Limitations of the Newtonian time scale in relation to non-equilibrium rheological states and a theory of quasi-properties

BY G. W. S. Blair, D.Sc. AND B. C. Veinoglou, Ph.D.

In collaboration with J. E. Caffyn, B.Sc.

National Institute for Research in Dairying, University of Reading

(Communicated by E. N. da C. Andrade, F.R.S.—Received 30 May 1946)

The behaviour of complex materials under stress is described in terms of entities which are not strictly ‘physical properties’. These so-called ‘quasi-properties’ range from entities hardly distinguishable from dimensionally true physical properties to concepts which are much less clearly defined.

Quasi-properties measure an ordered process towards equilibrium rather than a state of equilibrium. The Newtonian definition for equality of time intervals which leads to the concepts velocity, acceleration, momentum and force having whole-number dimensional exponents, does not apply to ‘quasi-equilibrium states’. In order to keep the Newtonian time scale, fractional differential equations are introduced.

The simplest fractional differential equation relating stress, strain and time integrates to a series equation whose first term is a simple power law (Nutting's equation) already known to describe the behaviour of many complex materials under constant stress. The physical meaning of the fractional differential is considered.

An apparatus is described for loading test-pieces of plastics and the like under tension or compression at constant stress to a preselected strain, and for following the subsequent stress dissipation; and the results of tests on thirty-eight materials are studied statistically.

Introducing a second term from the series equation (and, very rarely, a third term) greatly improves the fit for materials for which Nutting's equation is inadequate and explains hitherto unaccountable anomalies when the Nutting plot is otherwise satisfactory. Constants derived by the equation from constant-stress and constant-stain conditions are compared.

The form of the series equation suggests that the relative importance of the second term may sometimes disclose the presence of undissipated stresses in the materials.

The accuracy of tests on individual test-pieces is high, but, on account of frequent lack of homogeneity in the samples available, the use of the unmodified Nutting equation is often adequate even when the addition of a second term would significantly improve individual curves.

Some alternative treatments are discussed, but, both theoretically and practically, the fractional differential approach is preferred for most of the materials tested.

INTRODUCTION

It has been generally believed since the time of St Augustine (Confessions, Book xi) that, whereas space can be measured directly by the superposition of lengths, the measurement of time is indirect, being made either subjectively (as St Augustine thought, from memory engrams) or objectively, by definition, from some periodic physical process such as the rotation of the earth. St Augustine believed in an absolute time scale independent of the length of the day, and suggested that, even if the sun should be stayed in its course, time might still be measured by the rotation of the potter’s wheel.
In Newtonian physics, times are implicitly defined as of equal length where either light or some body free from extraneous influences traverses equal (i.e. superposable) distances in them. It is assumed that lengths are themselves invariant. Recently, other phenomena have been found to give the same or a simply related time scale; e.g. Dingle (1944) equates the times taken by a specified body to radiate equal amounts of energy.

The rotations of the earth give only approximate agreement with the Newtonian scale and, as Dingle (1942) points out, astronomers prefer to say that the earth is slowing down rather than to question the accuracy of the Newtonian laws.

Bodies are said to move at constant velocity when they move through equal distances in equal times; but, since equal times are already defined as above, this is no more than the definition of an entity, velocity, being the first differential of length with respect to time. Acceleration is defined as the second differential, and the products with mass as momentum and force respectively.

In other words, equality of time units is so defined as to produce these simple whole-number differential concepts and, when a body does not, in fact, travel at constant rectilinear velocity, i.e. changes its momentum, force, which was originally a psycho-physical concept, is defined as the rate of change of the momentum. Einstein's relativity, while correcting the Newtonian laws for the special case of high velocities, does not affect the Newtonian time scale itself. Milne's relativity is not so easily dismissed, since no single time scale is regarded as universal and the measure of time takes priority over that of length. For the intervals of time with which we are concerned in the testing of materials, however, Milne's theories do not in any way affect our present line of argument.

