

STRUCTURAL AND THERMODYNAMIC PECULIARITIES OF THE BOUNDARY
LAYERS OF LIQUIDS

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Gibbs' theory of capillarity, whose centenary anniversary of publication has recently been celebrated at the Leningrad Symposium, contemplates the surface zones at the interface as possessing properties that are different from those of phases in bulk. In that case, however, a question is left to be answered as to how the properties inside those zones are distributed and what is their thickness. Thus, Gibbs followers had to solve the problem of providing the specific contents for the general thermodynamic concept of Gibbs, starting from the molecular-statistical approach.

A further object consisted in examining the behaviour of such interlayers, in which the zones belonging to both surfaces are overlapped. This problem was in the main posed and developed by Soviet scientists. At first, the peculiarities and effects have been considered, that are not attributable to the changes in the structure of liquid (or solvent) as caused by the interface. In the first place, these comprise the effects depending on the surface fields of the Van der Waals origin and their overlapping (Lifshits' theory), and the effects depending on diffuse ionic atmospheres and their overlapping. It would be advisable to interpret those effects quantitatively for the case of plane-parallel interlayers as two components of disjoining pressure.

In the case of lyophobic systems, it is the taking into account of those two components that allowed the consecutive theory of stability of lyophobic colloids to be developed¹. In spite of the fact that this theory has been developing already during 42 years, there remains much to be supplemented. One of the main questions consists in finding correct boundary conditions in integrating Poisson-Boltzmann's equation. It is usually assumed that the potential is constant at the boundaries of a diffuse ionic layer. This condition is acceptable so far as the interlayer thickness is of the order of ionic atmospheres or thicker. It is just this thickness that corresponds to the force or potential barrier of the interaction of particles. So, this

justifies using the assumption of the potential constancy in the theory of stability of lyophobic colloids and in calculating the far potential pit. The situation, however, changes for the opposite case of an interlayer that is much thinner than the Debye length. This we have to deal with in the case of secondary black free or emulsion films, or at such aggregation state of colloidal particles, when the liquid interlayer between them remains even after the overcoming of the potential barrier. Certain authors² explain its existence and the possibility of its subsequent peptization in the following manner: at a rapid approach of particles to one another, the adsorption equilibrium has not time to change, owing to which the last step of approach occurs at constant charges of surfaces. It is their rather slow relaxation that is able to explain the impossibility of peptization after the lengthy aggregation state. This explanation, however, is inapplicable to the stability of secondary black films, which sometimes persists for years and arises also at the slow thinning out of primary films. Another approach, however, is possible, which should be suitable for interpreting the stability of any ultrathin interlayers.

In this approach, the mechanism of charging surfaces is used as the basis, which allows the surface charge to be calculated in a substantiated way as a function of the interlayer thickness. We limit ourselves to the simple case of a diluted solution containing only one ion-active tenside, as for example, anion-active sodium oleate. In the case of a sufficiently small thickness of the solution interlayer, which is much smaller than that of the ionic atmosphere, its content of free anions may be neglected. All the anions will be found in adsorbed monolayers at the interlayer surfaces owing to specific adsorption. Part of anions will be blocked by cations, and only the remaining part of the first determines the charge of the surfaces per unit area, σ .

In view of the condition of electrical neutrality, this charge is compensated for by the charge of cations that are present in the film volume:

$$2\sigma = \int_{-h}^{+h} c(x) dx, \quad (1)$$

where $c(x)$ is the concentration of cations at a distance of x from the symmetry plane of the film, h is its half-thickness (on subtracting the thickness of an adsorption monolayer). The adsorption isotherm will be determined by writing the condition of detailed equilibrium between the processes of adsorption and desorption of cations:

$$\sigma c_1 = b (\sigma_0 - \sigma), \quad (2)$$

where c_1 is the concentration of cations directly close to adsorption monolayers; σ_0 is the charge of surfaces when the adsorbed cations are absent, so that difference $(\sigma_0 - \sigma)$ is proportional to the number of the cations adsorbed; b is the equilibrium constant. The left side of Equation (2) is proportional to the adsorption rate, because σ is proportional to the number of "vacant places", which is determinable by the number of anions that are "not blocked" by cations. Instead of Equation (2), we may write:

$$c_1 + b = b \frac{\sigma_0}{\sigma}. \quad (3)$$

Poisson-Boltzmann's Equation gives:

$$\frac{d^2\psi}{dx^2} = - \frac{4\pi}{\epsilon} e c_\infty \exp\left(-\frac{e\psi}{\theta}\right), \quad (4)$$

