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Modern State of the Investigation of Long-Range Surface Forces[†]

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Development of the concept of surface long-range forces and, in particular, the equilibrium disjoining pressure of liquid and gaseous interlayers has been set forth. Considered are the molecular, adsorption, electrical, structural, and electronic components of disjoining pressure. The contribution of the disjoining pressure to the hydrodynamics of thin layers is considered. The first theory of the frost heaving of soils has been formulated. Stated are the investigations of surface forces, in particular, in the processes of the formation of new interfaces and arising phenomena of the emission of electrons, ions, photons, and neutrons.

In the Gibbs capillary theory the interfaces are characterized only by such extensive quantities as adsorption, free energy, and entropy. Thus a world of two dimensions was created, leaving unrevealed the structure of interfaces and distribution of the forces and other intensive parameters acting at interfaces. This world was reduced to a monolayer due to the experimental work of Releigh and Langmuir.

It is fairly obvious that the kinetics of surfaces and disperse systems can be interpreted only if the structure of interfaces is considered—that is, when passing over to the three-dimensional world.

This occurred first of all in developing the theory of electrokinetic phenomena, the first of which—electrophoresis—was detected by Reuss in 1809 in Moscow. Though it may be surprising, the cognate phenomenon—diffusiophoresis—had been detected only in 1947, also in Moscow, by the author of the present paper¹ with further participation of Dukhin, Ulberg, and Dvornichenko.^{2,3}

The two phenomena have a common feature in that both depend on the diffuseness of adsorption layers. One of the limit cases of diffuseness is a nonsolving volume studied

in several fundamental works by Dumansky.⁴ A difference consists in that diffusiophoresis is possible also in nonionic media under the condition of diffuseness of corresponding adsorption layers.⁵ Quite recently diffuseness of adsorption layers has gained a tremendous significance in connection with the application of reverse osmosis membranes to desalting and separating mixtures.

In this connection, I can't help but noting that the terms reverse osmosis membrane and reverse osmosis are essentially incorrect; for the membranes are permeable for a solute (dissolved component), and hence, these allow the capillary osmosis to occur,¹ which was investigated by Koptelova and co-workers at our department, rather than the osmotic pressure and osmotic transfer.⁶

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About 40 years ago, we had started investigations on the structural peculiarities of polymolecular boundary layers.⁷ In recent years, these investigations have been playing an undoubtedly major role in mastering membrane separation processes.⁸ These peculiarities determine changes in the dissolving power of those layers and thus also influence the membrane separation efficiency.

These structural peculiarities had been recognized approximately 50 years after the first publications substantiating their existence, and about 30–40 years since unambiguous proofs thereof had been obtained (in particular by Zorin and me⁹).

This, on one hand, is pitiful and, on the other, allows a statement to be made that those investigations have considerably outstripped their time.

There is another reason why the Gibbs capillarity theory, i.e., thermodynamics of heterogeneous systems, is completely insufficient (though it is indispensable) for interpretation of the properties of most disperse systems. The point is that these contain, either permanently or in the process of colloid particles approaching one another, disperse phase (or ambient medium) interlayers, in which the transient interphase layers overlap.

In such an interlayer there are absent parts whose intense properties are identical with those of the bulk phases of which the interlayer has been formed. As is known, Gibbs had not considered just such interlayers.

In 1931, W. Hardy had published a paper¹⁰ stating that a static counterpressure was set up when any interlayers (including those of air) became thinner. Although it had proved that corresponding measurements were absolutely erroneous (probably because of the foreign particles of vegetable origin getting into the gap between two plates), the idea itself of carrying out such experiments was quite progressive.

Also in 1931, I had published measurements indicating that thin water interlayers between quartz surfaces around 100-Å thick would reveal shear elasticity¹¹ (at an oscillation frequency of about 10–100 Hz). Partly under the influence of this work, and partly analyzing the causes of the stability of sols and suspensions, I had together with Obuchov and Kusakov carried out experiments establishing the existence of a regular connection between the pressure applied to a liquid interlayer and its thickness in the equilibrium state.¹²

This pressure for the equilibrium state was designated as the disjoining pressure.^{12a} Coincidence of the experimental results obtained, whether in the course of the gradual thinning-out of an interlayer or when its thickness increased, corroborated the equilibrium character of the

plotted isotherm of disjoining pressure.