From the Newtonian scale are derived all those physical properties which so conveniently give universal and generally integral indices of mass, length and time. But it has long been realized that the Newtonian time scale, in spite of its invaluable contribution to physics, remains an arbitrary scale. As Poincaré (1904) points out: 'La définition implicitement adoptée par les astronomes peut se résumer ainsi: le temps doit être défini de telle façon que les équations de la mécanique soient aussi simples que possible.' The Newtonian scale is the simplest for the study of most of the problems of physics.

For biological phenomena, however, du Noüy (1936) suggests an alternative time scale based on the rate of healing of aseptic wounds and points out that, since the units of this physiological time progressively increase in relation to the Newtonian time units, time will seem to pass more quickly as man ages. This raises an interesting parallel with Milne's theory, according to which the period of a pendulum shortens as we recede in time towards the finite 'beginning' of the atomic time scale.

This linking of physical, physiological and psychological time is especially interesting in view of recent experiments on the quantitative effects of temperature changes on the psychological time scale in man and in bees, ants, etc. (François 1928; Piéron 1945). Hoagland (1935) claims that the relationship between rate of
counting and absolute temperature of a feverish patient is governed by a law of the Arrhenius type.

Bergson (1889) gives a wider definition of the equality of time intervals: "Two intervals of time are equal when two identical bodies, in identical conditions at the beginning of each of these intervals and subject to the same actions and influences of every kind, have traversed the same space at the end of these intervals." It will be noticed that this definition postulates the existence of bodies whose conditions are not permanently affected by the actions and influences during the specified time. According to Bergson's philosophy, living matter could never qualify.

Schrödinger (1944) describes living matter as ""doing something", moving...and so forth, and that for a much longer period than we would expect an inanimate piece of matter to "keep going" under similar circumstances.

But there are many inanimate colloidal systems which behave in this way and hence do not qualify for Bergson's definition. In studying the behaviour of such systems one is at liberty either to use a non-Newtonian time scale, which is inconvenient since each system or group of systems has its own time scale; or, using the Newtonian definition, to make use of differentials of length with respect to time which are of fractional orders.

It will be seen that these alternatives are equivalent, since, as explained above, the definition of velocities and accelerations as first and second derivatives is effected by selecting the Newtonian definition of time equality. It is therefore proposed to keep to the Newtonian definition but to define two new generalized entities—motion, having dimensions $LT^{-\left(1+z\right)}$ and drive, with dimensions $MLT^{-\left(1+z\right)}$ in which $z$ is a fraction.

In the experiments described below, these ideas were developed in relation to two processes: (1) the straining (tension or compression) of cylinders or strips of various colloidal materials—plastics and the like—under constant stress, and (2) the relaxation of stress of the same materials when subsequently held at constant strain. It is clear that the concepts of motion and drive need only be applied to conditions within the materials tested. Thus straining may be done at constant stress and not at constant drive per unit area, since the loads applied to the test-pieces are naturally to be treated in the ordinary Newtonian manner. Within the test-piece, however, the concept of stress must be regarded with caution.

In order to approach this rather difficult problem it is best first briefly to review the real significance of the rheological equations of the simple prototypes, the Hookean solid and the Newtonian liquid. (To avoid confusion, the latter will be referred to as the 'true liquid'.)

The simple Hookean system is generally a crystalline structure with regularly spaced inter-atomic potential troughs. The linear relationship between stress and strain within the small elastic range represents no more than an approximate cancellation of opposite curvatures from the power laws of attraction and repulsion. The most convenient entity by which to express the stress-strain relation is the rigidity modulus $(n)$ $(ML^{-1}T^{-2})$, i.e. the simple ratio of (Newtonian) stress to strain.
Both the states of stress and of strain can be described by tensors made up of the three spatial components of the tractions and displacements (respectively) on each of the three faces of the unit cube. These ninefold tensors are symmetrical, for isotropic systems, so the only concern in this case is with six components. The appropriate vectors can be selected from these tensors to give the usual elastic constants, though in the work described in this paper volume changes can safely be ignored.

At the other end of the scale are the amorphous systems which tend to fluid behaviour. Here the reaction of the material may be regarded as uninfluenced by previous straining, so that the simple relationships between stresses and strain rates are independent of the magnitude of the strain and can thus be derived by a simple differentiation of the elasticity equations, for pure deformations.

