Influence of surface forces on the formation of structural peculiarities of the boundary layers of liquids and boundary phases

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Abstract – The paper deals with the research of changing
structure and the properties depending on it in the bounda-
ry layers of liquids under the influence of surface forces
of solid support. Examples are given of global importance
of these changes of structure.

The surface forces acting beyond the range of boundary monolayers,
are able to change the concentration of dissolved ions and molecules. In
the first case, diffuse ionic layers are formed, which was known already
long ago, and which is mainly associated with the electrical component of
the surface field. The ionic atmospheres and the electric fields associa-
ted with these, may be formed in the case of electrolyte solutions (ref. 1)
In the second case, i.e. in that of molecular solutions, the field of sur-
face forces, in the first place the dispersion component of this field can
form the diffuse adsorption layers of molecules. These were for a long ti-
me ignored. For the first time, their existence was proven as a result of
investigating the capillary osmosis in the work done by Derjaguin and Kop-
telova (ref. 2). The existence of diffuse molecular adsorption layers
leads to that the diffusiophoresis phenomenon (ref. 3), which was discove-
red in 1947, may be observed, in distinction from electrophoresis, in non-
-ionic media, too (ref. 4).

The overlapping of the boundary diffuse layers of dissolved molecules in
an interlayer between two phases causes the third "adsorption component of
disjoining pressure". The theory thereof (ref. 5-9) was confirmed in pa-
pers (ref. 10). A case of the multilayer, negative adsorption provided
the basis for Dumansky and a number of other authors (ref. 11) to speak of
the existence of a "non-dissolving volume", as for example, in the water
layers close to the hydrophilic surface. An attempt to develop a quantita-
tive theory of that phenomenon was published by me (ref. 12). Generally
speaking, the negative adsorption of dissolved molecules may be brought
about by the balance of dispersion forces. In this case, however, the ne-
gative adsorption cannot attain the values observed at the surface of
strongly lyophilic bodies. In the latter cases, a change in the structure
of the layers of a polar solvent near the hydrophilic surface, under its
influence, may serve as an explanation. As regards the mechanism of that
phenomenon, it should include the direct influence of the lyophilic sur-
face on a solvent monolayer which is directly adjacent to it, this influ-
ence changing the structure thereof, for example, by creating a definite
orientation. This monolayer of changed structure imparts its structure
to the layers situated farther, by means of some kind of relay mechanism.
The British famous scientist, Hardy, had for the first time indicated the
possible existence of such a mechanism, and called it diachysis (ref.13).

In my paper written in 1953 (ref. 14), I had put forward a supposition
that in some cases such a structure must, at a certain distance from
the lyophilic surface, disappear jumpwise, passing over into the struc-
ture of the bulk liquid.

This then enabled me to put forward a concept on the boundary phases. At a
later date, the complete and definite confirmation of the real existence of
the boundary phases was obtained by investigating the behaviour and proper-
ties of the polymolecular nitrobenzene layers wetting the surface of glass
or quartz. At first, it was shown by the use of a calorimeter, that the spe
cific heat capacity in thin layers was different by a few per cent from its
bulk value (Ref.15). In this case, this difference remains constant until
a certain thickness is obtained, as the distance from the substrate increa-
ses; and when that thickness is exceeded, the difference disappears jumpwi-
se. The thickness of such boundary phases having a changed heat capacity

gradually diminishes, as temperature is raised. Measurement of the heat absorbed, when temperature is gradually raised, allowed the latent specific heat of phase transition to be determined. With regard to the order of magnitude, it proved to be equal to the transition heat, when liquid crystalline phases are formed of a corresponding mesogen liquid. In distinction from the latter, however, in the case of the boundary phases the transition heat evolves, not at once at the liquid–crystalline phase–isotropic phase equilibrium temperature, but gradually as temperature is raised, and as the boundary phase grows thinner.

Still more distinct and obvious results that are characteristic of the boundary nitrobenzene phases, were obtained by a method involving translucence of a wedge-shaped nitrobenzene layer between the glass and the quartz surface to transmitted polarized light (Fig. 1) (Ref.6). Scanning this wedge-shaped layer, one could have plotted a dependence of the light damping logarithm on the layer thickness (Fig. 2).

