

VI. *The Phenomena of Rupture and Flow in Solids.*By A. A. GRIFFITH, *M. Eng. (of the Royal Aircraft Establishment).**Communicated by G. I. TAYLOR, F.R.S.*

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1. *Introduction.*

IN the course of an investigation of the effect of surface scratches on the mechanical strength of solids, some general conclusions were reached which appear to have a direct bearing on the problem of rupture, from an engineering standpoint, and also on the larger question of the nature of intermolecular cohesion.

The original object of the work, which was carried out at the Royal Aircraft Establishment, was the discovery of the effect of surface treatment—such as, for instance, filing, grinding or polishing—on the strength of metallic machine parts subjected to alternating or repeated loads. In the case of steel, and some other metals in common use, the results of fatigue tests indicated that the range of alternating stress which could be permanently sustained by the material was smaller than the range within which it was sensibly elastic, after being subjected to a great number of reversals. Hence it was inferred that the safe range of loading of a part, having a scratched or

grooved surface of a given type, should be capable of estimation with the help of one of the two hypotheses of rupture commonly used for solids which are elastic to fracture. According to these hypotheses rupture may be expected if (a) the maximum tensile stress, (b) the maximum extension, exceeds a certain critical value. Moreover, as the behaviour of the materials under consideration, within the safe range of alternating stress, shows very little departure from HOOKE'S law, it was thought that the necessary stress and strain calculations could be performed by means of the mathematical theory of elasticity.

The stresses and strains due to typical scratches were calculated with the help of the mathematical work of Prof. C. E. INGLIS,\* and the soap-film method of stress estimation developed by Mr. G. I. TAYLOR in collaboration with the present author.† The general conclusions were that the scratches ordinarily met with could increase the maximum stresses and strains from two to six times, according to their shape and the nature of the stresses, and that these maximum stresses and strains were to all intents and purposes independent of the absolute size of the scratches. Thus, on the maximum tension hypothesis, the weakening of, say, a shaft 1 inch in diameter, due to a scratch one ten-thousandth of an inch deep, should be almost exactly the same as that due to a groove of the same shape one-hundredth of an inch deep.

These conclusions are, of course, in direct conflict with the results of alternating stress tests. So far as the author is aware, the greatest weakening due to surface treatment, recorded in published work, is that given by J. B. KOMMERS,‡ who found that polished specimens showed an increased resistance over turned specimens of 45 to 50 per cent. The great majority of published results indicate a diminution in strength of less than 20 per cent. Moreover, it is certain that reducing the size of the scratches increases the strength.

To explain these discrepancies, but one alternative seemed open. Either the ordinary hypotheses of rupture could be at fault to the extent of 200 or 300 per cent., or the methods used to compute the stresses in the scratches were defective in a like degree.

The latter possibility was tested by direct experiment. A specimen of soft iron wire, about 0.028-inch diameter and 100 inches long, which had a remarkably definite elastic limit, was selected. This was scratched spirally (*i.e.*, the scratches made an angle of about 45 degrees with the axis) with carborundum cloth and oil. It was then normalised to remove initial stresses and subjected to a tensile load. Under these conditions the effect of the spiral scratches was to impart a twist to the wire, the twisting couple arising entirely from the stress-system due to the scratches. It was found that if the load exceeded a certain critical value, a part of the twist, amounting

\* "Stresses in a Plate due to the Presence of Cracks and Sharp Corners," 'Proc. Inst. Naval Architects,' March 14, 1913.

† 'Proc. Inst. Mech. Eng.' December 14, 1917, pp. 755-809.

‡ 'Intern. Assoc. for Testing Materials,' 1912, vol. 4A and vol. 4B.

in some cases to 15 per cent., remained after the removal of the load. It was inferred that at this critical load the maximum stresses in the scratches reached the elastic limit of the material. This load was about one-quarter to one-third of that which caused the wire to yield as a whole, so that the scratches increased the maximum stress three or four times. The readings were quite definite even in the case of scratches produced by No. 0 cloth, which were found by micrographic examination to be but  $10^{-4}$ -inch deep. Control experiments with longitudinal and circumferential scratches gave twists only 2 or 3 per cent. of those found with spiral scratches, and there was no permanent twist.

This substantial confirmation of the estimated values of the stresses, even in very fine scratches, shows that the ordinary hypotheses of rupture, as usually interpreted, are inapplicable to the present phenomena. Apart altogether from the numerical discrepancy, the observed difference in fatigue strength as between small and large scratches presents a fundamental difficulty.

## 2. *A Theoretical Criterion of Rupture.*

In view of the inadequacy of the ordinary hypotheses, the problem of the rupture of elastic solids has been attacked from a new standpoint. According to the well-known "theorem of minimum energy," the equilibrium state of an elastic solid body, deformed by specified surface forces, is such that the potential energy of the whole system\* is a minimum. The new criterion of rupture is obtained by adding to this theorem the statement that the equilibrium position, if equilibrium is possible, must be one in which rupture of the solid has occurred, if the system can pass from the unbroken to the broken condition by a process involving a continuous decrease in potential energy.

In order, however, to apply this extended theorem to the problem of finding the breaking loads of real solids, it is necessary to take account of the increase in potential energy which occurs in the formation of new surfaces in the interior of such solids. It is known that, in the formation of a crack in a body composed of molecules which attract one another, work must be done against the cohesive forces of the molecules on either side of the crack.† This work appears as potential surface energy, and if the width of the crack is greater than the very small distance called the "radius of molecular action," the energy per unit area is a constant of the material, namely, its surface tension.

In general, the surfaces of a small newly formed crack cannot be at a distance apart greater than the radius of molecular action. It follows that the extended theorem of minimum energy cannot be applied unless the law connecting surface energy with distance of separation is known.

\* POYNING and THOMSON, 'Properties of Matter,' ch. xv.

† The potential energy of the applied surface forces is, of course, included in the "potential energy, of the system."

There is, however, an important exception to this statement. If the body is such that a crack forms part of its surface in the unstrained state, it is not to be expected that the spreading of the crack, under a load sufficient to cause rupture, will result in any large change in the shape of its extremities. If, further, the crack is of such a size that its width is greater than the radius of molecular action at all points except very near its ends, it may be inferred that the increase of surface energy, due to the spreading of the crack, will be given with sufficient accuracy by the product of the increment of surface into the surface tension of the material.

The molecular attractions across such a crack must be small except very near its ends; it may therefore be said that the application of the mathematical theory of elasticity on the basis that the crack is assumed to be a traction-free surface, must give the stresses correctly at all points of the body, with the exception of those near the ends of the crack. In a sufficiently large crack the error in the strain energy so calculated must be negligible. Subject to the validity of the other assumptions involved, the strength of smaller cracks calculated on this basis must evidently be too low.

The calculation of the potential energy is facilitated by the use of a general theorem which may be stated thus: In an elastic solid body deformed by specified forces applied at its surface, the sum of the potential energy of the applied forces and the strain energy of the body is diminished or unaltered by the introduction of a crack whose surfaces are traction-free.

This theorem may be proved\* as follows: It may be supposed, for the present purpose, that the crack is formed by the sudden annihilation of the tractions acting on its surface. At the instant following this operation, the strains, and therefore the potential energy under consideration, have their original values; but, in general, the new state is not one of equilibrium. If it is not a state of equilibrium, then, by the theorem of minimum energy, the potential energy is reduced by the attainment of equilibrium; if it is a state of equilibrium the energy does not change. Hence the theorem is proved.

Up to this point the theory is quite general, no assumption having been introduced regarding the isotropy or homogeneity of the substance, or the linearity of its stress-strain relations. It is necessary, of course, for the strains to be elastic. Further progress in detail, however, can only be made by introducing HOOKE'S law.

If a body having linear stress-strain relations be deformed from the unstrained state to equilibrium by given (constant) surface forces, the potential energy of the latter is diminished by an amount equal to twice the strain energy.† It follows that the net reduction in potential energy is equal to the strain energy, and hence the total decrease in potential energy due to the formation of a crack is equal to the increase in strain energy less the increase in surface energy. The theorem proved above shows that the former quantity must be positive.

\* The proof is due to Mr. C. WIGLEY, late of the Royal Aircraft Establishment.

† A. E. H. LOVE, 'Mathematical Theory of Elasticity,' 2nd ed., p. 170.

### 3. *Application of the Theory to a Cracked Plate.*

The necessary analysis may be performed in the case of a flat homogeneous isotropic plate of uniform thickness, containing a straight crack which passes normally through it, the plate being subjected to stresses applied in its plane at its outer edge.

If the plate is thin, its state is one of "plane stress," and in this case it may, without additional complexity, be subjected to any uniform stress normal to its surface, in addition to the edge tractions. If it is not thin, it may still be dealt with provided it is subjected to normal surface stresses so adjusted as to make the normal displacement zero. Here the plate is in a state of "plane strain." The equations to the two states are of the same form,\* differing only in the value of the constants; they will therefore be taken together.

The strain energy may be found, with sufficient accuracy, in the general case where the edge-tractions are arbitrary; it is necessary in the present application, however, for the resulting stress-system to be symmetrical about the crack, as otherwise it is not obvious that the latter will remain straight as it spreads. The only stress distribution which will be considered, therefore, is that in which the principal stresses in the plane of the plate, at points far from the crack, are respectively parallel and perpendicular to the crack, and are the same at all such points. This is equivalent to saying that, in the absence of the crack, the plate would have been subjected to uniform principal stresses in and perpendicular to its plane. It is also necessary, on physical grounds, for the stress perpendicular to the crack and in the plane of the plate to be a tension, otherwise the surfaces of the crack are forced together instead of being separated, and they cannot remain free from traction.

In calculating the strain energy of the plate use will be made of the solution obtained by Prof. INGLIS for the stresses in a cracked plate, to which reference has already been made. The notation of Prof. INGLIS'S paper will be employed. In that notation  $\alpha, \beta$ , are elliptic co-ordinates defined by the family of confocal ellipses;  $\alpha = \text{const.}$  and the orthogonal family of hyperbolæ  $\beta = \text{const.}$  The crack is represented by the limiting ellipse or focal line  $\alpha = 0$ . The axis of  $x$  coincides with the major axes, and the axis of  $y$  with the minor axes of the ellipses. The cartesian co-ordinates  $x, y$ , are connected with the elliptic co-ordinates  $\alpha, \beta$ , by the relation

$$x + iy = c \cosh (\alpha + i\beta).$$

$R_{\alpha\alpha}, u_{\alpha}$ , are the tensile stress and displacement respectively along the normal to  $\alpha = \text{const.}$

$R_{\beta\beta}, u_{\beta}$ , are the corresponding quantities in the case of the normal to  $\beta = \text{const.}$

$S_{\alpha\beta}$  is the shear stress in the directions of these normals.