where ψ is the potential, ϵ is the permittivity; $\theta = kT$, where k is the Boltzmann constant, T is the Kelvin temperature, c_∞ is the concentration of cations in the bulk phase, with which the interlayer is in contact or in the full thermodynamic equilibrium (in the case of an isolated film). Using Boltzmann's equation,

$$c_x = c_\infty \exp\left(-\frac{e\psi}{\theta}\right), \quad (5)$$

it will be possible to convert the integral of Equation (4) to:

$$\frac{2\pi}{\epsilon\theta} \sigma^2 = c_1 - c_0 = c_0 \operatorname{tg}^2\left(\frac{h}{2d_0}\right), \quad (6)$$

where

$$d_0 = \frac{1}{e} \sqrt{\frac{\epsilon\theta}{2\pi c_0}} = \sqrt{\frac{2c_\infty}{c_0}} d \quad (7)$$

designates some length which may be much smaller than d , i.e. the thickness of ionic atmospheres in the solution bulk, if c_0 - the concentration of cations in the symmetry plane of the film is much higher than c_∞ ; this is realized at sufficiently small values of h .

For further simplification, we shall examine limit cases of small and great thicknesses. When

$$\frac{h}{2d_0} \ll 1 \quad (8)$$

then tg may be replaced by its argument, and after carrying out rather simple calculations, we find:

$$\sigma = z e c_0 \frac{h}{2}. \quad (9)$$

As the interlayer thickness h decreases, the values of c_0 and $c_1 > c_0$ increase. Let us first consider the case, when c_1 and c_0 still remain much smaller than β , which has a great value. In this case, we obtain from Equation (3):

$$\sigma \approx \sigma_0.$$

In such a case, we derive from Equation (9):

$$c_0 = \frac{2\sigma_0}{ze h}. \quad (10)$$

As is known, according to Langmuir³, the electrostatic component of disjoining pressure, Π_e , is equal to:

$$\Pi_e = \theta (c_0 - c_\infty). \quad (11)$$

Hence, taking into account that for sufficiently small values of h

$$c_0 \gg c_\infty, \quad (12)$$

$$\Pi_e = \theta \frac{2\sigma_0}{ze h}. \quad (13)$$

This is yet not a limit law. At still smaller values of h , the concentration of c_1 will be increased to such an extent that the inverse condition will be realized:

$$c_1 \gg \beta \quad (14)$$

and simultaneously $c_1 \approx c_0$. Then from Equations (3) and (9), we derive:

$$\sigma \approx \frac{\beta \sigma_0}{c_1}, \quad (15)$$

$$c_0 \approx \sqrt{\frac{2\beta \sigma_0}{ze}} h^{-1/2}, \quad (16)$$

$$\Pi \approx \theta \sqrt{\frac{2\beta \sigma_0}{ze}} h^{-1/2}. \quad (17)$$

We shall have another limit case, when the tangent argument in formula (6) will tend to $\frac{\pi}{2}$, and when accordingly $c_0 \ll c_1$. Supposing, however, that condition $c_0 \gg c_\infty$ is preserved, we obtain:

$$h = \pi d_0 \ll \pi d; \quad (18)$$

Consequently:

$$C_1 \gg C_\infty, \quad \frac{e\psi}{\theta} \gg 1, \quad (19)$$

$$C_0 = \frac{\pi}{2} \frac{\varepsilon \theta}{e^2} h^{-2}, \quad (20)$$

$$\Pi_e = \frac{\pi}{2} \frac{\varepsilon \theta^2}{e^2} h^{-2}. \quad (21)$$

Formula (21) coincides with Langmuir's formula that has been derived for the case where h is substantially smaller than the thickness of ionic atmospheres, while the dimensionless potential of surfaces is much greater than unity, which coincides with conditions (18) and (19). An essential peculiarity of Equation (12) consists in that Π_e depends on adsorption parameters σ_0 and β .

As regards σ_0 , its value is within a narrow range, when the monolayer is dense and close to saturation. The value of β may vary within a wide range. It will be the higher, the easier the adsorbed molecules dissociate and the cations pass over from the monolayer into the film bulk. In this respect, lithium and sodium ions occupy the first place in aqueous solutions, both kinds of ions exhibiting an increased hydration energy. On having assessed possible values of β , the following can be established by simple calculations: transition with a decrease in h from formula (21) to formulas (13) and (17) is accompanied by a drastic (by several orders of magnitude) increase in Π_e . The reverse - owing to a more drastic increase in Π_e with a decrease in h in formula (21) - can be attained only at unrealistically small values of h (less than 10^{-9} cm). Π_e would achieve still higher values in the case when the charge should remain constant as the thickness of h diminishes. However, this is incompatible with the equilibrium conditions; therefore, the lengthy stability of, for example, black soap films cannot be attributed to that circumstance.

