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The Depth of the Surface Zone of a Liquid*

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I. INTRODUCTION

IS the surface zone of a liquid strictly monomolecular with unaltered liquid immediately underneath; or is it not rather a zone in which the outside monomolecular layer conditions the orientation and properties of the underlying liquid to a depth of many molecules?

Following the concept introduced in 1912 by W. B. Hardy (59)** and popularized by Reychler (132), Harkins, and Langmuir, it is now universally accepted that the outermost layer of a liquid consists of a monolayer of oriented molecules. The recognition of this truth came at the same time as the rejection of the assumption of classical physics that direct intermolecular forces are of long range, of the order of one micron. The long range forces were abandoned in favor of electrical forces directly effective for only a few angstrom units. Subsequently attention has been so focused on the dominant role of the outermost layer of molecules that the inevitable polarizing effect of this oriented layer upon the molecules immediately adjacent to it has been overlooked.

The fact that liquid molecules are already close-packed and that they are therefore readily oriented by any directed force of polarization was described, very inconspicuously, in Hardy's important paper of 1912 (59), in which the following words may be found: "The radius of the sphere of influence of a single molecule···has an extremely small value, not much greater than the diameter of the molecule itself. Quite another kind of range of molecular action is possible in close-packed structures such as fluids and solids, namely, a strain transmitted from molecule to molecule···. It is this irradiation of strain in a close-packed structure which may extend so deeply as to modify the molecular state of a skin some hundreds of microns in depth," that is, some millions of angstroms. The accepted analysis of x-ray evidence by Warren (162) is to the effect that in a liquid a molecule and its immediate neighbors, if they are elongated, mostly lie side by side and end to end, long-chain compounds being essentially straight. Recent authors approach the structure of liquids from the standpoint that the immediate neighbors of a molecule in a liquid lie almost in the position they would occupy if they were beginning to build a crystal. If appreciable couplings between neighboring molecules exist, the question is how they are intensified by the proximity of a thoroughly oriented monolayer of exposed surface.

The concept is therefore that, although the powerful forces involved are of very short range, they are transmitted by successive polarization of neighboring molecules to an impressive depth. The analogy is with a magnet of very limited range of appreciable direct attraction which nevertheless can lift or hold a piece of iron at a considerable distance if there is an intermediate chain of iron filings or pieces of iron in between. In the close-packed liquid such oriented chains or layers are subjected to thermal vibration and will be con-

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** The numbers in parentheses refer to items in the list of references given at the end of the article.

tinually breaking and reforming. The question is to what extent they occur and how their existence is manifested. In many isolated branches of science such as electrokinetics, clay technology, multilayer adsorption, etc., it is taken for granted that immobilized layers of water or other liquid of considerable thickness may occur. Hence it is timely to assemble the evidence that has been accumulating during recent years in this subject.

Currently the Dutch school and others envisage direct forces intermediate in range, i.e., longer than a few angstroms but shorter than those of the classical physicists. The fundamental nature of these forces, if they exist, is at present not completely understood. For a review of the conflicting formulations the reader is referred to two papers and ensuing discussion at a meeting of the Faraday Society in 1946 (159, 88). Langmuir's contributions to this subject are also significant (86).***

A basic theoretical treatment has not been attempted in this paper, not for lack of relevant literature, but in the belief that it must await acceptance of the broad base of experimental fact.

The experimental evidence for orientation of molecules in liquid surfaces extending to a considerable depth with consequent modification of the properties of the liquid in this surface zone, has been divided into three groups.

1. The data that appear to constitute definite proof of deep surface orientation are mainly from x-ray and electron diffraction studies. To these is added the most conclusive of the evidence showing that surface properties differ from those of the bulk liquid.
2. The data to which several kinds of more or less *ad hoc* objections may be raised, each in a single field of study. However, the objections are often found to be applicable to one kind of data only, and sometimes contradict the objections directed at other data.
3. Those that, standing alone, are readily discounted, but viewed in the light of the theory of deep surface orientation, appear reasonable and readily understood.

II. DIRECT EVIDENCE OF DEEP SURFACE ORIENTATION

This group of experimental data constitutes the most cogent and direct evidence of an effective depth of the liquid surface. The results appear not to have been contested in published papers, with the possible exception of the interpretation of x-ray diffraction from soaps. In this case the uncertainty lies only in the nature of the soap micelles, and in the magnitude of their separation by the aqueous medium.

A. Refractive Index

Optical anisotropy in homogeneous liquids is evidence of molecular orientation. Taylor and King (150) found anisotropy several degrees above the melting point of long-chain fatty acids (normally isotropic) to a distance of a wave-length of light from a glass surface; that is, 4000A, or about 200 molecules deep. The effect ceased abruptly at a certain temperature, which correlates with the behavior of lubricating oils reported by Brummage (21) and summarized in Section II D.

It is well established that certain liquids have the property of being oriented as "liquid crystals." The orientation may be observed readily by the extinction of polarized light and may be seen to proceed from the wall of the container until the whole mass of the liquid is birefringent. The influence of the solid wall has been elegantly demonstrated by Zocher and Coper (174). They brought about an orientation of the surface of a glass plate merely by rubbing it with filter paper or cotton. The orientation could be detected by evaporating on the glass an alcoholic solution of a dye, the deposit of which was seen to be birefringent, whereas on any untreated surface it is isotropic. The induced orientation of liquid crystals was demonstrated by melting *p*-azoxyanisole on such an oriented glass surface, warming until the liquid became isotropic, and allowing it to cool; the anisotropy in the liquid state was then found to follow the direction of the orientation of the glass plate.

It seems reasonable to suppose that this orienting ability, possessed to an extreme degree by a few liquids, is to some degree the normal property of all liquids; that the influence relayed through *p*-azoxyanisole to a distance of centimeters differs only quantitatively from the influence relayed through tens or hundreds of angstroms in the common liquids that furnish most of the examples in the present review.

B. Multimolecular Adsorption

Adsorption of a liquid in more than monomolecular layers is evidence of forces extending from the solid and from one molecule to another in the liquid. Lenher (87) and McHaffie and Lenher (107) exposed various plane surfaces to atmospheres nearly, but not quite, saturated with water or benzene vapor. Films of definite limited thickness were obtained, the proof of which was that equilibrium was approached from both sides. The films ranged in thickness from 45A for water on silica, to 5300A for water on glass. Benzene films on platinum were as much as 930A, but on glass only 110A. The high value for the water film on glass is illustrative of the peculiar power that glasses and clays have in orienting water, as will be shown later in this review. The effect of fissures in the solid surface was minimized by using blown glass and silica and burnished platinum surfaces. A correction has been applied to these data to take into

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*** B. V. Deryagin has pointed out (private communication) that he originated the method of calculation of the force of repulsion between weakly charged particles in an electrolyte; Bull. acad. sci. U.R.S.S., Ser. ohim. 5, 1153–64 (1937).

account the roughness of the glass. A roughness factor between 3 and 10 was suggested by one author. A value of 4.75 was found on the basis of radioactivity measurements with tritium. Lenher's films were thus calculated by Joris and H. S. Taylor (77) to be 18 to 62 monolayers in thickness.

Bangham, Mosallam, and Saweris (6) produced abnormal liquid films thick enough to show interference colors, i.e., several thousand angstroms thick, when a stream of super-saturated benzene vapor was directed at a solid mica surface. Bangham (7) showed that these abnormal films condensed only on incompletely wetted solids, and the abnormality persisted only to a definite distance from the solid surface. The criterion of dissimilarity between the adsorbed film and the bulk liquid was that a drop of the liquid would not coalesce with the film. The drop might flatten, but it did not lose its identity until the abnormal film had been built up to a critical thickness, at which point additional vapor condensed in the form of the bulk liquid. Additional references demonstrating multimolecular saturated films were given in this paper.

Determinations of thickness of multimolecular films have also been made by direct weighing. Rinse (136) condensed the vapor of mercuric iodide on glass surfaces and found layers 500 molecules deep at temperatures far above the melting point and just below the point at which the vapor should be saturated (580°). Two interconnected bulbs, one containing glass powder, were sealed with a known amount of mercuric iodide and brought to equilibrium. They were then sealed off and the adsorbate in each bulb was driven into a capillary side arm, separated, and weighed. The bulb containing glass powder was found to contain an excess of mercuric iodide. Similar results were obtained from determinations of pressure of vapor. The pressure-temperature curves failed to break sharply at the saturation point, providing a quantitative measure of adsorption. Mercuric bromide and chloride and iodine gave similarly abnormal pressure-temperature curves, but mercurous chloride and mercury behaved normally. The possibility that the results were due to reaction with the glass was eliminated by prolonged heating of the system 70° above the saturation point.

C. X-Ray Diffraction

In an exceptionally careful and elaborate x-ray study of methemoglobin, Boyes-Watson, Davidson, and Perutz (18) showed that the layers of protein molecules making up crystals of the methemoglobin are separated by layers consisting of varying amounts of water. The solid, though not hard, was crystalline and could only have retained its shape if a layer of water 15A to 25A thick constituted part of the crystal structure. The water layer must not, however, be considered solid in the sense that ice is solid, since ions diffused readily into it and at the isoelectric point did not alter the layer spacing. On the other hand, if the water did not form a series of identical layers, the x-ray pattern and the crystallinity would not be possible. Recently the molecules of a crystalline virus have similarly been shown to be separated by layers of water 78A thick (14a).