Changing the incident beam polarization plane, it has been established that the boundary layer is optically anisotropic. As appears from the Lambert-Bougerr law, the obtained profile shows that the optical properties of the boundary phases are uniform; yet these differ from those of the bulk liquid by a smaller absorption coefficient, which proves the homeotropic orientation. Knowing μ and the bulk phase absorption coefficient, μ_o , the structural ordering degree, S could be determined from the formula

$$S = 1/2 \left(3 < \cos^2 \vartheta > -1\right) = 1 - \mu/\mu_o \ ,$$

where ϑ is the angle between the long axis of a molecule and the normal to the substrate surface. The parameter S and the thickness h proved to be increasing with the cleaning and lyophilization degree; and on being treated in the hydrogen flame, S would obtain the values of 0.32 ± 0.1 and h=65 nm, respectively, at 295° K. The same method was applied to detecting and investigating the boundary phases of a number of other liquids having benzene rings in molecules. Such a choice of objects is in some sense occasional, and is not associated with that the boundary phases do not form liquids having a different structure of molecules. The point is that a sufficiently strong absorption of the beam of a chosen region of the light spectrum is required for measurements. The boundary phases of about thirty derivatives of benzene were investigated. It appears that the thicknesses and the order parameters of all these liquid layers are fairly close to one another. The developed theory (Ref.16) explains quite well the mechanism of the formation of the boundary phases and the dependence of their thickness, h, and the order parameter, S, on temperature.

The character of orientation is preset by the short–range forces of the substrate; and its propagation according to the relay mechanism by the interaction forces between the molecules of liquid. The thickness of the boundary phase is determined by the effect of the molecular long–range forces, reducing the excess free energy of the boundary phase interlayer. The boundary phases can undoubtedly be also formed by other polar liquids, as, for example, by hydrocarbons. The results of investigation of the viscosity of liquids by the blow-off method as a function of distance from the substrate, are indicative of that (Ref.18). In some cases, it has been detected that viscosity changes jumpwise at a certain distance, thereby indicating an abrupt change in structure (Refs. 9,19). In the case of a series of liquids, in the first place of water, the available data indicate rather a gradual decay of the structural peculiarities, as the distance from the substrate increases.

A special structure of the boundary layers of water was for the first time indicated by the isotherms of polymolecular adsorption of the vapours of water and ethyl alcohol, intersecting the saturation axis (p/p_s =1) with a thickness close to 100 Angström (ref.20). In this case, the thickness corresponding to p/p_s =1 proved to be strongly dependent on temperature, approaching a monolayer at 70°C (Ref.21). It was found to be impossible to ascribe such a run of the isotherm to the joint effect of molecular and ionic-electrostatic forces. These forces explain, however, another, β– branch of the adsorption isotherm, separated from the first, $\measuredangle$ branch by the region of unstable thicknesses. In accordance with the Frumkin-Derjaguin theory (Refs.22,23), the existence of both this region and the shape of the $\measuredangle$-branch of the isotherm explain the incomplete wetting of glass and mica by water.

The special structure of the boundary layers underlies the difference of a number of their properties from the bulk ones. Thus, investigation of the expansion of water in pores (about 50 Å in size) between the particles of silica-gel powder (Fig. 3) revealed an essentially different shape of the isotherm, with which the minimum volume disappears, whilst the density at 20°C exceeds the bulk density by about 2% (Ref.24). In view of the presence,
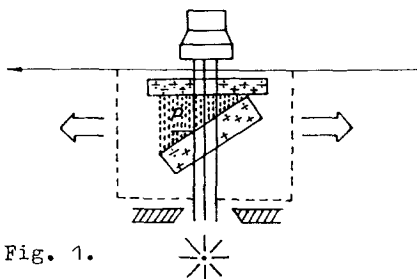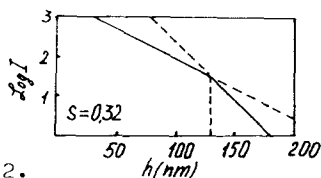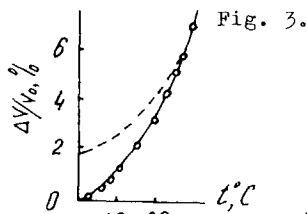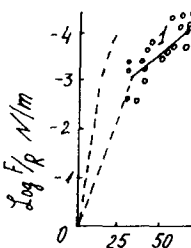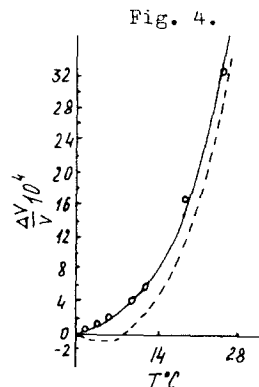
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

part of the effect may be attributed to the content of the pores in silica particles. This would somewhat underrate the evaluation of corresponding effective thicknesses, which the effect observed must be correlated with. The measurements of the free expansion of water in the pores of aerosil powder made up of particles having no internal pores and the interparticle interstices of the order of 60 A, are free of that disadvantage(Fig. 4)

