Historical Notes upon Surface Energy and Forces of Short Range.

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THE following notes were completed about fifteen years ago for a purpose not now likely to be fulfilled. They seem worthy of publication because the early history of the subject, which is to be found in Clerk Maxwell's essay on "Capillary Action,"[1] and is based upon a report made by Challis to the British Association in 1834, seems to be wrong in material points. Challis does less than justice to the eighteenth-century philosophers.

According to Poggendorff, Leonardo da Vinci must be considered as the discoverer of capillary phenomena, but a fact so patent to all can scarcely have been discovered by a single man. The ascension of water and other liquids in capillary tubes was "noticed by the Academy del Cimento at Florence early in the seventeenth century, but seems not to have been much regarded in the sequel."[2] Communications to that academy were anonymous. Probably Leslie's authority was "une anecdote curieuse qui a été publiée par M. Nelli ('Saggio di storia letteraria,' etc., p. 92) sçavoir que le véritable auteur de cette expérience fut Nicolas Aggiunti, mort le 6 décembre, 1635 . . . l'un des Fondateurs de l'Académie del Cimento."[3]

The beautiful volume issued by the Academy in 1667 is devoted mainly to experiments in a vacuum. Amongst these is a demonstration of the rise of fluid in a capillary tube *in vacuo*.

The phenomenon was still novel when Boyle demonstrated capillary rise "to the no small wonder of various mathematicians."[4] Boyle tried, but failed, to observe whether the rise took place in a vacuum, and he also inquired why the capillary surface should be concave with water and convex with mercury.

If Leslie is to be trusted, the revival of the subject was part of that great revival of physical experiment which followed the promulgation of the Newtonian system at the close of the seventeenth century. At any rate, though Hauksbee was the first whose published work needs consideration, he was not the first to make experiments, for he writes of many attempts to "solve this Appearance. . . . Some have argued from the impeded or diminished Action of the Air,[5] others from the Innixion or Resting of the Parts of the Fluid on the Pores and Asperities of the Glass; others again from the Congruity and Incongruity of the Parts of Matter one to another."[6]

Argument was direct and frequently personal in the pamphleteering times of the eighteenth century, and Hauksbee goes on to say that the "First two ways of solving the Difficulty have this advantage above the other, that they are perspicuously False; whereas this latter is more mysteriously so . . . because of the hard Words of Congruity and Incongruity."

Nothing tangible has survived from these earliest discussions, and we begin the subject with Hauksbee, whose merit was twofold; he was an exact experimenter, and he succeeded in interesting Newton in the problem. His first paper appeared in the Philosophical Transactions for 1709. This led Newton himself to make experiments, and it is a nice question how far the speculations concerning the constitution and intimate forces of matter which appear in the incomparable[7] thirty-first query are owing to his attention being thus directed to the problem of cohesion. The thirty-first query appeared for the first time in the second edition of the "Opticks" of date 1718. Be this as it may, though exact experiment and induction begin with Hauksbee, what may be called in eighteenth-century phrase the philosophy of the subject begins with Newton.

Hauksbee experimented with capillary tubes and also on the rise of fluid between planes of glass, marble, and metal. As fluids he used water, alcohol, and various oils. He noticed that the phenomenon of the rise of fluid in small spaces is not peculiar to one fluid or one solid, and that it is not due to the presence of air, since the rise occurs in a vacuum. His most important experimental result was that the height to which fluid rises is the same in two tubes of the same diameter, but one "at least ten times as thick as the other." Comparing this with the magnet, which can be broken into smaller and smaller pieces each of which will exert the force, he argues that the attraction of the solid for the fluid is limited to the surface of the solid.