It is quite obvious that the interlayers whose disjoining pressure is different from zero are not "Gibbs": the boundary layers in such interlayers are overlapped. The overlapping itself is both the *necessary* and *sufficient* cause of the arising of disjoining pressure. Recognition of this connection served exactly as the general basis for developing the theory of different components of disjoining pressure. In the first place, the ionic–electrostatic and the molecular components of disjoining pressure were derived thus allowing a quantitative theory of coagulation and stability of lyophobic colloids to be developed.¹³ This theory was further applied to heterocoagulation phenomena,¹⁴ and finally, with participation of Churaev, it was expanded by including the structural component of disjoining pressure.¹⁵ The structural component of disjoining pressure was for the first time definitely detected already in 1951, when I was investigating together with Zorin the polymolecular adsorption layers close to vapor saturation—that is, in a nonsymmetrical system.^{9,16} The aforesaid data cannot at all be attributed to the effect of molecular and ionic–electrostatic forces. In a nonsymmetrical system, a liquid layer whose structure has been modified under the effect of a lyophilic substrate is overlapped by a liquid–gas interface. After Hell,¹⁷ Adamson,¹⁸ and other had published their works yielding cognate results, Kitchener and Pashley have shown that the thickness of adsorption layers close to saturation would increase several times, attaining 300 Å, if the substrate is thoroughly hydrophilized and if all hydrophobic sites are removed.¹⁹ This only reinforces our concept of the existence of the structural long-range action of surfaces. Other works that also mentioned this long-range action, were reviewed by Henniker in 1949.

This concept is in good agreement also with the theoretical research undertaken, for example, by Ninham, Marceija, et al., for the purpose of interpreting the interaction of lyophilic surfaces.²⁰

These theoretical researchers were based on calculation of the structural changes imposed on the liquid by an adjacent phase and on their decay as the distance from the surface of the latter was increased. The successes achieved in this case are generally known. Yet three major supplementary remarks will have to be made. First suggested²¹ and quite recently experimentally detected²² by Israelachvili and Pashley, the disjoining pressure of water interlayers between hydrophobic surfaces may be negative, extending at a distance of the order of 100 Å and being of the explicitly structural nature. These forces are, of course, of the nature cognate with the lyophobic forces generated by separate molecules or ions of a solution.

However, the stride occurring in passing over to the collective effect of lyophobic sites arranged on the interface

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and in the adjoining boundary layers of an adjacent liquid phase must not be ignored and/or underestimated. The point is that Gui-Chapman's diffuse ionic layers and Debye-Huckel's ionic atmospheres are usually sharply distinguished, not only historically, but also conceptually.

Pashley's tendency to reduce the aforementioned structural repulsion forces to hydration of ions²⁴ especially contradicts physical logic (as well as the available experimental data, as has been shown by Low²³).²⁴ This is all the more inadmissible because the radius of action of the surface structural forces may exceed by 2 orders of magnitude the thickness of the hydrate shell of ions and because in many cases these forces are generated by the surface-active sites of the hydrophilic nature (for instance, on quartz).

The second supplement resides in a necessity of distinguishing the structural effects or forces of two kinds with essentially different origins.

Calculations and direct measurements of the disjoining pressure of aqueous and other interlayers between the molecular-smooth mica surfaces allowed an oscillating shape of the isotherm of disjoining pressure to be detected at small thicknesses on the order of a few monolayers.²⁵ The period of these oscillations corresponds to a monolayer thickness, and hence, the oscillations themselves are due to the discrete structure of liquid and are not associated with the long-range action forces. Thus, it will be natural to call the corresponding effects and forces microstructural.

At larger distances, the oscillations decay and the long-range forces remain, dependent on the molecular and the structural components of disjoining pressure. It will be quite rational to denominate the forces corresponding to the latter component as macrostructural ones.

In distinction from the microstructural forces depending essentially on Born's forces, the macrostructural ones depend on the van der Waals, dipole, and quadrupole forces, and finally for water, on the hydrogen bond. The long-range action of hydrogen bonds is determined by the fact that the correlation length of hydrogen bonds is on the order of 10 Å. In this connection, I note that under real conditions the oscillations, in which the microstructural forces show up, decay at considerably shorter distances from the surfaces that are not atomically smooth; therefore, these oscillations do not play any substantial part in the colloids stability problem. These are also blurred near nonrigid liquid-fluid interfaces. Therefore, in particular, these oscillations due to the microstructure do not show up distinctly when plotting the isotherms of adsorption of vapour even on the atomic-smooth surfaces.

For a long time, the existence of long-range structural forces and the direct proofs of their existence either have been ignored or the experiments have been referred to, in which these forces were not detected.