Analogous results were obtained in (Ref.25). It is essential that such a structural-sensitive property as the viscosity of the boundary layers near to the lyophilic surface, is substantially higher than that in bulk (Refs. 26,9). An important consequence of a changed structure of the boundary layers of water consists in the appearance of a positive structural component of disjoining pressure in the course of their overlapping inside a water interlayer. The disjoining pressure was for the first time detected in (Ref.27), as well as in (Ref.28), both for the wetting and symmetrical interlayers. Some authors, who had observed the same component of disjoining pressure, persevere in calling it differently; namely, – hydration or solvation forces. In doing this, they avoid indicating their nature and mechanism, attributable to a special structure of the boundary layers, but not to "hydration of ions", which is present to the same extent in the bulk of liquid, too. Both the thickness of the boundary layers and their differences from the bulk values may be reduced by changing in some way the degree of lyophility (or hydrophilicity) of the surface. Moreover, the disjoining pressure reverses its sign and becomes a negative one in the course of hydrophobization of the surface. The possibility of this was indicated for the first time in Ref. (29). Israleachvili was the first to have detected this phenomena (Ref.30); Rabinovich and Derjaguin (Ref.31) had done it (independently of Israelachvili) somewhat later (Ref.31). By applying the method of crossed filaments on the hydrophobic surface, we have not only detected the structural attractive forces, but also shown that their radius of action is substantially longer than that of the structural repulsive forces (Fig. 5). The negative component of disjoining pressure may probably, lead to the superfast coagulation of the sols of hydrophobic particles, too.

I would like to state that the global significance of the influence of hydrophilic substrates on the structure of the adjacent layers of water shows up in decreasing their freezing point. Therefore, the layers of unfrozen moisture are found in contact with hydrophilic soil particles in the Northern regions, where the ground is at a temperature of zero to minus 5°C. In the theory developed by me and Churaev (Ref.35), it has been shown that transfer of moisture in these interlayers proceeds in the direction of decreasing temperature at a very considerable rate, because it is proportional to the latent heat ice fusion. This allowed a quantitative theory of the frost heaving of soils to be developed for the first time, which had experimentally been rigorously checked in model experiments (ref.34). Another manifestation of the structural component of disjoining pressure – the swelling of a number of clays, was thoroughly investigated by P.Low (Ref.28). It would be essential to state additionally that, as was shown by Green–Kelly and me (Ref.35), the swelling water in Na – montrmorillonite does show up birefrigerence in the layers up to 200 A thick. This emphasizes the special structure of the swelling water similarly to the birefrigerence of the boundary layers of benzene derivatives.

It would be important to substantiate this also for other cases, as for example, for wetting films. By the way, the hydrodynamics of the wetting films, developed by us on the basis of introducing a term with the gradient of disjoining pressure (Ref.36), is also of the global significance; for it underlies the calculation of the mass transfer in grounds and soils. For instance, this enabled one to explain the formation of subterranean lakes having the surface area of many thousand square kilometers in the Karakoum desert (Ref.37). These lakes were formed owing to migration of the water films wetting the ground particles, under the influence of surface forces, the films forming due to rare preapitation of rain.