There the matter was allowed to rest so far as the paper of 1709 is concerned. In the paper of 1711 the movements of a drop of oil of oranges between two glass planes inclined to one another at an angle are rightly referred to variations in the area of the surface of contact between fluid and solid, but the statement that the power of attraction must increase in proportion to that surface cannot now be defended. His papers of 1712 and 1713 are devoted to careful measurements of the curves which the surface of water forms when enclosed between glass planes. Brooke Taylor in 1712 had already pointed out that the curve was an hyperbola.

There is little theory in Hauksbee's papers. He was essentially an experimenter,[8] but in his book he draws certain definite conclusions from his experiments for which he has not received due credit.

"That very great Man, Sir Isaac Newton (the Honour of our Nation and Royal Society), has set both these Laws of Attraction in a very clear Light"—namely, that amongst the greater bodies of the universe the attraction decreases reciprocally as "the Squares of the Distances do encrease," and that the smaller portions of matter tend to each other by a law very different and unknown, but one according to which the "attractive Forces do decrease in a greater proportion than that by which the Squares of the Distances do encrease." Hauksbee then goes on to make this

[1] "Encyc. Brit.," 9th edition.

[2] Leslie, Tilloch's *Phil. Mag.*, vol. 14, p. 194, 1802. This academy was perhaps the first such body devoted to natural science, though it is stated by Vasari and others that da Vinci founded one at Milan. It was active in Florence during the years 1657–67, and deserves remembrance for the quality of its work.

[3] *Journal des Sçavans* (Amsterdam), November 1768, p. 74.

[4] "New Experiments, Physico-mechanical." (London, 1682.)

[5] [*E.g.* Hooke.]

[6] Hauksbee, "Physico-mechanical Experiments," p. 156. (London, 1709.)

[7] "Our Incomparable President," Jurin, 1718. Also Halley wrote concerning the "Principia" in 1686, "an incomparable treatise on motion."

[8] "There's no other way of Improving Natural Philosophy but by Demonstrations and Conclusions, founded upon Experiments judiciously and accurately made."

perfectly definite statement that "the attractive Power of small Particles of Matter acts only on such Corpuscles as are in contact with them, or removed but infinitely little Distances from them," thus anticipating Segner by nearly half a century.[1]

Obviously, it follows that (in anticipation of Clairaut) the water in the interior of capillary tubes is held up by the attraction of the particles of the walls of the tube, to those particles of water at the surface which are "urged strongly towards the Glass." Lastly, Leslie was not the first to show that the attraction is everywhere normal to the surfaces of the solid, as Maxwell states, for Hauksbee says: "The Parts of the Liquid adjoining to the concave Surface of the Tube are strongly attracted by it, and that in a Direction perpendicular to the sides of the Cylindrick Glass."

A comparison of contemporary references with the actual writings of Newton leads to the conclusion that much which is attributed to him was made public verbally during the discussions at the Royal Society. An interesting instance is furnished by the note to Dr. Jurin's paper.[2] At any rate, the hints scattered through the Queries to his "Opticks" as to the existence of forces acting between the particles of matter "which reach to so small distances as hitherto to escape observation," and which sprang in the first instance from his study of the diffraction of light, became a compact body of doctrine accepted in England before 1720. Hauksbee, as we have seen, wrote in 1709, nine years before the thirty-first Query was published, of intermolecular forces of insensible range, which fall off according to some higher power than the square of the distance, and Jurin in 1719 speaks of the "universally acknowledged" attractive force between the particles of a fluid (water), and refers to the sphericity of drops of rain, and the fusion of drops of water when in contact, as examples of the operation of the force; in both cases reference is made to Newton.

This doctrine, which, I believe, was shaped by the discussions at the Royal Society, may be embodied in a series of propositions as follows:—

(1) That, in addition to the force of attraction which acts between larger bodies and varies in intensity according to the inverse square of the distance, there is another attractive force which acts between the ultimate particles of matter, has a range of insensible magnitude, and varies inversely according to some power of the distance higher than the square.

(2) At distances less than a certain minute value this attractive force gives place to a repulsion.