$c$  is the half-length of the focal line.

\* A. E. H. LOVE, 'Mathematical Theory of Elasticity,' 2nd ed., p. 205.

$h$  is the modulus of transformation,  $\sqrt{\frac{2}{c^2 (\cosh 2\alpha - \cos 2\beta)}}$ .

$\mu$  is the modulus of rigidity of the material.

$E$  is YOUNG'S modulus.

$\sigma$  is POISSON'S ratio.

$p = 3 - 4\sigma$  in the case of plane strain, and

$$\frac{3 - \sigma}{1 + \sigma} \text{ in the case of plane stress.}$$

The state of uniform stress existing at points far from the crack (*i.e.* where  $\alpha$  is large) will be specified by the three principal tensions P, Q and R. P is normal to the plate, and in the case of plane stress it is the same everywhere. Q and R are parallel respectively to the axes of  $x$  and  $y$ , and R is positive.

The strain energy of the plate is a quadratic function of P, Q and R, and hence, in accordance with the theorem proved above, the increase of strain energy due to the crack must be a positive quadratic function of P, Q and R. The general form of this function may be found by evaluating a sufficient number of particular cases.

The following particular cases are sufficient:—

I.— $Q = R$  (and  $P = 0$  in the case of plane stress).

Boundary of crack given by  $\alpha = \alpha_0$ .

The stresses are

$$R_{\alpha\alpha} = R \frac{\sinh 2\alpha (\cosh 2\alpha - \cosh 2\alpha_0)}{(\cosh 2\alpha - \cos 2\beta)^2}, \dots \dots \dots (1)$$

$$R_{\beta\beta} = R \frac{\sinh 2\alpha (\cosh 2\alpha + \cosh 2\alpha_0 - 2 \cos 2\beta)}{(\cosh 2\alpha - \cos 2\beta)^2}, \dots \dots \dots (2)$$

$$S_{\alpha\beta} = R \frac{\sin 2\beta (\cosh 2\alpha - \cosh 2\alpha_0)}{(\cosh 2\alpha - \cos 2\beta)^2}, \dots \dots \dots (3)$$

while the displacements are given by

$$\left. \begin{aligned} \frac{u_\alpha}{h} &= \frac{c^2 R}{8\mu} \{ (p - 1) \cosh 2\alpha - (p + 1) \cos 2\beta + 2 \cosh 2\alpha_0 \} \\ \frac{u_\beta}{h} &= 0 \end{aligned} \right\} \dots \dots (4)$$

The strain energy of the material within the ellipse  $\alpha$ , per unit thickness of plate is

$$\frac{1}{2} \int_0^{2\pi} \frac{u_\alpha}{h} \cdot R_{\alpha\alpha} \cdot d\beta + \frac{1}{2} \int_0^{2\pi} \frac{u_\beta}{h} \cdot S_{\alpha\beta} \cdot d\beta. \dots \dots \dots (5)$$

On substituting and integrating, it is found that, as  $\alpha$  becomes large, the strain energy tends towards the value

$$\frac{\pi c^2 R^2}{8\mu} \left\{ \frac{1}{2} (p - 1) e^{2\alpha} + (3 - p) \cosh 2\alpha_0 \right\} \dots \dots \dots (6)$$

Hence  $W$ , the increase of strain energy due to the cavity  $\alpha_0$ , is given by

$$W = \frac{\pi c^2 R^2}{8\mu} (3 - p) \cosh 2\alpha_0 \dots \dots \dots (7)$$

or, on proceeding to the limit,  $\alpha_0 = 0$ ,

$$W = \frac{(3 - p) \pi c^2 R^2}{8\mu} \dots \dots \dots (8)$$

for a very narrow crack of length  $2c$ .

II.— $R = 0$  (=  $P$  in the case of plane stress)  $\alpha_0 = 0$ .

Here the stresses are entirely unaltered by the crack, at every point of the plate except the two points  $x = \pm c, y = 0$ , where  $R\alpha\alpha = -Q$ . It follows that  $W = 0$ .

III.— $Q = R = 0, \alpha_0 = 0$ .

Here, again, the stresses are unaltered, and  $W = 0$ .

The only positive quadratic function of  $P, Q$  and  $R$  which is compatible with these three particular cases is that given by equation (8); this is therefore the general form of  $W$ , and rupture is determined entirely by the stress  $R$ , perpendicular to the crack.

A point of some interest, with regard to equation (8), may be noticed in passing. Since  $W$  cannot be negative it follows that, in real substances, where  $\mu$  is positive,  $3 - p$  must be positive. Hence  $\sigma$  cannot be negative in real isotropic solids.

The potential energy of the surface of the crack, per unit thickness of the plate is

$$U = 4cT \dots \dots \dots (9)$$

where  $T$  is the surface tension of the material.

Hence the total diminution of the potential energy of the system, due to the presence of the crack, is

$$W - U = \frac{(3 - p) \pi c^2 R^2}{8\mu} - 4cT. \dots \dots \dots (10)$$

The condition that the crack may extend is

$$\frac{\partial}{\partial c} (W - U) = 0,$$

or

$$(3 - p) \pi c R^2 = 16\mu T, \dots \dots \dots (11)$$

so that the breaking stress is

$$R = 2 \sqrt{\frac{\mu T}{\pi \sigma c}}, \dots \dots \dots (12)$$

in the case of plane strain, and

$$R = \sqrt{\frac{2ET}{\pi \sigma c}} \dots \dots \dots (13)$$

in the case of plane stress.

Formula (13) has been verified experimentally. In connection with the experiments, interest attaches not only to the magnitude of  $R$ , but also to the value of the maximum tension in the material, which occurs at the extremities of the crack. This stress may be estimated if the radius of curvature of the boundary of the crack, at the points in question, can be found.

Expression (2) gives the maximum tension as

$$2R \sqrt{\frac{c}{\rho}} \dots \dots \dots (14)$$

in case I. above,  $\rho$  being the radius of curvature at the corners of the elliptic crack. Prof. INGLIS shows that this expression may also be used, with little error, for cracks which are elliptic only near their ends. The foregoing expressions for the stresses are obtained, however, on the assumption that the displacements are everywhere so small that their squares may be neglected. At the corner of a very sharp crack, it cannot be assumed, without proof, that the change in  $\rho$  leaves formula (14) substantially unaffected.

In the case under consideration the displacements at the surface of the crack, due to a small tension  $dR$  at distant points, are given by

$$\left. \begin{aligned} \frac{u_\alpha}{h} &= \frac{c^2 dR}{E} (\cosh 2\alpha_0 - \cos 2\beta) \\ \frac{u_\beta}{h} &= 0 \end{aligned} \right\} \dots \dots \dots (15)$$

Whence, by resolution, the displacements parallel respectively to the major and minor axes are

$$\left. \begin{aligned} u_x &= \frac{2dR}{E} c \sinh \alpha_0 \cos \beta \\ u_y &= \frac{2dR}{E} c \cosh \alpha_0 \sin \beta \end{aligned} \right\}, \dots \dots \dots (16)$$

which may be written

$$\left. \begin{aligned} u_x &= \frac{2dR}{E} x \tanh \alpha_0 \\ u_y &= \frac{2dR}{E} y \coth \alpha_0 \end{aligned} \right\} \dots \dots \dots (17)$$



Equations (17) show that the effect of the small stress  $dR$  on the elliptic cavity is to deform it into another ellipse. If  $a$  and  $b$  are the major and minor semi-axes of the ellipse, when the plate is subjected to a stress  $R$ , then, by (17),

$$\left. \begin{aligned} \frac{da}{dR} &= \frac{2b}{E} \\ \frac{db}{dR} &= \frac{2a}{E} \end{aligned} \right\} \dots \dots \dots (18)$$

on making use of the relation  $b = a \tanh \alpha_0$ .

The solution of these simultaneous differential equations is

$$\left. \begin{aligned} a &= a_0 \cosh \frac{2R}{E} + b_0 \sinh \frac{2R}{E} \\ b &= a_0 \sinh \frac{2R}{E} + b_0 \cosh \frac{2R}{E} \end{aligned} \right\} \dots \dots \dots (19)$$

where  $a_0$  and  $b_0$  are the values of  $a$  and  $b$  in the unstrained state.

With the help of equations (19) it is possible to find the maximum stress,  $F$ , due to an applied stress,  $R$ , taking account of the change in the shape of the cavity. From (2)

$$\frac{dF}{dR} = 2 \frac{a}{b} \dots \dots \dots (20)$$

whence

$$\begin{aligned} F &= 2 \int_0^R \frac{a_0 \cosh \frac{2R}{E} + b_0 \sinh \frac{2R}{E} dR}{a_0 \sinh \frac{2R}{E} + b_0 \cosh \frac{2R}{E}} \\ &= E \log \left( \cosh \frac{2R}{E} + \frac{a_0}{b_0} \sinh \frac{2R}{E} \right), \dots \dots \dots (21) \end{aligned}$$

and in the case of a narrow crack which is elliptic only near its ends,  $\frac{a_0}{b_0}$  may, as in (14),

be replaced by  $\sqrt{\frac{c}{\rho}}$ .

In the general case, where  $Q$  is not equal to  $R$ , the quantity  $R - Q$  must be added to the value of  $F$  given by (21).

Formulæ (19) and (21) are not, of course, exactly true. The application of integration to equations (18) and (20) involves the assumption that the strains are so small that they can be superposed. If the strains are finite, this involves an error in the stresses depending on the square of the strains. In the case of ordinary solids, it is improbable that this assumption can alter the calculated stress by as much as 1 per cent.

#### 4. *Experimental Verification of the Theory.*

In order to test formula (13), it was necessary to select an isotropic material which obeyed HOOKE'S law somewhat closely at all stresses, and whose surface tension at ordinary temperatures could be estimated. For these reasons glass was preferred to the metals in common use. A comparatively hard English glass,\* having the following properties, was employed:—

Composition—SiO<sub>2</sub>, 69·2 per cent. ; K<sub>2</sub>O, 12·0 per cent. ; Na<sub>2</sub>O, 0·9 per cent. ;  
Al<sub>2</sub>O<sub>3</sub>, 11·8 per cent. ; CaO, 4·5 per cent. ; MnO, 0·9 per cent.

Specific gravity—2·40.

YOUNG'S modulus— $9·01 \times 10^6$  lbs. per sq. inch.

POISSON'S ratio—0·251.

Tensile strength—24,900 lbs. per sq. inch.

