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UMI
A THEORY OF IMPERFECT ELASTICITY

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and

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A THEORY OF IMPERFECT ELASTICITY

It is well known that the so-called elastic materials show, in varying degree, departures from perfect elasticity such as elastic afterworking, elastic hysteresis, damping of vibrations and the like. In fact, as Stokes (1) observed, every degree of behavior from the elastic solid to the viscous fluid is found in actual materials so that it is impossible to make a sharp division between the two classes. However, it has been convenient in the past to set up certain "ideal" materials, each representative of a class of actual materials. Among such ideal materials might be mentioned the perfectly elastic solid, elastico-viscous material, visco-elastic material, and viscous fluids. (infra).

The theory given in this paper might be said to present a new ideal material which shows the phenomena of afterworking, elastic hysteresis, and damping and which includes as special cases the ideal materials mentioned above. The theory is applied here particularly to metals although much of what is said is also true of non-metallic crystalline aggregates and of vitreous solids.

Our knowledge of the nature of the binding forces in metallic crystals and, indeed, of homopolar binding in general is still so meager that at the present time
a structure theory of the mechanical properties of metals cannot be given. Born's atomic theory of the solid state has met with some success in the case of polar crystals such as those of the alkaline halides but for metallic crystals the theory breaks down. It predicts, for example, that Cauchy’s relations hold true for cubic crystals, such as iron and tungsten, whereas conclusive experimental evidence has long since discredited Cauchy’s theory. One of Cauchy’s relations is $c_{23} = c_{44}$ where these are physical constants of the crystal. For tungsten, Bridgman found $c_{23} = 15300$ and $c_{44} = 20500$.

Furthermore, single crystals do not seem to show afterworking and hysteresis, so that for the seat of these phenomena we have to consider, in the case of quasi-isotropic materials (crystalline aggregates), the rather amorphous arrangement of molecules between the crystal grains. Here some statistical theory might be applied but again the nature of the cohesive forces between the non-polar molecules is so poorly understood that even where physical models have been proposed to explain individual phenomena the treatment is in effect purely phenomenological. It is rather interesting to note that while great advances have been made in understanding the electrical and magnetic properties of crystals, the mechanical properties have presented the most obstinate resistance to theoretical attack.
With these difficulties in mind, we think it useless to make any pretence of giving here anything other than a phenomenological treatment. One can be guided, however, by the idea that in the amorphous layers the molecules or atoms have a certain amount of freedom of motion about points more or less fixed in relation to neighboring molecules; that they are attracted to their equilibrium positions by elastic forces; that while "straining" they are opposed by frictional forces; and that under strain, readjustment of molecular positions gives some relaxation of the forces necessary to preserve that strain.

If we restrict ourselves to isothermal changes, a perfectly elastic solid may be defined as one for which the stress components are given by single valued functions of the strain components, whether or not those functions are linear. If they are linear, the functions express the generalized Hooke's Law. If they are not linear, they are approximately so for sufficiently small strains. The tensile stress below which a material behaves elastically is called the elastic limit, and the stress below which the stress strain relationship can be regarded as linear is called the limit of proportionality. Strictly speaking, it is doubtful whether a finite elastic limit exists for actual materials since precise measurement shows a small amount of plasticity (with permanent set) even under very small stress.
The departures from perfect elasticity which have been referred to above are not found in bulk compressions. In the experiments of Bridgman, for example, no departures from perfect elasticity were detected for non-porous materials, even when stressed to many times their elastic limits as given by tensile tests.

A history of the theories which have been put forward to account for imperfect elasticity is given, for example, by von Karman. Only the three theories which have been most fruitful are mentioned here.

The first, given by Maxwell and later by Butcher and Jeffreys, is a modification of Hooke's Law of the form:

\[ \dot{P} = \alpha \dot{E} - \beta \dot{P} \]

where \( P \) is the stress, \( E \) the strain, and \( \alpha \) and \( \beta \) are constants. Material which conforms to this law is called elastico-viscous. Such material continues to deform as long as stress is applied. For constant strain the stress falls off asymptotically to zero with time. For constant velocity of strain, stress increases with time approaching asymptotically the condition of a viscous fluid.

The second theory is due to Voigt. It has been used extensively by Jeffreys and others in geophysical applications and a formal treatment has
been given recently by Thompson. Hooke's Law is modified as follows:

\[ \rho = \gamma E + \delta \dot{E} \]

where \( \gamma \) and \( \delta \) are constants. Such material is called visco-elastic. The rate of strain is at first proportional to the applied stress but falls off asymptotically with time. This theory predicts that for vibrations the logarithmic decrement of amplitude will be inversely proportional to the period. This is not in agreement with the results of experiments by Lord Kelvin on torsional pendulums, which indicated that the logarithmic decrement was more constant than this law would imply. However, Voigt found that, of more than a dozen metals investigated by the torsional pendulum method, two, copper and nickel, seemed to obey the visco-elastic law.

The third theory, due to Boltzmann, is of the general form:

\[ \rho = \delta E - \phi \]

where \( \delta \) is a constant, and \( \phi \) is an integral covering the past history of the material. For particular assumptions as to the form of the integrand, this theory becomes identical with one or other of the above theories. This theory has been dealt with by Volterra, who calls it a "heredity" theory. The integral con-
tains "heredity coefficients" which require further postulation. Boltzmann's particular form of the theory leads to the conclusion that the logarithmic decrement of amplitude of torsional vibrations should be independent of period. Voigt found this true, in a narrow band of periods, only for cadmium.