(3) The attractive force "performs the Chymical Operation"; it is the source of cohesion, and cohesion brings about the movement of fluids in small spaces.

(4) Heat is a quality of matter, not a substance. It is the agitation of the particles of matter, and if "the Heat is big enough to Keep them in (adequate) Agitation, the Body is fluid."

(5) The ultimate particles of matter are of definite shapes—not always spheres—and are impenetrable.

Dr. Jurin, secretary of the Royal Society during a portion of Newton's term as president, was led to the subject of capillarity by "an ingenious Friend" who proposed a plausible method for "making a perpetual Motion" founded upon Hauksbee's experiments. The method is of little interest, but Jurin was led directly by it to the discovery that the height to which fluid is raised is determined by the "periphery of the tube to which the upper surface of the water is contiguous," and he argues that, as this is the "only part of the tube from which the water must recede upon its subsiding," it is consequently "the only one which by the force of its cohesion or attraction opposes the descent of the water." Hence the rise must be inversely proportional to the diameter of the tube. Newton and Machin pointed out that Jurin's "'periphery' . . . is really a small surface, whose base is that periphery (of the tube), and whose height is the distance to which the attractive power of the glass is extended."[3]

In the interval between Jurin's papers a book appeared "by a very learn'd and ingenious member of this [the Royal] Society," whose name I have not succeeded in tracing. It deserves mention because in it the effect of the attractive power of the water for itself is exactly considered. Jurin demonstrated the attraction in a striking manner when he showed that if the tube at the lower part of a funnel is drawn out to capillary dimensions and the funnel inverted with the open mouth under water, then if it be filled by drawing water up into the capillary it will remain full. The experiment succeeded in a vacuum. He infers that the lower mass of water in the funnel must be suspended by its cohesion to the column within the capillary. At the end of the memoir is a series of propositions, of which Nos. 4 and 6 assert that the particles of water are more strongly attracted by glass than by each other, but the particles of quicksilver are attracted more strongly by each other than by the glass—hence the rise of water and the depression of quicksilver in a tube.

Though the theories of Hauksbee and Jurin were generally adopted—as, for instance, in the memoirs of Bilfinger[4] and Weitbrecht[5]—there was a body of opinion which contested the existence of attractive forces of cohesion.[6]

The cause of this widespread interest and discussion of capillary phenomena in the eighteenth century cannot be better stated than in the words of the astronomer, de la Lande[7]: "Many phenomena are regarded as allied to those of capillary tubes, . . . *e.g.* the suction of sugar and of sponges, the origin of springs in elevated sites; the secretions in the human body seem to be due to the same cause. . . ." These phenomena illustrate the general attraction of matter, contested too long. "Capillary tubes put into our hands an obvious example of the generality of this law, which is the keystone of physical science." But M. de la Lande's attempts to explain the phenomena were not very illuminating!

In the eighteenth century the force of cohesion was so closely identified with chemical action that Guyton

[1] Maxwell therefore is wrong in saying that "these early speculators . . . do not distinctly assert that this attraction is sensible only at insensible distance."
[2] Phil. Trans., 355, p. 739, 1718.

[3] Phil. Trans., 1718, p. 747.
[4] *Mémoires de l'Acad. de St-Pétersbourg*, vols. 2 and 3, 1727–28.
[5] *Ibid.*, vols. 8 and 9, 1736–37.
[6] *E.g.* Paulian, "Traité de paix entre Newton et Descartes," vol. 3, p. 199; Gerdil, "qui a fait un Livre tout entier contre l'attraction des Tubes Capillaires"; Abat and others. Mairan, who explained cohesion as being due to electrical action, etc.
[7] *Journal des Sçavans* (Amsterdam), vol. 35, November 1768, p. 75. De la Lande, in his system of astronomy, incorrectly refers his own paper to the October number.

de Morveau, for example, in 1773, in his examination of the nature of chemical affinity, attempted to determine the relative affinities of a variety of substances from the force required to detach small plates of glass from their surfaces.[1] The experimental method was investigated mathematically by Laplace and Duprè, and used widely as a means of measuring surface tension.

