, θ_0
			K	K_0	
10	100	25	0	0	$5^\circ 30'$
8	100	20	0	0	7°
7	75	20	0	0	12°
6	75	15	0	0	13°
5	65	0	0	0	14°
2	0	0	-2×10^7	0	15°

^a At $C = 10^{-2}$ mol/L.

published the first results of such a calculation of the contact angle for water on the quartz surface.²³ The values of the contact angle of around 5° , in good agreement with the experimental data, were obtained by using the known values of the potentials of quartz (Ψ_1) and film (Ψ_2) surface, the spectral characteristics of water and quartz, and the known parameters of the isotherm of structural forces. Such an agreement could not have been obtained without taking into account the structural forces.

Now let us determine which suppositions on the dependence of the structural forces on the concentration and pH of electrolyte solutions have to be adopted, for the purpose of obtaining agreement with the experimental values of the contact angles,²⁹ given in the last columns of Tables I and II.

The contact angles were calculated with eq 1 by using the known isotherm of molecular forces, $\Pi_m(h)$, for water films on quartz²³ and the isotherm of electrostatic forces, $\Pi_e(h)$, calculated from Devereux and de Bruyn's tables on the basis of the values of Ψ_1 and Ψ_2 , as given in Tables I and II. For definition of the values of Ψ_1 , we used the results of electrokinetic measurements, while for the values of Ψ_2 , the results of measurement of the potentials of the solution-gas interfaces.²³ The parameters of the isotherms $\Pi_s(h)$ of structural forces, K and K_0 , were used as the fitting ones, for the purpose of attaining agreement between the values of θ_0 calculated from the total $\Pi(h)$ isotherm and the experimental ones. For the isotherm of structural forces we have used the following equation:

$$\Pi_s(h) = K \exp(-h/l) + K_0 \exp(-h/l_0) \quad (2)$$

where $l = 20$ Å and $l_0 = 2.5$ Å.²³ The values obtained for these parameters are given in Tables I and II.

As appears from Table I, good agreement between theory and the experimental data is obtained if we assume that as the electrolyte concentration increases, the structural repulsion forces ($K > 0$) at first decrease and then, at $C = 10^{-2}$ mol/L, do not show up noticeably ($\Pi_s = 0$), whereas at $C \geq 10^{-1}$ mol/L, these forces reverse their sign:

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thereby causing not the repulsion of the film surfaces but their attraction ($K < 0$). This is also confirmed by the data of Table II. From this table, it follows that at the solution ionic strength of around 10^{-2} mol/L (with the exception of pH 2), it would be sufficient to use only two components of disjoining pressure, $\Pi_m(h)$ and $\Pi_e(h)$, for explaining the dependence of the contact angle on the pH values.

Both the state of the substrate and its interaction with the aqueous solution determine the character and the degree of modification of the boundary layers and, hence, the value and sign of structural forces. The latter, in turn, determine the value of the contact angle, which is characteristic of the substrate hydrophilicity. For instance hydrophobization may be considered as a treatment which causes a reversal of the sign of structural forces. The direct measurements by Israelachvili and Pashley³⁰ have proved the appearance of the forces of structural attraction in the case of hydrophobic surfaces instead of those of structural repulsion in the case of hydrophilic surfaces. The loss of stability of water interlayers between hydrophobic surfaces has also been confirmed by Shchukin and Yaminsky.³¹

The formation of large contact angles cannot be explained without including the structural forces in the calculation of wetting. For instance, Zorin et al.³² and Whalen et al.³³ have experimentally detected an increase in the contact angle of water up to about $40-60^\circ$ as temperature is raised up to around $70-80^\circ\text{C}$. This may be explained only by a marked decrease in the forces of structural repulsion due to thermal destruction of the boundary layers. As is known, the molecular and electrostatic forces are relatively weakly sensitive to temperature.

As follows from the numerical experiments carried on by the methods of Monte Carlo and molecular dynamics¹¹⁻¹⁸ near the hydrophobic walls water dipoles are oriented parallel to the surface. The effect of orientation extends a considerable distance and is the long-range one. Such an arrangement of water molecules is conducive to a decrease in density near the walls and facilitates the mobility of molecules in the tangential direction, which may be interpreted as a reduction in the viscosity of boundary layers. Macroscopically, this effect may show up as the slip of liquid over the lyophobic substrate.