The importance of Hooke's Law in problems concerned with perfect elasticity suggests that a linear relationship of stress and strain and their first order time derivatives might be of equally far reaching application in problems involving imperfect elasticity. The modification of Hooke's Law which forms the hypothesis for this paper may be stated simply (but not exactly) for comparison with the above theories in the form:

$$\rho + a \dot{\rho} + b \dot{E} + c \ddot{E} = 0$$

where $a$, $b$, and $c$ are constants. The usual assumption is made that the changes in stress-strain are isothermal. This means that for vibrations a small thermoelastic effect is neglected. The materials considered are isotropic or quasi-isotropic. No particular difficulty is encountered in extending the theory to the anisotropic case. The elastic constants become fourth order tensors in three dimensions with a number of relations between the components given by the degree of symmetry of the material.
Before proceeding with the theory proper, it is of interest to note that the equation just given would follow from the assumptions that in a polycrystal (a) the crystals are perfectly elastic, and (b) the intercrystalline material is visco-elastic. Let the total strain $E$ consist of the strain in the crystals $E_1$ together with the strain in the matrix $E_2$. We have then

\[
P = f E, \\
\dot{P} = g E + h \dot{E}_2, \\
\dot{\dot{P}} = f \ddot{E},
\]

or,

\[
g P = g f E, \\
f P = g f E + f h \dot{E}_2, \\
h \dot{P} = f h \dot{E},
\]

and summing,

\[
(g+f) P + h \dot{P} = g f E + f h \dot{E}
\]

which, with new constants, becomes

\[
P + a \dot{P} + b E + c \dot{E} = 0
\]
Let the stress and strain tensors be represented by

\[
P = \begin{pmatrix}
p_{11} & p_{12} & p_{13} \\
p_{12} & p_{22} & p_{23} \\
p_{13} & p_{23} & p_{33}
\end{pmatrix}
\quad \text{and} \quad
E = \begin{pmatrix}
e_{11} & e_{12} & e_{13} \\
e_{21} & e_{22} & e_{23} \\
e_{31} & e_{32} & e_{33}
\end{pmatrix}
\]

with \( p_{ik} = p_{ki} \) \quad \text{and} \quad e_{ik} = e_{ki}

If the displacement vector is \((u_1, u_2, u_3)\) where \(u_1, u_2,\) and \(u_3\) are functions of the space coordinates \(x_1, x_2, x_3,\) then

\[
e_{ik} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right)
\]

provided that the strains are sufficiently small so that products of the \( \frac{\partial u_i}{\partial x_k} \) may be neglected.

The mean tension and mean extension are given by

\[
p_0 = \frac{1}{3} p_{ii} \quad i = 1, 2, 3
\]

\[
e_0 = \frac{1}{3} e_{ii} \quad i = 1, 2, 3
\]

with the usual convention of summation over dummy indices.

In this notation Hooke's Law is

\[
p_{ik} = 3\lambda e_0 \delta_{ik} + 2\mu e_{ik} \quad (1)
\]

where \(\lambda\) and \(\mu\) are Lame's constants and \(\delta_{ik}\) is the unit tensor. \(\mu\) is also the modulus of rigidity.

We shall find it convenient to distinguish between strains which result in change of volume without change of shape on the one hand, and strains which show
change of shape without change of volume on the other. These may be called dilations and distortions respectively. Any small strain may be resolved into a dilation and a distortion. Since a material may behave in one way (say with perfect elasticity) for dilations, and in another way (say with imperfect elasticity) for distortions, the following resolution of strain is useful.

Let

\[ p^o = \begin{pmatrix} p_{11}^o & p_{12}^o & p_{13}^o \\ p_{21}^o & p_{22}^o & p_{23}^o \\ p_{31}^o & p_{32}^o & p_{33}^o \end{pmatrix} \]

and

\[ E^o = \begin{pmatrix} e_{11}^o & e_{12}^o & e_{13}^o \\ e_{21}^o & e_{22}^o & e_{23}^o \\ e_{31}^o & e_{32}^o & e_{33}^o \end{pmatrix} \]

Then \( E^o \) represents a strain without change of volume, that is to say, a distortion. (\( e_{11}^o = 0 \)).

By (1),

\[ 3 p^o = p_{ij} = 9 \lambda e^o + 6 \mu e^o \]

\[ p^o = 3 \kappa e^o \]

where \( \kappa = \lambda + \frac{2}{3} \mu \) is the bulk modulus.

Furthermore,

\[ p^o_{ik} = p^o_{ik} - p^o \delta_{ik} = 3 \lambda e^o \delta_{ik} + 2 \mu e^o_{ik} - (3 \lambda + 2 \mu) e^o \delta_{ik} \]

\[ = 2 \mu (e^o_{ik} - e^o \delta_{ik}) \]

\[ = 2 \mu e^o_{ik} \]
Hooke's Law is now simply:

\[ P^0 = 2\mu E^0 \]
\[ \rho_0 = 3K e_0 \]

In the modification of Hooke's Law which follows, these equations become

\[ P^0 = 2 ME^0 \]
\[ \rho_0 = 3K e_0 \]

where \( M \) and \( K \) are linear fractional operators.

According to our hypothesis we have for a simple shear \( \gamma \), with strain \( \sigma \), the relationship

\[ \gamma + \frac{\eta}{2} \dot{\gamma} - 2\mu \sigma - 2\eta \dot{\sigma} = 0 \]

or,\(^\#\)

\[ \gamma = 2 \frac{\mu + \eta \rho}{1 + \frac{\eta}{2} \rho} \sigma \]

where \( \rho = \frac{\partial}{\partial t} \), and the constants \( a, b, \) and \( c \) are written \( \frac{\mu}{\eta}, -2\mu, \) and \( -2\eta \).

Since a distortion \( E^0 \) is equivalent to the superposition of less than six shears, we have also the tensor equation

\[ P^0 = 2 \frac{\mu + \eta \rho}{1 + \frac{\eta}{2} \rho} E^0 \]

\(^\#\) A rigorous treatment of this and other operators is given, e.g., by H. Jeffreys in the Cambridge Tract on Operational Calculus in Mathematical Physics.
For dilations, our hypothesis gives
\[ p_e + \frac{\eta'}{\nu'} p_e - 3k e_e - 3\eta^e e_e = 0 \]
\[ p_e = 3 \frac{k + \eta^e p}{1 + \eta^e_p} e_e \]
so that
\[ M = \frac{\mu + \eta^e p}{1 + \eta^e_p} \]
\[ K = \frac{\mu + \eta^e p}{1 + \eta^e_p} \nu' \]
For \( \eta, \eta' = 0 \) and \( \frac{\eta}{\nu}, \frac{\eta'}{\nu'} = 0 \), these reduce to
\[ M = \mu \]
\[ K = \kappa \]
the condition of perfect elasticity.