Many solids show the property of swelling when wetted by certain liquids. Often great pressures are exerted. When it is shown that the water between particles of solids exists in layers many molecules deep, it is apparent that the forces in the water extend far more than molecular distances. Several investigations of the swelling of clays by water have been made. Hofmann and Bilke (73) investigated the hydration of montmorillonite; they found a thickness of intercrystalline swelling by x-ray methods to be 10A for calcium and hydrogen montmorillonites and 20A for sodium montmorillonite. The relative thickness of the clay unit crystal and the separating layer of water have been confirmed by electron microscopy by Shaw (145). Various organic liquids such as glycerol may take the place of the water layer. In montmorillonite the layers were from 1 to 3 molecules thick, depending on the organic liquid adsorbed (105).

Many studies of soap micelles have been made with x-rays since the extensive pioneer work of Hess and his collaborators (71, 72, 79). While the soap micelle is not a solid in the ordinary sense of the term, the oriented molecules of soap appear to act as a surface from which orientation of water molecules proceeds. The micelles appear to consist of layers of soap molecules with their hydrocarbon ends in contact and their polar ends facing out toward the water. Successive layers of soap are separated by layers of water which for 9.12 percent sodium oleate were found to be 42A thick. Hughes, Sawyer, and Vinograd (75), like other investigators, found a short spacing of 4.4A in micelles of potassium laurate and a long spacing varying from 50A to 125A, the double length of the soap molecules themselves being only 40A. They found that the long spacing varied inversely as the soap concentration, which indicates that it was affected by the amount of water between the layers of soap. When toluene or another liquid was solubilized by these micelles, their spacing and the intensity of the long spacings were affected by the amount and nature of the toluene or other liquid. This indicates that the toluene molecules penetrated between the layers of soap molecules and were oriented, as was the water. Their influence on the long spacings proved that they were part of the same diffraction pattern. Harkins, Mattoon, and Corrin (67) used a similar concept to explain their results with soap micelles. They found that a mixture of isoprene and styrene gave as much as a 16A increment in spacing. McBain and Marsden (104) have obtained comparable results with non-ionic detergents. They have found a variation in x-ray spacing, depending on the concentration of the detergent. Spacings as high as 90A are reported. In more recent experiments (94) they have detected micelles in an anhydrous solution of triethanolamine laurate in benzene. Thus is completed the series of three kinds of laminar micelle containing oriented liquid layers of water, water and oil, and oil, respectively.

The same kind of structure has been demonstrated in a very different system by the x-ray work of Palmer (119, 120). An emulsion of mixed nerve lipides containing cephalin appeared to consist of bimolecular leaflets. The long spacing increased with decreasing concentration of the emulsion, and in a 25 percent emulsion it reached 150A. The water layer must have occupied at least 85A, since only 65A could have been accounted for by the lipide molecules. Ions had a profound effect on the structure, 0.076 *N* calcium chloride being enough to expel the water layer.

Palmer and his colleagues have produced new evidence of structure in intracrystalline water in their work on pectinic and pectic acids (121). The water contents of the solid materials increased with the relative humidity of the environment, and concurrently the x-ray spacing between the polymer chains increased, though only from 6.1 to 7.4A. Moreover the crystallinity revealed by the x-ray patterns was perfected as the water content and the spacing increased. This suggests that the structure of the solid as a whole had been enhanced by intermolecular forces in the water. The behavior of the most methylated samples (10.9 percent methyl ester content) was peculiar; the x-ray spacing remained nearly constant at all water contents. It was suggested that the prevalence of the hydrophobic methyl groups had prevented the chains coalescing when water was removed. However, it seems to the writer that this may have been due to a more rigid water structure than in the less methylated material, since in the latter, the spacing at the highest water content exceeded the constant spacing of the high methoxy acids. This is supported by the fact that the low methoxy acids are not as water-soluble as the high methoxy acids.

D. Electron Diffraction

Brummage (21) in his study of the heating of films of straight chain organic compounds on metals discovered a disorientation temperature, often well above the melting point, up to which the film gave a pattern by electron diffraction. The disorientation temperature increased with film thickness up to about 20 molecular layers and then remained constant up to 100 molecular layers. This indicates that the metal surface had an orienting effect on the liquid film to a depth of thousands of angstroms. The ability of the metal surface to orient molecules in the liquid phase was further illustrated by the fact that disorientation temperatures of films deposited from solution in isohexane were the same as those of films deposited by the Blodgett technique.

E. Surface Viscosity

The evidence for abnormally high viscosity in the neighborhood of a solid surface is extensive. Unfortunately, many of the experiments involve the relative motion of two solid surfaces in close proximity and hence are open to criticism on the basis of possible asperities of the surfaces. Then, too, the data on abnormal viscosity in capillaries are subject to the uncertainty of the diameter of the passage and to the possibility of electrostatic effects.

Several investigations, however, have been made in which the film of liquid was confined between a solid surface and a gas phase. In these cases asperities or dust particles cannot appreciably affect the results. In 1944 Deryagin and his colleagues (41) announced a method for comparing the viscosity of an oil near the solid surface with that farther away from it. A shearing force on a layer of oil was produced by blowing a stream of air over it in a narrow rectangular slit. The thickness of the resulting film was estimated from interference patterns set up by the reflection of monochromatic light. Several oils, including a vaseline oil containing 0.4 percent oleic acid, did not show any anomaly in viscosity beyond 1000A from the wall, but a turbine oil containing additions of aluminum naphthenate up to 2 percent showed anomalous interference bands corresponding to a tenfold increase in viscosity within 5000A of the wall. The same additive caused deviations from Newtonian viscosity in the bulk liquid. The authors interpreted the wall effect as an intensified or preferential development of a colloid structure in the proximity of the oil-metal interface.

The blow-off technique was improved (42) by using a wedge-shaped instead of rectangular slit. This produced an interference pattern, which when photographed gave a direct representation of the viscosity of the oil as a function of the distance from the wall. The sensitivity of the method was later improved by blowing the air radially over the oil layer (84).

Equally positive results were obtained by Deryagin and his colleagues (37, 38) in 1939 in studying the film of liquid between a bubble and a smooth mica surface immersed in a liquid. When the bubble was brought rapidly up to the mica, the film of liquid that remained, observed by interference bands, was thicker in the center than at the periphery. By recording the gas pressure in the bubble and the rate of collapse of the liquid layer it was possible to calculate the viscosity in the thin annulus. Abnormally high viscosity was found. The range of forces responsible appears to be of the order of 1200A, which was the film thickness. Elton (46) has shown the importance of streaming potential in such a case, but has not given a quantitative evaluation of its contribution to the viscosity observed in these experiments.

F. Adhesion

Joints made with liquids between plane polished metallic surfaces show effects of the metal through many molecular layers of the liquid. Hardy and Nottage (63), using butyl, octyl, or undecyl alcohol between steel and copper polished surfaces, found the adhesion between dissimilar metals was the mean of those between similar metals, not the minimum as would be expected were the joint strength determined at the metal surface.

In the same paper Hardy states that the same final maximum value of adhesion is attained whether the adhesive layer is formed by squeezing out an excess of liquid or by allowing the liquid to run in between dry surfaces in contact. The thickness of the liquid layer was a fraction of a millimeter. Significantly, the equilibrium was reached far more quickly in increasing the liquid layer than in decreasing it. In the words of Hardy, "When the cylinder rises (end of cylinder resting on a flat plate), fluid of low viscosity is drawing in, when it falls, it presses out lubricant whose molecules are locked in place by the attraction fields of the solids. It is the difference between drawing in a light spirit and expressing a jelly."

G. Extension of Orientation

An orienting effect extending through organic films was observed by Bradley (19). Ammonium iodide normally crystallizes in a cubic pattern. On the surface of mica it crystallized in oriented tetrahedral crystals. When a film of cellulose acetate or rubber 1000A thick was first deposited on the mica and the ammonium iodide was deposited on top of this, it again crystallized in the tetrahedral form. This indicates a propagation of the orienting effect of the mica through the organic film. The particular importance of this work lies in one experiment in which Bradley spread octane on mica in a film thick enough to show interference colors, and showed that the orienting effect was transmitted through this liquid layer. The possibility that the effect occurred via holes in the blanket layer was minimized by three observations: no cubic crystals were formed along with tetrahedrons; crystals of intermediate form grew on films too thick to subdue completely the cubic orientation; a film of gold 1100A thick, but seen under the microscope to be porous, entirely inhibited tetrahedral crystals.

H. Compressive Strength

A striking demonstration of the compressive strength of thin films of liquids was made by Deryagin and Kusakov (37, 38). They pressed a bubble of hydrogen against a plane mica surface immersed in various liquids and measured the thickness of the intervening film of liquid by photographing the Newton rings. A film of water reached an equilibrium thickness of 300A in a few minutes and did not diminish in 24 hours.

The film was demonstrated to be in thermodynamic equilibrium; it thinned on warming, but regained its thickness on cooling to the original temperature. If the vapor pressure of the film had not been equal to that of the inside of the bubble, there would have been a transfer of liquid from the film during the heating and cooling. Of the liquids tested, water produced the thickest film.