This conclusion is in good agreement with the direct measurement results.³⁴ The water slip effect was quantitatively investigated owing to the application of micrometer quartz capillaries having the molecularly smooth hydrophobized (methylated) surface. The experiments give a value of the water slip coefficient, which is equal to around 3×10^{-4} cm³/dyn s.

In the case of interlayers confined by hydrophilic surfaces, the situation changes. Thus, as has been shown by Anastasiou et al.,¹⁴ close to the surface of a NaCl ionic crystal, water dipoles are oriented normal to the surface, mainly due to the electrostatic attraction between Na^+ ions and the oxygen atoms of water molecules. A similar conclusion follows also from the numerical experiments con-

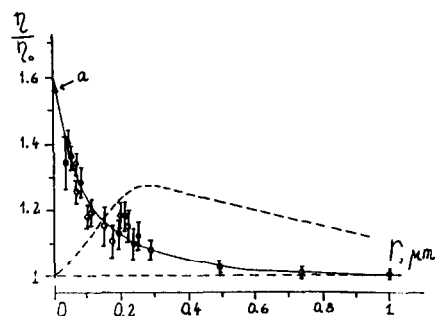


Figure 1. Dependence of the mean viscosity of water on the radius of quartz capillaries.

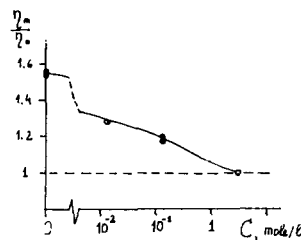


Figure 2. Influence of the KCl concentration on the viscosity of a solution in fine pores ($r = 35 \text{ \AA}$) of a nonselective glass membrane.

ducted by Marcelja et al.¹⁷ and Scott et al.¹⁵ In distinction from hydrophobic walls, some increase in density and a reduction in the tangential mobility of water molecules take place, which must show up macroscopically as growth of the viscosity of the boundary layers of water.

In Figure 1 are represented the results of the direct measurement of the viscosity of water in fine hydrophilic quartz capillaries and fine-pore glasses.³⁵ The average viscosity of water increases as the radius of the capillaries decreases. When interpreting the measurement results, however, a possible influence of the electroosmotic counterflow under the influence of the streaming potential (i.e., electroviscosity) will have to be taken into account. A dashed line indicates the results of the calculation of electroviscosity according to the theory of Dukhin et al.³⁶ The value of quartz surface potential $\Psi_1 = -150$ mV was used for calculation, measured in the same capillaries.³⁷ From Figure 1, the maximum influence of electroviscosity should have been observed at the capillary radius of around $0.3 \mu\text{m}$. The absence of the influence of electroviscosity in the experiments conducted on capillaries is explained by measurements being carried out with a liquid column of practically constant length, i.e., in the absence of a noticeable mass transfer. When the meniscus was shifted to about $100-200 \mu\text{m}$, the overflow volume amounted only to about $10^{-11}-10^{-12}$ cm³, and this proved to be insufficient to form a noticeable streaming potential.

The results of measurements of viscosity in a porous glass ($r = 35 \text{ \AA}$) are indicated by the point in Figure 1.

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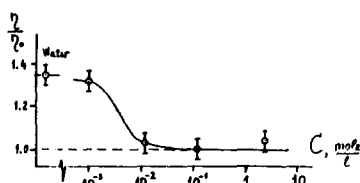


Figure 3. Viscosity of water and KCl solutions of different concentrations, as measured in the same quartz capillary ($r = 0.073 \mu\text{m}$) at $t = 20.1^\circ\text{C}$; η_0 are the bulk values of the viscosity of water and solutions.

Here the influence of electroviscosity was rather small in view of the strong overlapping of the electrical double layers. In this case, theory gives a correction for electroviscosity, which does not exceed 1%.³⁸

An increase in the viscosity of thin interlayers of water between the hydrophilic surfaces of quartz is a well-established experimental fact following not only from these measurements but also from earlier measurements effected by Zachavaeva and Derjaguin,⁶ as well as by Low on clays,³⁹ measurements by Tovbina on silica gels,³⁹ and those by Apel et al. on nucleopores.⁴⁰

Let us now consider what factors, aside from the hydrophilicity of surface, are able to influence the properties of the boundary layers and the structural forces.