But recently the situation has changed under the influence of both new experiments and theoretical research. However, that the forerunners were right has mostly not been noted. In these cases, instead of the terms introduced by those pioneers—structural forces or the structural component of disjoining pressure—the following term has been used: hydrate or solvate forces. The term structural forces possesses an advantage consisting in that it simultaneously indicates unambiguously the nature of those forces. Yet the term *solvate forces* appeals to the notion

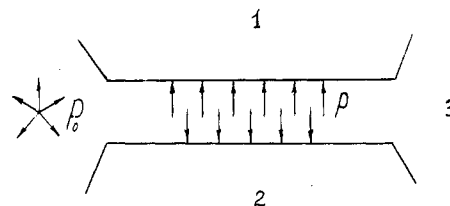


Figure 1. Direct determination of the disjoining pressure value.

of solvation, which, though it has frequently been used, has not been unambiguously defined.

Essentially, only the concept on structural peculiarities is apt to characterize the basic distinctive feature of solvate (or hydrate) layers. Therefore, introduction of the term solvate forces instead of structural forces should be refuted as entering misunderstandings and unclearness in the very fundamentals of colloid science.

Remember that in accordance with Biblical legend the construction of the Babylon tower was stopped when the common language had ceased to be used. However, in distinction from the mentioned problem, the foundation of the tower was already finished and did not suffer because of this.

At present, there are available an immense number of applications of the colloid science to most diverse regions of industry, agriculture, and medicine. If its standing among other science branches is rather underestimated in several countries, the main cause resides in that its general fundamentals are underestimated or ignored, as well as that the foundation itself remains so far unfinished. Thus, it is quite obvious that first of all a common language has to be developed, for the purpose of reinforcing and enlarging the fundamentals of the science of colloid-surface phenomena.

Establishing concise terminology and the exact definition of basic concepts should play a major part. The general concept of disjoining pressure is one of these.

Almost 50 years have elapsed since the concept on "disjoining pressure" has been introduced in the science of colloids and surface phenomena. During this time, it has come to diverse uses in treating the problems dependent on the behavior and the properties of polymolecular liquid layers. Unfortunately, the defacto usage of this concept is frequently masked by the omission of the term itself.

The frequency of the implicit usage of disjoining pressure may be illustrated by the use of a formula in thousands of works, which was published by me in 1934²⁶ and allows the calculation of any equilibrium interaction F of any convex body due to surface forces to be reduced to that of the free energy, $U(H)$, of the interaction of plane-parallel surfaces of the same nature, separated by a gap, H , which is equal to the distance of the nearest approach of both bodies:

$$F = GU(H) \quad (1)$$

where G is the geometrical factor dependent on the curvature of the surfaces of bodies near the approach zone.

In the course of derivation of the formula, the interaction of different elementary "zones" of the surfaces of both bodies, separated by an identical gap " h ", is considered. Further, all these "elementary" interactions are summed up (Figure 1). It is obvious (though it is usually not underscored) that all these elementary interactions are equivalent to corresponding disjoining pressures that are

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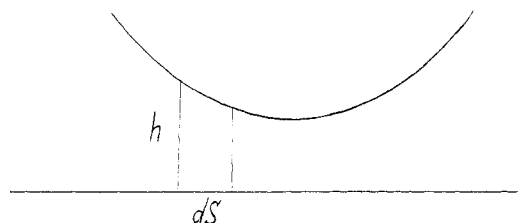


Figure 2. Derivation of B. V. Derjaguin's formula.

functions of the local thickness, h . In this case, it will have to be borne in mind that this is meant to be a general definition of disjoining pressure, which is applicable to any interlayer, including a gaseous one; in the case of attraction forces, the disjoining pressure may have a negative sign. Only under this condition, the general applicability of formula 1, which has come into wide use, to numerous cases with any interlayers and acting forces of any nature would be justified. All this proves simultaneously the importance of establishing the precise term and determining the concept on "disjoining pressure". Now, in the IUPAC collection there is written only that the disjoining pressure is a derivative of the free energy of a thin interlayer with respect to its thickness. So there is essentially no direct definition of the disjoining pressure, proper, and the latter is merely a result of a mathematical operation.

Yet long ago and many times I formulated the *direct* physical definition of the disjoining pressure as an excess one compared with the pressure of the bulk phase, the thin layer being part thereof.²⁷ The drawback of the definition adopted by the IUPAC does not consist only in that. It equates the disjoining pressure to the derivative with respect to thickness of the Helmholtz free energy. However, the direct definition of disjoining pressure, as will be easy to show, coincides with the derivative of the Gibbs free energy with respect to the interlayer thickness.