The three last-named quantities were determined by the usual tension and torsion tests on round rods or fibres about 0·04-inch diameter and 3 inches long between the gauge points. The fibres had enlarged spherical ends which were fixed into holders with sealing wax. A slight load was applied while the wax was still soft, to ensure freedom from bending. The possible error of the extension measurements was about  $\pm 0·3$  per cent., and HOOKE'S law was obeyed to this order of accuracy. No "elastic after-working" was observed with this glass, though more accurate measurements would doubtless have indicated its existence.

The problem of estimating the surface tension of glass, in the solid state, evidently requires special consideration. Direct determinations appeared to be impracticable, and ultimately an indirect method was decided on, in which the surface tension was found at a number of high temperatures and the value at ordinary temperatures deduced by extrapolation.

On the accepted theory of matter, intermolecular forces in solids and liquids consist mainly of two parts, namely, an attraction which increases rapidly as the distance between the molecules diminishes, balanced by a repulsion (the intrinsic pressure), which is due to the thermal vibrations of the molecules. It is reasonable to assume that the attraction, at constant volume, is sensibly independent of the temperature; this amounts merely to supposing that the attraction exerted by a molecule does not depend on its state of motion. On this view, the temperature variation, at constant volume, of the intermolecular forces is determined entirely by the change in thermal energy. Hence, it may be inferred, on the accepted theory of surface tension,† that the surface tension of a material, at constant volume, is equal to a constant diminished by a quantity proportional to the thermal energy of the substance. In the case of solids, nearly the same result should hold at constant pressure, as the temperature-volume change is small.

\* Supplied in the form of test-tubes by Messrs. J. J. Griffin, Kingsway, London.

† POYNTING and THOMSON, 'Properties of Matter,' ch. xv.

The specific heat of glass is greater at high than at low temperatures, but the temperature coefficient is not large. Hence its surface tension may be expected to be nearly a linear function of the temperature, and extrapolation should be fairly reliable. This was found to be the case with the glass selected for the present experiments.

In the neighbourhood of 1100° C. the surface tension was found by QUINCKE'S drop method. At lower temperatures this method was not satisfactory, on account of the large viscosity of the liquid glass; but between 730° C. and 900° C. the method described below was found to be practicable. Fibres of glass, about 2 inches long and from 0.002-inch to 0.01-inch diameter, with enlarged spherical ends, were prepared. These were supported horizontally in stout wire hooks and suitable weights were hung on their mid-points. The enlarged ends prevented any sagging except that due to extension of the fibres. The whole was placed in an electric resistance furnace maintained at the desired temperature. Under these conditions viscous stretching of the fibre occurred until the suspended weight was just balanced by the vertical components of the tension in the fibre. The latter was entirely due, in the steady state, to the surface tension of the glass, whose value could therefore be calculated from the observed sag of the fibre. In the experiments the angle of sag was observed through a window in the furnace by means of a telescope with a rotating cross wire. If  $w$  is the suspended weight,  $d$  the diameter of the fibre,  $T$  the surface tension, and  $\theta$  the angle at the point of suspension between the two halves of the fibre, then, evidently,

$$\pi \cdot d \cdot T \cdot \sin \frac{1}{2}\theta = w.$$

For this method of determining the surface tension to be valid, it is evidently necessary that the angle of sag shall reach a steady value before the development of local contractions, arising from the instability of liquid cylinders, becomes appreciable. That this requirement is satisfied is shown by the following experimental results. After heating for two hours at about 750° C. the angle of sag of a particular fibre was 18°·25. Two hours later it had increased by less than 0°·1. The temperature was then raised momentarily to 940° C., and quickly reduced again to 750° C. The angle was then found to be 20°·2. After two hours further heating at 750° C. the angle had *decreased* to 18°·4, agreeing within permissible limits of error with the former value. That is to say, substantially the same limiting angle of sag was reached whether the initial angle was above or below that limit.

Above 900° C. it was found that the viscosity was insufficient to enable an observation to be made before the fibre commenced to break up into globules. Below 730° C., on the other hand, observations made on fibres of different diameters were inconsistent, the apparent surface tension being higher for the larger fibres. The obvious meaning of this result is that below 730° C. the glass used was not a perfect viscous liquid and hence the method was inapplicable. The transition from the viscous liquid state was quite gradual. The maximum tension (apart from surface tension) which could be permanently sustained, was zero at 730° C., 1.3 lbs. per sq. inch at 657° C., and 24 lbs.

per sq. inch at 540° C. At lower temperatures the rates of increase, both of this "solid stress" and the viscosity, were enormously greater. At 540° C. a fibre took about 70 hours to reach the steady state.

Table I. below gives the values of the surface tension obtained from these experiments. That for the temperature 1110° C. is the mean of five determinations by the drop method. The remaining figures were obtained from the sag of fibres.

TABLE I.—Surface Tension of Glass.

Temperature.	Surface Tension.
° C.	lb. per inch.
1110	0·00230
905	0·00239
896	0·00250
852	0·00249
833	0·00254
820	0·00249
801	0·00257
760	0·00255
745	0·00251
15	0·0031*

So far as they go, these figures confirm the deduction that the surface tension of glass is approximately a linear function of temperature. Moreover, as the actual variation is not great, the error involved in assuming such a law and extrapolating to 15° C. is doubtless fairly small. The value so obtained, 0·0031 lb. per inch, will be used in the present application.

Rigorously, expressions (13) and (21) above are true only for small cracks in large flat plates. In view, however, of the difficulties attendant on annealing and loading large flat glass plates, it was decided to perform the breaking tests on thin round tubes and spherical bulbs. These were cracked and then annealed and broken by internal pressure. The calculation cannot be exact for such bodies, but the error may obviously be reduced by increasing the ratio of the diameter of the bulb or tube to the length of the crack. It will be seen from the results of the tests that the variation of this ratio from two to ten caused little, if any, change in the bursting strength, and hence it may be inferred that the error in question is negligible for the present purpose.

The cracks were formed either with a glass-cutter's diamond, or by scratching with a hard steel edge and tapping gently. The subsequent annealing was performed by heating to 450° C. in a resistance furnace, maintaining that temperature for about one hour, and then allowing the whole to cool slowly. The question of the best annealing temperature required careful consideration, as it was evidently necessary to relieve the

\* By extrapolation.

initial stresses due to cracking as much as possible, while at the same time keeping the temperature so low that appreciable deformation of the crack did not occur. It was found that the bursting strength increased with the annealing temperature up to about 400° C., while between 400° C. and 500° C. very little further change was perceptible. From this it was inferred that relief of the initial stresses was sufficient for the purpose in view at a temperature of 450° C.

The principal stresses at rupture,  $Q$  and  $R$ , were calculated from the observed bursting pressure by means of the usual expressions for the stresses in thin hollow spheres and circular cylinders, the thickness of the glass near the crack being measured after bursting. In the case of the tubes the cracks were parallel to the generators, and provision was made for varying  $Q$  by the application of end loads.

In dealing with the longer cracks, leakage was prevented by covering the crack on the inside with celluloid jelly, the tube being burst before the jelly hardened. In the case of the smaller cracks leakage was imperceptible and this precaution was unnecessary.

The time of loading to rupture varied from 30 seconds to five minutes. No evidence was observed of any variation of bursting pressure with time of loading.

The results of the bursting tests are set down in Tables II. and III. below.  $2c$  is the length of the crack,  $Q$  and  $R$  are the calculated principal stresses respectively

TABLE II.—Bursting Strength of Cracked Spherical Bulbs.

$2c$	$D$	$Q$	$R$	$R\sqrt{c}$
inch.	inch.	lbs. per sq. inch.	lbs. per sq. inch.	
0·15	1·49	864	864	237
0·27	1·53	623	623	228
0·54	1·60	482	482	251
0·89	2·00	366	366	244

TABLE III.—Bursting Strength of Cracked Circular Tubes.

$2c$	$D$	$Q$	$R$	$R\sqrt{c}$
inch.	inch.	lbs. per sq. inch.	lbs. per sq. inch.	
0·25	0·59	—621	678	240
0·32	0·71	—176	590	232
0·38	0·74	—31	526	229
0·28	0·61	55	655	245
0·26	0·62	202	674	243
0·30	0·61	308	616	238

parallel and perpendicular to the crack, and  $D$  is the diameter of the bulb or tube. The thickness of the bulbs was about 0·01 inch and the tubes 0·02 inch.

The average value of  $R\sqrt{c}$  is 239, and the maximum 251.

According to the theory, fracture should not depend on  $Q$ , and  $R\sqrt{c}$  should have, at fracture, the constant value

$$\sqrt{\frac{2ET}{\pi\sigma}}.$$

In the case of the glass used for these experiments,  $E = 9.01 \times 10^6$  lbs. per sq. inch,  $T = 0.0031$  lbs. per inch, and  $\sigma = 0.251$ , so that the above quantity is equal to 266.

These conclusions are sufficiently well borne out by the experimental results, save that the maximum recorded value of  $R\sqrt{c}$  is 6 per cent., and the average 10 per cent., below the theoretical value. It must be regarded as improbable that the error in the estimated surface tension is large enough to account for this difference, as this view would render necessary a somewhat unlikely deviation from the linear law.

A more probable explanation is to be obtained from an estimate of the maximum stress in the cracks. An upper limit to the magnitude of the radius of curvature at the ends of the cracks was obtained by inspection of the interference colours shown there. Near the ends a faint brownish tint was observed, and this gradually died out, as the end was approached, until finally nothing at all was visible. It was inferred that the width of the cracks at the ends was not greater than one-quarter of the shortest wave length of visible light, or about  $4 \times 10^{-6}$  inch. Hence  $\rho$  could not be greater than  $2 \times 10^{-6}$  inch.

Taking as an example the last bulb in Table II. and substituting in formula (21), it is found that

$$\frac{a_0}{b_0} = \sqrt{\frac{c}{\rho}} \geq 478$$

$$\frac{2R}{E} = 8.13 \times 10^{-5},$$

whence the maximum stress  $F \geq 344,000$  lbs. per sq. inch. The value given by the first order expression

$$F = 2R\sqrt{\frac{c}{\rho}}$$

is 350,000 lbs. per sq. inch.

A possible explanation of the discrepancy between theory and experiment is now evident. In the tension tests, the verification of HOOKE'S law could only be carried to the breaking stress, 24,900 lbs. per sq. inch. There is no evidence whatever that the law is still applicable at stresses more than ten times as great. It is much more probable that there is a marked reduction in modulus at such stresses. But a decrease in modulus at any point of a body deformed by given surface tractions involves an increase in strain energy, and therefore in the foregoing experiments a decrease in strength. This is in agreement with the observations.