Thus, in the most general case, six constants are required to specify the mechanical properties of the material. In addition to the static moduli \( \mu \) and \( \kappa \), we have also the instantaneous moduli \( \nu \) and \( \nu' \), and the viscosities \( \eta \) and \( \eta' \), for shear and dilation respectively. \( \eta' \) has the dimension of time and may be called the relaxation time.

The assumption has been made\(^{(15)}\) that all solids and liquids are perfectly elastic for bulk compressions. This is justifiable, as pointed out above, and is adopted here although it is not essential to the theory. Further experimental evidence might lead us to retain \( K \) in its most general form. Here we take \( K = k \).

We have now as fundamental equations:

\[ p^0 = 2 \frac{\mu + \eta^e_p}{1 + \eta^e_p} E^0 \]  -- -- -- -- -- -- (2)
\[ p_e = 3 \frac{k + \eta^e p}{1 + \eta^e_p} e_e \]  -- -- -- -- -- -- (3)
These include as special cases:

1) $\mu = \eta = \frac{\eta}{\nu} = 0$  \hspace{1cm} $P^0 = 0$  \hspace{1cm} Perfect fluids
2) $\mu = 0$, $\nu = \infty$  \hspace{1cm} $P^0 = 2\eta E^0$  \hspace{1cm} Viscous fluids
3) $\eta = \frac{\eta}{\nu} = 0$  \hspace{1cm} $P^0 = 2\mu E^0$  \hspace{1cm} Perfect elasticity
4) $\mu = 0$  \hspace{1cm} $P^0 + \frac{\eta}{\nu} \dot{P}^0 = 2\eta E^0$  \hspace{1cm} Elastico-viscosity
5) $\nu = \infty$  \hspace{1cm} $P^0 = 2\mu E^0 + 2\eta E^0$  \hspace{1cm} Visco-elasticity

In the generalization here given, it is seen how the various "ideal" materials blend into one another with the variation of three physical constants.

Equation (2) shows immediately that our new ideal material has this property: for a suddenly applied $P^0$, $p = \infty$, and $P^0 = 2\gamma E^0$, while for a slowly applied load, $p = 0$, and $P^0 = 2\mu E^0$.

**APPLICATIONS**

As an illustration of the behavior of material under the modified equations (2) and (3), consider a rod of uniform cross section $A$ placed in tension by a load $W$. If $Y$ is Young's modulus, the extension $e$ as given by Hooke's Law would be

$$e = \frac{1}{Y} \frac{W}{A}$$

or, since

$$\frac{1}{Y} = \frac{1}{9\kappa} + \frac{1}{3\mu}$$

$$e = \left(\frac{1}{9\kappa} + \frac{1}{3\mu}\right) \frac{W}{A}$$
Replacing $\mu$ by $M = \frac{\mu + \eta \beta}{1 + \eta \beta} = \frac{\nu}{\nu + \frac{\mu}{2}}$

$$e = \frac{1}{9 \nu} \frac{W}{A} + \frac{1}{3 \nu} \frac{p + \frac{\mu}{2}}{p + \frac{\mu}{2}} \frac{W}{A}$$

$$= \frac{1}{9 \nu} \frac{W}{A} + \frac{1}{3 \mu} \frac{W}{A} \left[1 + \left(\frac{\mu}{2} - 1\right)e^{-\frac{\nu}{2} t}\right]$$

Thus, for $t = 0$,

$$e = \frac{1}{9 \nu} \frac{W}{A} + \frac{1}{3 \mu} \frac{W}{A} \frac{\mu}{\nu}$$

$$= \left(\frac{1}{9 \nu} + \frac{1}{3 \mu}\right)\frac{W}{A}$$

and for $t \gg 0$,

$$e = \left(\frac{1}{9 \nu} + \frac{1}{3 \mu}\right)\frac{W}{A}$$

The material receives an initial strain as if its modulus of rigidity were $\nu$ (the instantaneous rigidity), and this is followed by afterflow. The strain approaches an equilibrium value which is the same as that given by the hypothesis of perfect elasticity. Thus for static (i.e. very slow) tests the material behaves perfectly elastically, but in dynamic tests afterflow appears. It must be pointed out that many solids show a small amount of hysteresis even in a static test. This has been called "plastic hysteresis". It is not a property of our ideal material inasmuch as we have excluded permanent set.

However, the material shows elastic hysteresis. Consider the behavior of the rod when the load $W$ is removed at time $t_1$. We superimpose on the strain already found the strain due to a load $-W$ applied at time $t_1$. 
We had
\[ e = \frac{1}{2\pi} \frac{W}{A} + \frac{1}{3\mu} \frac{W}{A} \left[ 1 + \left( \frac{\mu}{\lambda} - 1 \right) e^{-\frac{\mu}{\lambda} t} \right] \]

The strain due to \(-W\) is
\[ e' = -\frac{1}{2\pi} \frac{W}{A} - \frac{1}{3\mu} \frac{W}{A} \left[ 1 + \left( \frac{\mu}{\lambda} - 1 \right) e^{-\frac{\mu}{\lambda} (t-t_0)} \right] \]

Then
\[ e'' = e + e' = \frac{1}{3\mu} \frac{W}{A} \left( \frac{\mu}{\lambda} - 1 \right) \left[ e^{-\frac{\mu}{\lambda} t} - e^{-\frac{\mu}{\lambda} (t-t_0)} \right] \]
\[ = \frac{1}{3\mu} \frac{W}{A} \left( \frac{\mu}{\lambda} - 1 \right) e^{-\frac{\mu}{\lambda} t} (1 - e^{-\frac{\mu}{\lambda} t}) \]

At \( t = t_1 \)
\[ e'' = \frac{1}{3\mu} \frac{W}{A} (1 - \frac{\mu}{\lambda})(1 - e^{-\frac{\mu}{\lambda} t_1}) \]

and for \( t = \infty \)
\[ e'' = 0 \]

In this way a loop is described in the stress-strain plane, that is, we have elastic hysteresis. The hysteresis loop is considered more extensively later.