For evaluating the stabilizing role of Π_e in "superthin" films, the expression (17) for Π_e will have to be compared with the expression for Π_m , the molecular component of disjoining pressure, which is equal to

$$\Pi_m = \frac{A}{6\pi h_e^3}, \quad (22)$$

where h_e is the effective thickness of the film, exceeding h but being of the same order of magnitude with it⁴. At values A of the order of

10^{-12} to 10^{-13} , and at possible values of β , it has been found that even at $h \approx 10^{-8}$ cm

$$\Pi_e > \Pi_m.$$

Thus, the mechanism of stabilization of "ultrathin" interlayers by ion-active tensides considered proves to be very efficient.

Of course, the calculation made becomes incorrect at the values of h on the order of a few monolayers, when the effect of the discrete character of the structure of monolayers begins to become perceptible. Muller and Derjaguin⁵ have shown that the discrete character of the distribution of adsorbed ions decreases their electrostatic repulsion and may even lead to their attraction. In the study of Martinov and Smilga⁶ it has been shown that the normally oriented dipole layers are attracted at very close distances. Nonetheless, it should not be underestimated that the long-time stability of "black films" speaks in favour of developed calculations.

Our calculations are simultaneously applicable to the case, also, where the surface is charged as a result of dissociation of ionogen functional surface groups. This corresponds to the limit case $C_\infty \rightarrow 0$ in the aforementioned calculations.

Recently, the behaviour of "ultrathin" liquid interlayers has attracted a great attention in connection with the technical and biological problem of the membrane separation, for example, in the process of "reverse osmosis". In that case, contrary to their denomination, there are used, not the osmotic membranes, but such that are permeable for all the molecules of the mixture to be separated. In such membranes, the capillary osmosis may be observed⁷ rather than the ordinary osmosis. The following is quite obvious: the separation effect is determined by how the concentration of the "dissolved" component is distributed across the section of a pore which, for the sake of simplicity, we assume to be slit-shaped, and inasmuch that concentration is different from that in the solution to be separated. In view of a small thickness of the liquid interlayer, the surface zones will overlap. First of all, let us consider the case of an electrolyte solution. If it were strongly ion-active, then, as we have seen, only counterions would be present in the interlayer bulk. The ions of a dense monolayer possess but a slight mobility, and the flow of counterions would infringe on the electrical neutrality. In other words, the formation of the flow of counterions would cause the appearance of the contrary drop of potential. Therefore, the membrane will be able to purify the solution from such an electrolyte.

Of course, at high filtration rates the purification degree will drop owing to the fact that the entraining and the carrying away of counterions will be accompanied by desorption of adsorbed ions.

Now, let us consider the flow of a solution of nonelectrolytes through the membrane. The author and his coworkers examined the capillary osmosis of solutions of nonelectrolytes. The existence of the latter in the light of the theory developed by the author ⁷ proves the diffuse structure of the movable part of an adsorption layer. Using this as the basis, the separation effect of reverse osmosis will have to be examined; it would be more correct to designate it as "reverse capillary osmosis". The factor common to both effects are the molecular forces acting upon the molecules dissolved close to the interface. By analogy with Lifshits' method for deriving the forces of paired interaction of molecules, the energy of effective attraction of dissolved molecules of a diluted solution to phase surfaces was established in a study dealing with the theoretical and experimental investigation of capillary osmosis ⁸ :

$$U(h) = - \frac{A}{h^3}, \quad (23)$$

where

$$A = \frac{\hbar}{16\pi^2} \int_0^\infty \frac{(\epsilon_3 - \epsilon_2)}{(\epsilon_3 + \epsilon_2)} \frac{1}{\epsilon_1} \left(\frac{\partial \epsilon_1}{\partial C} \right) d \frac{\xi}{\xi}, \quad (24)$$

where h is the distance from the interface, \hbar is the Planck constant, ϵ_1 is the solution permittivity, ϵ_2 is the permittivity of the solvent, ϵ_3 is the permittivity of the wall, C is the number of molecules that are dissolved in the solution volume unit. All ϵ_i are taken as a function of imaginary frequency $i \frac{\xi}{\xi}$. Using Boltzmann's equation, we find the concentration of dissolved molecules in an interlayer of thickness h by formula:

$$C = C_\infty \exp \left(\frac{A}{x^3} + \frac{A}{(h-x)^3} \right). \quad (25)$$

In the case if A is positive, we have:

$$C > C_\infty. \quad (26)$$

This, as was shown by Churaev ⁹, is conducive to the fact that filtration of a solution through a membrane is accompanied by a concentration drop of dissolved molecules, which will just be characteristic of its separation effect.