As follows from the experiments with a nonselective glass membrane,⁴¹ an increase in the electrolyte concentration causes a gradual decrease in the difference of the solution viscosity from the bulk values (Figure 2). Here the nonpolar CCl_4 was used as a reference liquid for absolute measurements of viscosity. A similar result (Figure 3) has also been obtained by the viscosity measuring in single fine capillaries.⁴² Hence, the concentration destruction of the special structure of boundary layers is observed. The possibility of the formation of the special boundary structure decreases under the effect of ions and solute molecules. This should have been reflected also by the concentration dependence of structural forces. Thus, the data presented in Table I confirm the weakening of the structural repulsion forces in aqueous films. However, the results of other model experiments, as, for example, those conducted on hydrophilic macroscopic bodies, do not provide fitting data. For instance, in the experiments conducted by Rabinovich et al.²² on glass and quartz, the concentration weakening of structural forces has been established. In the work done by Peschel et al. on quartz,¹⁹ the effect was brought out in a much weaker manner; while in the experiments of Israelachvili and Pashley on mica,^{20,21} it either did not occur at all or had even the reversed sign. This seems to be associated with the insufficient accuracy of the calculation of the contribution of the electrostatic forces in the region of short distances between bodies. These difficulties arise due to the changes in potential and surface charge when surfaces approach one another, the changes being associated with changes in the adsorption of ions.

Another method for the weakening or destruction of the special structure of the boundary layers of water is

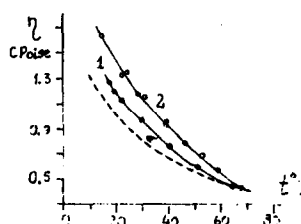


Figure 4. Influence of temperature on the mean viscosity of water in quartz capillaries having the radii $r = 0.17 \mu\text{m}$ (curve 1) and $r = 0.05 \mu\text{m}$ (curve 2). The dashed curve illustrates variation in the viscosity of bulk water.

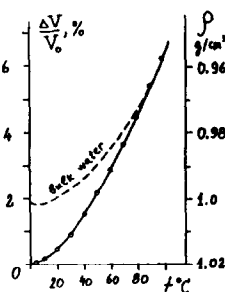


Figure 5. Comparative runs of the thermal changes in volume, $\Delta V = V - V_0$ (where V_0 is the volume at 0°C), for bulk water (dashed curve) and for water in fine pores (continuous curve).

physically obvious. As is known, an increase in temperature causes the weakening of hydrogen bonds in water, which must restrict the possibility of the formation of boundary layers, having a modified architecture of hydrogen bonds. In Figure 4 is represented a temperature dependence of the viscosity of water in fine hydrophilic quartz capillaries (curves 1 and 2) in comparison with the temperature dependence of the viscosity of bulk water (dashed curve). As the temperature is raised up to $\sim 65\text{--}70^\circ\text{C}$, the differences of viscosity from the bulk values decrease, which means a decrease in the thickness of the boundary layers. As has been shown earlier, an increase in temperature up to $\sim 65\text{--}70^\circ\text{C}$ breaks the thermosmosis of water in fine pores,⁹ and the water filtration rate in porous bodies and membranes increases noticeably.^{43,40}

The thermal destruction of the boundary layers of water leads also to a decrease in the stability of hydrophilic colloids. This is shown by Chernoberezhsky and co-workers^{44,45} for quartz and diamond dispersions. As has been demonstrated by Glazman,⁴⁶ stabilization of colloid systems due to the adsorption of nonionic surfactants is associated with the formation of the boundary layers of water near the polar groups of surfactant molecules. In this case also, an increase in temperature leads to a loss of the stability of sols,⁴⁷ micellar solutions,^{48,49} and films.⁵⁰

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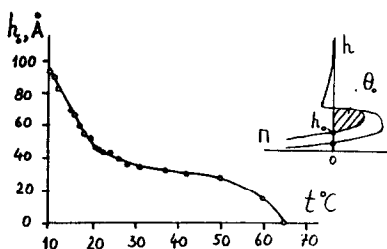


Figure 6. Dependence of the thickness, h_0 , of the polymolecular adsorption water films on the quartz surface (at $p/p_s = 1$) on temperature.

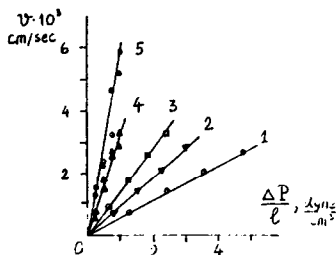


Figure 7. Dependence of the shear velocity, v , of ice columns under the effect of gas pressure, ΔP , in a cylindrical quartz capillary ($r = 9 \mu\text{m}$) on temperature: $t = -2.05^\circ\text{C}$ (1); -1.5°C (2); -1°C (3); -0.5°C (4); -0.25°C (5).