*5. Deductions from the Foregoing Results.*

The estimate of maximum stress obtained above appears to lead to a peremptory disproof of the hypothesis that the maximum tension in this glass, at rupture, is always equal to the breaking stress in ordinary tensile tests. If HOOKE'S law was obeyed to rupture, and the squares of the strains were negligible, the maximum tension in the above cracked tube could not have been less than 344,000 lbs. per sq. inch; but, in the tensile tests, HOOKE'S law was obeyed up to the breaking stress, the squares of the strains were negligible, and the maximum stress was only 24,900 lbs. per sq. inch. Hence the stresses could not have been the same in the two cases. Moreover, the order of the results obtained suggests (though this is not rigorously proved, as the assumptions have not been checked at stresses above 24,900 lbs. per sq. inch) that the actual strength may be more than ten times that given by the hypothesis.

Similar conclusions may be drawn regarding the "maximum extension," "maximum stress-difference" and "maximum shear strain" hypotheses which have been proposed from time to time for estimating the strength of brittle solids.

These conclusions suggest inquiries of the greatest interest. If the strength of this glass, as ordinarily interpreted, is not constant, on what does it depend? What is the greatest possible strength, and can this strength be made available for technical purposes by appropriate treatment of the material? Further, is the strength of other materials governed by similar considerations?

Some indication of the probable maximum strength of this glass may be obtained from the bursting tests already described. There is no reason for supposing that, in those tests, the radii of curvature at the corners of the cracks were as great as  $2 \times 10^{-6}$  inch. It is much more likely that they were of the same order as the molecular dimensions. Considering, as before, the last bulb in Table II., and putting  $\rho = 2 \times 10^{-8}$  inch in formula (21), it is found that the maximum stress,  $F$ , is about  $3 \times 10^6$  lbs. per sq. inch. Elastic theory cannot, of course, be expected to apply with much accuracy to cases where the dimensions are molecular, on account of the replacement of summation by integration, and the probable diminution of modulus at very high stresses must involve a further error. Taking these circumstances into consideration, however, it may still be said that the probable maximum strength of the glass used in the foregoing experiments is of the order  $10^6$  lbs. per sq. inch.

It is of interest to enquire at this stage whether there is any reason for ascribing similar maximum strengths to other materials. On the molecular theory of matter the tensile strength of an isotropic solid or liquid is of the same order as, though less than, its "intrinsic pressure," and may therefore be estimated either from a knowledge of the total heat required to vaporise the substance or by means of VAN DER WAAL'S equation.\* It may be noted that these methods of estimating the stress indicate that

\* POYNTING and THOMSON, 'Properties of Matter,' ch. xv.

it should be, approximately at least, a constant of the material. TRAUBE\* gives the following as the intrinsic pressures of a number of metals, at ordinary temperatures :—

TABLE IV.—Intrinsic Pressures of Metals (TRAUBE).

Metal.	Intrinsic Pressure.
	lbs. per sq. inch.
Nickel . . . . .	$4.71 \times 10^6$
Iron . . . . .	$4.70 \times 10^6$
Copper . . . . .	$3.42 \times 10^6$
Silver . . . . .	$2.34 \times 10^6$
Antimony . . . . .	$1.74 \times 10^6$
Zinc . . . . .	$1.58 \times 10^6$
Tin . . . . .	$1.06 \times 10^6$
Lead . . . . .	$0.75 \times 10^6$

These are of the same order as the direct estimate obtained above for glass, but they are from 20 to 100 times the strengths found in ordinary tensile and other mechanical tests.

In the case of liquids, the discrepancy between intrinsic pressure and observed tensile strength is much greater. According to VAN DER WAAL'S equation, water has an intrinsic pressure of about 160,000 lbs. per sq. inch, whereas its tensile strength is found to be about 70 lbs. per sq. inch. It has been suggested that this divergence may be due to impurities, such as dissolved air, but DIXON and JOLY† have shown that dissolved air has no measurable effect on the tensile strength of water.

Thus the matters under discussion appear to be of general incidence, in that the strengths usually observed are but a small fraction of the strengths indicated by the molecular theory.

Some further discrepancies between theory and experiment may now be noticed. In the theory it is assumed that rupture occurs in a tensile test at the stress corresponding with the maximum resultant pull which can be exerted between the molecules of the material. On this basis the applied stress must have a maximum value at rupture, and hence, if intermolecular force is a continuous function of molecular spacing, the stress-strain diagram must have zero slope at that point. This, of course, is never observed in tensile tests of brittle materials; in no case has any evidence been obtained of the existence of such a maximum anywhere near the breaking stress.

Again, the observed differences in strength as between static and alternating stress tests are at first sight inexplicable from the standpoint of the molecular theory, if the

\* 'Zeitschr. für Anorganische Chemie,' 1903, vol. xxxiv., p. 413.

† 'Phil. Trans.,' B, 1895, p. 568.



breaking load is regarded as the sum of the intermolecular attractions. According to the theory, large changes in the latter can only occur as a result of large changes in the thermal energy of the substance, such as would be immediately evident in alternating stress tests, if they took place.

Lastly, as indicated above, the strain energy at rupture of an elastic solid or liquid should on the molecular theory be of the same order as its heat of vaporisation. Hence rupture should be accompanied by phenomena, such as a large rise of temperature, indicative of the dissipation of an amount of energy of this order. It is well known that tensile tests of brittle materials show no such phenomena.

If, as is usually supposed, the materials concerned are substantially isotropic, there is but one hypothesis which is capable of reconciling all these apparently contradictory results. The theoretical deduction—that rupture of an isotropic elastic material always occurs at a certain maximum tension—is doubtless correct; but in ordinary tensile and other tests designed to secure uniform stress, the stress is actually far from uniform so that the average stress at rupture is much below the true strength of the material.

Now it may be shown, with the help of elastic theory, that the stress must be substantially uniform, in such tests, unless the material of the test-pieces is heterogeneous or discontinuous. It is known that all substances are in fact discontinuous, in that they are composed of molecules of finite size, and it may be asked whether this type of discontinuity is sufficient to account for the observed phenomena.

With the help of formula (13) above, this question may be answered in the negative. Formula (13) shows that a thin plate of glass, having in it the weakest possible crack of length  $2c$  inch, will break at a tension, normal to the crack, of not less than  $266/\sqrt{c}$  lbs. per sq. inch. This result, however, is subject to certain errors, and experiment shows that the true breaking stress is about  $240/\sqrt{c}$  lbs. per sq. inch. But such a crack is the most extreme type, either of discontinuity or heterogeneity, which can exist in the material. Hence it is impossible to account for the observed strength, 24,900 lbs. per sq. inch, of the simple tension test specimens, unless they contain discontinuities at least  $2 \times \left(\frac{240}{24,900}\right)^2$  inch, or say,  $2 \times 10^{-4}$  inch wide. This is of the order  $10^{-4}$  times the molecular spacing.

The general conclusion may be drawn that the weakness of isotropic solids, as ordinarily met with, is due to the presence of discontinuities, or flaws, as they may be more correctly called, whose ruling dimensions are large compared with molecular distances. The effective strength of technical materials might be increased 10 or 20 times at least if these flaws could be eliminated.

It is easy to see why the presence of such small flaws can leave the strength of cracked plates, such as those of the foregoing experiments, practically unaffected. The most extreme case of weakening is that where there is a flaw very near the end of the crack and collinear with it. Here the result is merely to increase the effective length of the crack by less than  $10^{-3}$  inch. This involves a weakening of less than 0.1 per cent.

### 6. *The Strength of Thin Fibres.*

Consideration of the consequences of the foregoing general deduction indicated that very small solids of given form, *e.g.*, wires or fibres, might be expected to be stronger than large ones, as there must in such cases be some additional restriction on the size of the flaws. In the limit, in fact, a fibre consisting of a single line of molecules must possess the theoretical molecular tensile strength. In this connection it is, of course, well known that fine wires are stronger than thick ones, but the present view suggests that in sufficiently fine wires the effect should be enormously greater than is observed in ordinary cases.

This conclusion has been verified experimentally for the glass used in the previous tests, strengths of the same order as the theoretical tenacity having been observed. Incidentally, information of interest has been obtained, somewhat unexpectedly, concerning the genesis of the flaws, and it has been found to be possible to prepare quite thick fibres in an unstable condition in which they have the theoretical strength.

Fibres of glass, about 2 inches long and of various diameters, were prepared. One end of a fibre was attached to a stout wire hanging on one arm of a balance, and the other end to a fixed point, the medium of attachment being sealing wax. A slight tension was applied while the wax was still soft, in order to eliminate bending of the fibre at the points of attachment. The other arm of the balance carried a beaker into which water was introduced from a pipette or burette. The weight of water necessary to break the fibre was observed, and the diameter of the latter at the fracture was found by means of a high-power measuring microscope. Hence the tensile strength was obtained.

At first the results were extremely irregular, though the general tendency of the strength to increase with diminishing diameter was clear. It was found that the irregularities were due to the dependence of the strength on the following factors:—

(1) The maximum temperature of the glass.—To secure the best results it was found necessary to heat the glass bead to about 1400° C. to 1500° C. before drawing the fibre.

(2) The temperature during drawing.—If the glass became too cool before drawing was complete, a weak fibre was obtained. This temperature could not be very closely defined, but it is perhaps the same as the limiting temperature of the viscous liquid phase, namely, 730° C. This effect made the drawing of very fine fibres a matter of some difficulty, as the cooling was so rapid.

(3) The presence of impurities and foreign bodies.

(4) The age of the fibre.—For a few seconds after preparation, the strength of a properly treated fibre, whatever its diameter, was found to be extremely high. Tensile strengths ranging from 220,000 to 900,000 lbs. per sq. inch were observed in fibres up to about 0.02 inch diameter. These strengths were estimated by measuring the radii to which it was necessary to bend the fibres in order to break them. They are therefore probably somewhat higher than the actual tenacities. The glass appeared to be

almost perfectly elastic up to these high stresses. The strength diminished, however, as time went on, until after the lapse of a few hours it reached a steady value whose magnitude depended on the diameter of the fibre.

Similar phenomena have been observed with other kinds of glass, and also with fused silica.

The relation between diameter and strength in the steady state was investigated in the following manner. Fibres of diameters ranging from  $0.13 \times 10^{-3}$  inch to  $4.2 \times 10^{-3}$  inch, and 6 inches long, were prepared by heating the glass to about  $1400^{\circ}$  C. to  $1500^{\circ}$  C. in an oxygen and coal-gas flame and drawing the fibre by hand as quickly as possible. The fibres were then put aside for about 40 hours, so that they might reach the steady state. The test specimens were prepared by breaking these fibres in tension several times until pieces about 0.5-inch long remained; these were then tested by the balance method already described. The object of this procedure was the elimination of weak places due to minute foreign bodies, local impurities and other causes.