Though the range of the force of cohesion was recognised as being insensible by these earlier writers, nowhere, so far as I know, did they draw the conclusion that the surface layer of a fluid must be the seat of special forces, though a strong hint appears in Newton's comments upon Hauksbee's experiments. The enunciation of the secondary principle of surface tension was reserved for Segner.[2] Segner appears to have had little or no acquaintance with other work on the subject; he refers only to Clairaut (" Figure de la Terre," 1743), whose book, however, he could not obtain (" quesitum nancisci non potui ") : " Cupiebam autem inspicere, propter articulos quasi episodicos . . . rotunditatem guttarum . . . elevationemque et depressionem fluidorum in tubis capillaribus, spectantes. Ea ergo qualia sint, quantumque cum meis consentiant, dicere nequeo." The subject matter of Segner's paper is, in the first instance, the equilibrium of drops of fluid ; the equilibrium in tubes is treated from the point of view of the curvature of the free surfaces. The important theorems are Nos. 2 and 3, which assert that if in any drop the volume be divided into a shell, the thickness of which is that of the range of the force of attraction, and an interior mass, the forces on any particles in the latter contribute nothing to determining the form of the drop, but only those forces on any particles in the surface shell which can be resolved along the normal to the surface and in the tangent plane. In his calculations of the effects of the surface tension so produced Segner made the mistake, afterwards corrected by Laplace, of taking account only of the curvature of a meridian section of the drop, neglecting the effect of the curvature in a plane at right angles to this section. To Segner, however, belongs the credit of being the first to deduce the phenomena of capillarity from the surface tension.

The existence of a surface tension was demonstrated objectively when Leidenfrost showed, in 1756,[3] that a soap bubble tends to contract. In 1787 Monge[4] applied the principle to explain the apparent attractions and repulsions between bodies floating on a liquid.

Reference is made by Leslie (see later) to experiments on the subject made in Holland by Musschenbroek. I have not succeeded in tracing these. The only reference in his " Cours de Physique " of 1769 is to the experiments of Hauksbee, and theory is limited to the statement that " l'explication se présente naturellement à l'esprit " ![5]

Leslie, in a curiously polemical and pedantic paper,[6] attempts to replace Jurin's " explication " of the rise in capillary tubes, which " is almost universally adopted. It is repeated in all the elementary books of natural philosophy." The attraction of the glass, everywhere normal to the surface and of narrow range, gives rise to an increase in pressure in the layer of water next to the surface of the glass. The result of this pressure is that a drop of water tends to spread out over the surface of the glass and consequently to mount upwards in a tube. " But why should the mere tendency of the water to the surface of the glass occasion a dispersive motion ? The reason is that the external particles could not approach without spreading themselves and extending the film : and analogy will instruct us, that the attraction of water to glass must increase in proportion to the proximity of its approach." The liquid film flows up the walls of the tube, carrying with it water which adheres to it, and equilibrium is reached when the weight of the column balances the force by which the film spreads itself over the glass. " This explanation of the action of the solid is equivalent to that by which Gauss afterwards supplied the defect of the theory of Laplace, except that, not being expressed in terms of mathematical symbols, it does not indicate the mathematical relations between attraction of individual particles and the final result."[7] Maxwell gives to Leslie the credit of being the first to explain correctly the rise of fluid in a capillary tube. " He [Leslie] does not, like the earlier speculators, suppose this attraction [of the solid] to act in an upward direction so as to support the fluid directly." Yet a few pages further on Maxwell himself speaks of the tension of the solid as though it intervened actively as an upward pull !