**TORSIONAL VIBRATIONS**

As far as we know it has not been possible on the basis of any theory hitherto given to account even quantitatively for the variation of logarithmic decrement \( \delta \) with the period \( T \) of a torsional pendulum. According to the visco-elastic theory \( \delta \) should vary inversely with \( T \) for any one material. According to Boltzmann's theory \( \delta \) should be constant. However, Voigt's experiments on several metals showed that, for some, \( \delta \) decreased when \( T \) increased; for some, \( \delta \)
was about constant; while for others, \( \delta \) increased with \( T \), a condition not given by any of the theories.

In the present theory it will appear that each material has a characteristic period \( T_0 = \frac{2\pi \rho}{\sqrt{\mu \nu}} \).

For \( T \) approximately equal to \( T_0 \), the logarithmic decrement is about constant. For \( T > T_0 \), \( \delta \) decreases when \( T \) increases; and for \( T < T_0 \), \( \delta \) increases with \( T \).

Voigt's experiments were all performed within the same small range of periods so that each metal behaved in one of these three ways depending on how its \( T_0 \) was related to the test periods.

The differential equation for the oscillation of an undamped torsional pendulum is

\[
L \ddot{\theta} + \mu \theta = 0
\]

where \( L \) depends on the dimensions of the wire and on the inertia of the disc. \( \theta \) is the angular displacement. The solution of this equation is

\[
\theta = A e^{i \sqrt{\frac{\mu}{L}} t}
\]

so that

\[
T' = 2\pi \sqrt{\frac{L}{\mu}}
\]

where \( T' \) is the period of the undamped vibrations.

Replace \( \mu \) in (4) by \( M \).

\[
L \rho \ddot{\theta} + \frac{\mu + \nu \rho}{1 + \frac{\nu}{\rho}} \theta = 0
\]
Let
\[ \theta = A e^{(-\beta + i\omega)t} \]

\( \beta \) is the damping constant, and \( \omega \) the angular frequency. Then
\[ p = -\beta + i\omega \]

and we have from (6)
\[ L \frac{n}{v} p^3 + L p^2 + \eta p + \mu = 0 \]

Substituting for \( p \), and equating the real and imaginary parts to zero,
\[ -L \frac{n}{v} \beta^3 + L \beta^2 + (3L \frac{n}{v} \omega^2 - \eta) \beta + \mu - L \omega^2 = 0 \quad \cdots \cdots \quad (7) \]
\[ 3L \frac{n}{v} \omega \beta^2 - 2L \omega \beta - L \frac{n}{v} \omega^3 + \eta \omega = 0 \quad \cdots \cdots \quad (8) \]

Since, in (8) \( \omega \neq 0 \), we have
\[ 3L \frac{n}{v} \beta^2 - 2L \beta - L \frac{n}{v} \omega^2 + \eta = 0 \quad \quad \cdots \cdots \quad (9) \]
\[ \omega^2 = 3\beta^2 - 2 \frac{\nu}{\eta} \beta + \frac{\nu}{L} \quad \quad \cdots \cdots \quad (10) \]

Substituting this value of \( \omega^2 \) in (7) we get
\[ 8\beta^3 - 8 \frac{\nu}{\eta} \beta^2 + 2(\frac{\nu}{L} + \frac{\nu^2}{L^2}) \beta - \frac{\nu}{L} (\nu - \mu) = 0 \]

For hard solids, the damping constant \( \beta \) is very small while \( \nu/\eta \) is large; thus the term in \( \beta^3 \) can be neglected and the remaining quadratic solved for \( \beta \).
\[ \beta = \frac{2(\frac{\nu}{L} + \frac{\nu^2}{L^2})}{16 \frac{\nu}{L}} \left( 1 - \sqrt{1 - \frac{32 \frac{\nu^2}{L^2} (\nu - \mu)}{4 (\frac{\nu}{L} + \frac{\nu^2}{L^2})^2}} \right) \]
The second term in the root is small so that

approximately

\[
\beta = \frac{\frac{v}{l} + \frac{v^2}{l^2}}{8 \frac{v}{l}} \left(1 - \left[1 - \frac{1}{2} \frac{8 \frac{v^2}{l^2} (v - \mu)}{(\frac{v}{l} + \frac{v^2}{l^2})^2} \right]ight)
\]

\[
= \frac{1}{2} \frac{\eta (v - \mu)}{\eta^2 + \mu v} \quad \quad \quad \quad \quad (11)
\]

For small damping the period of the oscillation is very nearly the period of the undamped pendulum. This is easily seen by solving (10) for \( \omega \). The period of the undamped pendulum results if \( \eta^2 \) is neglected when added to \( \omega^2 \). Using (5) we take

\[
\omega = \left(\frac{T}{2\pi}\right)^\mu
\]

so that

\[
\beta = \frac{1}{2} \frac{\eta (v - \mu)}{\eta^2 + \mu v (\frac{T}{2\pi})^2}
\]

The logarithmic decrement is given by

\[
\delta = \beta T = \frac{T}{2} \frac{\eta (v - \mu)}{\eta^2 + \mu v (\frac{T}{2\pi})^2} = \frac{2 \pi^2 T \eta}{\mu v} \frac{(v - \mu)}{(\frac{T}{2\pi})^2 + T^2}
\]

or, putting

\[
\delta = \frac{2 \pi^2 T \eta}{\mu v} \left(\frac{T}{2\pi}\right)^\mu \quad \quad \quad \quad \quad \quad (12)
\]

\[
\delta = \frac{T T_0}{2 \eta} \frac{(v - \mu)}{T^2 + T_0^2} = \frac{(v - \mu) T_0}{2 \eta} \frac{T}{T^2 + T_0^2} \quad \quad \quad \quad \quad (13)
\]

