

Rigidity and other Anomalies in Colloidal Solutions.<sup>1</sup>

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THE technical definition of the term rigidity is arrived at by considering a cube of an elastic solid one face of which is held while a tangential force is applied to the opposite one. The cube undergoes a deformation called a 'shear' and resists it by virtue of a property called its rigidity, which causes it to return to its original shape when the force ceases to act. The terms of the experiment lead to a quantitative expression, the modulus of rigidity, that is, the force which, applied to a cube of unit dimensions, would produce unit deformation.

In a transparent isotropic material, such as gelatin jelly, a further change accompanies the deformation: the material becomes double refracting. This accidental double refraction is easily observed in polarised light and is a delicate means of detecting strains in transparent media.

It must be added that the rigidity of a perfectly elastic material does not vary with time, so that the stress required to maintain a given deformation remains constant.

Rigidity is one of the most characteristic properties of the solid state and absent in all normal liquids. The difference between solids and liquids is best realised by considering the ideal case of a liquid between two indefinitely extended parallel planes, one of which is fixed. If now a force, however small, is applied to the other, it moves, not only a small distance as with the elastic solid, but also continuously so long as the force acts and comes to rest when it ceases to do so. The force required to maintain a given velocity is proportional to the area of the plates and the velocity gradient, that is, the velocity of the moving plate divided by its distance from the fixed one, and depends on the viscosity of the liquid. A quantitative expression again suggests itself from the terms of the mental experiment: the force per unit area required to maintain unit velocity when the plates are unit distance apart; this is called the viscosity coefficient. In all liquids it decreases with rising temperature.

A very remarkable feature of this physical constant is that in all normal liquids it is quite independent of the velocity gradient. If all else is kept constant, the forces required to maintain two different velocities are exactly proportional to these velocities.

Instead of expressing the viscosity coefficient in the absolute units of the definition, it is customary in work on solutions, such as we shall consider, to express it as 'relative viscosity,' the viscosity of a standard liquid, generally the solvent itself, being taken as unity. Thus the relative viscosity of a 60 per cent. solution of cane sugar at 20° is 56.5.

Since a normal liquid yields at once to the smallest force, no deformation can be set up in it, nor the accompanying phenomenon of double refraction.

<sup>1</sup> Discourse delivered at the Royal Institution on Friday, Mar. 18.

Attempts to detect such an effect at very high shear gradients were first made by Kundt in 1881, and afterwards by other physicists, with negative results except in a few liquids which we now know to be colloidal solutions.

The arrangement of two parallel planes with liquid between them, from which the definition of the viscosity coefficient was deduced, is not realisable experimentally. We can, however, without materially altering the conditions, so to speak 'roll up' the two planes, and confine the liquid between two coaxial cylinders, the outer of which is rotated while the inner is at rest. Such an arrangement can be used for measuring viscosities and will be referred to again.

Historically, it is not the first device used for this purpose. The study of viscosity was begun by Poiseuille, who in 1841 discovered empirically the law, called after him, which governs the flow of a liquid through a capillary tube. This 'transpiration method,' as it was originally called, attracted the interest of Thomas Graham, the founder of colloid chemistry, who applied it to many colloidal solutions. He was so much struck with the changes in viscosity caused by the addition of electrolytes or by mere ageing, that in his famous paper on silicic acid he made the often quoted remark that "a liquid transpiration tube may be employed as a colloidoscope."

The transpiration tube, or, as it is now called, the capillary viscometer, was used by a large number of observers, generally in the simple form given it by Wilhelm Ostwald, in which the pressure causing the flow of liquid is produced by a column of the liquid itself. As measurements accumulated it became evident that many colloidal solutions did not behave like normal liquids, but the instruments in general use were theoretically inadequate to reveal the nature of their anomalies. On a somewhat different footing stands an investigation by Garrett, published at Heidelberg in 1903. He studied the viscosity of a number of colloidal solutions both in the capillary and by a method not used before. If a circular, horizontal disc suspended from a wire is made to oscillate round its axis in a liquid, the viscosity coefficient can be calculated from the damping effect. Garrett found in this way that colloidal solutions exhibited a number of bewildering anomalies. The values found by the disc method did not agree with those determined by the capillary; they were not even consistent among themselves, but varied with the amplitude of the oscillations and altered even during the course of the experiment. This investigation is quoted in all the text-books published about 1910 to show the complexity of the problem, but no very definite attitude towards it is taken up by the authors.

The first deliberate attempts to bring some light into the matter were made about this time by Prof. W. R. Hess, of Zürich, and by myself, working

in ignorance of each other. Hess had been induced to attack the problem by practical considerations: measurements of the viscosity of blood had become a clinical method, but the results obtained by various observers were difficult to reconcile. Hess showed in an improved capillary viscometer that the viscosity of blood and of some colloidal solutions like gelatin was not a constant but varied with the shear gradient; the faster these liquids were sheared the less viscous they appeared to be, until above a certain gradient the viscosity coefficient became a constant.