Another important corollary of Equation (25) consists in that it proves to be impracticable to apply Dzyaloshinskij, Lifshits and Pitaevskij formula to the calculation of the disjoining pressure of an solution interlayer, the formula supposing the uniformity of the interlayer. This problem was solved by Churaev and me ¹⁰ by using Gibbs-Duhem's equation which allowed the disjoining pressure of the interlayer of nonelectrolyte binary solution to be expressed by formula:

$$\Pi = - \int_{-\infty}^{\mu} \frac{\partial \Gamma(h)}{\partial h} d\mu + \Pi_m, \quad (27)$$

where $\Gamma(h)$ is the excess number of dissolved molecules in the system at a given value of the chemical potential of the solute, μ , and the prescribed values of pressure p and temperature T , the number of the molecules of the solvent and the concentration of dissolved molecules C_∞ in the solution bulk, at a distance of plates h as compared with distance $h \rightarrow \infty$. Π_m designates the disjoining pressure of an interlayer of the pure solvent at the same thickness h . The value of Π_m can be accurately calculated by Lifshits et al'.¹¹ formula, if, of course, the structural peculiarities of the solvent close to interfaces with plates be disregarded. Formulas (23), (24), (25) and (27) allow calculating Π .

Analysis of the equations derived has shown the following: the dispersion component of disjoining pressure may be positive, if constant A is positive and sufficiently great (supposing that the influence of electromagnetic retardation is not yet essential). This consequence of our theory is in qualitative agreement with findings of Sheludko and Ekserova¹² relative to the stability of free films of butyric acid aqueous solutions. It will be of interest to check the developed theory for the case where both surfaces are unlike, $\Pi_m = 0$, and, hence, Π is completely determined by the overlapping of adsorption atmospheres. In the studies of Kuny, Rusanov and Brodskij¹³, the disjoining pressure of the interlayers of solutions is interpreted on the basis of taking into account paired interactions and without using formulas (24) and (27) derived by us. This does not allow obtaining quantitative results, when using macroscopic constants as the starting point.

At present, there has been accumulated a great amount of experimental data showing that in a number of cases the considered components of disjoining pressure are insufficient for explaining the interaction of phases separated by thin interlayers. In particular, the interaction arising changes

abruptly with the nature of the surface as a result of adsorption of ion-nonactive tensides. There are relevant grounds available to believe that the fourth component of disjoining pressure appears when the boundary layers are overlapped, whose structure has been changed as compared with the bulk one under the influence of the interface. Hereinbelow, we shall designate that component as the structural one. The existence of this component is recognized but with a great delay, owing to the fact that the theory has been developed yet insufficiently, and due to a small number of studies, in which the structural features of the boundary layers of liquids have been proved unambiguously.

Therefore, referring to a number of original studies that have been carried out recently by Ninham et al.¹⁴, we limit ourselves to setting forth the experimental proofs of the existence of the structural component of disjoining pressure. The most direct and unambiguous proofs were obtained by examining the isotherm of disjoining pressure of wetting films of water on hydrophylic surfaces of quartz, glass, mica (muscovite). In Fig.1 are presented the experimental results of various authors^{15,16,17} determining $\Pi(h)$

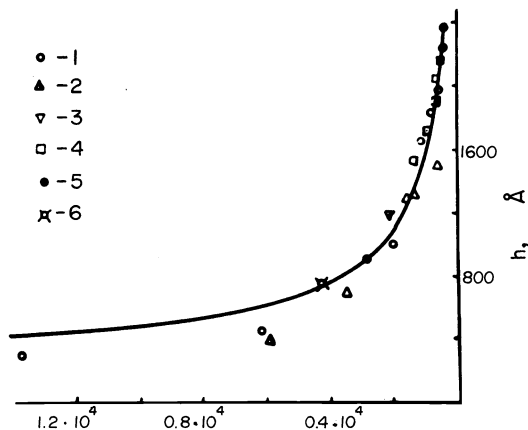


Fig. 1. Disjoining pressure isotherms for wetting β -films

1. Water on mica¹⁵
2. Water on glass¹⁵
3. $2 \cdot 10^{-5}$ N aqueous KCl solution on quartz¹⁶
4. 10^{-4} N aqueous NaCl solution on glass¹⁵
5. Water on quartz¹⁶
6. Water on quartz¹⁷