This function has a maximum at \( T = T_0 \), since

\[
\frac{d \delta}{dT} = \frac{(v - \mu) T_0}{2 \eta} \frac{T_0 - T^2}{(T^2 + T_0^2)^2}
\]

becomes zero when \( T = T_0 \), where \( \delta_0 \)

\[
\delta = \delta_0 = \frac{\pi}{2} \frac{v - \mu}{\sqrt{v \mu}} \quad \quad \quad \quad \quad (14)
\]
Thus, if the coefficient of rigidity $\mu$ is known for a material, and $T_0$ is determined experimentally, $\delta_0$ gives the value of $\nu$, and $T_0$ gives $\zeta$.

In Fig.1 equation (13) is plotted for three different sets of values of $\mu$, $\nu$, and $\zeta$. If $R$ is a small range of period under investigation, it is seen that materials such as (1) would show $\delta$ increasing with $T$, those such as (2) $\delta$ about constant, and those such as (3) $\delta$ decreasing as $T$ increases.

In Fig.2 the results of Voigt\(^{(9)}\) and of Subrahmaniam and Gunnaiya\(^{(16)}\) for steel wires are shown graphically and a theoretical curve is drawn (equ. 13) for the particular values of the constants $\mu = 8 \times 10^6$ dynes/sq.cm, $\nu = 8.019 \times 10^6$ dynes/sq.cm, and $\zeta = 1.8 \times 10^6$ dyne-sec./sq.cm. An exact fit would hardly be expected since different steel wires were used, but some idea is obtained of the relative values of the constants for steel.

Since Voigt found an almost constant logarithmic decrement for cadmium, the periods he used must correspond about to the critical period for cadmium. Taking from Voigt’s data

$$\delta_0 = .0311 \quad \text{and} \quad T_0 = .715$$

and using the rigidity $\mu = 2.4 \times 10^6$ dynes/sq.cm given in the Smithsonian Tables, we get from (12) and (14)

$$\nu = 2.45 \times 10^6 \text{ dynes/sq.cm.}$$

$$\zeta = 2.76 \times 10^6 \text{ dyne-sec./sq.cm.}$$

$$\frac{\zeta}{\nu} = .113 \text{ sec.}$$
MEMORY

A frequently observed phenomenon connected with afterflow has been called memory. If, for example, a wire is given a positive twist, then a negative twist, and is finally released, the displacement does not always return to zero with constant sign. It may show "memory" of its past history. In the example before us the displacement may return to a positive value and then slowly approach zero. According to our theory, this occurs as follows:

Let $T = \text{the applied torque}$
$
\theta = \text{the twist}
$
$l = \text{length of wire}
$
$r = \text{radius of wire}

By Hooke's Law:

\[
\theta = \frac{T}{\mu} \frac{2l}{\pi lr^2}
\]

Replacing $\mu$ by $M$ we get

\[
\theta = \frac{T}{M} \frac{2l}{\pi lr^2} \left[ 1 - \left(1 - \frac{M}{\mu} \right) e^{-\frac{M}{\mu} t} \right]
\]

and letting $k = \frac{2l}{\mu \pi r^2}, \quad c = 1 - \frac{M}{\mu}, \quad \alpha = \frac{M}{\mu}$

\[
\theta = k \left( 1 - c e^{-\alpha t} \right)
\]

We assume that for small strains, the strains due to separate torques can be superimposed by addition.

Let torque $T$ be applied at time $t = 0$

" " $-2T$ " " $t = t_1$

" " $T$ " " $t = t_2$

Thus after $t_2$ there is no applied torque.
\[ \theta = Th(1 - ce^{-\alpha t}) - 2Th(1 - ce^{-\alpha(t-t_1)}) + Th(1 - ce^{-\alpha(t-t_2)}) \]

\[ = Thc\left[-e^{-\alpha t} + 2e^{-\alpha(t-t_1)} - e^{-\alpha(t-t_2)}\right] \]

\[ = Thc e^{-\alpha t}[-1 + 2e^{\alpha t_1} - e^{\alpha t_2}] \]

So, if \( 2e^{\alpha t_1} \approx 1 + e^{\alpha t_2} \) (or, for small \( t_1 \) and \( t_2 \), if \( t_2 < 2t_1 \)), then \( \theta \) is positive after \( t_2 \) and there is a memory effect. If, however, \( t_2 \) is too large compared with \( t_1 \), the material "forgets" its earlier experience, in the sense that \( \theta \) remains negative as it approaches zero.

\[ \begin{align*}
\theta & \quad t \quad t_1 \\
\text{With memory} & \quad \text{Without memory}
\end{align*} \]

**Fig. 3**

**Continuously varying torque.** If the torque varies continuously but slowly enough for the neglect of inertia effects, we have the problem of superimposing successive infinitesimal strains.