Table V. below gives the results of these tests. Diameters are in thousandths of an inch, and breaking stresses in lbs. per sq. inch.

TABLE V.—Strength of Glass Fibres.

Diameter.	Breaking Stress.	Diameter.	Breaking Stress.
0.001 inch.	lbs. per sq. inch.	0.001 inch.	lbs. per sq. inch.
40.00	24,900*	0.95	117,000
4.20	42,300	0.75	134,000
2.78	50,800	0.70	164,000
2.25	64,100	0.60	185,000
2.00	79,600	0.56	154,000
1.85	88,500	0.50	195,000
1.75	82,600	0.38	232,000
1.40	85,200	0.26	332,000
1.32	99,500	0.165	498,000
1.15	88,700	0.130	491,000

It will be seen that the results are still somewhat irregular. No doubt more precise treatment of the fibres would lead to some improvement in this respect, but such refinement is scarcely necessary at the present stage.

The limiting tensile strength of a fibre of the smallest possible (molecular) diameter may be obtained approximately from the figures in Table V. by plotting reciprocals of the tensile strength and extrapolating to zero diameter. This maximum strength is found to be about  $1.6 \times 10^6$  lbs. per sq. inch, which agrees sufficiently well with the rough estimate previously obtained from the cracked plate experiments.

\* From the tensile tests previously described.

In 1858, KARMARSCH\* found that the tensile strength of metal wires could be represented within a few per cent. by an expression of the type

$$F = A + \frac{B}{d} \quad \dots \dots \dots (22)$$

where  $d$  is the diameter and  $A$  and  $B$  are constants. In this connection it is of interest to notice that the figures in Table V. are given within the limits of experimental error by the formula

$$F = 22,400 \frac{4 \cdot 4 + d}{0 \cdot 06 + d} \quad \dots \dots \dots (23)$$

where  $F$  is in lbs. per sq. inch and  $d$  is in thousandths of an inch. Within the range of diameters available to KARMARSCH, this expression differs little from

$$F = 22,400 + \frac{98,600}{d}, \dots \dots \dots (24)$$

which is of the form given by KARMARSCH. Moreover, the values of  $B$  found by him for the weaker metals, *e.g.*, silver and gold, in the annealed state, are of the same order as that given by formula (24) for glass.

To a certain extent this correspondence suggests that the mechanism of rupture, as distinct from plastic flow, in metals, is essentially similar to that in brittle amorphous solids such as glass.

The remarkable properties of the unstable strong state referred to on p. 180 above are exhibited most readily in the case of clear fused silica. If a portion of a rod about 5 mm. diameter be made as hot as possible in an oxyhydrogen flame, and then drawn down to, say, 1 mm. or less and allowed to cool, the drawn-down portion may be bent to a radius of 4 or 5 mm. without breaking, and if then released will spring back almost exactly to its initial form. If instead of being released it is held in the bent form it will break spontaneously after a time which usually varies from a few seconds to a few minutes, according to the degree of flexure. To secure the best results the drawing should be performed somewhat slowly.

When fracture occurs it is accompanied by phenomena altogether different from those associated with the fracture of the normal substance. The report is much louder and deeper than the sharp crack which accompanies the rupture of an ordinary silica or glass rod, and the specimen is invariably shattered into a number of pieces, parts being frequently reduced to powder. This shattering is not confined to the highly stressed drawn-out fibre; it usually occurs also in the unchanged parts of the original thick rod and sometimes in the free ends, which are not subjected to the bending moment. The experiment is most striking, for it appears at first sight that the 5 mm. rod has been broken by a couple applied through the fibre, which may be only 0.5 mm. in

\* 'Mittheilungen des gew. Ver. für Hannover,' 1858, pp. 138-155.

diameter. As a matter of fact, however, the shattering is probably merely one of the means of dissipating the strain energy of the strong fibre, which at fracture is perhaps 10,000 times that of silica in the ordinary weak state. An elastic wave is doubtless propagated from the original fracture, and the stresses due to this wave shatter the rod.

Confirmation of this view is obtainable if the fibre is broken by twisting instead of by bending. The thick part of the rod is in this case found to contain a number of spiral cracks, at an angle of about  $45^\circ$  to the axis, showing that the material has broken in tension, but the cracks run in both right- and left-handed spirals, so that the surface of the rod is divided up into little squares. This shows that the cracking must be due to an alternating stress, such as would result from the propagation of a torsional wave along the rod.

Another phenomenon which has been observed in these fibres is that fracture at any point appears to cause a sudden large reduction in the strength of the remaining pieces. Thus, in one case a glass fibre was found to break in bending at an estimated stress of 220,000 lbs. per sq. inch. One of the pieces, on being tested immediately afterwards, broke at about 67,000 lbs. per sq. inch.

### 7. *Molecular Theory of Strength Phenomena.*

From the engineering standpoint the chief interest of the foregoing work centres round the suggestion that enormous improvement is possible in the properties of structural materials. Of secondary, but still considerable, importance is the demonstration that the methods of strength estimation in common use may lead in some cases to serious error.

Questions relating to methods of securing the indicated increase in tenacity, or of eliminating the uncertainty in strength calculations, can scarcely be answered without some more or less definite knowledge of the way in which the properties of molecules enter into the phenomena under consideration. In this connection it is of interest to enquire whether any indication can be obtained of the nature of the properties which are requisite for an explanation of the observed facts.

For this purpose it is convenient to start with molecules of the classical type, whose properties may be defined as (a) a central attraction between each pair of molecules which decreases rapidly as their central distance increases, and which depends only on that distance and the nature of the molecules; (b) translational and possibly rotational vibrations whose energy is the thermal energy of the substance. In the unstrained state, the kinetic reactions due to (b) balance the central attractions (a).

In a body composed of such molecules, the flaws which have been shown to exist in real substances might consist of actual cracks. But experiment shows that under certain conditions the strength of glass diminishes with lapse of time. On the present hypothesis this would require the potential energy of the system to increase

spontaneously by the amount of the surface energy of the cracks. This view must therefore be regarded as untenable.

Again, the observed weakening might conceivably occur if at any instant the vibrations of a large number (at least  $10^8$ ) of near molecules synchronised and were in phase, provided the energy of these molecules was approximately that corresponding with the temperature of ebullition of the substance. Except in the case of a material very near its boiling point, the probability of such an occurrence must be so small as to be quite negligible. Hence this hypothesis also must be discarded.

The foregoing discussion seems to suggest that the assumed type of molecule is too simple to permit of the construction of an adequate theory. An increase in generality may be obtained by supposing that the attraction between a pair of molecules depends not only on their distance apart, but also on their relative orientation. The properties of crystals seem definitely to require the molecules of anisotropic materials to be of this type, but those of isotropic substances have usually been assumed to be of the simpler kind. In view of the author, however, molecular attraction must be a function of orientation even in substances, such as glass, metals and water, which are usually referred to as "isotropic."

Consider a solid made up of a number of such molecules, initially oriented at random. Doubtless the mechanical properties of the substance, while it is in this amorphous condition, will differ little from those of a substance composed of molecules of the simpler type, having an attraction of appropriate strength. If this is so, the tensile strength of the material must be that corresponding with its average intrinsic pressure.

In general, however, this initial condition cannot be one of minimum potential energy.

It is clear that under suitable conditions the tendency to attain stable equilibrium can cause the molecules to rotate and set themselves in chains or sheets, with their maxima of attraction in line. The formation of sheets will commence at a great number of places throughout the solid, *i.e.*, wherever the initial random arrangement is sufficiently favourable. Evidently it is possible for the number of such "sufficiently favourable" arrangements to be enormously less than the total number of molecules, so that the ultimate result will be the formation of a number of units or groups, each containing a large number of molecules oriented according to some definite law. The relative arrangement of the units will, of course, be haphazard.

Now, in each unit there will, in general, be a direction which is, approximately at least, that of the minimum attractions of the majority of the molecules in the unit. Hence if the ratio of the maximum to the minimum attractions is sufficiently great, each unit can constitute a "flaw," and there appears to be no reason why the units should not be as large as the flaws have been shown to be in the case of glass. Thus, in order to explain the spontaneous weakening of glass, it is only necessary to suppose that the thermal agitation at about  $1400^\circ$  C. is sufficient to bring about the initial random formation.

It will be remembered that in the case of the freshly drawn fibres the reduction in tenacity required several hours for completion, so that the time taken was large compared with the time of cooling. Expressed in terms of molecular motion, this means that the molecules resist rotation very much more than they resist translation. This is in keeping with the conclusions of DEBYE,\* who found that, on the basis of the quantum theory, the phenomena associated with the specific heat of solids could be explained only if the thermal vibrations of the molecules were regarded as practically irrotational. The same thing is shown more roughly, without introducing the quantum theory, by the law of DULONG and PETIT, which requires that each molecule shall have only three degrees of freedom.

The theory here put forward makes the spontaneous weakening a consequence of the attainment of a molecular configuration of stable equilibrium; it therefore suggests that the weakening should be accompanied, in general, by a change in the dimensions of the solid. This has been verified by direct observation with a high-power microscope; in the course of half an hour a spontaneously weakening glass fibre increased in length by about 0.1 per cent., while the length of a silica fibre decreased by about 0.03 per cent.

On account of the random arrangement of the molecular groups, this spontaneous change in unstrained volume must set up internal stresses, which may be sufficiently large to start cracks along the directions of least strength. In this connection it may be mentioned that irregularly shaped pieces of glass, of which some parts had been put into the strong unstable state by heating, have sometimes been observed to break spontaneously about an hour after cooling was practically complete.

It was remarked on p. 184 that cracks could not form spontaneously in a substance composed of molecules having spherical fields of force, as the process would involve an increase in potential energy. This is no longer true when the attraction is a function of orientation, as the surface energy of the cracks may be more than counterbalanced by the decrease in potential energy accompanying the molecular rearrangement.

For this reason, it is impossible to deduce the ratio of the maximum to the minimum molecular attractions from the ratio of the maximum and minimum strengths of the material, as it is possible that the spontaneous weakening is always accompanied by the formation of minute cracks, of the same size as the molecular groups.

It is probable that, in many cases, the most stable orientation of the molecules at a free surface is that in which their maxima of attraction lie along the surface. Such an orientation would in turn lead to a similar tendency on the part of the next layer of molecules, and so on, the tendency diminishing with increasing distance from the surface. There would therefore be a surface layer having the special property that in it the "flaws" ran parallel to the surface.

Hence this layer would be of exceptional strength in the direction of the surface. This suggests a reason for the experimental fact that the breaking load of wires and

\* 'Ann. der Physik,' 39 (1912), p. 789.

fibres consists mainly of two parts, one proportional to the area, and the other to the perimeter of the cross-section. The process of drawing, too, might predispose the molecules to take up positions with their maxima of attraction parallel to the surface.