for water on quartz and glass K-8. These data, like the first measurements made by Derjaguin and Kusakov¹⁵, were obtained by resorting to a method of pressing a gas bubble to a flat plate, and of measuring the equilibrium

thickness of a wetting film h and the capillary pressure of the bubble, which correspond to each other. It is obvious that for great thickness and, accordingly, small values of Π , the experimental points of different authors are located close to a curve that was plotted according to Langmuir¹⁸ equation

$$\Pi_e = \frac{\varepsilon \varepsilon_0}{8} \left(\frac{\theta}{e} \right)^2 h^{-2} \quad (28)$$

This equation defines the ionic-electrostatic component of the disjoining pressure of a wetting film in the assumption that the substrate potential is very great ($\psi_0 > 100$ mV), the charge of the free surface is equal to zero, while the (dimensionless) thickness is small:

$$\chi h \ll 1. \quad (29)$$

However, when Π of the wetting film increases and it accordingly grows thinner, it goes beyond the boundary of stability (or rather metastability). In such a case, there occur local breakups, in which there form thinner sections. Eventually, the greater part of the film acquires a smaller stable thickness, while the remaining part of the initial thicker film breaks up into small lenses forming with the thin film the final contact angle of the order of 5 to 10°. The branch of the isotherm of disjoining pressure corresponding to thinner wetting films was obtained in a number of studies¹⁹, by plotting the dependence of the thickness of polymolecular "adsorbed" films of water on the relative pressure of vapour p/p_s beginning with $p/p_s = 1$, where p_s is the pressure of vapour over the flat surface of the same liquid in bulk. Fig. 2 represents on one graph both section^s of the $\Pi(h)$ isotherm, i.e. that of thicker, β -layers and that of thinner,

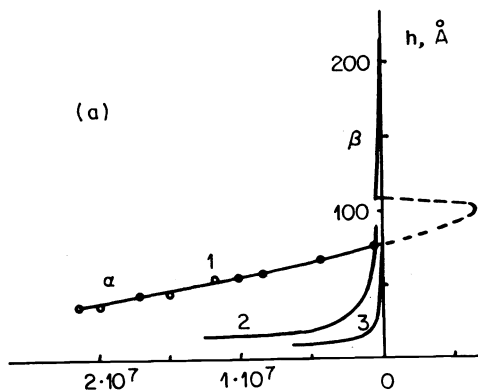


Fig. 2. h vs Π dyn/cm² isotherm for water on glass,

β -film¹⁵, α -film¹⁹ (curve 1);

h vs Π_e isotherm (curve 2); h vs Π_m isotherm (curve 3).

α -layers²⁰. The lower part of β -section corresponds to the metastable states of a wetting film. A remarkable fact is that α -section of thinner layers of $\Pi(h)$ isotherm intersects the ordinate corresponding to the value $\Pi=0$ at a finite value $h=h_0$. The values $h>h_0$, $\Pi(h)<0$ of α -branch of $\Pi(h)$ isotherm correspond to metastable states. The section in which inequalities are valid:

$$\frac{d\Pi}{dh} > 0, \quad \Pi < 0. \quad (30)$$

(if it does exist), obviously corresponds to the labile states of the wetting layer. This is a corollary of the fact that a following condition is simultaneously fulfilled:

$$\frac{dp}{dh} < 0. \quad (31)$$

Owing to this condition, any variation in thickness will increase due to an exchange with the vapour phase. On the same figure, curve 2 represents Π_e isotherm which has been plotted according to equation (28) that gives the maximum possible limit of Π_e values within the range of small thicknesses. Curve 3 represents the dispersion component, Π_m , which for $h < 200 \div 300 \text{ \AA}$ satisfies equation:

$$\Pi_m = \frac{-A}{6\pi h^3}. \quad (32)$$

Constant A , which was calculated by N.V.Churaev²⁰ according to E.M.Lifshits et al.' theory on the basis of quartz and water absorption spectra, has value