Derjaguin, Karasev, and Khromova⁵¹ have shown that as temperature is raised up to ~ 70 – 80°C , the differences in thermal expansion of bulk water and water in thin silica pores ($\sim 50 \text{ \AA}$) disappear. Coincidence of both curves of the thermal expansion in the high-temperature region (Figure 5) also allowed changes in the density of water, ρ , in fine hydrophilic pores to be quantitatively estimated. As is apparent from Figure 5, the density of the overlapped boundary layers of water has increased by approximately 1.5% at 20°C .

Experiments conducted on the water films adsorbed on the quartz surface also enable one to follow well the influence of temperature on the structural effects. As can be seen from Figure 6, an increase in temperature causes a gradual decrease in the thickness of α -films, due to a reduction in the thickness of the boundary layers of water.⁶² From these measurements, it follows in particular that at a temperature of about 65 – 70°C , the thickness of the boundary layers reduces to a monolayer, which fits well the results of experiments discussed above. As is shown in Figure 6, the observed reduction in the thickness of α -films should enhance the intrusion of the $\Pi(h)$ isotherm into the region of negative values of disjoining pressure, and hence, in keeping with eq 1, it must lead to an increase in the contact angle. As has been demonstrated by Zorin, Eaipova, and Ershov,³² just this actually takes place.

As is shown, an increase in temperature leads to destruction of the boundary layers. A decrease in temperature must, in contrast, enhance the structural effects. This, in particular, is manifested by the boundary fusion of ice. This well-known effect is readily observed in strictly cylindrical, fine capillaries (Figure 7) having a molecularly

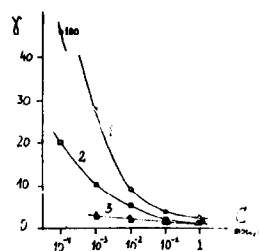


Figure 8. Dependence of the partition coefficient, γ , on the pore sizes in reverse-osmosis membrane and on the concentration of equilibrium KCl solution. $r = 7 \text{ \AA}$ (1); 10 \AA (2); 18.5 \AA (3).

smooth surface.⁶³ As the temperature approaches the melting point, the ice columns become easily mobile, because of the formation of a sufficiently thick nonfreezing water interlayer at the ice-quartz interface. This interlayer possesses the properties of a viscous Newtonian liquid. In accordance with theory,⁵³ the dependencies of the shift velocity of ice columns on applied gas pressure are linear (Figure 7). As temperature decreases, the flow rate diminishes owing both to a reduction in the thickness of interlayers (i.e., freezing out) and to an increase in their viscosity.

Taking into account the peculiarities of nonfreezing interlayers enables us to derive, on the basis of thermodynamics of irreversible processes and the theory of disjoining pressure, the flow equations relating the moisture transfer velocity in frozen soils and porous bodies to the heat of ice melting.⁶⁴ This theory has been quantitatively confirmed by experiments on nonfreezing films on the surface of quartz capillaries.⁶⁵

The change in the structure of water in fine pores, where the boundary layers are overlapped, is not merely of general theoretical interest. The reverse-osmosis separation of aqueous solutions is based on the structural effects—that is, on a reduced dissolving power of thin water interlayers between hydrophilic surfaces (in accordance with Dumansky⁶⁶). A decrease in the dissolving power is a consequence of several effects, namely, disturbances of the structure of bulk water, containing voids accommodating dissolved molecules, and a reduction in its dielectric permittivity. The second effect is especially important for the case of electrolyte solutions. It leads to the so-called dielectric exclusion investigated by Dukhin and Yaroshchuk,^{57,68} residing in changing the self-energy of a ion under the effect of Born's forces and the image forces in pore walls.

The change in the dissolving power may be characterized by the ratio of the solute concentration in membrane pores, C_p , to that in the equilibrium bulk solution, C_0 . In Figure 8 are represented the partition coefficient values, $\gamma = C_p/C_0$, obtained in the experiments on glass porous membranes. As is apparent, the dissolving power of water is reduced the smaller the mean radius of pores, i.e., the higher the boundary overlapping degree. In this case, as in measuring viscosity, the effect of the concentration

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break-up of the boundary layer structure under the influence of incorporated hydrated molecules and ions does distinctly show up. An increase in the concentration of solutions causes a decrease in the difference between the dissolving power of water in fine pores and in bulk.