The validity of these results was challenged by Elton (46, 47) on both theoretical and experimental grounds. He attributed the long duration of the film to the effect of normal viscosity and electroviscosity (the retarding action of a streaming potential built up by the presence of an electrical double layer on the wall of the channel). Elton presented experimental values of the film thickness as a function of time for bubbles in benzene, ether and 1 *N* KCl (liquids having electrical double layers of negligible thickness), and showed that the plots could be extrapolated to a thickness of zero. His estimated experimental error was 50A, so that his finding is not in disagreement with the statement of Deryagin and Kusakov that the film of alcohol on glass was too thin to be measured by the optical method in use. Elton showed no such plot for water, the liquid which both he and the Russian investigators had found to give the thickest films. The actual thicknesses were comparable; 180A after 3 hours for water on quartz under 2800 dynes/cm^2 by the former; 300A after periods from a few minutes to 24 hours for water on mica under 1500 dynes/cm^2 by the latter.

Elton, in his theoretical treatment of the problem, tabulated the effect of electroviscosity on the rate of approach of two plane solid surfaces in a liquid. He showed that, for instance, the time required for two plates to come within 500A is 20 times as great for an ionic as for a non-ionic liquid. But this does not seem to be sufficient by itself to account for the experimental result that the thickness of a film of water after 24 hours was greater than that of a film of vaseline oil after one hour, since the normal viscosity of the oil was probably many times that of water.

Elton has made an important contribution in his theoretical treatment of electroviscosity and his corroboration of the experimental work of others, but he has not disproved the reality of the compressive strength of multimolecular liquid films.

An equation has been derived by Schofield (144), the application of which is in good agreement with the data of Deryagin and Kusakov on the thickness of films of water (containing up to $N/10$ NaCl) on mica and glass, hexyl alcohol on glass, and hexane on steel.

III. *PRIMA FACIE* EVIDENCE OF DEEP SURFACE ORIENTATION

These data are less definitive than those in the first group, and may be contested on various grounds. However, the objections apply to some data and not to others, and are not always consistent among themselves. For example, Voet's interpretation of the dielectric constant of dispersions (Section III B) might be contested by assuming point contact between particles of aluminum suspended in oil, the contacts being diminished when the mixture was under mechanical shear, the effect of which would have to be assumed independent of the concentration of the dispersion. The most obvious criticism of the lubrication data (Section III G) is that foreign particles were present that wedged between solid surfaces moving under considerable perpendicular pressure. The two objections contradict one another.

A. Electrical Conductance of Oils

Watson and Menon (163) made a study of the high conductance reported to occur in thin films of oils ordinarily regarded as good insulators. A wedge-shaped passage between plane polished surfaces of glass and steel was set up by separating a pair of plates at one side by thin leaves of mica. Oil that was allowed to flow in at the wide end of the passage showed a precipitous increase in conductivity at the point where the film had narrowed to 10 microns. The change was not due to a normal breakdown since the bulk value of the dielectric strength was 25 volts per micron, while the increased conductance in the film started under a stress of only 0.2 volt per micron. Whatever the nature of the change in oil that had occurred, it was certainly conditioned by the presence of solid surfaces.

The anomaly of a thin film of an insulating oil providing a low resistance path has been found in the course of several other investigations (23, 115, 171). In all cases the conductivity of the thin oil films is described as "very high" or "metallic" and appears suddenly as the film is made thinner. In an investigation comparable to that of Watson and Menon it seems certain that normal electrical breakdown of the oil was not responsible (115). The bulk value of the dielectric strength of the lubricating oil was not measured but is not likely to have been less than 5 volts per micron, while high conductivity was recorded in a 1-micron film under only 0.025 volt per micron.

Wilson and Barnard (171) measured the resistance of a film of oil pressed between two polished metal plates. On the passage of a 1000-cycle alternating current, only 1 percent of the current passed under a direct potential, the resistance fell rapidly to one-tenth of its former value. In a comparable experiment with films of guttapercha, collodion, and paraffin wax, 5 to 25 microns thick, Branly (20) found the conductance was increased by an oscillatory discharge in the vicinity.

B. Dielectric Constant

Voet (160) measured the dielectric constant of conducting particles in oils, both at rest and under mechanical shear perpendicular to the electrical field. In all cases the effect of shear above a certain concentration, the same concentration at which the viscosity became non-Newtonian, was to lower the dielectric constant. In the case of plate-like aluminum and copper particles the "form factor," which is a measure of the deviation of the particles from spherical shape, was independent of concentration, both at rest and under shear. Voet considered this to mean that in these dispersions the particles were not agglomerated, but gave rise to thixotropy by orienting themselves and remaining separated at points of potential energy minima. This type of thixotropy he called the "ferric oxide type," distinguished by slow setting. Characteristic of the other type of thixotropy ("bentonite type") is rapid setting and a structure dependent on orientation and point contact of particles. An example is a dispersion of nearly spherical zinc particles, in which the form factor at rest increased with concentration.

If Voet's interpretation of the ferric oxide type of thixotropy is correct, it provides an example of a liquid acting to keep solid particles apart and having sufficient rigidity to give the dispersion a yield value. However, a rigid demonstration has not yet been provided. Work has been undertaken in this laboratory to confirm and extend these results.

C. Multimolecular Adsorption

The theoretical basis for adsorption in multimolecular layers is firm. The isotherm of Brunauer, Emmett, and Teller (22) is based on more than one layer and is experimentally justified.

Harkins and Jura (66) in developing a method for the determination of surface area of a powder demonstrated the reality of multimolecular layers by a calorimetric technique which measured the energy of emersion of each succeeding layer of water adsorbed on finely ground titanium dioxide. The value of the energy of emersion fell off exponentially with the distance from the surface. These workers, however, ignored the possibility of pores in the "plane surface."

Frazer, Patrick, and Smith (54), by evaluating curves of pressure of water vapor in equilibrium with glass as a function of temperature, showed the presence of more water on glass surfaces than corresponded to molecular thickness, but they did not accept the possibility of multimolecular films, explaining their results in terms of increase of the surface of the glass as a result of washing by water.

A direct determination of the amount of liquid remaining indefinitely on the inner surface of a 0.3-mm glass capillary was made by Weber and Lewin (165). Thicknesses for all liquids examined were of the order of 1 micron.

There is a possibility that swelling of the glass could be responsible for the presence of all but a monomolecular film of liquid in these reports. However, a much greater swelling with water than with other liquids would be expected but was not observed. Moreover, there are several cases in which the adsorbing surface is a liquid-gas interface and hence not open to the criticism of sorption within a solid.

A number of experimental tests of the Gibbs adsorption equation were reviewed by McBain and DuBois (99). Several indicated adsorption greater than that predicted theoretically. Their own experimental data, using a foaming technique developed by McBain and Davies (97), indicated that bubbles rising through the solutions carried on their surface from two to eight times the amount of solute predicted, the amounts being equivalent to two to four times that required to form a monomolecular layer of closely packed, oriented molecules of solute. This shows that, at least on the surface of a moving bubble, forces are operative to several molecular lengths.

Herzfeld has deduced an equation expressing surface tension in terms of concentration of the solute and distance from the surface (70a). He found that if the range of intermolecular forces at a liquid surface is of the order of 10A, the calculated increase in surface tension is in agreement with experimental data.

Deep adsorption at an oil-air interface has been measured by Kaminski (78), using the microtome developed by McBain and Wood (103) for aqueous solutions. The microtome blade passed at about 30 feet per second just below the surface of solutions of lauric acid or lauryl alcohol in medicinal white oil. The concentration of solute in the sample so collected was then compared with that of the bulk solution by means of an interferometer. The excess of solute, deduced from the refractive index of the surface samples collected on solutions of less than 0.03 percent concentration, was equivalent to a layer of pure solute over 800A deep, or deeper if diluted with oil, existing on the stationary solution. These experiments should be repeated or amplified with a chemically homogeneous solvent.

Bartsch (9) measured the adsorption of oleic acid on minerals in water suspension by saponifying and determining the soap by surface tension of the solution. Chalcopyrite adsorbed a layer 0.55 micron thick, or 9500 molecular layers.

D. X-Ray Diffraction

The x-ray investigation of the orientation of molecules of lubricants near surfaces has been extensive. Trillat in a series of papers has shown that orientation perpendicular to a solid surface extends far enough into the liquid to produce sharp x-ray patterns. These could only come from a relatively large number of molecular layers. The first estimate in 1926 set the range of orientation at 50,000A (153). A tangential x-ray beam directed onto liquid films of fatty acids on the surface of a mercury drop showed spacings that were apparently due to the distance between oriented chains (154). No determination of depth of orientation was made in this case, but patterns from the air-liquid interface of molten lead oleate (154) gave also a 27A spacing corresponding to the chain length. Marsden, at the Stanford Research Institute, is testing this method for experimental error. The nature of the solid support, which was 2-mm from the surface, had no influence. X-ray examination of several liquid fatty acids, alcohols, and triglycerides was reported later (155, 156). Here again an orientation perpendicular to the air-liquid surface was demonstrated, there being evidence of some thermal agitation of the diffracting layers.