For \( n \) finite torques \( T_i \) applied at times \( t_i \) we have as above

\[ \theta = \sum_{i=1}^{n} T_i h[1 - ce^{-\alpha(t-t_i)}] \]

Letting \( n \) increase without limit,

\[ \theta = h \int_{t_i}^{t} d\tau [1 - ce^{-\alpha(t-\tau)}] \]
If $T$ has a continuous derivative, we can write

$$\theta = h \int_{-\infty}^{t} T'(\tau) [1 - ce^{-\alpha(t-\tau)}] d\tau$$

(16)

Suppose, for example, that an alternating torque

$$T = T_0 \sin \omega \tau$$

is applied at time $t = 0$.

$$T'(\tau) = \omega T_0 \cos \omega \tau$$

$$\theta = h\omega T_0 \int_{0}^{t} \cos \omega \tau [1 - ce^{-\alpha(t-\tau)}] d\tau$$

$$= hT_0 \sin \omega t - hT_0 \omega ce^{-\alpha t} \int_{0}^{t} \cos \omega \tau e^{\alpha \tau} d\tau \quad \ldots \quad (17)$$

$$= hT_0 \left[ \sin \omega t - \omega c \left( \frac{1}{\alpha^2 + \omega^2} \cos \omega t + \frac{\omega}{\alpha^2 + \omega^2} \sin \omega t - \frac{\alpha}{\alpha^2 + \omega^2} e^{-\alpha t} \right) \right]$$

After a long time has elapsed, the last term can be neglected, and we have then

$$\theta = hT_0 \left[ (1 - \frac{\omega^2 c}{\alpha^2 + \omega^2}) \sin \omega t - \frac{\omega \alpha c}{\alpha^2 + \omega^2} \cos \omega t \right]$$

$$= AhT_0 \sin (\omega t - \varepsilon)$$

(18)

where

$$A = \frac{\sqrt{(\alpha^2 + \omega^2 - c\omega^2)^2 + (c\omega \alpha)^2}}{\alpha^2 + \omega^2}$$

and

$$\varepsilon = \tan^{-1} \frac{c\omega \alpha}{\alpha^2 + \omega^2 - c\omega^2}$$

or, for small $c$,

$$A = 1 - \frac{c\omega^2}{\alpha^2 + \omega^2}$$

(19)

$$\varepsilon = \tan^{-1} \frac{c\omega \alpha}{\alpha^2 + \omega^2}$$

(20)
Now let the torque be removed by applying at time \( t = t_1 \) a torque \( T_1 = -T_0 \sin \omega \tau \). Write this
\[
T_1 = T_{11} + T_{12} = -(T_0 \sin \omega t) - (T_0 \sin \omega \tau - T_0 \sin \omega t,)
\]

We had (17)
\[
\theta = h T_0 \sin \omega t - h T_0 \omega c e^{-\alpha t} \int_0^t \cos \omega \tau e^{\alpha \tau} d \tau
\]

The strain due to \( T_{11} \) is by (15)
\[
\theta_{11} = -h T_0 \sin \omega t \left[ 1 - c e^{-\alpha (t-t_1)} \right]
\]

and that due to \( T_{12} \) is by (16)
\[
\theta_{12} = h T_0 \left[ -\sin \omega t + \sin \omega \tau + \omega c e^{-\alpha t} \int_{t_1}^t \cos \omega \tau e^{\alpha \tau} d \tau \right]
\]

The total strain is
\[
\sum \theta = -h T_0 \omega c e^{-\alpha t} \int_0^t \cos \omega \tau e^{\alpha \tau} d \tau + h T_0 c (\sin \omega t) e^{-\alpha (t-t_1)}
\]

But
\[
\int_0^t \cos \omega \tau e^{\alpha \tau} d \tau = e^{\alpha t} \left[ \frac{\alpha \cos \omega t_1 + \omega \sin \omega t_1}{\alpha^2 + \omega^2} \right] - \frac{\alpha}{\alpha^2 + \omega^2}
\]

Neglecting the last term for large \( t_1 \), we have
\[
\sum \theta = \frac{\omega T_0}{\alpha^2 + \omega^2} \left( \alpha \sin \omega t_1, -\omega \cos \omega t_1 \right) e^{-\alpha (t-t_1)}
\]
\[
= \frac{\alpha c T_0}{\sqrt{\alpha^2 + \omega^2}} e^{-\alpha (t-t_1)} \sin (\omega t, -5)
\]

where \( 5 = \tan^{-1} \frac{\omega}{\alpha} \)

Thus \( 5 > \epsilon \) of equ. (20)
This means that there will be memory (in the same sense as before) only if the torque is released at a time $t_1$ such that
\[ \pi n + \varepsilon < \omega t_1 < \pi n + 5 \]
\[ n = \text{integer} \]
(see Fig. 4 in appendix)

**Hysteresis loss per cycle.** It was found (18) that the twist lagged behind the torque by a small amount. Thus each cycle will be represented by a loop in the torque-twist diagram. We have
\[ T = T_0 \sin \omega t \]
\[ \theta = \theta_0 \sin (\omega t - \varepsilon) \]

Where $\theta_0 = A h \theta_0$.

The energy lost per cycle is given by the area of the loop.
\[ W = \int_c Td\theta = \theta_0 T_0 \int_0^{2\pi} \sin \omega t \cos (\omega t - \varepsilon) \, d(\omega t) \]
\[ = \pi T_0 \theta_0 \sin \varepsilon \]

Substituting the value of $\theta_0$ and approximating $\sin \varepsilon$ by $\tan \varepsilon$ we have
\[ W = \pi A h T_0^2 \tan \varepsilon \]
\[ = \frac{\pi h T_0^2 (\alpha^2 + \omega^2 - c^2)}{\alpha} \frac{c \omega}{(\alpha^2 + \omega^2)^2} = \pi h T_0^2 \frac{c \omega}{\alpha} \text{ for long periods.} \]

If $P$ is the period,
\[ \omega = \frac{2\pi}{P} \]
\[ W = \frac{2\pi^2 hc T_0^2}{\rho \alpha} = \frac{2\pi^2 T_0^2}{P} \frac{\eta (\nu - \mu)}{\nu \mu} \text{ for long periods.} \]
The energy loss per cycle varies inversely as the period and so the energy loss per second varies as the square of the period.

**ARBITRARY DECAY FUNCTION**

In what has preceded $e^{\alpha t}$ might be called the decay function. Suppose that some other decay function, say \( \frac{1}{1+\beta t} \) is found to be in better agreement with the experimental facts. We can show that $e^{-\alpha t}$ may still be the true decay function microscopically, if $\alpha$ varies from point to point in the material, or from one elementary region to another. It is then of interest to find, for a given empirical decay function, what the $\alpha$ distribution is.