The discussed results have demonstrated sufficiently good agreement between the investigation of the physical properties of the boundary layers of water and the structural forces. At high surface hydrophilicity, the structural forces are positive and cause the repulsion of surfaces, the viscosity and density are enhanced, and the dissolving power is reduced. In the case of hydrophobic surfaces, these effects have opposite signs. A wide intermediate range is disposed between these two limit cases, where the degree of the structural peculiarities of the boundary layers may be relatively low.

The structural changes in the boundary layers of liquids, the structural and microstructural forces, represent a physiscal reality. However, the conditions under which the structural effects can actually show up will have to be clearly defined, and these should not be used for clarification of deviations from the existing theories in the cases where the structural effects had not to be present at all. The maxima of structural effects are to be expected in two extreme cases—that of the highly lyophobic and that of the highly lyophilic surface.

Further efforts should be aimed at the development of a quantitative theory of structural forces. This will permit their incorporation in the general theory of long-range surface forces and disjoining pressure.

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Structural Component of Disjoining Pressure in Wetting Films of Nitrobenzene Formed on the Lyophilic Surface of Quartz[†]

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It has been shown that a structural component of disjoining pressure, Π_s , decreasing according to the exponential law as the layer thickness increases, arises in the wetting films of nitrobenzene formed on the lyophilic surface of quartz. A family of isotherms, Π_s , have been obtained within a temperature range 293–333 K. The dependence of parameters on temperature has been determined, the parameters being characteristic of the transition of a wetting film into a thermodynamically nonequilibrium state.

The electrostatic and the molecular components of disjoining pressure have earlier been investigated in ref 1 and 2. The structural component Π_s , arising when the interphase boundary layers overlap, whose structure is different from that of bulk liquid,³ has been considerably less investigated.

The existence of the structural component of disjoining pressure has been shown experimentally for α -films of water, formed on the quartz surface,⁴ and for free and wetting films of nematic liquid crystals.⁵

An attempt was made to calculate theoretically the structural component, Π_s , for water films on the lecithin surface.⁶ The exponential dependence of the structural component of disjoining pressure on thickness, obtained in the cited work, qualitatively agrees with the data.⁴

Yet the theoretical diagram used ref 6 contains a number of simplifications that considerably reduce its merits. The structural component of disjoining pressure was theoret-

ically calculated for comparatively thick films of the nematic phase of liquid crystals, $h \sim 1 \mu\text{m}$, in ref 7 and 8 within the framework of the continual theory of liquid crystals. A satisfactory agreement with experiment was thus obtained. However, the continual theory is probably inapplicable to the orientation-ordered wetting films of nonmesogenic liquids having thickness within the range $h \sim 10$ to 60 nm.

The structural component, Π_s , has not up to now been directly experimentally investigated in such films.

Using the theory of a self-consistent field as the basis,⁹ B. V. Derjaguin assessed the structural component of disjoining pressure for thin, nonsymmetrical wetting films. It has been shown that a positive component of disjoining pressure arises as a film gets thinner and the near-to-wall orientation-ordered layers overlap. However, no quantitative results have been obtained.

As has been shown earlier,¹⁰ some nonmesogen polar

Table I

h, nm	t, °C									
	20		30		40		50		60	
	Δ	Ψ	Δ	Ψ	Δ	Ψ	Δ	Ψ	Δ	Ψ
20	14.59	6.52	13.81	6.52	13.03	6.54	12.21	6.56	11.50	6.57
25	17.91	6.31	16.97	6.33	16.00	6.35	16.06	6.37	14.10	6.40
30	21.10	6.06	19.94	6.09	18.79	6.12	17.66	6.16	16.54	6.19
35	24.04	5.79	22.70	5.83	21.30	5.87	20.00	5.91	18.76	5.96
40	26.73	5.49	25.20	5.54	23.68	5.59	22.20	5.65	20.75	5.71
45	29.13	5.17	27.41	5.24	25.72	5.30	24.07	5.37	22.46	5.44
50	31.20	4.84	29.29	4.92	27.43	4.99	25.62	5.07	23.85	5.16
55	32.89	4.50	30.80	4.59	28.77	4.68	26.80	4.77	24.89	4.87
60	34.13	4.16	31.86	4.25	29.67	4.36	27.56	4.47	25.52	4.58

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