Clark and co-workers (32) found that chlorinated esters would assist in the orientation of films of lubricating oil up to a distance of 6000A near metal surfaces. The chlorinated esters by themselves, which are solids, gave films 9000A in thickness. They found the nature of the metal to have an effect on the extent of orientation. It is not clear whether the oil films were frozen during the x-ray examination. But even if they were not liquid, the fact that widely different depths of orientation were found, depending on the oil, the nature of the solid surface, and the presence of additive, indicates that orientation had occurred in the liquid condition.

Ghosh (56) allowed an x-ray beam to graze the surface of methyl alcohol and obtained peaks resulting from monomer, dimer, and trimer of the alcohol and also resulting from oriented molecules.

It should be noted that no pattern would have been obtained unless several molecular layers had been oriented.

Macey (90) pointed out a coincidence in the lattice dimensions of silicate minerals and ice and showed that one lattice fits almost perfectly on the other. The distance between oxygen atoms in ice is 4.52A, that in silicate is 4.51A. On this basis he postulated an almost perfect crystal structure of water on the surface of clay particles, extending outward until it is overcome by thermal agitation and the presence of ions. This structure he considers to account for several properties of wet clay, such as the low permeability to water in contrast to that of organic liquids under the same conditions. Norton and Johnson (118), in support of Macey's theory, pointed out that calculations based on heat of wetting led to water pressures at the crystal face that correspond to the formation of ice at ordinary temperatures. Mering (108) considers it established (by x-ray data) that the water taken up by montmorillonite at a relative humidity above 50 percent is adsorbed and is in addition to water of hydration that is fixed between the silicate sheets in a hexagonal pattern in one, two, three, or four superimposed layers. The structure of the water held by clays, and the mechanism of its attachment have been well reviewed by Williamson (169). He postulates that the water is present in two forms; water of low density directly adjacent to the clay surface, and compressed water associated only with the exchangeable cations.

Similar conclusions as to the ice-like structure of water in close connection with a solid were arrived at by Kolkmeijer and Favejee (80). They took x-ray photographs of hydrated starch and of ice under equivalent conditions and found coincidence of a majority of the resulting lines. They concluded that the water film had the structure, more or less deformed, of ordinary ice.

E. Schiller Layers

Zocher (173) observed interference bands originating in layers in inorganic sols. As the sol coagulated, the layer spacing contracted by losing water. The shrinkage was observed as a change in the color of reflected light from second-order green through to first-order green. Assuming the index of refraction to be normal in the water that was expelled during coagulation, the thickness of the layers was calculated to have been 2500A. In a later paper (13) third-order red interference bands were reported. This observation extends the thickness of the Schiller layers to 8000A. Tactoids and Schiller layers definitely exist. They are explained by the expansive effect of the diffuse double layer between the surfaces together with some debatably postulated attractive forces acting over a distance of several thousand angstroms. The Dutch school ascribes these to London-van der Waals forces. Langmuir (86) gives a different explanation of the spatial equilibrium.

F. Soap Films

The stability of soap films is in itself evidence of rigidity in water near surfaces. As early as 1883 Reinold and Rucker (129) measured the thickness of large numbers of stable soap films by an interferometric method and found the thinnest film was 72A thick. This is in quantitative agreement with modern x-ray data on micelles in soap solutions in bulk, the interpretation of which indicates stable layers of water between monolayers of soap. Such a layer structure in thick soap films is evident from the work of Perrin (123), who found by an interferometric method that the thickness is always an exact multiple of the thickness of the thinnest black film. Bubbles from solutions of lauryl sulfonic acid are stable, and in this case there is no possibility of their being maintained by materials that are solid in bulk. Films consisting of water between layers of oleic acid, which were reported by Hardy (62), also serve to show that stable films may consist entirely of liquid materials. The stability is not due to slowness of drainage of water, since calculations based on complete mobility of surfaces indicate that a bubble should reach a film thickness of less than a wave-length of light in a fraction of a second; it is well known that "black films" are not reached until after very long standing. It has been suggested that the repulsion force between the two sides of a soap film may be simply electrostatic instead of structural. The presence of electrical double layers in soap films has been demonstrated (130). They may actually enhance the stability of a film, but the fact that changes in the ionic concentration have relatively little effect on micelles or on soap films, while profoundly altering the electrical properties of the solvent, requires the action of a force other than electrostatic.

The bubbles of liquid paraffin studied by Berdennikov and co-workers (12) thinned precipitously to black-film thickness (between 100A and 1000A) and were as stable as bubbles formed with adsorption layers. The results were obtained with a monoparaffin prepared by electrolysis and recrystallized many times.

More direct evidence of structure at the surface of a soap solution was obtained by Bacon (5). He reflected polarized light from the liquid surface and by determining the deviation in ellipticity of the light arrived at a depth of inhomogeneity of 70A. This depth corresponds to over two molecular lengths as determined by x-ray methods in the solid soap and is the approximate thickness of unit or McBain lamellar micelles.

G. Mechanical Strength of Liquid Films

The first three investigations are of particular significance since in each case one or both of the confining surfaces was liquid, thus avoiding the possibility that the rigidity observed was due to dust particles in the liquid layer or asperities at the boundary.

Berdennikov and co-workers (12), using films of paraffin 2 or 3 degrees above the melting point, found evidence of a compressive strength in the liquid. They found that a layer 100A thick remained between liquid mercury surfaces that were pressed together and prevented their coalescence. In the same year Tausz and Szekeley (149) found that a film of lubricating oil under a steel ball dipped into mercury was remarkably stable. Non-polar oils gave a film about 5000A thick, which broke only after two days. Films of polar oils maintained themselves for as long as sixty-five days. In these cases the films were between 300 and 1000A thick.

The gradual formation of a rigid liquid layer around air bubbles rising through oil was studied by Robinson (136). A diameter of the air bubble was measured optically, but by Stoke's law the effective radius of the bubble was 150 microns greater. The rigid shell was acquired during the period of 170 seconds in which the bubble rose to the surface of the oil.

Needs (115) has made extensive investigation of thin oil films. A 10,000A film sheared between metal disks showed normal viscosity tangentially, but a rigidity radially that withstood compressive loads up to 800 pounds per square inch. After the disk was allowed to stand for some time, the rigidity was observed in a circumferential direction when torque was applied just long enough to make a measurement. When rotation was resumed, this rigidity gradually disappeared. Static film thicknesses of the order of 7500A were observed under a load of 0.2 pound per square inch. The radial rigidity and low tangential viscosity of these films led Terzaghi (115) to surmise that rigidity extended out to the midpoint between the two metal faces. Criticism of the results was mainly on the basis of the possibility of the presence of foreign particles in the oils. Needs had only centrifuged or settled his oils before use.

Marcelin (92) showed that a moving shaft could be supported on a film of oil a few microns thick. When the original film was broken by excessive pressure, a layer only one or two molecules deep remained.

A sudden decrease in the coefficient of friction for a lubricated bearing above a certain speed was reported by Beeck and co-workers (11). The new phenomenon was called "wedging," since it occurred only in the presence of excess oil and appeared to be due to a drawing-in of oil. The onset of wedging was also observed in a sudden increase in electrical resistance between the metal surfaces. It was correlated with molecular orientation as observed by electron diffraction. White oil, which is non-polar, and ricinoleic acid, which adsorbs flat-wise, showed no wedging. Film thicknesses were not measured directly, but it seems certain, especially in view of the above references, that wedging consists of the building up of thick oriented films.

Some action such as wedging appears to have been responsible for the remarkable behavior of oil films in a bearing as described by Marx and his students (95). Under loads of only a few pounds per square inch, in flooded lubrication, the shaft rose above the center of the bearing, in some cases rising nearly to the maximum that the clearance of the bearing allowed. Apparently the oil below the shaft, subjected to a load perpendicular to the oil film, had acquired rigidity.

Griffiths (58) demonstrated rigidity in a thin film of paraffin oil between steel surfaces. A steel ball fell freely down a dry steel tube 2.5 microns wider than the ball, but when the tube was wetted, no motion was observed on standing one week. Apparently the rigidity does not occur in a liquid that does not wet the walls, since with water the effect could be obtained only on one occasion.

The writer has been unable by this method to find any evidence of rigidity in the film of a lubricating oil between the ball and glass tube in a Hoeppler viscosimeter. The ball was gold plated and was 6.7 microns smaller in radius than the tube. Griffiths' positive result may be attributed to the smaller clearance and to the peculiar ability of steel to orient oils. This orienting ability has been demonstrated in the study of lubrication.

H. Flow in Narrow Passages

Local increases in viscosity in the immediate region of solid surfaces can scarcely be explained except in terms of strong forces extending from the solid surface many molecules deep into the liquid. The viscosity of liquids flowing through capillary tubes and through plugs of fine particles has been quite extensively studied. Duff (45) first reported abnormally high viscosity in liquids flowing through capillaries. In 1934 Wolkowa (172) calculated the radii of pores in three samples of clay and in silica gel. All non-polar liquids studied gave the same value of the radius for any given solid, but the calculated radius decreased with increasing polarity of the liquid and was very small for water. The reasons suggested were peptization, oriented films, swelling and wetting hysteresis. All these explanations, with the exception of oriented films, are inapplicable in one or another of the cases that follow.