We had in (15)

$$\theta = Th \left( 1 - C e^{-\alpha t} \right)$$

But, if $f(t)$ is given empirically,

$$\theta = Th \left( 1 - C f(t) \right) \quad (21)$$

Let $q_i$ be the fraction of the number of particles which has $\alpha = \alpha_i$ \quad ($i = 1, 2, \ldots \ldots \ldots m$). Then

$$\theta = Th \left( 1 - C \sum_{i=1}^{m} q_i e^{-\alpha_i t} \right)$$

Letting $m$ increase without limit, let $q(\alpha) d\alpha$ represent the fraction of the number of particles which has values of $\alpha$ between $\alpha$ and $\alpha + d\alpha$. 
Then
\[ \Theta = \mathcal{N} \left( 1 - C \int_0^\infty Y(x) e^{-\alpha t} \, dx \right) \]  

and we have from (21) and (22)
\[ f(t) = \int_0^\infty Y(x) e^{-\alpha t} \, dx \]

to determine \( Y(x) \).

The \( r(t) \)'s in which we are interested can be developed into series in negative powers of \( t \). Let
\[ f(t) = F \left( \frac{1}{t}, \frac{1}{t^2}, \ldots, \frac{1}{t^n}, \ldots \right) \]

within the region of convergence.

By definition
\[ \Gamma(n) = \int_0^\infty x^{n-1} e^{-x} \, dx \]

Let \( x = \alpha t \)
\[ \Gamma(n) = \int_0^\infty \alpha^{n-1} t^n e^{-\alpha t} \, d\alpha \]
\[ \frac{1}{t^n} = \int_0^\infty \frac{\alpha^{n-1}}{\Gamma(n)} e^{-\alpha t} \, d\alpha \]

If the \( n \) are integers, \( \Gamma(n) = \frac{n-1}{n-1} \), and
\[ \frac{1}{t^n} = \int_0^\infty \frac{\alpha^{n-1}}{\Gamma(n)} e^{-\alpha t} \, d\alpha \]
\[ f(t) = F \left( \frac{1}{t}, \frac{1}{t^2}, \ldots, \frac{1}{t^n}, \ldots \right) = \int_0^\infty F(1, \ldots, \frac{\alpha^{n-1}}{\Gamma(n-1)}, \ldots) e^{-\alpha t} \, d\alpha \]
\[ Y(x) = F(1, \ldots, \frac{\alpha^{n-1}}{\Gamma(n-1)}, \ldots) \]  

If \( n \) is not an integer the gamma function is retained. As an application of equation (23), consider the empirical decay function \( r(t) = \frac{1}{1 + \beta t} \)
\[
\frac{1}{1 + \beta t} = \frac{1}{\beta t} - \left(\frac{1}{\beta t}\right)^2 + \cdots + (-1)^{n-1}\left(\frac{1}{\beta t}\right)^n + \cdots = F\left(\frac{1}{t}, \frac{1}{\beta t}, \cdots\right)
\]

Therefore,
\[
\varrho (\alpha) = \frac{1}{\beta} \cdot 1 - \frac{1}{\beta^2} \frac{\alpha}{t} + \frac{1}{\beta^3} \frac{\alpha^2}{t^2} + \cdots + \frac{1}{\beta^n} (-1)^n \frac{\alpha^n}{t^n} + \cdots
\]
\[
= \frac{1}{\beta} \left[ 1 - \frac{\alpha}{\beta} + \frac{(\alpha/\beta)^2}{t^2} + \cdots + \frac{(-\alpha/\beta)^n}{t^n} + \cdots \right]
\]
\[
= \frac{1}{\beta} e^{-\frac{\alpha}{\beta}}
\]

Or, since \( \alpha = \frac{\beta \ell}{t} \)
\[
\varrho \left( \frac{\beta \ell}{t} \right) = \frac{1}{\beta} e^{-\frac{\beta n}{t}}
\]

Fig.5

With this distribution of viscosities we will have a macroscopic decay function \( \frac{1}{1 + \beta t} \).

CONCLUSION

When more is known about the nature of the cohesive forces in solids, it should be possible to work this problem in the opposite direction, and, from the distribution of the viscosity and other coefficients, to deduce the general equations for imperfect elasticity. Here, however, we find that the equations
lead to descriptions, if not explanations, of many of the departures of solids from perfectly elastic behavior.

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TEMPERATURE SHIFT OF THE TRANSMISSION BAND OF SILVER

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THE TEMPERATURE SHIFT OF THE TRANSMISSION BAND OF SILVER

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Abstract

It is shown that by Kronig’s quantum theory of dispersion in metals one can account for the shift of the frequency at which maximum transmission is found for silver when the temperature is varied. The calculated rate of shift is in fair agreement with experiment.

It has been known for some time that, although for wave-lengths up to 5μ the optical constants of metals show little or no temperature dependence, there is a marked temperature effect in the case of silver in the region of the minimum of reflecting power, around 3160Å. Ebeling\(^1\) first noted that raising the temperature from 15°C to 200°C produces a displacement of the reflection minimum toward the red of about 100Å and an increase of reflecting power at the minimum from 4.2 to 20 or 30 percent. The reflection measurements of de Selincourt\(^2\) at temperatures from −183 to 156°C showed that a similar effect extended throughout this range. It is to be expected that with the minimum of reflection would be associated one of absorption. Minor’s experiments on silver at ordinary temperatures\(^3\) showed minima of absorption index, reflecting power, extinction coefficient, and absorption coefficient at 3140, 3160, 3160, and 3220Å respectively. Lord Rayleigh\(^4\) first investigated the effect of temperature on the absorption minimum (transmission maximum) by passing light through silver foil at temperatures from −180 to 254°C. The transmission maximum behaved much in the same manner as the minimum in the earlier reflection experiments.