On few subjects has more been written than on capillarity, and yet the exact way in which the attractive forces act in causing the rise of fluid in capillary tubes and the spreading of fluids over solid or fluid surfaces is still obscure. Leslie's account is probably the best, and if true it carries an important corollary—namely, that the layer of fluid attracted by the glass is at least two molecules in depth. Recent writers, if I understand them rightly, would restrict the influence to a layer only one molecule deep.

Leslie's paper is original and powerful, and even now very little out of date. It includes many observations which are still of great interest ; of these the only one I have space to mention is the discovery of the fact that the " assimilation " of fluid by porous bodies is accompanied by a rise of temperature. He was, I believe, the first to detect this fact.

In the early years of the nineteenth century the subject received attention at the hands of two remarkable men—Dr. Thomas Young and the Marquis de Laplace. Their methods were entirely dissimilar. Young founded his theory on the principles of surface tension, or " superficial cohesion," as he calls it. " Since the time of Segner," he says, " little has been done in investigating accurately and in detail the various consequences of the principle." He begins by making two assumptions—the first, which he attributes to Monge " and others," that the cohesive attraction of the superficial particles causes the free surface of fluids to " be formed into curves of the nature of lintearіæ which are supposed to be the results of a uniform tension of a substance " ; and the second, " which appears to be new," that the angle of contact

[1] He used " la méthode du Docteur Taylor [Brooke Taylor] . . . qui, par le choix des matières employées, peut servir à faire connoître que l'attraction que les Chymistes nomment affinité a nécessairement quelque part à cette adhésion," *Jour. de Physique*, vol. 1, p. 172, 1773.

[2] " De Figuris Superficierum Fluidarum," Comm. Soc. Reg. Sci. Gottingensis, vol. 1, p. 301, 1751.

[3] " De aquae communis nonnullis qualitatibus tractatus." (Duisburg.)

[4] *Mémoires de l'Acad. des Sciences*, p. 506, 1787.

[5] Pencilled on the margin of my MS. is the note " Not altogether just." At this distance of time I cannot elucidate the remark.

[6] Tilloch's *Phil. Mag.*, vol. 14, p. 193, 1802.

[7] Clerk Maxwell, art. " Capillary Action," " Encyc. Brit.," 9th edition.

of a liquid surface and a solid is constant and characteristic of any given pair of liquids and solids.

If a curved line is equally stretched, the force that it exerts along the normal at any point is directly as its curvature, and the same is true of a surface of simple curvature—*e.g.* a cylindrical surface. When the curvature is double, each curvature has its appropriate effect, and the normal force will vary as the sum of the curvatures. As this sum is the same for all perpendicular directions, the normal forces will be proportional to the sum of the greatest and least curvatures. Since the force is always directed to the centres of curvature it will elevate the fluid in a capillary tube when the surface is concave, and depress it when convex. When the surface is cylindrical and therefore curved only in one direction, as when water rises between two glass plates, the curvature must be everywhere as the height of the volume of fluid. When the curvature is double, the sum of the curvatures must be as the ordinate. This is the relation expressed by Laplace's fundamental equation, and Young's essay[1] contains the solution of most of the cases afterwards solved by Laplace. Peacock, Lowndian professor at Cambridge from 1836 to 1858, the editor of the Works of Young, appends the following note: "In the original essay the mathematical form of this investigation and the figures were suppressed, the reasoning and the results to which it leads being expressed in ordinary language; even in its altered form the investigation is unduly concise and obscure." Clerk Maxwell says of Young's methods of demonstration that, "though always correct and often extremely elegant [they] are sometimes rendered obscure by the scrupulous avoidance of mathematical symbols."