The gradual plugging of capillary passages by the flow of oil has been reported in several papers. The effect was first observed by Wilson and Barnard (171) in 1922, using lubricating oils in metal tubes. Plugging was prevented by treating the oil with pyrophoric iron, which was thought to have removed impurities that were responsible. The effect was increased by the addition of a small percentage of stearic acid.

The plugging phenomenon was confirmed by Dover (44). Bulkley (26) repeated some of this work with glass and platinum capillaries and also found plugging. However, when the oil was filtered through cotton wool immediately before use, there was no plugging. The capillary radius calculated from the bulk viscosity of the oil and rate of flow was less than the radius measured optically, by 200 or 300A, which was the limit of experimental measurement. This would permit that thickness to be completely solidified oil, or a greater thickness to be partially solidified. Filtration through cotton also prevented plugging by oil containing 1 percent oleic acid, though the percentage of acid was very little reduced in filtration.

Neale (114) found in measuring the viscosity of oil in engine bearings that the apparent viscosity is only a small fraction of the normal value. (This is in contrast to Needs, who observed a viscosity five times the normal value.) The viscosity of axial flow was greater than predicted classically and is considered to be due to orientation parallel to the direction of rotation. Neale (114) also found that the boundary layers of a jet of oil emerging at a high speed from an orifice are birefringent. The angle of extinction was 45 degrees to the stream lines.

Direct measurements of the viscosity in liquid films were made by Bastow and Bowden (10), but they found no sign of rigidity in normal liquids in films 1000A thick or more, even at temperatures down to one-tenth of a degree above the freezing point. Deryagin (36) pointed out, however, that these results do not conflict with the upper limit of rigidity (1500A) previously reported by him (35).

Terzaghi (152) found the viscosity of water to be many times the bulk value in the passage between glass plates 1000A apart. Macaulay (89) found a tenfold increase in the viscosity of water between glass plates 2500A apart.

The resistance of clays to the pressure of a water-permeable piston was used as further evidence of the rigidity of layers of water; Norton and Johnson (118) found that the rigid water film in plastic clay averaged 50A in thickness under a pressure of 200 pounds per square inch. At zero pressure the water film thickness was estimated to be 300A.

There is another explanation, however, suggested by Ruth (141), that is at least qualitatively valid. Whenever a double layer exists at the wall of a channel in which a liquid is flowing, there will tend to be an accumulation of the charge of the diffuse half of the double layer at the downstream end of the channel. In a narrow channel this streaming potential may not be dissipated by an ion flow in the reverse direction, since the double layer may occupy a great part of the volume of the capillary. The net effect of a streaming potential will be to retard the flow of charged liquid in the capillary and even to reverse the flow in the outer layer in which the concentration of the mobile charges is greatest. The quantitative evaluation of this effect has been worked out recently by Elton (46). His equation gives the apparent viscosity in terms of the bulk viscosity, dielectric constant, conductivity and the radius of the capillary, for the case of a univalent electrolyte. When the thickness of the double layer is small in comparison with the radius of the tube, the equation reduces to a simple fraction involving the above quantities. It may account for at least some of the viscosity anomalies reported for very narrow channels. For instance, in Duff's classical experiments (45) the high viscosity vanished when the capillary was silvered on the inside; this could be interpreted as a short-circuiting of the streaming potential by the silver film. Bishop, Urban, and White (15) detected a brief reverse flow after passing a dilute solution of potassium chloride through a cellulose acetate film. This suggests the presence of a streaming potential that took an appreciable time to be dissipated after the forward flow had ceased. They also found that the resistance to flow gradually increased, but not when thorium replaced the univalent cation. This too is suggestive of an effect depending on the double layer, whose thickness is very much diminished by polyvalent ions.

The studies in electrosmosis by Fairbrother and Balkin (52) indicate that zeta-potentials between organic liquids and glass could account for a retardation of flow in non-aqueous media.

Bull and Wronski (27) measured the viscosity of several aliphatic alcohols in pores in solids. They found that the rate of flow was a function not only of bulk viscosity but of the attraction of the liquid for the solid. The permeability of filter beds was found by Ruth (141) to be several times greater for gases than for liquids. Reekie and Aird (128) made quantitative measurements of this effect using a plug of rouge particles. From microscopic examination of the particles they estimated that the pores were 1500A in diameter. This value was checked satisfactorily by the flow of air. But when water was passed through the plug, the apparent viscosity was five to ten times the bulk value.

Such comparisons of permeability to air and water are not proof of abnormally high viscosity of water since gases may exhibit the phenomenon of "slip" when the diameter of the passage is of the order of the mean free path which would result in a low apparent viscosity of the gas (133). For air at standard conditions the mean free path is about 900A, somewhat longer at room temperature.

Deryagin and Krylov (40) have reported anomalous viscosity of water in capillaries 1000A in diameter. They describe the flow as no longer viscous but nearly plastic, following Bingham's law. At high pressures the flow became normal, following Poiseuille's law. Coating the pores with oleic acid resulted in a sevenfold increase in flow, which is ascribed to dehydration by the oleic acid. An aspect of this which occurred to the writer is that a monolayer of oleic acid might entirely replace the double layer, leaving no unbalanced charge to extend its influence out from the surface. The water in the capillary would be electrically neutral and would be bounded not by a negatively charged solid surface but by a neutral surface consisting of the ends of hydrocarbon chains. The decrease in viscosity then is strongly suggestive of the phenomenon of boundary lubrication.

Fairbrother and Varley (51) in experiments on electrosmosis of aqueous solutions through sintered glass diaphragms found that both endosmosis and flow under hydrostatic pressure decreased with time. They considered this to be due to swelling of the glass.

These experiments are significant in regard to the streaming potential effect mentioned above. If we assume that the electrosmosis system was in dynamic equilibrium with respect to the regions outside the capillary, the potentials at the ends of the capillaries were fixed. Thus the slowing action could not be caused by a gradual building up of a stream potential. The explanations that remain are the swelling of glass mentioned by Fairbrother and Varley and the concept of the deep surface layer. The swelling of glass is not eliminated in the case of aqueous media but is improbable in the many cases involving hydrophobic liquids.

Lachs and Kronman (85) also observed an increase in hydraulic resistance with time in glass capillaries, using dilute aqueous systems. They proposed swelling of the glass as an explanation.

Other effects of time have been observed in the building up of surface viscosity. Wentworth (166) found that when water, aqueous electrolytes, benzene, and xylene flowed through narrow passages between surfaces of rock or of brass, the flow decreased with time. He considered this to be caused by adsorption of a molecular film on the wall. Arismendi and Nibley (4) found that solutions of detergents flowing through a bed of sand gradually plugged the pores in the sand.

Meyerott and Margenau (110) caused water to flow radially toward the center of the space between two glass disks. In one experiment the flow decreased 50-fold in 12 days. The effect was thought to be cumulative with flow rather than dependent on time, but this point is rendered uncertain by variations in temperature. There appeared to be a slight decrease in flow with rising temperature, which is explained in terms of the formation of bubbles which were actually seen microscopically. The suggested mechanism is that the water absorbs air at the open surface and precipitates it on the glass surface because the solubility of the air is "affected by the small separation of the plates." If this air bubble hypothesis is correct, it indicates an interesting effect of a solid on the solubility of a gas in a liquid boundary layer, but not an effect that has been observed elsewhere. They considered that the 50-fold retardation was caused by such air bubbles and not by an orientation effect.

A demonstration of high viscosity in thin films has been made by Miles, Shedlovsky, and Ross (111). They measured the flow of liquid down columns of foam and found that one solution having a higher bulk viscosity than another flowed more rapidly through the foam. The liquid content of the foam was maintained constant. Further evidence of surface viscosity was obtained in these experiments. For a given liquid content of the foam, the rate of flow was greater in large bubbles than in small. Presumably this was the result of greater film thickness associated with a smaller total area of film.

I. Adhesion

McBain and Lee (96) measured the adhesion of water and several liquid esters and natural oils between optically plane metal surfaces. The breaking loads were 10 to 30 pounds per square inch. The adhesive films were formed by wringing the surfaces together with a sliding and twisting motion; their thickness was one or two hundred molecular layers.

IV. CIRCUMSTANTIAL EVIDENCE OF DEEP SURFACE ORIENTATION

The suspicion that plane solid surfaces in close proximity may be held apart by asperities or by submicroscopic particles of dust or abrasive has made it necessary to defer some otherwise excellent data to this section. In particular, some of the data on rigidity in liquids, on surface viscosity, and on friction are subject to criticism in this respect. There have been some careful studies of the roughness of surfaces made by electron diffraction. For example, Heidenreich and Matheson (70) developed a stereoscopic electron diffraction technique that employs the method of mathematical analysis used in terrestrial mapping by aerial photography. They polished a steel plate with magnesium oxide on a felt wheel that was contaminated with aluminum oxide and evolved profile diagrams of several regions on the surface. The occasional larger scratches produced by the aluminum oxide were no more than 450A deep, and the maximum difference in level between adjacent plateaus was 130A. No evidence of isolated peaks, such as asperities or foreign particles, was indicated.