REFERENCES

1. B.V.Derjaguin, G.A.Martynov, Dokl. AN SSSR, 152, 140 (1963).
2. B.V.Derjaguin et al.,Disc.Farad.Soc., N 40, 246 (1965). N 5, 692 (1969); Coll. Res. in Surface Forces, N.Y.; L., 64, p.182 (1975). B.V.Derjaguin, N.V.Churaev, J.Colloid a. Interface Sci., 62, 369 (1977); 87, 543 (1982).
3. B.V.Derjaguin et al., Kolloidn.zh., 9, 335 (1947).
4. B.V.Derjaguin, Z.P.Ul'berg, S.S.Dukhin, G.L.Dvornichenko, N.N.Ivzhenko, Koll.zh., 48, 435 (1986); 48, 673 (1986).
5. B.V.Derjaguin a. N.V.Churaev, Dokl. AN SSSR, 222, 554 (1975); J.Colloid a. Interf. Sci., 62, 3, 369 (1977).
6. B.V.Derjaguin, Colloid a. Polym.Sci., 258, 433 (1980).
7. D.Y.Chan, D.J.Mitchell, B.W.Ninham, B.A.Pailthorpe, J.Coll.a.Interf.Sci., 68, 462 (1979).
8. B.V.Derjaguin a. N.V.Churaev, J.Colloid a.Interface Sci., 87, 543 (1982)
9. B.V.Derjaguin, N.V.Churaev, V.M.Muller, Surface Forces. Plenum, N.Y.,(1987).
10. E.Manev, M.Buleva, Coll. Polymer Sci., 256, 375 (1978). A.D.Sheludko, D.Ekserova, Izv. Khim. Inst. Bulg. Akad.Nauk, 7, 105 (1960). L.B.Boino-vich and B.V.Derjaguin, Koll.zh., 49, 631 (1987).
11. A.V.Dumansky, Lyophility of disperse systems, Kiev, published in Russian by the USSR Academy of Sciences (1960).
12. B.V.Derjaguin, Koll.zh., 5, 257 (1939), 605 (1939).
13. W.Hardy, Phil.Trans. A., 230, 827 (1931).
14. B.V.Derjaguin. Proc. II Internat.Congr. Surface Activ. London, 2, 145 (1957).
15. B.V.Derjaguin, Yu.M.Popovsky, Dokl. AN SSSR, 159, 897 (1964); 175, 385 (1967).
16. B.V.Derjaguin, Coll. Liquid Crystalline State of the Wall-Adjacent Lay-ers of Some Polar Liquids, ed. by C.A.Croxton. Wiley (1986), p.739.
17. B.V.Derjaguin, Yu.M.Popovsky, A.A.Goryuk, Langmuir, 3, 628 (1987).
18. V.V.Karasev, B.V.Derjaguin, Dokl. AN SSSR, 62, 761 (1948), Kolloidn.zh., 15, 365 (1953).
19. B.V.Derjaguin, and B.V.Karasev, Dokl. AN SSSR, 101, 289 (1955). Wear, 1, 277 (1958).
20. B.V.Derjaguin a. Z.M.Zorin, Proc. II Intern. Congr. Surface Activ., London, 2, 145 (1957).
21. B.V.Derjaguin, Z.M.Zorin, N.V.Churaev, V.A.Shishin, In Coll. Wetting, Spreading a. Adhesion, London, Acad.Press, p.201 (1977).
22. A.N.Frumkin, Zh.fisich.khim., 12, 387 (1938).
23. B.V.Derjaguin, Zh.fisich khim., 14, 137 (1940).
24. B.V.Derjaguin a. V.V.Karasev, Res. in Surface Forces, N.Y., Consult. Bur., 3, 25 (1971), J.Coll. a. Interf.Sci., 78, 274 (1980).
25. B.V.Derjaguin, V.V.Karasev, N.B.Ur'ev, Colloids and Surfaces, 25, 387 (1987).
26. B.V.Derjaguin, N.N.Zachavaeva, A.M.Lopatina, In Coll.Res. in Surf.For-ces, 1, 162, Consult.Bur., N.Y. B.V.Derjaguin, N.V.Churaev, Coll."Res. in Surf. Forces", 3, 261 (1971), Consult.Bur., N.Y.
27. B.V.Derjaguin, M.M.Kussakov, Acta physicoch. URSS, 10, 25; 153 (1939); K.H.Adlfinger, G.Peschel, Z.phys.chem. N.F., 70, 151 (1970); 108, 145 (1977). G.Peschel a. al. Coll. a. Polymer Sci., 260, 444, (1982). Koll. zh., 48, 1090 (1986). J.N.Israelachvili, Philos.Mag. A, 43, 753 (1981). Ya.I.Rabinovich, B.V.Derjaguin, N.V.Churaev, Adv.Coll.a.Interf.Sci.,16, 63 (1982); Ya.I.Rabinovich, B.V.Derjaguin, Langmuir, 3, 625 (1987).
28. P.F.Low, Soil Sci. Soc. Amer., 44, 667 (1980). J.L.Oliphant, P.F.Low, J.Coll.a. Interf.Sci., 89, 366 (1982). B.E.Viani, P.F.Low, C.B.Roth, J.Coll.a.Interf.Sci., 96, 229 (1983). F.Low, Koll.zh., 48, 1081 (1986).
29. B.V.Derjaguin, N.V.Churaev, J.Coll.a.Interf.Sci., 49, 249.
30. J.N.Israelachvili, Nature, 300, 341 (1982). B.M.Pashley, P.M.McGuiggen, B.W.Ninham, Science, 229, 1088 (1985); D.F.Evans a. B.W.Ninham, J.Phys. Chem., 90, 226 (1986).
31. Ya.I.Rabinovich a. B.V.Derjaguin, Colloids a. Surfaces, 30, 243 (1988).
32. Yu.M.Chernoberezhskii a. al., "Langmuir", 3, 654 (1987).
33. B.V.Derjaguin, N.V.Churaev, J.Coll. a. Interf. Sci., 67, 391 (1978). Cold Regions Sci. Technol., 12, 57 (1986).
34. B.V.Derjaguin, N.V.Churaev, J.Coll. a. Interf. Sci., 84, 182 (1981).
35. D.Green-Kelly, B.V.Derjaguin, Trans.Farad.Soc., N 60, 449 (1964); Coll. Res. in Surf. Forces, 2, 115, N.Y., Consult.Bur.
36. B.V.Derjaguin, and N.V.Churaev, The Wetting Films, published in Russian by "Nauka". Moscow (1984), Chapter II.
37. M.M.M.M.Chubarov, Feeding up of the Ground Water in a Sand Desert through an Aeration Zone. Moscow. Published in Russian by "Nedra",(1972).