$$A = -1,12 \cdot 10^{-3} \text{ erg}. \quad (33)$$

Thus, it is obvious that the superimposition of components Π_e and Π_m of disjoining pressure is not able to give, even approximately, the isotherm which was observed within the region of α -layers. Moreover, by this means it is impossible to explain the reversing of the sign of $\Pi(h)$ at $h=h_0$. This is an unambiguous proof that α -branch of the isotherm stems from the structural peculiarities of water layers that are adjacent to the quartz surface. This is also substantiated by the temperature dependence of the characteristic thickness h_0 of α -layers. The value of h_0 decreases as temperature is raised, and at $t^\circ = 70^\circ$ it is reduced to the monolayer thickness²¹. That the observed isotherm of disjoining pressure cannot be ascribed to Van der Waals forces also results from the fact that hydropho-

bization of glass with a monolayer leads to the disappearance of polymolecular layers of water under any pressures of water vapour. This cannot be explained on the basis of the molecular attraction laws.

Now, the isotherms of the disjoining pressure of wetting films of non-polar liquids on some substrates may be fully identified with the molecular component of disjoining pressure, Π_m . In Fig. 3, there is represented as an example the isotherm of the disjoining pressure of *n*-hexane wetting

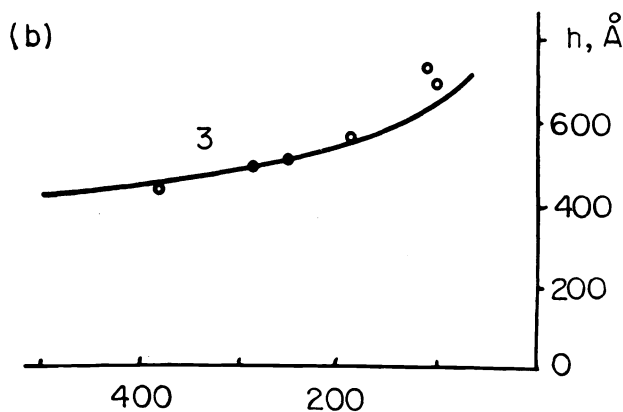


Fig. 3. Π dyn/cm² vs thickness of *n*-hexane films on steel.

film on steel²². Measurements were limited to the films having thickness more than 400 Å. Therefore, instead of formulas (32), a formula was applied to plotting the theoretical isotherm:

$$\Pi_m = \frac{-B}{h^4}, \quad (34)$$

where constant $B = -1.6 \cdot 10^{-19}$ erg.cm and corresponds to the interaction with the film, which is independent from the kind of metal used, in the limit case of the full effect of electromagnetic retardation²³. In case of water, it would be natural to ascribe the structural peculiarities to a change in the architecture of hydrogen bonds under the effect of active centers of the substrate. Such a disturbed architecture can be restored at distances from the surface of the order of correlation length, which is for water on the order of scores Ångström. At temperatures higher than 70°C, the heat motion disturbs the system of hydrogen bonds; therefore, the structural component of disjoining pressures disappear, too. This fact also refutes the assumption of the possible influence of quartz solubility on the structural component, for solubility is able only to grow with temperature.

Examination of the viscosity of thin layers of water serves as a further substantiation of structural peculiarities. An increased viscosity of

those layers on the quartz-glass interface was detected on observing whether the flow of water in quartz capillaries ²⁴ up to 200 Å in radius, or the flow of thin water films wetting glass and quartz ²⁵. In layers about 50 Å thick, at a temperature of about 20°C there is observed an increase in viscosity by several times as compared with the bulk value. It is remarkable that this increase in viscosity disappears at the same temperature of 70°C, at which the structural component of disjoining pressure disappears.

Finally, the structural peculiarities of boundary layers of water were independently proved by examining thermoosmosis which was detected in 1947. This phenomenon consists in the flow of liquid through glass capillaries or diaphragm pores under the effect of a temperature gradient ²⁶. In accordance with Derjaguin's theory ²⁶ based on using thermodynamics of irreversible processes, the thermoosmotic flow rate j through a capillary having the form of a slit with thickness h is equal to:

$$j = \chi \frac{\text{grad } T}{T}, \quad (35)$$

where

$$\chi = - \int_0^{h/2} \frac{\Delta H(x) x (h-x) dx}{h \eta}, \quad (36)$$

where ΔH is the excess of the enthalpy density as compared with the bulk value, η is viscosity, x is the coordinate which is read off one surface of the slit. It is supposed that the width of the capillary is much greater than the width of layers in which the specific enthalpy is different from the bulk value. Part of the change in the enthalpy may be ascribed to the effect of ionic atmospheres that form close to the slit surfaces. For water, this part is small, as follows, firstly, from an insignificant influence of the electrolyte concentration, and secondly, from the fact that thermoosmosis intensity which decreases as temperature increases, disappears at a temperature of 70°C ²⁷. Peculiar is the dependence of the thermoosmotic flow on the capillary radius (see Fig.4). At great radii (on the order of 1 μm), the thermoosmotic flow is directed towards the increasing temperature, and its flow rate is comparatively small. As the capillary radius (see Fig.4) decreases below 500 Å, the direction of the thermoosmotic flow changes to the directly opposite one, i.e. in the direction of decreasing temperature, and, what is the most surprising, it increases with a further decrease in the radius. The change in the direction of thermoosmosis to the directly opposite

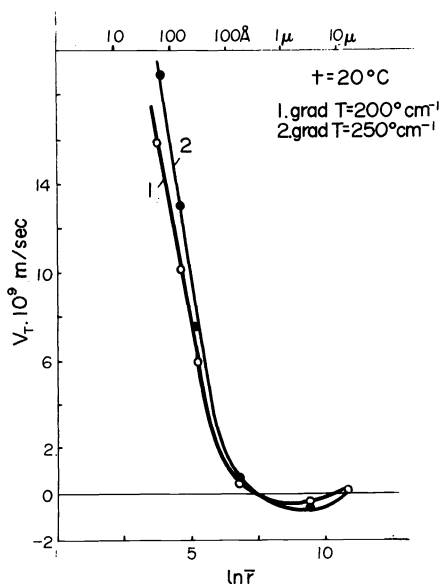


Fig. 4. Thermoosmosis rate vs capillary radius.

one with the layer thickness proves unambiguously that the boundary layer of water consists at least of two layers, for one of which ΔH is positive, and for the other negative²⁸. However, it is impossible to indicate unambiguously why at greater thicknesses h or radii of capillaries, the influence of one layer is greater, whereas at smaller thicknesses h or radii the influence of another layer prevails; for as the boundary layers overlap one another the structure of each of them changes. Without such a change in the structure, it would be impossible to explain an increase in the thermoosmotic flow as the capillaries narrow themselves.

It is the presence on the surface of an adjacent phase, of active functional groups (for example, OH) and charged centers that determines the appearance of structural peculiarities of boundary layers. Hence, the surface of lyophobic bodies (or lyophobic colloid particles) can be modified under the effect of monolayer adsorption. As a result, there appears the structural component of disjoining pressure which is able to guarantee the stability of a corresponding colloid system. As an example, there may be mentioned the change of lyophobic hydrosol of silver iodide into lyophilic one that coagulates only under the effect of additions of concentrated solutions of electrolytes (independently of the valence of the counterion). According to Glazman's study²⁹ that modification is achieved by adding non-ionogen surfactants to the aqueous medium, the surfactants being, for example, polyglycol esters having oxethyl chains of different lengths.

It proved to be impossible to ascribe that effect to simple steric effect which arises when adsorption monolayers contact and repulse one another. There are many other cases of stability of colloid systems, which cannot be ascribed to the steric repulsion, nor to the ionic-electrostatic component of disjoining pressure. Those cases serve as an indirect substantiation of the existence of the structural component of disjoining pressure and its importance in the colloidal chemistry.