It may be worth noting that the compression stress on isolated asperities might be far greater than any material would withstand. For instance, a weight of only one gram resting on a particle 500A in diameter would create a stress of the order of 200,000 tons per square inch.

In this group also have been included several studies of thin layers of amorphous material, not truly liquid. Such experiments cannot be regarded as more than circumstantial evidence, but were they repeated with true liquids, some very significant data might be obtained. Thus, they have been included here (particularly in Sections B, F, and G), as indications of directions in which significant studies may be expected.

A. Rigidity

Deryagin (34, 35) showed directly that water is rigid in thin layers near surfaces of solids. He measured the modulus of rigidity of water in layers up to 1500A thick between a convex lens and a flat surface. The modulus was calculated from the damping of torsional oscillations of the convex lens. These experiments showed that films 350A thick had the rigidity of metallic lead (36).

In measuring the distance between a quartz lens and a quartz plate by means of Newton's rings, Eversole and Lahr (50) showed that a layer of rigid water existed, which supported the weight of the disk. This was based on the observation of a shift of 100A when water was introduced between the quartz faces. They considered that the effect could not be due to osmotic pressure since the presence of ions in the water had no effect on film thickness. Elton (46) repeated the experiments, but concluded that any stable film must be less than 25A thick.

Terzaghi (151) allowed water to evaporate from between glass plates and found that evaporation stopped when the plates were 1000A apart. This indicated that the force in the liquid extended to at least 500A.

B. Elasticity

Kumler (83) showed that the patterns seen in the grease on the lid of a desiccator were due to an elasticity in the grease. The two glass surfaces spring apart by a force which was shown not to be due to entrained air. The film was between 2500 and 6500A in thickness. An orientation existed in the grease which was made visible by polarized light. The liquid nature of greases could be questioned, but it will be recalled that on long standing the surface of greases becomes rounded and highly reflecting, indicating flow due to surface tension.

C. Viscosity

Macey's work (90) on the drying of clay suspensions showed that the permeability of clay to water obeys a relation which cannot be explained by the usual laws of viscosity. Macey found that the rate of flow through clay for organic liquids was many thousand times greater than that for water. Erbring, Broese, and Bauer (48), also working with clays, found maxima in viscosity at certain velocities of flow of 10 percent dispersions of bentonite, to which salt had been added. Additional salt shifted the viscosity maxima until a normal structural viscosity curve was obtained.

Hauser (69) has reviewed the rheology of dispersions of clays and draws the conclusion that forces operative to a considerable distance (up to 5000A) in the liquid may act to hold the particles at an equilibrium distance.

Mysels and McBain (113) observed surface conductivity and a slow increase of resistance to hydraulic flow in fritted glass membranes. The diaphragm was kept wet for several months, sometimes with distilled water, sometimes with dilute (0.0005 *N*) or concentrated (0.1 *N*) potassium chloride. During fifty days the electrical resistance rose nearly 3 percent for the dilute solution but was unchanged for the concentrated. At the same time the resistance to flow was estimated to have increased 100-fold. Ions had no effect on the rate of flow. However, when the membrane was cleaned with nitric acid, the electrical resistance dropped sharply and the hydraulic resistance returned to the original state.

Mysels pointed out that the increase in hydraulic resistance could not be due to stream potential since the latter would have varied widely with the change in ion concentration that did not affect the flow. He considers that either swelling of the glass or sorption of thick films may account for his data.

In one investigation, Deryagin and Samygin (39) observed the flow of a bubble of air trapped in a tube of liquid. The film of water, 1000A thick, gave a viscosity nearly double the normal value; and a film 200A thick, a viscosity nearly five times the normal value. The effect was especially marked in films of nonane 1900A thick and in films of heptanoic acid. The point of uncertainty here is not the possibility of asperities or dust, but the difficulty of measuring accurately the thickness of the film of liquid. The method was to observe the volumes of the full portions of the tube during the motion of the bubble and at rest. Since a bubble could not be made to flow in a tube less than several millimeters in diameter, it appears that the error in determining a 1000A film might be large.

Hatschek (68) calculated the thickness of adsorbed layers of water on the surface of colloidal sulfur by observing the relative viscosity of sols of different particle size. The water layer was found to be 8.7A thick. This value is based on the assumption that the water is completely solidified and of the same thickness on all particles.

D. Vapor Pressure

Several investigators have reported anomalies in the vapor pressure of liquids resulting from condensation on solid surfaces, in all of which cases the anomaly could not be explained satisfactorily in terms of surface tension effects or monomolecular layers. Shereshefsky (146) found that the Kelvin equation for vapor pressure lowering did not account for the decrease in vapor pressure in glass and silica capillaries 2 to 5 microns in radius. The liquids used were water and toluene. Vapor pressures in the capillaries were determined by isothermal distillation into and out of them from a bulk liquid whose vapor pressure was lowered a known amount. Shereshefsky had no explanation for his results other than to assume a 23-fold increase in surface tension. The writer has recalculated the data, using the Kelvin equation, assuming the surface tension and molal volume to be normal. The effective radii of the capillaries are found to be from one-half to one-eighth the true value for silica, and one-seventeenth for glass. If we assume that the apparent contraction of the capillary is due to condensed liquid, the film thicknesses would have to be 2 microns for water on silica and 4 microns for toluene on silica. The value of 3 microns for water on glass is subject to a downward revision because of solubility of the glass. Such a long-range surface effect is not impossible since it was observed under conditions of equilibrium, where the only forces acting against the surface force would be very small. The temperature variation of the thermostat, for instance, would introduce changes in vapor pressure that would be comparable to the effect of the surface force at a considerable distance. The experimental variation was 0.002°C, which would be equivalent to 2 or 3 percent of the observed vapor pressure lowering, or 0.25 percent of the calculated film thickness. The presence of ionic impurities would not change the surface tension enough to explain the results. The Jones-Ray effect, which is a decrease in surface tension, is the reverse of what is found.

The attempt to explain the results in terms of a surface film should not be taken as a denial of a possible increase in surface tension. Moreover, a change in surface tension would itself be evidence of an effect of the capillary wall through to the air-liquid interface.

Similarly, in 1935 Wilsdon, Bonnell, and Nottage (170) found that the Kelvin equation did not agree with the values of adsorption of water in clays and sands found by hydrostatic-tension methods. Wilsdon and co-workers accounted for their results by Hardy's concept of the oriented surface layer. Chapek (31) found that on evaporation of water suspensions of quartz and kaolin the adsorption of water occurred at relative vapor pressures (0.32 to 0.55) at which capillary condensation is unlikely. His particles were of the order of 70 to 500 microns in diameter, but no estimate of pore size was made.

E. Friction

Some of Hardy's pioneer work on lubrication is significant in a study of thick films (60). The static friction between highly polished glass surfaces, one plane and the other spherical, lubricated with long-chain fatty acids or alcohols, reached the same steady value no matter how the system was assembled; this is considered to be the condition of boundary lubrication, involving monolayers only. But the initial friction of the system was not constant. Immediately after bringing the surfaces and fluid together, the friction coefficient was high (0.57 for caprylic acid, which will serve as a representative lubricant). Hardy considered that the liquid had not had time to orient and had been rapidly squeezed out, leaving only a poorly oriented primary film. When, however, the glass surfaces were allowed to come to equilibrium with the liquid before being placed together, the friction was low (0.26) rising rapidly to 0.44. This period was interpreted as temporary hydrodynamic lubrication, ending in boundary lubrication by a somewhat incomplete primary film. The friction subsequently dropped to the steady value (0.34), which corresponds to the complete monolayer. The initial low value (hydrodynamic) was absent between surfaces in equilibrium with only the vapor of the lubricant, which indicated poorly oriented primary films in this case also.

In some of Hardy's later work on lubrication the coefficient of static friction was measured between a plane slider and a plane face. Under these conditions the normal pressure was low enough to insure viscous, rather than boundary, lubrication. Using several organic liquids, Hardy and Bircumshaw (61) found that after a "latent period" the friction coefficient reached a steady value that was in inverse proportion to the normal pressure on the slider. An assumption that the thickness of the film decreased with increasing pressure would indicate that the friction coefficient was a function of the film thickness. (At higher pressures the friction coefficient was constant. Hardy considered this final condition to be boundary lubrication dependent on a small number of molecular layers.) It should be mentioned that the occurrence of static friction in multimolecular layers is itself evidence of a yield value in the liquid.

In a later paper, Hardy (65) measured the separation between the plane surfaces and found a gradual change in the friction coefficient for alcohol between steel surfaces as the film decreased from 70,000A to 4000A. Bowden (17), however, using alcohol between steel surfaces found that the friction coefficient was negligible until a film thickness of 3600A was reached, below which point it rose rapidly. He considered that the friction in the thicker films previously reported must have been due to contamination of the liquid. Deryagin (36) pointed out that these data do not contradict his evidence of deep surface orientation extending to 1500A since Bowden merely denied complete rigidity extending over 1000A into a liquid. Later Deryagin and Smolinanskii (43) reported that the friction coefficient of films of paraffin oil containing aliphatic acids or alcohols could be used as a measure of adsorption. Films from 1000A to 10 microns thick were involved in this study.