To determine the disjoining pressure only through free energy is also to a certain degree detrimental. The point is, as follows from examination, for instance, of Lifshitz et al.'s papers,²⁸ that, as a rule, a direct theoretical calculation of the disjoining pressure proves to be much simpler and more unambiguous than that of free energy. This in particular pertains to determination of the ionic-electrostatic component of disjoining pressure. As has been shown, it is a function only of charges and potentials of the diffuse part of an electric double layer in the given state of the system.²⁹

The Gibbs free energy depends on how the surface charges or potentials change as the layer thickness diminishes from infinity (∞) to a given thickness. These dependencies will have to be taken into account also in calculating a derivative of free energy with respect to thickness.

In view of the aforesaid, it has become both necessary and important to carry out direct determination of the disjoining pressure, and, with this as the basis, a corrected relationship between the latter and the Gibbs free energy of a thin interlayer has been obtained.

The suggested definition is as follows: "The disjoining pressure of a plane-parallel interlayer of phase 3 (including a vacuum) between phases 1 and 2 is equal to a difference between the pressure applied by the interlayer to the

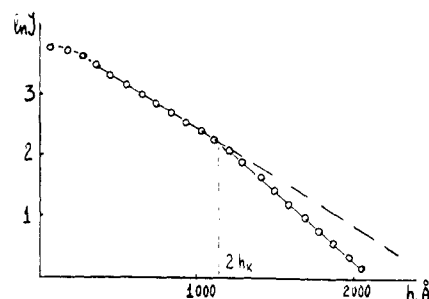


Figure 3. Dependence of the logarithm of the intensity of transmitted light on the nitrobenzene layer thickness.

phases confining it, and the pressure in the bulk part of phase 3 in the state of the isothermal and isobaric equilibrium" (Figure 2).

The additional Gibbs free energy of such a non-Gibbsian system, representing the amount of work involved in the thinning-out of the interlayer in the isobaric-isothermal process from infinity to the given thickness, h , is equal to a corresponding integral of the disjoining pressure over the thickness of the interlayer multiplied by its area.

As a first approximation, the disjoining pressure may be adopted to be equal to a sum of components of different nature: a molecular component, dependent on the effect of molecular or dispersion forces; an ionic-electrostatic component, dependent on the overlapping of diffuse ionic atmospheres; an adsorption component, dependent on the overlapping of diffuse atmospheres of adsorbed molecules; a structural component; and an electronic component, dependent on the overlapping of near-to-surface layers of liquid metals, in which the wave functions of electrons are different from the bulk ones. This component has been revealed for mercury films surrounded by octane.

The reports covering the structural peculiarities of the boundary layers of polar liquids play an important part in the program of our symposium. In this connection, I would like to emphasize a special significance of dependence of the structural peculiarities of boundary layers on their distance from an adjacent phase.

Yet as early as in 1952, I had put forward a supposition³⁰ that the special structure of boundary layers may at some distance from the substrate surface jumpwise disappear by transforming into the isotropic structure of the bulk phase. Thus, the existence of some sort of a liquid-crystalline phase of a limited thickness, being a function of temperature, has been admitted. Popovsky and I were the first to have obtained a substantiation of the existence of such "epitropic" phases, with a thickness on the order of 0.1 μm , in the course of investigation of thermodynamic properties³¹ and later also of the optical birefringence of nitrobenzene layers on the surface of glass or quartz specially activated during cleaning.³²

Popovsky and Altoiz, on having measured the decay of plane-polarized light passing through the interlayer dependent upon its thickness (Figure 3), have demonstrated in a most obvious, rigorous, methodically transparent and simple manner the liquid-crystalline nature of the wetting layers of nitrobenzene.³³ They have detected the bire-

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(31) Popovsky, Yu. M.; Derjaguin, B. V. *Dokl. Akad. Nauk SSSR* **1964**, *159*, 897; **1967**, *175*, 385; in *Research in Surface Forces*; Consult. Bureau; New York, 1971; b. 3, p 128.

(32) Derjaguin, B. V.; Popovsky, Yu. M.; Silenko, G. P. *Dokl. SSSR* **1972**, *207*, 1153.

frigence of these layers, their optical uniformity, and the jumpwise transition to the properties of an isotropic, bulk phase at a distance of around $0.06\ \mu\text{m}$ from the substrate. Measurements allowed the parameter of the order, S , and its dependence, as well as that of the epitropic phase thickness, on temperature to be determined. Similar results were obtained on 20 liquids—aniline and a series of benzene substituents. Thus, the formulated hypothesis of boundary phases has fully been corroborated. Yet the following reservation has to be made: for water and many other polar liquids a gradual change in structure as the distance from the substrate increases should be adopted.