In a theoretical paper published early in 1911, I had reached the conclusion that colloidal solutions of a certain type should have a variable viscosity which should become constant above a certain velocity gradient. I proceeded to test these conclusions in a modification of the concentric cylinder apparatus which was first used by Couette in 1890.

This apparatus consists of an outer cylinder, which can be rotated at constant speed, and an inner cylinder coaxial with it and suspended from a wire. When the outer cylinder revolves, the viscous drag of the liquid carries round the inner one, until the torsion of the wire balances this drag. If all end effects are eliminated—which can be accomplished by screening the ends of the inner cylinder by suitable fixed guards—theory shows that the deflexion of the inner cylinder, which is read with telescope and scale, is exactly proportional to the product of angular velocity into viscosity.

The first results obtained with this apparatus were published in 1913. Dilute gelatin solutions were investigated, and the viscosity was found to decrease rapidly with increasing velocity: at 10° per sec. it was about 2.5 times as great as at 100° per sec. The curves representing the variation of viscosity with velocity all show a tendency to become horizontal at high velocities, and to rise asymptotically at low velocities. The same behaviour has been found in a very large number of colloidal solutions, examined either in the concentric cylinder apparatus or in improved forms of the capillary instrument, in which the rate of flow can be varied. In a few instances apparent exceptions have been found by some observers, *i.e.* viscosities which appeared to be constant. These discrepancies have been cleared up by extending the range of investigation to much lower velocity gradients, when the usual behaviour could be demonstrated again. Increasing viscosity with decreasing shear gradient may now be considered a general property of colloidal solutions.

Since this behaviour is thus characteristic of a large and important class of liquids, and in the most striking contrast to that of normal liquids, it is of great importance to find some explanation of it. One suggested by several authors, including Prof. Freundlich, is that these solutions, unlike normal liquids, possess rigidity as well as viscosity. It can indeed be shown mathematically, by making the simplest assumption regarding this rigidity, that the result will be what has been

found experimentally, namely, decreasing viscosity with increasing velocity gradient.

The suggestion that solutions which nobody could hesitate to describe as liquids should possess one of the fundamental properties of solids is so surprising, that one is naturally anxious to have a direct demonstration rather than an inference from mathematical treatment. There is no difficulty in providing this demonstration with delicate apparatus, which permits measurements of the modulus to be made. I have, however, been fortunate enough to discover a solution, the rigidity of which can be demonstrated without any apparatus at all, namely, dilute ammonium oleate. If a freshly prepared solution is given a rotary movement in a beaker it gradually comes to rest like any other liquid, but then *rotates backwards*.

The ammonium oleate solutions are mechanically very labile systems, the elastic properties of which depend on their age and previous treatment. In view of their marked rigidity they appeared to be excellent test objects for the assumption that it was this property which caused variable viscosity. Examination, however, revealed the further striking anomaly that these solutions had viscosities which varied even at constant velocity gradient and oscillated periodically between well-marked maxima and minima.

This anomaly fortunately is unique, although a decrease in viscosity after continued shearing is quite common. As regards rigidity, no other solution so far examined shows it in the same striking manner as ammonium oleate, and special apparatus is necessary to demonstrate it and to measure the modulus. The first measurement of this kind was carried out by Schwedoff in 1889 on a 0.5 per cent. gelatin solution; a series of such solutions was investigated by Rohloff and Shinjo at Göttingen in 1907. We were desirous of studying solutions other than gelatin, more especially those which had shown markedly variable viscosity, and employed Schwedoff's method for the purpose.

This method again uses the artifice of confining the liquid between concentric cylinders, the inner one being suspended from a wire. If now a certain torsion is given to the wire, and if the liquid between the cylinders is merely viscous, the suspended cylinder begins at once to follow the wire and continues to do so, until no torsion is left in the wire. If, however, the liquid has rigidity, the cylinder does not follow, but describes a much smaller angle than that by which the wire has been twisted, and remains in this position for some time, the rigidity of the hollow cylinder of liquid now balancing the torsion. From the two angles and the constants of the apparatus the modulus of rigidity can be calculated.

All the liquids we have examined lose their rigidity at or below 40°, and, to obtain a satisfactory zero, they are charged into the apparatus at this temperature and allowed to cool in it for twenty-four hours before measurements are made. The moduli are of the order of *milligrams per sq. cm.*, whereas the modulus of 10 or 12 per cent. gelatin jellies is about 100 grams per sq. cm. and that of metals

of the order of tons per sq. cm. Solutions of ammonium oleate, gelatin, benzopurpurin, and cotton yellow (two dyes), and of mercury-sulphosalicylic acid, have been studied in this fashion. In all of them the modulus increases with age; a corresponding increase in viscosity has been known to occur for some time.