Schnurmann (143), in reviewing the effect of surface contaminants on friction coefficient, states that the friction only becomes independent of the nature of the solid surface when the fluid film is at least 5 microns thick. When the film is thicker, friction is governed by purely hydrodynamic laws.

Macaulay (89) found that the shear force between two glass plates was greater when the plates were separated by a layer of water than when they were dry. The plates were apparently 1500A apart though distortion of the glass might have brought the center parts of the plates closer together. This is in contrast to the lubricating effect of water in clay dispersions and of oils between metal surfaces. Oils appear to possess a certain rigidity that prevents their being squeezed out of a bearing, as is mentioned elsewhere in this paper, but they appear to have the special property of low friction coefficient between monomolecular layers.

F. Extension of Orientation

When a solid surface in contact with a liquid has the effect of determining the structure of a solid growing on it from solution in the liquid, it is apparent that the solid must have an orienting effect on the layer of liquid adjacent to it. None of the following examples is proof of deep orientation at liquid surfaces, but it is felt that they are of sufficient significance to this study to be included. Some of the experiments might be modified to demonstrate the transfer of an orientation effect through multimolecular layers of liquid.

The work of Clark and co-workers (32) included a study of the orientation of wax by chlorinated esters. When wax crystals were allowed to grow in the presence of the ester additive, they followed a honeycomb pattern characteristic of the polar compound. Moreover, the orientation did not extend beyond a definite limit.

Talmud (148) found that a monomolecular layer on a solid surface had a profound effect on the compressive strength of paraffin in a layer 40,000A thick. A mass of sand particles coated with the paraffin had a compressive strength of 12 kilograms per square centimeter. However, if a monolayer of amyl alcohol was first adsorbed on the sand, the mass showed a compressive strength of 28 kilograms per square centimeter. A similar effect on silica gel was observed by adsorbing paratoluidine on the surface of silica. The phenomenon was called "molecular soldering." Further examples were supplied by Konstantinova (82).

The function of the filler in a rubber composition such as is used in an automobile tire seems to be another example of induced orientation. Park (122) looked upon the carbon black, which constituted nearly one-third of the rubber composition, as forming centers around which plastic films develop. He noted that the character of the pigment is important, and he pictured the attractive force between pigment particles being balanced by the strength of the plastic film.

The role of active fillers in rubber was clarified by Rebinder, Ab, and Veiler (127). They showed that the fillers that produced the highest tensile strength in milled vulcanized rubber also produced a yield value in a 10 percent sol of rubber in toluene which by itself showed only Newtonian viscosity. The difference between fillers was illustrated by the inactivity of quartz dust as contrasted with active silica of the same specific surface. Also cited was the increased strength of rubber in which a monolayer of stearic acid was adsorbed on the filler. This orienting effect recalls Talmud's molecular soldering (148).

The same kind of effect on suspended particles was mentioned by Robertson in a discussion on paints (135). For example, stearic acid, which is adsorbed by some pigments but is insoluble in the oily vehicle, is particularly effective in preventing settling of the pigment.

The recent work by Rothen (139) on immunological reactions shows a similar effect through organic films. Films of antigen were plated onto a solid surface. Such films are capable of adsorbing the homologous antibody. The antigen was then covered with layers of organic substances such as barium stearate, octadecylamine, and several plastics as much as 200A thick. These substances alone will not adsorb the antibody. On bringing the antibody in contact with the organic film, it was found the antigen was able to adsorb the antibody through the intervening layer. The possibility that this was due to holes in the blanket layer was minimized since the thickness of the blankets required for this effect depended on the nature and thickness of the underlying layer of antigen.

Rothen (138) demonstrated the same kind of effect with an enzyme. In this case antigen bovine albumin was coated on a metal plate and covered with an organic blanket layer. Thick blanket layers protected the antigen from the action of trypsin, but the enzyme was able to deactivate the antigen through thin (65A to 150A) layers. In this case also the thickness of the blanket layer required for protection was a function of the number of layers of antigen beneath.

Rothen's effect involves a solid rather than a liquid film, but it seems that whatever orientation is responsible is more likely to have originated while the blanket film was liquid than after it had solidified. The entire series of experiments has been criticized on the basis that the blanket layers were porous. However, an early resolution of the controversy may be expected in view of its importance to the general theory of enzyme action.

As far back as 1869 a comparable effect was observed by Quincke (125). He laid a wedge-shaped collodion film on glass and observed the contact angle of water droplets standing on the film. At the point where the film was 800A thick, the contact angle deviated from that of the thicker parts of the collodion film. Here it does not seem that submicroscopic porosity would be decisive. An extension of this work to true liquid films might give very significant results.

The effect of urea on the crystal habit of sodium chloride has long been known (57). Other cases, such as the effect of dyes on the crystal habit of thallous chloride have been mentioned by Saylor (142). It is significant that the dye may not enter into the structure of the crystal whose habit it influences. A more recent case is the effect of a dye on the growth of sodium bromate as observed by Blomquist and France (16). This orientation effect can be explained if the liquid layers in the immediate neighborhood of the growing crystal are oriented in such a way as to produce the peculiar crystal growth. The extensive study of tobacco mosaic virus by Bernal and Fankuchen (14) included an x-ray examination of the dry gel. Orientation in two dimensions parallel to the air-liquid surface of the drying mass was recorded.

Hudson (74) has shown that smooth amalgamated metals carry a film of mercury several microns deep on the surface which may be subject to thixotropic setting. Apparently the mercury is not contaminated with an appreciable amount of the solid metal, which minimizes the possibility of a network structure in the mercury layer, and infers an orientation of the mercury by the underlying solid metal.

G. Adhesion

Adhesion with solid adhesives has been extensively studied. In particular, McBain and Hardy and their respective colleagues including Bowden have found the strength of joints to depend on the solid surfaces that were joined. These results would not be introduced into a treatise on liquids were the adhesives all crystalline solids. In that case it would be reasonable to assume that the effect of the wall was transmitted by solid crystals, much as the growth of a single crystal is oriented at the growing face. The adhesives used, however, were amorphous solids, in which it is perhaps more reasonable to assume that the molecules were oriented by the wall while still in the liquid state rather than in the form of a clearly disordered solid mass. The effect of the wall was demonstrated in a number of ways by McBain and his colleagues. Comparing the tensile strength of films of the adhesive alone with the strength of joints, it was found that the metal increased the strength of the adhesive several fold (98). In the same paper it was reported that the strength of a joint increased with diminished thickness. For example, joints of soft shellac between nickel surfaces were increased in strength seven times in diminishing the thickness from 0.010 inch to 0.003 inch. This is thought to be caused by the elimination of 0.007 inch of the relatively unorganized central part of the adhesive layer.

Studies with a number of metals showed (96, 98) that for a given adhesive the identity, and to a lesser extent the surface condition, of the metal faces influenced very strongly the strength of the joints. It was found that the strength increased greatly with the hardness, elasticity, and tensile strength of the metal and decreased with its atomic volume and compressibility.

One of the most striking demonstrations was made by J. G. Morrison and reported by Fuller (55). A beeswax joint between two tungsten surfaces had an average tensile strength of 260 pounds per square inch; that between copper surfaces, 795 pounds per square inch. A similar joint between a copper and a tungsten surface would be expected to show the strength of the weaker joint were the strength determined solely at the surface. However, the actual strength was 600 pounds per square inch, showing that the copper had transmitted its influence across the adhesive layer. A similar result was obtained using de Khotinsky cement between copper and tungsten

In these investigations the thickness of the adhesive layer was not measured, but after breaking the joints, layers of visible thickness remained on each face. This demonstrates the range of the forces to be of the order of microns.

Hardy and Nottage (64) also investigated joints between dissimilar metals, with comparable results. Copper and steel joined by solid paraffins and fatty acids in layers 4 microns thick showed a strength that was the mean, not the minimum, of the joints between similar metals.

Bowden (17) using solid myristic acid as an adhesive, also found the strength to depend upon the solids. In addition he contrasted the tensile strength of bulk myristic acid (6 kg per square centimeter) with its strength in the role of an adhesive (19 kg per square centimeter).

It has been shown in other ways that water can act as an adhesive. Pettijohn (124) shook particles of quartz and glass in a flask and added water in small increments. He found that the amount of water required to cause the particles to stick to the glass wall was much greater than the amount he calculated to be necessary if the particles adhered by means of surface tension only. Several organic liquids also were used, and these required the same volume as did the water. Von Buzagh (28) made similar measurements with suspensions of glass and quartz. He also measured the angle at which layers of sedimented particles had to be tilted before they would be disturbed. Von Buzagh used particles from 2 to 12 microns in diameter but made no measurement of film thickness. In a later paper (30) von Buzagh investigated the activity coefficients of electrolyte solutions functioning as adhesives. At concentrations below the isoelectric point there was a direct relation between cation activity coefficient and adhesiveness. This points to the electrical double layer as having a profound effect on the mechanical properties.

H. Thixotropy

Thixotropy in suspensions of solids may well be a manifestation of long-range forces extending out from or between solid particles, but the possibility of a skeleton of particles being present prevents the general phenomenon of thixotropy being included as evidence of deep surface orientation. Thixotropy in homogeneous isotropic liquids, however, is significant.