References

1. B.V.Derjaguin, *Izvest.Acad.Sci., Ser.Chim.*, No.5, 1153 (1937);
B.V.Derjaguin, *Trans.Farad.Soc.*, 36, 203, 730 (1940);
B.V.Derjaguin a. L.D.Landau, *Acta phys.-chim.URSS*, 14, 633, 1941;
J.Exper.Theor.Phys., 11, 802 (1941); 15, 633 (1945);
E.J.W.Verwey a. J.Th.G.Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
2. J.Th.G.Overbeek, *Proc.of the IVth Internat.Congress on Surface Active Subst.*, Brussels, 1954, vol.II. Gordon a. Breach Sci.Publ., London, New York, 1967, p. 19.
3. I.Langmuir, *J.Chem.Phys.*, 6, 873 (1938).
4. W.A.B.Donners, J.B.Rijnbout a. A.Vrij, *J. of Colloid a. Interface Sci.*, 60, 540 (1977).
5. B.V.Derjaguin a. V.M.Muller, *Dokl.Akad.Nauk SSSR*, 225, No.3 (1975);
Koll.Journ. (russ.) 38, No. 6 (1976).
6. G.A.Martynov a. V.P.Smilga, *Koll.Journ.(russ.)* 27, 250 (1965).
7. B.V.Derjaguin, G.P.Sidorenkov, E.A.Zubashchenko, and E.V.Kiseleva, *Kolloidn.zhurn.*, 9, 335 (1947). *Doklady AN SSSR*, 159, No.2 (1964).
8. B.V.Derjaguin, J.E.Dzyaloshinsky, M.M.Koptelova a. L.P.Pitaevsky, *Disc. Farad.Soc.*, No.40, 246 (1965).
9. N.V.Churaev, *Theoret.Osnovy Chimich.Technol.*, 13, No.12 (1979).
10. B.V.Derjaguin and N.V.Churaev, *Kolloid.zhurn.*, 37, 1075 (1975).
11. I.E.Dzyaloshinskij, E.M.Lifshits and L.P.Pitaevskij, *Zhurn.eksper.teoret. fiziki*, 37, 229 (1959).
12. A.D.Sheludko and D.Ekserova, *Izv.khimich.institutu Bolgar.Akad.Nauk*, 7, 105 (1959).
13. F.M.Kuny, A.I.Rusanov and E.N.Brodskaya, in *Coll.Research in Surface Forces*, v.4, p. 240. Consultants Bureau, N.Y., 1975.
14. S.Marselja and N.Radic, *Chem.Physics Letters*, 42, 129 (1976);
D.J.Mitchell, B.W.Ninham, B.A.Pailthorpe, *J.Coll.Interf.Sci.*, 64, 194 (1978);

- D.V.C.Chan, D.J.Mitchell, B.W.Ninham, *Molecul.Physics*, 35, 1669 (1978).
15. B.V.Derjaguin and M.M.Kusakov, *Acta Physicochim.URSS*, 10, 25, 153 (1939).
16. A.D.Read and J.A.Kitchener, *J.Coll.Interface Sci.*, 30, 391 (1972);
T.D.Blake and Kitchener, *J.Chem.Soc., Farad.Soc.I*, 68, 1435 (1972).
17. H.J.Schulze and G.Z.Cichos, *Z.Phys.Chem.*, 251, 252 (1972).
18. I.Langmuir, *J.Chem.Phys.*, 6, 873 (1949).
19. B.V.Derjaguin a. Z.M.Zorin, *Zh.Fiz.Khim.*, 29, 1755 (1955);
B.V.Derjaguin, Z.M.Zorin, N.V.Churaev, V.A.Shishin, *Wetting, Spreading and Adhesion, Symp. at Loughborough Univ.*, 27-29 Sept., 1976;
A.C.Hall, *J.Phys.Chem.*, 79, 2742 (1970).
20. B.V.Derjaguin a. N.V.Churaev, *J.Colloid. a. Interface Sci.*, 49, 249 (1974)
21. G.F.Ershova, Z.M.Zorin, N.V.Churaev, *Koll.Zhurn.*, 37, 208 (1975).
22. M.M.Kusakov a. A.S.Titijewskaja, *Dokl.Akad.Nauk SSSR*, 28, 333 (1940).
23. I.F.Dzjaloshinski, E.M.Lifshitz, *Zhur.Eksperim.Teoretich.Fisiki*, 37, 229 (1959).
24. N.V.Churaev, V.D.Sobolev a. Z.M.Zorin, *Thin Liquid Films and Boundary Layers*, Acad.Press, London, N.Y., 1971, p. 213.
25. Z.M.Zorin, A.V.Novikova, A.K.Petrov, N.V.Churaev, *J.Coll. Interf.Sci.*, 48, No.2 (1974).
26. B.V.Derjaguin a. G.P.Sidorenkov, *Doklady AN SSSR*, 32, 622 (1941).
27. P.A.Voznij, N.V.Churaev, *Koll.zhurn.*, 39, 264, 433 (1977);
B.V.Derjaguin a. N.V.Churaev, *Croatica Chemica Acta*, 50, 187 (1977).
28. B.V.Derjaguin, J.Sutor, S.V.Nerpin a. M.A.Arutyunyan, *Doklady Acad.Nauk SSSR*, 161, 147 (1965); S.V.Nerpin a. A.F.Chudnovskij, *Physics of Soil*, Moscow, "Nauka" (1967); W.Drost-Hansen, *Ind.Eng.Chem.*, 61, 10 (1969);
I.F.Efremov, *J.phys.chimii (russ.)* 38, 2350 (1964).
29. Yu.M.Glazman, *Disc.Farad.Soc.*, No.42, 255 (1966).