Now, the problem of the special structure of the boundary layers of liquids has been for a long time underestimated; yet the phenomena of fundamental significance due to that structure do exist quite really. This is why I have paid such attention to that problem.

Dependent upon that structure is the stability of many sols and suspensions, as, for example, those of quartz, and diamond, according to Chernoberezhsky's data³⁴ within a definite range of pH values of a dispersion medium). In accordance with Low's data,^{23,35} the swelling of many clays depends on structural repulsion. Most cases of membrane separation cannot be explained without taking into account the structural peculiarities of boundary layers.

Finally, it is impossible to explain the existence of unfrozen water interlayers in soils and grounds at subzero temperatures. Now, their existence and ability to migrate in the direction of colder places explain quantitatively, as has been shown in the Churaev and Derjaguin's theory of crystallization flow, the frost heaving of soils.³⁶ This is a phenomenon of worldwide importance, which represents an engineering problem of tremendous significance for the Northern regions of Siberia and Canada to be tackled.

The formation of thick ice cones is also explained by a similar thermocrystallization flow.

Another worldwide phenomenon, associated with migration of polymolecular wetting water layers into soils under the influence of a disjoining pressure gradient (at positive or above-zero temperatures), resulted in the formation of immense—extending over many hundred kilometers—subterranean lakes in the region of the Kara Kum desert in the USSR. These lakes were formed as a result of migration of rare rainfalls.

The mechanism of this migration process undoubtedly includes the structural component of disjoining pressure. It will have to be noted that the thickness of structurally modified layers of water depends on the substrate nature; it is close to zero on some surfaces, as, for instance, on the surface of silver iodide. The use of silver iodide crystals, for the purpose of inducing rainfall from cumuli through crystallization of supercooled droplets, is probably associated with the aforesaid. However, there are no reasons for believing that only the surface of silver iodide but also other surfaces are lacking thick hydrate layers. This reminds me of a certain case from the history of ancient Egypt. Travelers, on having returned from the Babylonian regions, told among other curiosities that the Euphrates and Tigris rivers flowed from the North toward the South. Those who had listened to them objected that this could

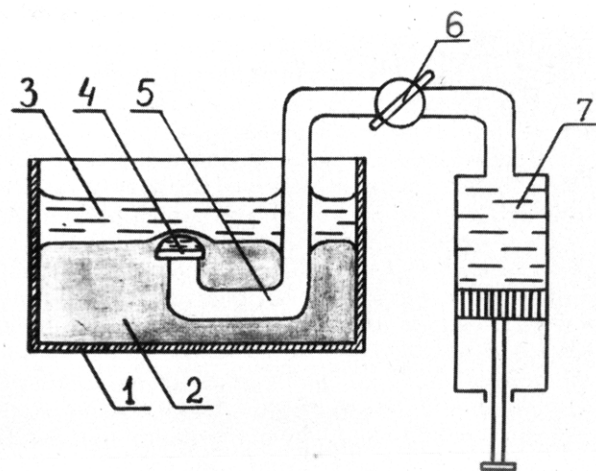


Figure 4. Schematic diagram illustrating the observation of the stability of mercury films.

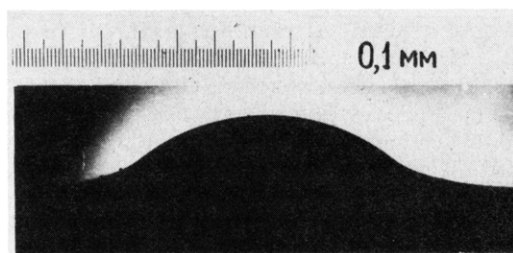


Figure 5. Profile of the stable free mercury film in octane.

be true because every Egyptian knows quite well that all rivers flow from the south toward the north.

In conclusion, I will mention two more components of disjoining pressure.