Since these liquids can support a small deformation, one may expect them to exhibit accidental double refraction, and they all do so, though in very different degrees. The phenomenon is most strikingly shown by quite dilute solutions of cotton yellow and of mercury-sulphosalicylic acid, when they were stirred or caused to flow. This accidental double refraction disappears with the rigidity on heating.

Although the solutions described exhibit measurable rigidities, the properties of the liquid state yet manifest themselves inasmuch as, unlike elastic solids, they do so for a short time only; very soon the phenomenon called by Maxwell 'relaxation' sets in and, in the apparatus described, the inner cylinder gradually follows the wire. From the constants of the apparatus and the time required for a given angular displacement the viscosity of the liquid at extremely low velocity gradients can be calculated; a number of determinations have been made at speeds which correspond to one revolution of the viscosity apparatus described above in 7.5 days, while the lowest speeds so far used have been of the order of one revolution in 2.5 minutes. At these very low velocity gradients the relative viscosities (water=1) approach 100,000, which confirms the result of a very large body of measurements at ordinary gradients, namely, that the viscosity with decreasing gradient grows asymptotically and at infinitely small velocities really becomes infinite.

We thus have a considerable body of evidence for the existence of rigidity in many of the solutions which exhibit anomalous viscosity, and numerous series of measurements of the latter over a wide range of velocity gradients. As regards the causes of these anomalies we are still in the dark, although there has been no lack of the *ad hoc* hypotheses which are characteristic of a vigorously growing discipline like colloid chemistry. To explain the anomalies it has been suggested that the particles forming these solutions have peculiar shapes and arrange themselves in a special manner; although the particles are of much larger than molecular sizes, they are yet supposed to be modelled on the shape of the molecule. Thus the long chain molecules of the fatty acid salts, or the long chains of amino-acids forming proteins like gelatin, are assumed to produce filamentous aggregates or ramifying structures. There is little direct evidence of such structures, since most of the solutions in question show no particles in the ultra-microscope, and the extreme chemical diversity of the substances the solutions of which show anomaly makes the explanation at least inadequate. While compounds like the oleates undoubtedly have long chain molecules, the mercury-sulphosalicylic acid

is a very simple aromatic compound of a type which makes chain formation difficult to conceive.

It is, however, not only the extreme diversity of chemical structures which makes such attempts at explanation unconvincing, but also we have experimental evidence showing beyond any doubt that variable viscosity can be produced by simply suspending in a normal liquid a small volume percentage of microscopic particles of nearly spherical shape. I showed in 1916 with Dr. Edith Humphrey (and the measurements have since been repeated and extended) that such suspensions (of rice starch in an indifferent organic liquid of the same density) exhibited viscosities which varied with the velocity gradient exactly as do the viscosities of colloidal solutions: with decreasing velocity the viscosity grows asymptotically, while with increasing velocity it approaches, and in the lower concentrations reaches, a constant value.

There is no evidence, and certainly no probability, that such particles aggregate into chains, and the cause of the variable viscosity must therefore be sought, not in their configuration, but in some effect which they produce on the surrounding liquid. There is a very large amount of evidence drawn from the most diverse phenomena to show that particles in a liquid are surrounded by films or layers of it in which the properties of the liquid are altered. The viscosity measurements on suspensions suggest that these layers must extend some distance into the bulk of the liquid and must be sufficiently labile to be affected by the shearing of the liquid. These considerations would apply to all particles, whatever their shape or arrangement, and the combined effect of these factors would necessarily be complicated.

There is a further strong argument for the view that the cause of the anomalies of these solutions has to be sought partly or largely in some change in the solvent, and that is the striking uniformity of their behaviour regarding temperature. Solutions of substances differing as widely as possible in their chemical constitution behave alike, inasmuch as they lose their rigidity about the same temperature, namely, 40°. It seems natural to look for the reason of this uniformity in the factor common to all the solutions, the water, for the properties of which this temperature is significant.

There is no doubt that the anomalies here discussed have an important bearing on processes in organisms, all of which consist largely of colloidal material. It is impossible to enter on so vast a subject, but attention must be directed to the general physical aspect of rigidity and variable viscosity in colloidal solutions. It is known that under enormous pressures solids behave like liquids, *i.e.* flow; colloidal solutions exhibit the converse behaviour: under exiguous stresses they approximate to the behaviour of solids by exhibiting rigidity and enormous viscosities. Many of them pass continuously into jellies which, within limits, behave more and more like elastic solids, and these colloidal systems thus provide a remarkable series of transitions from the liquid to the solid state.