Val'dman (158) found that all lubricating oils that he studied showed a thixotropic effect and anomaly in viscosity at low temperatures. Previous workers have found the same effect in some oils. In this case there is no effect of a surface, but one must assume a structure in the oil resulting from the length of the molecules. Van Wazer (164) has found that solutions of saponin have a surface layer 10 to 40 microns thick, which consists of a stiff gel which requires several hours to form. The surface gel appears not to be in equilibrium with the liquid phase and gradually dissolves in spite of the fact that it formed spontaneously originally. It is noteworthy that solid saponin dissolves readily in water; hence it appears that some surface effect other than adsorption is operating here.

Mardles (93) in measuring the rheological properties of non-Newtonian liquids found that spheres falling in greases gave complicated relationships between depth and time of fall, indicating an increased rigidity at greater depth. With thin plates, however, this effect was not observed.

Conseiller (33), working with solutions of macromolecules such as nitrocellulose, also found an increase in viscosity with time. These experiments were conducted in capillary tubes and between closely spaced glass plates which would allow a wall effect to be of importance.

Marcellin (91) rolled a ball down a sloping cylinder full of oil. The ball rolled more slowly after the oil had stood for twelve hours. It is not clear whether this was the effect of slow building up of surface viscosity or of thixotropy, but it seems definite that long-range orientation was involved.

I. Electrokinetic Potential

A mathematical approach was used by Eversole and Lahr (49). They derived an equation for the zeta-potential involving the concentration of electrolyte, a wall potential, and the thickness of the assumed immobile layer. The data led to the assumption of rigid layers of water between 8 and 63A in thickness.

J. Electron Diffraction

Electron diffraction studies of lubricating layers have been made but the film thicknesses penetrated are too small to prove orientation at greater than a few molecular lengths. Andrew, for instance (2), found that the best boundary lubricants were those with maximum orientation. He also showed that non-orienting oils containing a grease were oriented at the air interface of films at least 200 microns thick. Murison (112) rubbed organic substances, some of them liquids, on metals and obtained electron diffraction patterns resulting from the distance between carbon atoms in the chains. He concluded that the molecules are oriented perpendicularly to the surface and show a strong attraction to the metal. The data of Suge (147) are similar. Saturated fatty acid films on metal were oriented, but unsaturated acids were not oriented unless they were capable of combining chemically with the metal. The orientation of the molecules was established as perpendicular to the surface.

The correlation of "wedging" of lubricating oils and electron diffraction evidence of orientation has been discussed above (Section III G).

Orientation originating at the free surface of liquids has also been reported. Wierl (168) obtained electron diffraction patterns from the surface of mercury which showed a perfectly defined crystalline structure. Precautions were taken to avoid impurities and oxide films. Other electron diffraction patterns (12) from a mercury meniscus showed a highly oriented structure of the liquid surface whose lattice distance was that of solid mercury. Orientation at the air interface was also observed by Buhl and Rupp (25), using the reflection of slow electrons from mineral oil. Trillat failed to confirm these results (157) but did not question their validity.

K. Change in Surface Tension

Changes in surface tension have been observed which proceed so slowly that they cannot be accounted for by diffusion. Addison (1) has observed such changes in the surface tension of solutions of decoic acid and considers them to be caused by rearrangements in adsorbed layers when the changes require hours or days. Ward and Tordai (161) have analyzed the time dependence of boundary tensions of solutions and conclude that they are not accounted for by diffusion and must be due to an activation barrier that determines the rate of adsorption.

Antonoff (3) has reported that thick suspensions of carbon black in olive oil exhibit surface tensions of several hundred dynes per centimeter. McGee (106) has obtained very high values for concentrated suspensions of carbon black in lauryl alcohol, but the methods used (drop weight, sessile drop, and ring methods) show interference by thixotropy and a yield point. However, with a 30 percent suspension, a rise of 2 dynes per centimeter in surface tension was obtained by the ring method, with no evidence of yield point. Comparable results were obtained with the other two methods. In the sessile drop method wetting of the orifice was conveniently eliminated by constructing the tip of teflon (polytetrafluorethylene). The carbon black was heated to 600°C to eliminate any surface active agent, and the solvent recovered from the suspension by filtration was shown to have retained its original surface tension.

Since the size of the carbon particles was several hundred angstroms, it is apparent that forces must have acted on the liquid surface through many molecular layers around the solid particles. A surface excess of particles is considered unlikely since it would be expected to lead to a decrease in surface tension rather than an increase.

L. Turbulent and Laminar Flow

It is well known that when a liquid is moving in turbulent flow, a zone exists next to a stationary solid wall in which flow is laminar. This laminar region, in which glide planes in the liquid are of a rather permanent character, has not been fully explained. The concepts of deep orientation at the surface and of cybotaxis in the bulk liquid may well contribute to the understanding of laminar and turbulent flow.

An example of the experimental basis for the concept of the laminar surface region is the work on heat transfer by Meyer (109). The thickness of the layer was calculated by using the bulk value of heat transfer coefficient and assuming that the liquid in turbulent motion outside the film was at a constant temperature. The values for water on copper were between 60 and 90 microns. He quotes similar observations by Gratz, who found between 18 and 43 microns, depending on the rate of flow.

Nernst and Brunner (24, 116) used known values of diffusion coefficients in an analogous way to arrive at the thickness of the non-turbulent film through which a reagent must pass from a turbulent solution to reach a solid body with which it reacted. The thickness found ranged from 20 to 52 microns.

More recent observations by Davis and Crandall (33a) confirm the older data. The movement of particles suspended in water was examined by a low power microscope. In quiescent water, the particles within 400 microns of the surface were stationary, those below being seen to move freely under the influence of random currents. When the liquid was stirred at 1000 r.p.m., the quiescent film was diminished to 45 microns, which is comparable to Brunner's quiescent layers in agitated liquids.

In the course of an examination of anomalous viscosity in the surface of soap solutions, Wilson and Ries also observed deep orientation (171a). An ultramicroscope was focused on the surface of a solution of sodium stearate containing precipitated barium sulfate. In a few minutes the violent Brownian motion of the particles gave way to a slower vibration in unison. The region of Brownian movement gradually receded until it reached 10 to 40 microns from the surface.

M. Density

Early determinations of the density of metals by Rose (137) gave values as high as 26 for finely divided precipitated platinum. Johnston and Adams (76), also using a water immersion method, though more refined than that of Rose, found no effect of compressing metals except that the density was slightly lower after the first pressing but was restored by a second pressing. The high apparent density of platinum recorded by Rose is unexplained except in terms of the adsorption of a high-density layer of water on the surface of the platinum. Calculations by the writer indicate that very thin layers of water whose density was only 5 percent above normal would account for Rose's results if the specific surfaces of his platinum were of the order of those found for colloidal particles. The possibility that the metal actually is abnormally dense in the finely divided state might be checked by determinations of density by immersion in several liquids.

N. Surface Conductance

Compatible with the theory of the diffuse double layer is the abnormally high electrolytic conductivity exhibited in the neighborhood of the surfaces of dielectrics.

Probably the earliest evidence is the abnormally high conductivity observed in soap films by Reinold and Rucker (131). They found the thickness of the thinnest films, as measured optically, was several times less than the value calculated from the observed conductance and the bulk conductivity of the soap solution. A comparable occurrence near a monolayer of stearic acid on water was reported by McBain and Peaker (100). The normally undissociated fatty acid appeared to be one-ninth ionized, providing free hydrogen ions that were responsible for the conductance. The surface conductivity of insoluble soap curd fibers was of the same magnitude (101). Some of this was ascribed to the Helmholtz part of the double layer because the magnitude was shown to be greater than could be due to the outer (mobile) part of the diffuse layer alone. In the light of data in other fields which show that ions may move freely in rigidly oriented water (18), this is not surprising.

Surface conductivity at glass surfaces has been demonstrated, but the reported values vary greatly (81, 102, 113, 117, 140, 167).

O. Super-Cooled Water

A remarkable discovery was recorded by Rau (126) and quoted by Frank (53). By repeated freezing of small droplets, Rau was able to cool water to −72°C in the liquid state. On warming the ice, it did not remain solid but melted at −70°C. The explanation suggested is that this low melting ice was the same as the high pressure "Ice VI" made by Bridgeman. Below about −50°C the water droplets began to flatten. The significance of this was pointed out by Bangham (8), who considered that the change was not a decrease in surface tension but a gradual change in the water, especially in its surface layers, from the normal form to the form in which it existed in a multimolecular adsorbed film on the supporting metal surface. This is analogous to the contention of Macey (90) that water adsorbed on clay takes on an ice-like structure.

V. SUMMARY

The surface zone of a liquid is not merely a monomolecular layer with unaltered liquid immediately underneath it, but it is a region in which orientation extends effectively to many molecular lengths. This hypothesis follows from a review of experimental data that show that physical constants of the surface region may differ from those of the bulk liquid, and that in a number of cases molecular orientation is directly observable to a considerable depth. The data are drawn from published studies of lubrication, fluid flow, foams, adsorption, adhesion, ionization, etc., etc. The effective depth of the surface zone is tens or hundreds of angstroms in low molecular weight liquids, thousands of angstroms in long-chain molecules.

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