The fourth or adsorption component of disjoining pressure arises owing to the overlapping of the diffuse, adsorption atmospheres of the molecules contained in a solution. The nonuniformity of a solution interlayer arising due to these atmospheres does not permit us to limit ourselves to the application of the Lifshitz et al. theory of dispersion forces. This theory, however, enabled me and my co-authors not only to determine the structure of diffuse adsorption atmospheres but also, by having recourse to the Onsager principle, to calculate a contribution made in the course of their overlapping, i.e., the adsorption component of disjoining pressure.³⁷

The obtained results allowed an explanation of some experimental works performed by Kusakov,³⁸ Sheludko and Ekserova,³⁹ and others.⁴⁰

Finally, quite recently Leonov and Yashin have demonstrated at our laboratory⁴¹ the stability of symmetrical mercury films enveloped by octane, which proved to be unlimited in time (Figures 4 and 5). A theory developed by Roldyghin and me⁴² explained this stability, reducing it to the fifth or electronic component of disjoining pressure. This component arises due to the overlapping of the

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domains near the surfaces of contact of a mercury interlayer with the ambient medium, in which the wave function of electrons is different from its value in the mercury bulk. In accordance with theory, the arising disjoining pressure sensibly depends on the conditions of collision of electrons with the ambient medium, and it can reverse its sign. This permits the observed stability of mercury interlayers in other organic liquids, which is limited in time, to be explained. This restricted stability (i.e., the time of existence of an interlayer until it is ruptured) sharply changes even among a series of organic liquids that are cognate in their nature (e.g., octane, nonane, decane, hexane, etc.).

Up to now, investigation of surface forces has allowed the long-range action to be detected, which does not exceed a micrometers. Therefore, special attention should be paid to the experiments carried out by a researcher of the Oncology Center of the Academy of Medicinal Sciences, Golovanov. Diluting the blood plasma by a 4-fold volume of a 10% salt solution, Golovanov has detected that leukocytes can repel the surrounding erythrocytes at a distance up to 80 μm .⁴³ It has also been shown that in the absence of erythrocytes, leukocytes that mutually repel one another form in a few hours a periodical lattice possessing hexagonal symmetry.^{43,44} In this case, the distance between the neighboring lattice sites occupied by leukocytes was on the order of about 60–70 μm . These investigations results unambiguously indicate that live cells are able to generate repulsion forces having a radius of action which many times exceeds that of the forces stemming from unorganized matter. An attempt was made to ascribe the forces due to leukocytes to diffusion fluxes resulting from live activity processes.

However, this explanation became invalidated when it was demonstrated that the repulsion forces are able to overcome material barriers in the form of filaments and wires.⁴⁵ This indicates that the nature of these forces is cognate with that of Frohlich's forces generated by coherent excitations,⁴⁶ emitting electromagnetic waves having the length of a few hundred micrometers. The next problem to be solved resides in finding a direct substantiation of this hypothesis.

Up to now, we have considered mainly the surface forces of equilibrium nature. Yet the forces arising when the contact of solids is broken up are of a different, substantially nonequilibrium character. In most cases, when both solids are of different nature and the contact between these

is broken up, the plates of a Helmholtz electrical double layer are simultaneously separated. As a rule, a delay of their discharge increases the difference of potentials and that of energies till the discharge moment. This leads to an irreversible consumption of the separation work which may, at the sudden tearing-off, exceed by several orders of magnitude the equilibrium separation work or the equilibrium adhesion.

For instance, the dependence of the films peeling-off work on the kind and pressure of the surrounding gas, detected by Krotova and me, may serve as one of numerous proofs thereof.⁴⁷ The arising electrical component of adhesion⁴⁸ is especially important for the rapid processes of separation of two bodies. Thus, Toropov has proven that a pulse, as required for tearing-off the particles sticking to a plate, is proportional to the square of a radius.⁴⁹

Further development of the theory has shown this may be explained, only by assumption that the resistance to the tearing-off is mainly determined by the electrical forces of attraction of the charges being separated. The role of molecular forces is insignificant.⁴⁹ Of primary importance is comparison with theory (of Muller, Toropov, and Mikhovich), accounting for the contact electrification, of the rebound phenomenon at a collision of fine particles against an obstacle.⁵⁰ It has been found that only taking into account the contact electrification allows the loss of energy at a collision and the critical velocity, below which a rebound does not occur, to be quantitatively assessed.

Dahneke's attempt to explain the same phenomena by taking into account molecular forces is completely based on a gross error.⁵¹ It should be noted that in the case of breaking-up adhesion and cohesion, the special properties of freshly formed surfaces are also associated with their charges. In particular, these explain the phenomena of emission from the juvenile surfaces of high-energy electrons (detected by Krotova, Karasev, and Derjaguin⁵²), ions, and X-rays,⁵³ as well as, in some cases, of neutrons.⁵⁴

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