The phrase "scrupulous avoidance" is quoted from Challis and is applicable only to the earlier essays. In the article on cohesion of 1816 and the "Elementary Illustrations of the Celestial Mechanics of Laplace," mathematical symbols are freely used, the analysis being by the method of fluxions. Owing to a charming devotion to Newtonian tradition, English mathematics was at its lowest ebb when Young was a student at Cambridge; the reforms which Woodhouse, of Caius, within a few days of the same age as Young, initiated in the Cambridge School in 1803 bore fruit only in 1817, through the action of Herschel, Babbage, and Peacock. A poor training in antiquated methods and a certain vanity in his powers of "clear and simple explanation,"[2] may account for the way in which Young concealed his mathematics. His spirited indictment of the "algebraical philosophers, who have been in the habit of deducing all these quantities from each other by mathematical relations, making, for example, the force a certain function or power of the distance, and then imagining that its origin is sufficiently explained," and of the geometricians who "convert the formulæ into a curve with as many flexures and reflections as the labyrinth of Dædalus," is of the earlier period[3] and probably traceable to his personal irritation with Laplace, whom he never forgave for a real or fancied appropriation of his (Young's) ideas.

[1] Phil. Trans., 1805.
[2] *Cf.* the sentence, pregnant with personal character, which closes the essay of 1804.
[3] Lecture 49 of the "Natural Philosophy," the preface date being 1807; p. 471 of the edition of 1845.

Young proceeds to consider the "Physical Foundations of the Law of Superficial Cohesion." This he finds in the nature of the forces of cohesion. Young's work, and especially his "wonderful speculation," as Rayleigh calls it, as to the magnitude of the pressure in the interior of water due to corpuscular forces, which he puts at 23,000 atmospheres, and the calculation based on this estimate of the range of the cohesive force and the size of molecules, are fully dealt with by that writer.[4]

The beginnings of Laplace's well-known theory are to be found more than half a century earlier in the work of Clairaut.[5] Clairaut, like Laplace, was an astronomer, and his treatise on the figure of the earth consists of a mathematical analysis of the condition of equilibrium of fluid masses. This leads to the proposition that "all the particles of a mass of fluid can be in equilibrium amongst themselves when the force which acts on it is the sum of the attraction which they exercise on one another, (namely) gravity, and the attraction of any body which touches the mass." Capillary phenomena are treated as a special case of the proposition. Clairaut's analysis of fluid equilibrium is based upon a consideration of the forces acting upon an infinitely narrow canal of any figure which traverses the mass. The value of the method is that it leads very directly to equipotential surfaces. In the special case of the rise in a capillary tube the canal starts from the meniscus and ends on the general surface of the fluid.

The force of attraction of glass for water is assumed to be the same function of distance as that of water for itself, and to differ only by coefficients of the intensities. Since the range of the force is small (not insensible), only the integrals of the attractive forces about the ends of the tube need be considered. The sum of these must balance the difference in the weight of the limbs of the capillary tube.

The integral of the forces acting on that end of the tube which is at the general surface of the fluid will clearly be equal and opposite to that of the forces on the fluid below the tangent plane to the meniscus; therefore the weight of the column within the capillary is supported by the whole attraction of the fluid of the meniscus above the tangent plane, and of the lower end of the glass tube on the parts of the canal within its range. This result differs from that of Laplace because, though Clairaut assumed the range of the force of attraction to be small, he did not make it insensible. Had he done so he would have got rid of the attraction of the lower end of the capillary tube on the axial canal and have arrived at substantially the same result as Laplace.

Many workers contributed to the subject in the nineteenth century. The curious may find a brief summary of their experiments and conclusions in the papers by Charles Tomlinson which appeared, mainly in the *Philosophical Magazine*, between the years 1870 and 1880. Specially interesting are the speculations from those of Volta onwards as to the cause of the movements of particles of camphor and of other volatile solids on water. Challis's account of Gauss's important memoir cannot be bettered. The substance of it is reproduced by Clerk Maxwell in the article on capillarity which he wrote for the "Encyclopædia Britannica."

[4] Rayleigh, *Phil. Mag.*, vol. 30, 1890, p. 285.
[5] "Théorie de la Figure de la Terre." (Paris, 1743.)