If a perfectly clean glass plate be covered with gelatine and set aside, the gelatine gradually contracts, and as it does so it tears from the glass surface thin flakes up to about 0.06-inch diameter and shaped like oyster shells.\* This tendency to flake at the surface is also observed when glass is broken by bending. This was particularly well shown in the specially prepared fibres used for the experiments described in the present paper. In almost all cases of flexural fracture the crack curled round on approaching the compression side, till it was nearly parallel to the surface. On two occasions the fracture divided before changing direction, the two branches going opposite ways along the fibre and a flake of length several times the diameter of the fibre was detached.

Surface flaking is also observed when some kinds of steel are subjected to repeated stress. Here the flakes are usually very small.

All these facts are evidently in complete agreement with the "surface layer" theory and, indeed, it is difficult to account for them on any other basis.

#### 8. *Extended Application of the Molecular Orientation Theory.*

On the basis of the present theory, the physical properties of materials must be intimately related to the geometrical properties of the molecular sheet-formation. In order that a substance may exhibit the characteristic properties of crystals, it is clearly necessary for the sheets of molecules to be plane. In this case the crystals are, of course, the molecule groups or "units" referred to above. In "amorphous" materials, on the other hand, the sheets are probably curved.†

In materials of the former type, there must exist planes on which, if they are subjected to a sufficiently large shearing stress, the portions on either side of the planes can undergo a mutual sliding through a distance equal to any integral multiple of the molecular spacing, without fundamentally affecting the structure of the crystal. It is well known that the phenomenon of yield in crystals, and especially in metals, is of this nature. The planes in question are, of course, the well-known "gliding planes," and it is further possible that they may be identified also with the surfaces of least attraction. The stress at which gliding occurs in a single crystal must be determined in the following manner. The molecules of a crystal are normally in a configuration of stable equilibrium, and if two parts of the crystal slide on a gliding plane through one molecular space the resulting configuration is also stable. Between these two positions there must, in general, be one of higher potential energy, in which the equilibrium is unstable, and the shearing stress is determined by the condition that the rate at which work is done, in

\* Lord RAYLEIGH, 'Engineering,' 1917, vol. 103, p. 111, and H. E. HEAD, 'Engineering,' 1917, vol. 103, p. 138.

† See QUINCKE, 'Ann. der Physik,' (4), 46, 1915, p. 1025.



sliding from the stable to the unstable state, must be equal to the greatest rate of increase in potential energy which occurs during the passage between the two states. This rate will depend on the shape of the molecular fields of force, and may in particular cases be zero. Liquid crystals are doubtless of this type. The average shear stress, during yield, of a random aggregation of a large number of crystals, is doubtless greater than that of a single crystal, as the angle between the gliding planes and the maximum shear stress must vary from crystal to crystal and can be zero in only a few of them.

As the mutually gliding portions of a crystal pass from the stable to the unstable state, the molecular cohesion between them (normal to the gliding plane) must, in general, become less. In particular instances it may diminish to zero before the position of unstable equilibrium is reached. In these cases, shearing fracture along the gliding planes will occur, unless the material is subjected to a sufficiently high "hydrostatic" pressure, in addition to the shearing stress. Thus, a crystalline substance may be either ductile or brittle, according to nature of the applied stress, or it may be ductile at some temperatures and brittle at others, under the same kind of stress as has been actually observed by BENGOUGH and HANSON in the case of tensile tests of copper. This rupture in shear explains the characteristic fracture of short columns of brittle crystalline material under axial compression. The theory indicates that such fracture can always be prevented and yield set up by applying sufficient lateral pressure in addition to the longitudinal load; this is in agreement with experiments on rocks such as marble and sandstone.\* Conversely, a ductile substance might be made brittle if it were possible to apply to it a sufficiently large hydrostatic tension.

In the case of an alloy of, say, two metals A and B, suppose, as an example, that the sequence of molecules on either side of a gliding plane is

$$\begin{array}{c} . A . B . B . A . B . B \\ B . B . A . B . B . A . \end{array}$$

Let sliding occur (through one molecular space) to an adjoining position of stable equilibrium, or, say, to the configuration

$$\begin{array}{c} . A . B . B . A . B . B . \leftarrow \\ . B . B . A . B . B . A \rightarrow \end{array}$$

Evidently, the structure in the neighbourhood of the gliding plane is in this case no longer the same as in the original crystal formation. It is therefore likely that the new state is one of higher potential energy, whence it is reasonable to suppose that the maximum rate of increase in potential, in sliding, is greater than it would have been had the potential of the two states been the same. Thus an alloy may be expected to have a higher yield-point than its most ductile constituent. This is in accordance with experience. For example, it is known that quenching from a high temperature

\* T. V. KARMAN, 'Zeitschr. Ver. Deutsch. Ing.,' 55, 1911.

hardens tool steel by preventing the separation of "ferrite," or iron containing no carbon.

In a single crystal the molecules are presumably in an equilibrium configuration of maximum stability. In this event, the equilibrium of molecules at or near inter-crystalline boundaries, in a body composed of a large number of crystals, must, in general, be less stable than that of the molecules in the interior of the crystals. In fact, where the orientation of the component crystals is haphazard, the stability of the boundary molecules may be expected to range from the maximum of normal crystallisation down to zero, *i.e.*, neutral equilibrium. If such a body be subjected to a shear stress, some of the molecules in or near neutral equilibrium must, in general, become unstable, and these will tend to rotate to new positions of equilibrium. This rotation, however, will be strongly resisted, as has been seen, by forces doubtless of a viscous nature, and its amount will accordingly depend on the time during which the stress is applied. If, therefore, the strain is observed it will be found to increase slowly as time goes on, but at a constantly decreasing rate, as the molecules concerned approach equilibrium. If now the load is removed, these molecules must rotate in order to regain their original positions of equilibrium, and this process in turn will be retarded by viscous forces. Hence a small part of the observed strain will remain after the removal of the load, and this will gradually disappear as time goes on. These properties, known as "elastic after-working," are, of course, well known to belong to crystalline materials. Moreover, the theory shows that they should not be possessed by single crystals, and this has been demonstrated experimentally.\*

There is a special type of gliding or yield which may occur at stresses below the normal yield point. Consider a pair of adjacent crystals, separated by a plane boundary. If these crystals are thought of as sliding relatively to each other, it will be seen that only in a finite number of the positions so taken up can the two be in stable equilibrium. Between each pair of such positions there must in general be one of unstable equilibrium. Suppose that, while near such an unstable position, the two crystals are embedded in a number of others. Under these conditions the boundary molecules of the two crystals will be pulled over in the direction of one or other of the two adjoining stable positions, and they will strain the solid in the process. If now the body is subjected to a shearing stress tending to cause relative displacement of the two crystals towards the other stable position, then at a certain value of this stress the molecules on either side of the boundary will be wrenched away, will pass through the position of instability, and will then take up a new position bearing the same relation to the second stable position as their original state did to the first. This new condition will, of course, persist after the removal of the load, as the original state cannot be regained without passing through unstable equilibrium, *i.e.*, a condition of maximum potential energy. To cause the crystals to pass through this condition it would be necessary to apply a load of opposite sign, and in this way the process might be repeated indefinitely. In a body composed

\* H. v. WARTENBERG, 'Deutsch. Phys. Gesell., Verh.,' 20, pp. 113-122, August 30, 1918.

of a large number of crystals there must be many arrangements of this type, in which adjacent crystals can execute inelastic oscillations about positions of unstable equilibrium, under alternating shear stresses below the ordinary yield stress. The consequent observed phenomena would correspond exactly with those known to be manifested in metals, under the name "elastic hysteresis."\*

Experimentally, elastic hysteresis is distinguished from elastic after-working by the circumstance that it is completed very much more quickly. This is just what would be expected theoretically, on the view that molecular translation occurs much more readily than rotation.

It has been remarked that when a single crystal of a pure substance is caused to yield, its structure is fundamentally unaltered. This cannot hold, however, in the case of an aggregate of a large number of crystals arranged at random, or a crystal embedded in amorphous material. True, the material in the interior of each crystal can retain its original properties, but near the crystalline boundaries the structure must be violently distorted. As a result, it may be expected that the number of the molecules of inferior stability will be largely increased. Elastic after-working in metals should therefore be increased by overstraining or "cold-working." This, again, agrees with experience.

The foregoing considerations lend support to the view that each crystal of a severely cold-worked piece of metal is surrounded by an amorphous layer of appreciable thickness. If such a piece of metal undergoes a shear strain greater than that which can initiate yield in the normal crystalline substance, the average stress which is set up must be above the normal yield stress, for the part due to the amorphous layers must be the elastic stress corresponding with the strain, and this, by hypothesis, is greater than the yield stress. This part, moreover, will increase with the strain. It follows that yield in cold-worked metal should be less sharply defined, and should occur at a higher shear stress than in the normal crystalline variety. That this is actually the case is, of course, well known.

In the case of very large strains an important part of the shear stress must be taken by the amorphous boundary layers, and as a result the maximum tensile stress may reach a value sufficient to cause rupture of some favourably disposed crystals across their planes of least strength. This is, perhaps, the actual mode of rupture in ductile materials. On this view, the "ductility" of a metal depends simply on the relation between the tensile strength of the "flaws" and the normal yield stress. A substance whose ductility is small may still be "malleable," as hammering need not give rise to large tensile stresses.

The formation of non-crystalline material at the intercrystalline boundaries, when a piece of metal is over-strained, appears to provide an explanation of the sudden drop in stress which occurs immediately after the initiation of yield† in ductile metals.

\* GUEST and LEA, "Torsional Hysteresis of Mild Steel," 'Roy. Soc. Proc.,' A, June, 1917.

† ROBERTSON and COOK, 'Roy. Soc. Proc.,' A, vol. 88, 1913, pp. 462-471.

Remembering that the surface tension of a substance is the work done in forming unit area of new surface, it will be seen that the tension of any surface of a crystal must depend on the angle it makes with the crystal axis. Thus the surface tension parallel to the planes of least strength must be less than that in any other direction. Consequently, in a body composed of a number of crystals there must exist a mutual surface tension at each intercrystalline boundary. Now, the theory of surface tension shows that the magnitude of such a mutual tension is greatly diminished by making the transition between the two bodies more gradual. Hence the formation of the amorphous boundary layer involves a reduction in the surface energy of the crystals, and this is shown in the experiments by a drop in the stress. If this account of the phenomenon is complete, the drop in stress must be determined by the condition that the loss of strain energy equals the reduction in surface energy. The mechanism of the process appears to be that the breaking up of the boundary, which must accompany yield, is resisted by the surface tension, and yielding therefore requires a higher stress for its initiation than for its maintenance.

