CERTAIN RESULTS OBTAINED IN RESEARCH ON LONG-RANGE
SURFACE FORCES

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The development of the theory of capillarity in the works of Clairaut, Laplace, Poisson, and Young on the basis of summation of pair molecular interactions, and in Gibbs' treatise on the basis of a thermodynamic approach, has brought forward the question of the radius of molecular action of surfaces, or, more precisely, the radius of action of surface forces. Rayleigh's first crude estimates led to distances on the order of $10^{-7}$ cm.

A more definite estimate was given by Langmuir, who advanced the view, one that had considerable influence, that the effect of the surface does not extend further than the first adsorbed monolayer. The first direct experimental refutation of this concept was based on the discovery and investigation of the disjoining pressure of polymolecular layers of liquids, both those that contain dissolved ions [1] and those that do not contain ions [2]. In the first case, the disjoining pressure can be attributed to overlapping of diffuse ionic atmospheres, the theory of which was worked out for the first time in [3]. However, even then, measurements of the disjoining pressure at various concentrations of electrolyte, including high concentrations, revealed the existence of still another component of the disjoining pressure, which I related to hypothetical structural features of layers of water close to hydrophilic surfaces such as silicates. In contrast, the disjoining pressure isotherms for straight-chain aliphatic hydrocarbons could be wholly attributed to the action of van der Waals forces. A full quantitative confirmation of this view was obtained much later by applying to these measurements the theory of dispersion forces of E. M. Lifshitz.

The first direct measurements of molecular attraction between solids in the absence of a liquid interlayer [4] showed that the measured forces are considerably smaller than calculated forces based on the formulas of London on the assumption of additivity of pair interactions. This could be explained by an electromagnetic retardation effect, which was examined for the first time by Casimir. The problem that had arisen, which we discussed with E. M. Lifshitz, led to the development of a macroscopic theory of molecular forces [5], and subsequently to the development of a theory of the molecular component of the disjoining pressure for the most general case of interaction of any phases in the presence of any interlayer [6].

In the Discussions of the Faraday Society, where the results of [4] were reported, results were also communicated from measurements of molecular attractive forces by a different method [7]. In contrast to the data of [4], the values recorded in [7] were several orders of magnitude greater than the values that follow from the theory of unretarded London molecular forces. An attempt to "improve" this theory did not receive any recognition, and it attracted no further attention. In contrast, the theory of [5, 6] is in good agreement with our measurements, both those that preceded its development and also the measurements made subsequently.

The measurements made by the method of [9], which is different from ours, proved to be consistent with our measurements and also with the theory of [5, 6]. As I demonstrated thoroughly in the Faraday Discussions [10] based on the papers [4] and [7], the reasons why the forces measured in [7] were overstated by several orders of magnitude can be found in electric charges on the surface that were not removed as thoroughly as they should have been.

Thus, studies of the disjoining pressure have led to an examination of its three components: ionic-electrostatic, molecular, and structural. It was assumed that in the case of lyophobic surfaces, the structural component can be neglected in the first approximation in comparison with the other two components, for which the dependence on thickness could be determined theoretically. I used this approach in constructing a theory for the stability of lyophobic colloids. Initially limiting the analysis to the case of low potential $\varphi$, the condition for the coagulation of weakly charged particles was derived [11]

$$\frac{e\varphi}{A\kappa} < 1$$

where $\varepsilon$ is the permittivity; $A$ is the Hamaker constant; $\kappa$ is the reciprocal of the Debye length; $\varphi$ is the potential of the diffuse layer. A condition was also derived for the coagulation of particles with a radius much smaller than the thickness of the ionic atmospheres [12]

$$\frac{eR\varphi}{kT} \leq 20$$

where $k$ is Boltzmann's constant; $T$ is the absolute temperature. Subsequently, a condition was derived for the coagulation of strongly charged lyophobic sols [13]

$$mA^2z^6/\varepsilon^3 (kT)^5 > c$$

where $m$ is the electrolyte concentration; $z$ is the charge of the counterion; $c$ is a constant that is weakly dependent on the valence of the co-ion. In these formulas, $A$, the constant in the expression for the energy of molecular interaction per unit area of plane-parallel surfaces, could be precalculated only after the appearance of the Lifshits theory. At first, therefore, the only aspect of the theory that was compared with experiment (supporting the theory) was that part relating to the dependence of the concentration threshold of coagulation on the valence of the counterion [14].

Using the Lifshits theory, the absolute values of the coagulation concentrations could be calculated in advance. Good agreement was obtained in [15-18].

Since the reliability of calculations of these components of the disjoining pressure had now been verified in this manner, it became possible in the case of films between hydrophilic surfaces to evaluate the third (structural) component of the disjoining pressure by subtracting the electrostatic and molecular components from the measured value of the disjoining pressure. This method was applied in [19] for the case of water films between quartz surfaces. For water films between mica sheets, analogous measurements and calculations were performed in [20]. In both cases, at distances less than 30-50 Å, a structural component of the disjoining pressure is manifested, dropping off exponentially with increasing distance.

It must be noted, however, that the quantitative values obtained for the structural repulsion will depend on the law according to which the potential of the surfaces increases as they are brought together. Nonetheless, the general conclusion as to the existence and the order of magnitude of the radius of action of surface structural forces still remains valid.

It was easier in an experimental sense to evaluate this radius of action by determining the disjoining pressure isotherm for wetting water films on hydrophilic substrates (quartz, glass, mica). The isotherm obtained in [21] on the basis of ellipsometric measurements consisted of two sections. The section corresponding to large thicknesses and small values of the disjoining pressure ($8$-film) could be expressed quantitatively and completely in terms of the ionic-electrostatic component of the disjoining pressure [22]. In contrast, the section corresponding to thicknesses less than 70-80 Å ($8$-film) could not be expressed in any sort of approximation through the sum of the ionic-electrostatic and molecular components of the disjoining pressure, even at the high limit of potential of the substrate surface. Thus, the presence of a structural component of the disjoining pressure has been demonstrated unambiguously. It is significant that for $8$-films with an assigned undersaturation $p/p_8$ of water vapor, and hence also with an assigned disjoining pressure $H = (RT/mv) \cdot \ln p_8/p$ that drops off