Quite recently, McLennan, Smith, and Wilhelm\(^5\) with greatly improved methods made measurements on the transmission band of silver at temperatures from 20°C down to −269°C using liquid air, hydrogen, and helium and found the transmission maximum to vary nearly linearly with the temperature over this large range. Before the appearance of the last named paper, the author repeated Lord Rayleigh’s experiments with modifications in order to determine the nature of the reported broadening of the transmission band and change in transmission intensity and found that these agreed qualitatively with the reflection experiments of de Selincourt. No quantitative explanation of the shift has been given but one should now be possible in view of

\(^1\) Ebeling, Zeits. f. Physik 32, 489 (1925).
\(^3\) Minor, Ann. d. Physik 10, 581 (1903).
\(^5\) McLennan, Smith, and Wilhelm, Phil. Mag. 12, 833 (1931).
the work on the quantum theory of dispersion in metals by Kronig. Extending Kronig’s theory, Schubin has shown that the quantum theory indicates the existence of an absorption minimum very near the second line of the resonance doublet of the corresponding metal vapor (for silver this line is found at 3280Å). Attention had been called to this coincidence by Ebeling in the paper cited above. Schubin also shows that general qualitative considerations lead one to expect a shift of absorption minimum toward the red with increasing temperature.

In Fig. 1 are shown the experimental values of the frequency at which the absorption minimum occurs for different temperatures as found by various investigators. It is seen that the values found by McLennan and by de Selincourt fall on straight lines. In both of these cases careful photometric measurements were made. Of course, the two lines are quite distinct since one represents transmission maxima and the other minima of reflecting power. There is also a difference in the physical condition of the silver used. Three of Lord Rayleigh’s values are on a straight line on which Minor’s value at room temperature also lies.

The quantum theory of dispersion in metals as given by Kronig is based on Bloch’s theory of metallic conduction. The conduction electrons play the part both of free and of bound electrons. These electrons are distributed among their various quantum states according to the Fermi-Dirac statistics. Under the influence of an applied electric field and as a result of collisions with the ions of the crystal lattice, which are in temperature vibration, the conduction electrons make transitions to other states. When the applied electric field is that due to incident light of short wave-length λ, (i.e., less than about 5000Å) it is shown that it is possible to neglect the collisions with the lattice.

In Kronig’s ideal cubical crystal lattice the quantum states of the conduction electrons are given by three quantities $\xi_1, \xi_2, \xi_3$. Possible transitions are those to states $\xi_1', \xi_2', \xi_3'$ where

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* Schubin, Zeits. f. Physik 73, 273 (1931).
\[ \xi' = \xi_i + 2\pi n_i \quad i = 1, 2, 3 \]

and \( n_i \) is any positive or negative integer. Light of frequency \( \nu \) will be absorbed by such electrons as can make such transitions under the condition

\[ E(\xi_i + 2\pi n_i) = E(\xi_i) + h\nu. \]

According to Kronig, absorption is found under these conditions for \( \nu = 0 \) (which corresponds to absorption by free electrons under the classical theory) and also for a band \( \nu_1 < \nu < \nu_2 \) (corresponding to bound electrons) where \( \nu_1 \) and \( \nu_2 \) are of the order \( 10^{18} \).

Now, experimentally just such an absorption band is found for silver from \( \nu_1 = 0.925 \times 10^{18} \) to \( \nu_2 = 1.56 \times 10^{18} \). This is best seen by comparing the conductivity calculated from Minor's experimental values of refractive index (\( n \)) and extinction coefficient (\( K \)) by Drude's expression

\[ 2\sigma/\nu = 2nK \]

where \( \sigma \) is the conductivity, with the conductivity calculated from Kronig's formula

\[ \sigma = \frac{\pi}{2} \frac{\Omega}{\nu} (\nu_2 - \nu)(\nu - \nu_1) \quad \nu_1 < \nu < \nu_2 \]

where \( \Omega \) is a constant for silver. This comparison is made in Fig. 2 where \( \Omega \) is taken equal to 18. It is seen that \( \nu_1 \) must have very nearly the value assigned above.

But the lower frequency limit of the absorption band will also be very nearly the upper frequency limit of the transmission band. What we propose to show is that this limit, \( \nu_1 \), depends on temperature and shifts linearly toward the red with increasing temperature. If the transmission band does not widen appreciably (and the photometric measurements of de Selincourt and of McLennan do not bear out the widening reported by others for which Schubin attempts an account), the rate of shift of transmission maximum with temperature will be very nearly that of \( \nu_1 \).
Kronig finds, as a theoretical value for \( \nu_1 \),

\[
\nu_1 = \frac{4\pi \omega}{h}(\pi - \rho_0)
\]

where

\( \omega = \beta \left( \frac{h^3}{8\pi^2 ma^2} \right) \)

\( \beta = \) binding constant < 1

\( \rho_0 = (6\pi^2 K)^{1/3} \)

\( 2K = \) number of conduction electrons per cell

\( a = \) the lattice constant.

Thus

\[
\nu_1 = \frac{\beta h(\pi - \rho_0)}{2\pi ma^2}
\]

where \( a \) alone is supposed to vary with temperature according to this theory.

Putting \( a = a_0(1 + \alpha t) \) where \( \alpha \) is the coefficient of linear expansion for silver and \( t \) is the temperature on the Centigrade scale and putting

\[
\nu_0 = \frac{\beta h(\pi - \rho_0)}{2\pi ma_0^2}
\]

we get

\[
\nu_1 = \frac{\nu_0}{(1 + \alpha t)^2} = \nu_0(1 - 2\alpha t + \cdots)
\]

\[
\frac{d\nu_1}{dt} = -2\alpha \nu_0 = -2 \times 10^{-6} \times 0.925 \times 10^{13}
\]

\[
= -3.5 \times 10^{10} \text{ very nearly.}
\]

Based on this calculation, a theoretical curve is shown in Fig. 1 for comparison with experiment. Its slope is seen to lie between that of McLennan’s curve for transmission maxima and that of de Selincourt’s curve for minima of reflecting power.

In conclusion the author wishes to thank Professor H. A. Wilson for suggestions and criticisms in connection with the above work.