According to this view, the loss of strain energy should be inversely proportional to the linear dimensions of the crystals. Hence the results of different experiments should show considerable variation in the magnitude of the drop in stress. This is actually the case; a single series of experiments on mild steel, by ROBERTSON and COOK, gave drops varying from 17 per cent. to 36 per cent., while in other experiments as little as 7 per cent. has been observed.

In the above series of experiments the average loss of strain energy was about 12 inch-lbs. per cubic inch. Assuming, for simplicity, that the crystals were cubes, of, say, 0.001-inch side (which is a fair value for well-treated mild steel), the area of the intercrystal surface was 3000 sq. inches per cubic inch. These figures give the average intercrystal surface tension as 0.004 lbs. per inch. This is certainly of the right order of magnitude.

Many of the phenomena discussed above will be more complicated, in practice, if the coefficient of expansion of the crystals is not the same in all directions. In such an event, internal stresses will be set up in cooling, on account of the random arrangement of the crystals, and these stresses must be taken into consideration in applying the theory.

There remains for consideration the problem of the fracture of metals under alternating stress. It is known that fatigue failure occurs as the result of cracking after repeated slipping on gliding planes, and the theory has been advanced\* that this cracking is due to repeated to and fro sliding and consequent attrition and removal of material from the gliding planes. This theory presents some difficulties, in that it does not explain how the attrition can occur, or the method of disposing of the debris.

A theory which is free from these objections may be constructed if it is supposed that a change in volume occurs on the passage of the metal from the crystalline to the amorphous state. This assumption is, of course, known to be valid for many substances

\* EWING and HUMFREY, 'Phil. Trans.,' A, 1902, p. 200.

at their melting points, but at lower temperatures there seems to be no definite information available.

This assumption being granted, suppose that a piece of material which contracts on decrystallising is being subjected to a stress cycle just sufficient to cause repeated slipping in the most favourably disposed crystals. As a result, the material at the boundaries of these crystals will become amorphous, and the quantity of amorphous material will increase continuously as long as the repeated slipping goes on. But, by hypothesis, the unstrained volume of the amorphous phase is less than the space it filled when in the crystalline state. Hence all the material in the immediate neighbourhood will be subjected to a tensile stress, and as soon as this exceeds a certain critical value a crack will form. It has been observed above that the application of a sufficiently large hydrostatic tension may be expected to make a ductile substance brittle. Hence the crack may occur either in tension or in shear, according to the properties of the material and the nature of the applied stress. Further alternations of stress will cause this crack to spread until complete rupture occurs. This theory makes the limiting safe range of stress equal to that which just fails to maintain repeated sliding in the most favourably disposed crystals.

It may be asked why such cracking does not take place in a static test where the quantity of amorphous material, once yield has fairly started, is presumably much greater. The answer to this is two-fold. In the first place, if the material becomes amorphous round all, or nearly all, the crystals of a piece of metal, it is evident that it will contract as a whole and no great tensile stress will be set up. In the case where only a few crystals yield, the tension arises from the rigidity of the unchanged surrounding metal.

In the second place, even if some crystals do crack, the cracks will not, in general, tend to spread through the ductile cores of the neighbouring crystals, unless the applied load is alternating, on account of the equalisation of stress due to yield.

The safe limit of alternating stress will usually be less than the apparent stress necessary to initiate yield in a static test, on account of initial stresses, including those due to unequal contraction of the crystals.

The theory indicates that the cracking of the first crystal marks a critical point in the history of the piece. At any earlier stage the effects of the previous loading may be removed by heat treatment, or possibly by a rest interval, but once a crack has formed this cannot be done. True, the tension may be relieved and the ruptured crystal may even be compressed somewhat, but this cannot, in general, close the crack, as cracking is not a "reversible" operation. An exception may occur if the top temperature of the heat-treatment is sufficient to bring the molecules on either side of the crack within mutual range by thermal agitation, but it is unlikely that this can happen save in the case of very small cracks.

If this theory is correct, it appears at first sight that the phenomenon of fatigue failure must be confined to substances which contract on decrystallising. This, however

is not necessarily so. If, for instance, a small thickness of material at the interface between two crystals were to increase in volume, it could not be said without proof that tensile stresses would not be set up thereby, in addition to compressions. In some cases, in fact, it is obvious that there must be tensions. Thus, if the outer layer of a sphere increases in volume, the matter inside must be subjected to a tensile stress.

The effect of overstrain on the density of metals is at present under investigation at the Royal Aircraft Establishment. The work is not yet sufficiently complete for detailed publication, but it may be mentioned here that the expected change in density has been found, and that the results already obtained are such as to leave little room for doubt that this change is in fact the cause of fatigue failure in metals. Thus, in overstraining mild steel by means of a pure shearing stress, a decrease in average density of as much as 0.25 per cent. has been observed.

Some progress has also been made in the direction of estimating the internal stresses set up as a result of the change in density, and it has been found that an average change of the magnitude mentioned above could give rise to a hydrostatic tensile stress in the cores of the crystals, of the order of 30,000 lbs. per sq. inch.

Dealing now with materials whose molecular sheet-formations are curved, it is at once evident that all yield, or slide, phenomena must be absent, as possible gliding planes do not exist. Thus, this case, though geometrically more complicated, is practically much simpler than that in which the sheets are plane. The theoretical properties of materials having the curved type of formation appear to correspond exactly with those known to belong to brittle "amorphous" substances. Exactly as in the case of crystalline materials, elastic after-working is explained by the inferior stability of molecules near the boundaries of the units of molecular configuration, but elastic hysteresis should not occur. If adequate precautions are taken to avoid secondary tensile stresses, fracture of short columns in compression should occur at stresses of an altogether higher order than in the case of crystals. In this connection it may be remarked that the compressive strength of fused silica is about 25 times as great as its ordinary tensile strength.

It appears from the foregoing discussion that the molecular orientation theory is capable of giving a satisfactory general account of many phenomena relating to the mechanical properties of solids, though closer investigation will perhaps show that the agreement is in some cases superficial only. Such questions as the effects of unequal cooling, foreign inclusions and local impurities, and the behaviour of mixtures of different crystals, have not been dealt with; it is thought that these are matters of detail whose discussion cannot usefully precede the establishment of the general principles on which they depend.

#### 9. *Practical Limitations of the Elastic Theory.*

It is now possible to indicate the directions in which the ordinary mathematical theory of elasticity may be expected to fail when applied to real solids.

It is a fundamental assumption of the mathematical theory that it is legitimate to replace summation of the molecular forces by integration. In general this can only be true if the smallest material dimension, involved in the calculations, is large compared with the unit of structure of the substance. In crystalline metals the crystals appear, from the foregoing investigation, to be anisotropic and they must therefore be regarded as the units of structure. Hence the theory of isotropic homogeneous solids may break down if applied to metals in cases where the smallest linear dimension involved is not many times the length of a crystal.

Similar considerations apply to solids such as glass, save that here the units of structure are probably curved.

The most important practical case of failure is that of a re-entrant angle or groove. Here the theory may break down if the radius of curvature of the re-entering corner is but a small number of crystals long. An extreme instance is that of a surface scratch, where the radius of curvature may be but a fraction of the length of the crystals.

In the case of brittle materials the general nature of the effect of scratches on strength may be inferred from the theoretical criterion of rupture enunciated in section 2 above. Whether the material be isotropic or anisotropic, homogeneous or heterogeneous, it is necessary on dimensional grounds that the strain energy shall depend on a higher power of the depth of the scratch than the surface energy. It follows that small scratches must reduce the strength less than large ones of the same shape. Hence, where the tenacity of the material, under "uniform" stress, is determined by the presence of "flaws," it must always be possible to find a certain depth of scratch whose breaking stress is equal to that of the flaws. Evidently such a scratch can have no influence on the strength of the piece. Deeper scratches must have some weakening effect, which must increase with the depth, until in the limit the strength of very large grooves may be found by means of the elastic theory and the appropriate empirical hypothesis of rupture.

In the case of ductile metals, the effect of scratches is important only under alternating or repeated stresses. On the theory advanced in the preceding section, fatigue failure under such stresses is determined by phenomena which occur at the intercrystalline boundaries. Hence the strength of a scratched piece is fixed, not by the maximum stress range in the corner of the scratch, but by the stress range at a certain distance below the surface. This distance cannot be less than the width of one crystal, and it may be greater. Elastic theory suggests that the stress due to a scratch falls off very rapidly with increasing distance from the re-entrant corner, so that the relatively small effect of scratches in fatigue tests is readily explained.

Possibly many published results bearing on this matter depend more on initial skin stresses than on sharp corner effects.

### 10. *Methods of Increasing the Strength of Materials.*

The most obvious means of making the theoretical molecular tenacity available for technical purposes is to break up the molecular sheet-formation and so eliminate the "flaws." In the case of crystalline material this has the further advantage of eliminating yield and probably also fatigue failure.

In materials which normally have curved sheets, the molecular fields of force are presumably asymmetrical, and the process indicated above would lead of necessity to a random arrangement, which might be unstable. It has been seen that in glass and fused silica it is actually unstable, except in the case of the finest fibres.

As regards crystalline materials, however, in which the fields of force must have some sort of symmetry, there seems to be no reason why there should not be possible a very fine grained stable configuration, which could be derived from the ordinary crystalline form by appropriate rotations of certain molecules to new positions of stable equilibrium, in such a way as to break up the gliding planes. The grain of such a structure need be but a few molecules long, and its strength would approximate to the theoretical value corresponding with the heat of vaporisation.

There is some evidence that mild steel which has been put into the amorphous condition by over-strain tends, under certain conditions, to take up a stable fine-grained formation of this kind, in preference to resuming its original coarse crystalline configuration, in that a temperature of 0° C. appears to prevent recovery from tensile over-strain.\*

These considerations suggest that if a piece of metal were rendered completely amorphous by cold-working, and then suitably heat-treated, its molecules might take up the stable strong configuration already described. The theory indicates, however, that over-straining tends to set up tensile stresses in the unchanged parts of the crystals which may start cracks long before decrystallisation is complete. Such cracking could be prevented if the over-straining were carried out under a sufficiently great hydrostatic pressure, and this line of research seems to be well worth following up. It might, of course, be found that the requisite pressure was so enormous as to render the method unworkable, but if the theory is sound there seems to be no other reason why definite results should not be obtained.

The problem may be attacked in another way. As has been seen, the theory suggests that the drop in stress at the initiation of yield is due to the surface energy of the inter-crystal boundaries. Thus the yield point may be raised by "refining" the metal, *i.e.*, so heat-treating it as to reduce the size of the crystals. The limit of refinement is, doubtless, reached when each "crystal" contains but a single molecule and the material is then in the strong stable state already described.

Refining is also of great value in connection with resistance to fatigue failure. Suppose, in accordance with the foregoing theory of fatigue, that one crystal has been fractured,

\* COKER, 'Phys. Rev.,' 15, August, 1902.



then the general criterion of rupture shows that the crack cannot spread unless the material is subjected to a certain minimum stress, which is greater the smaller the crack. Thus, reducing the size of the crystals increases the stress necessary to cause the initial crack to extend. There is therefore a critical size of crystal for which the stress-range necessary to spread the crack is equal to that necessary to start it. Until the refining has reached that stage it can have no effect on the magnitude of the safe stress range, but from that point on the range must increase progressively with refinement until the limit is reached, as before, when each "crystal" contains but one molecule.

It therefore appears that refining is one avenue of approach towards the ideal state of maximum strength. Strangely enough, another line of argument suggests that the reverse of refinement might be effective in securing the desired result, in certain special cases. If a wire is required to withstand a simple tension, it seems that the best arrangement is that in which the strongest directions of all the molecules are parallel to the axis of the wire. This is equivalent to making the wire out of a single crystal. The theoretical tenacity would not be obtained, however, if the gliding planes made with the axis angles other than  $0^\circ$  C. and  $90^\circ$  C., as yield would occur.

If, in passing from the normal crystalline to the strong fine-grained state, the necessary orientation of the molecules were performed in accordance with some regular plan, the resulting configuration would possess some kind of symmetry, and the material might therefore exhibit crystalline properties. In cases where a substance exists in nature in several different crystalline forms, of which one is much stronger than the others, it may be that the strong modification is of the fine-grained type here considered. Thus, diamond may be a fine-grained modification of carbon. If this view is correct, it suggests that the transformation of carbon into diamond requires, firstly, the existence of conditions of temperature and pressure under which diamond has less potential energy than carbon; and, secondly, the provision of means for causing relative rotation of the molecules. In the attempts which have so far been made in this direction, attention seems to have been concentrated on satisfying the former requirement, the possible existence of the latter one having been overlooked. The most obvious way of satisfying it, if the mechanical difficulties could be overcome, would appear to be the application of suitable shearing stresses in addition to the hydrostatic pressure.

### 11. *Application of the Theory to Liquids.*

A detailed discussion of the properties of liquids, in the light of the present theory, would scarcely fall within the scope of this paper. One prediction which has been made, however, and which has been verified experimentally, affords such a remarkable confirmation of the general theory that it is felt that no apology is necessary for introducing it here. Consider a solid composed of molecules whose attraction is a function of orientation, the molecules being arranged in groups, in accordance with the theory outlined in the preceding pages. If the temperature of this body be supposed to be increasing, it will be seen that at some temperature the kinetic reactions due to

the thermal vibrations must overcome the minimum attractions of the molecules in each group. It is clear, therefore, that at this temperature the substance will be unable to withstand shearing stresses. At the same time it cannot vaporise, as the molecules must still be held together in chains by their maximum attractions. In other words, the transformation which has been discussed is simply the liquefaction of the solid.

This view of the phenomenon of melting indicates that the molecules of liquids are in general arranged in groups or chains, of a length comparable with that of the structure ascribed to solids in the preceding work, or, say,  $10^4$  molecules.

If, therefore, a liquid be contained in a solid boundary which it wets, the ends of these chains may be expected to attach themselves to the solid; and if at any point the distance between the bounding walls is less than the length of the chains, some of the latter will attach themselves to both walls and hinder the free flow of the liquid and the relative movement, if any, of the boundaries. At such a point the liquid will act as a solid under any stress which is insufficient to break the chains.

This has been verified experimentally. The apparatus consisted of a polished steel ball 1 inch in diameter, and a block of hard tool steel containing a circular hole about 4 inches long. The hole was carefully ground, after hardening, to a diameter about 0.0001 inch greater, at its smallest part, than the diameter of the ball. When both were dry the ball passed freely through the hole. If, however, they were wetted with a liquid, considerable pressure was necessary to force the ball through. This resistance possessed the characteristic "stickiness" of solid friction, and was exactly the kind of resistance which would have been expected in forcing the dry ball through a hole which was too small for it.

To show that the resistance was a true "solid stress" and not due merely to viscosity, the apparatus was on one occasion left for a week, with the weight of the ball supported by the stress in the liquid (paraffin oil). The hole was vertical, so that there was no normal pressure between its surface and the surface of the ball. During this period no motion whatever could be detected.

It is essential to the success of these experiments that the ball and hole should be thoroughly wetted by the liquid. For this reason the liquids used have been chiefly paraffin oil and lubricating oils, but on one occasion the effect was obtained with water.

The present theory suggests a reason for the very low tensile strength of liquids. If a liquid is composed of a random aggregation of chains of molecules, it may reasonably be expected to contain regions of dimensions comparable with, but smaller than, the length of the chains, across which no chains run. Rupture of the liquid will evidently occur by the enlargement of these cavities. Now the tension,  $R$ , necessary to enlarge a spherical cavity of diameter,  $D$ , in a liquid of surface tension,  $T$ , is given by

$$R = 4T/D.$$

In the case of water, the tensile strength,  $R$ , is about 70 lbs. per sq. inch at ordinary temperatures, while  $T$  is about 0.00042 lbs. per inch. Hence the cavities, if spherical, must be at least 0.00024 inch in diameter. This is of the order indicated by the theory.

The foregoing conclusions are of especial interest in their relation to the theory of ROSENHAIN,\* on which many of the properties of metals, and particularly "season cracking" under prolonged stress, are explained by supposing that the crystals are cemented together by very thin layers of amorphous material having the properties of an extremely viscous undercooled liquid. The experiments described above show that fluidity is not a property which can be ascribed *a priori* to such films. Hence if the view of ROSENHAIN and ARCHBUTT were to be definitely established, it would be necessary to regard it, not as a theory of season cracking in terms of the known properties of materials, but as a deduction of the properties of the intercrystalline layers from the phenomena of season cracking. Looked at in this way, it would be of extreme interest, for it would show that the molecular arrangement of the intercrystalline layers could not be of the coarse-grained type characteristic of the normal states of solids and liquids.

It is clear that the foregoing theory of liquids is not free from objection, and that in some respects it appears to be less satisfactory than existing theories. The most obvious objection is that it seems to be incompatible with accepted determination of the molecular weight of liquids. Since, however, these experiments are based ultimately on kinetic considerations, the author believes that this difficulty will not in fact arise unless the requisite bonds between the molecules of each group are found to be sufficiently strong to cause appreciable modification of the average molecular kinetic energy.

## 12. Summary of Conclusions.

(1) The ordinary hypothesis of rupture cannot be employed to predict the safe range of alternating stress which can be applied to metal having a scratched surface. The safe range of an unscratched test piece appears to be slightly less than the yield range, but if the surface is scratched the safe range may be several times the range which causes yield in the corners of the scratches.

(2) The "theorem of minimum potential energy" may be extended so as to be capable of predicting the breaking loads of elastic solids, if account is taken of the increase of surface energy which occurs during the formation of cracks.

(3) The breaking load of a thin plate of glass having in it a sufficiently long straight crack normal to the applied stress, is inversely proportional to the square root of the length of the crack. The maximum tensile stress in the corners of the crack is more than ten times as great as the tensile strength of the material, as measured in an ordinary test.

(4) The foregoing observation is in agreement with the known fact that the observed strength of materials is less than one-tenth of the strength deduced indirectly from physical data, on the assumption that the materials are isotropic. The observed

\* W. ROSENHAIN and D. EWEN, "Intercrystalline Cohesion in Metals," 'J. Inst. Metals,' vol. 8 (1912); and W. ROSENHAIN and S. L. ARCHBUTT, "On the Intercrystalline Fracture of Metals under Prolonged Application of Stress (Preliminary Paper)," 'Roy. Soc. Proc.,' A, vol. 96 (1919).

strength is, in fact, no greater than it would be, according to the theory, if the test pieces contained cracks several thousand molecules long.

(5) It has been found possible to prepare rods and fibres of glass and fused quartz which have a tenacity of about one million pounds per square inch (approximately the theoretical strength) when tested in the ordinary way. The strength so observed diminishes spontaneously, however, to a lower steady value, which it reaches a few hours after the fibre has been prepared. This steady value depends on the diameter of the fibre. In the case of large rods it is the same as the ordinary tenacity, whereas in the finest fibres the strength diminishes but little from its initial high value. The relation between diameter and strength is of practically the same form for glass fibres as for metal wires.

(6) If it is assumed that intermolecular attraction is a function of the relative orientation of the attracting molecules, it is possible to construct a theory of all the phenomena mentioned in (3), (4) and (5) above. In the case of crystalline substances the theory also appears to explain yield and shearing fracture; elastic hysteresis; elastic afterworking; the fracture in tension of ductile materials and the flow of brittle materials under combined shearing stress and hydrostatic pressure; the drop in stress which occurs on the initiation of yield in ductile substances; fatigue failure under alternating stress; and the relatively slight effect of surface scratches on fatigue strength. In the case of non-crystalline materials the theory explains elastic afterworking and the great strength of short columns in compression.

(7) The theory shows that the application of the mathematical theory of homogeneous elastic solids to real substances may lead to error, unless the smallest material dimension involved, *e.g.*, the radius of curvature at the corner in the case of a scratch, is not many times the length of a crystal.

(8) It should be possible to raise the yield point of a crystalline substance by "refining" it, until at the ultimate limit of refinement the yield stress should be of the same order as the theoretical strength. It should also be possible similarly to increase the tenacity. Up to a certain stage the fatigue range should be unaffected by refining, but thereafter it should increase in the same degree as resistance to static stress.

(9) The theory requires that a thin film of liquid enclosed between solid boundaries which it wets should act as a solid. Experimental confirmation of this has been obtained.

In conclusion, the author desires to place on record his indebtedness to many past and present members of the staff of the Royal Aircraft Establishment for their valuable criticism and assistance, and also to Prof. C. F. JENKIN, at whose request the work on scratches was commenced.

[*Note.*—It has been found that the method of calculating the strain energy of a cracked plate, which is used in Section 3 of this paper, requires correction. The correction affects the numerical values of all quantities calculated from equations (6), (7), (8), (10), (11), (12) and (13), but not their order of magnitude. The main argument of the paper is therefore not impaired, since it deals only with the order of magnitude of the results involved, but some reconsideration of the experimental verification of the theory is necessary.]

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