The entity by which the stress-strain-time \((S:\sigma:t)\) relation is best described is the ratio of shear stress to rate of shear (viscosity, \(\eta\)). Just as Hooke's law is no more than an approximation, so Grunberg & Nissan (1945) have shown that even for true fluids the viscosity is only constant under limited conditions.

Although there are some important materials which approximate to Hookean or to truly fluid behaviour, these are the exception rather than the rule. Between the crystalline and amorphous materials are many others whose structure is defined to a greater or lesser degree. Many of the so-called 'high-elastic' materials show approximately Hookean behaviour over large ranges of strain. The mechanism of this is quite different from that of ordinary elasticity, but the behaviour of the material may be described in terms of a simple ratio of stress to strain where this is found to be approximately constant. For really large strains, however, the strain axes do not lie at 45° with the direction of shear, so that although shear stress is proportional to shear strain, tensile stress is not proportional to tensile strain. Under these conditions, Mooney (1940) proposes a second modulus (for rubber) which is called the 'Coefficient of Asymmetry.'

Much work has been done on 'high elasticity', but in many otherwise valuable contributions to the subject it has been forgotten that the equations relating the tensile and shear moduli of elasticity are derived only by making certain assumptions such as that strains are small; and that these equations are not valid for large strains even when Poisson's ratio is \(\frac{1}{2}\) (British Rheologists' Club 1946).

There still remain many materials—plastics, bitumens, pastes, unvulcanized rubbers, etc.—for which the inter-atomic potential troughs are very irregularly spaced and for which neither \(S/\sigma\) nor \(S + d\sigma/dt\) is constant. When these materials are strained, they are not, during the straining, in an equilibrium state in the usual sense of the term. By a system in equilibrium is generally meant one in which there are no unbalanced forces—force being here used in accordance with the Newtonian definition, although the term is also used less precisely to imply a balance of gains and losses, as when it is said that living matter maintains a state of equilibrium.

It is often necessary to study rheological behaviour in systems which are not in Newtonian equilibrium, and, as might be expected from what has already been said,
Limitations of the Newtonian time scale

it is found that the combinations of $S$, $\sigma$ and $t$ which are found to be constant do not prove to be physical properties in the sense that they do not have whole-number or even universal exponents of $M$, $L$ and $T$; nor is the process by which they are measured reversible, in that the states through which the material passes are not equilibrium states, so that tests, though reproducible, must be repeated on fresh samples.

As typical of such entities take 'firmness', which, for many complex industrial materials is of great practical importance, can be reproducibly measured on replicate samples and in some cases by quite independent physical methods but which has dimensions which depend on the material or group of materials.

It has often been pointed out that such entities are not to be regarded as 'physical properties' in the strict sense of the term, and it has been suggested that, except for purely ad hoc industrial purposes, treatments involving them should be avoided. The alternatives, however, are far from satisfactory: they are, either to ignore such materials altogether or to presume that they are mechanical mixtures of simple Hookean and true-fluid prototypes or at least that they may be treated as such.

This latter assumption is occasionally justified, but although it is usually possible to reproduce an experimental rheological curve by fitting a number of exponential terms and always possible to invent a new prototype on conveniently exponential lines, neither process does much to further our knowledge of the behaviour of real materials. We propose, then, to accept the entities of the kind described above and to refer to them as 'quasi-properties'. They are a measure rather of a process than of a state, but it is a steady process, and, though not at equilibrium in the Newtonian sense, we feel justified in describing it as a state of 'quasi-equilibrium'. Thus the 'process' of work-hardening of a metal under pressure from a sphere in an indentation hardness test is measured by the Meyer exponent—there are many illustrations.

While it is true that the measurement of a 'property' must not be altered by the process of measurement (the axiom underlying Heisenberg's principle), there would seem to be no objection to measuring the process of change produced by the test provided that the methods are standardized and the results are independent of the observer.

It is clear that quasi-properties will be of different 'orders'. Some will hardly differ from true physical properties in that the exponents of $MLT$, although fractional, will be the same (within the limits of experimental error) for quite large groups of materials, and the quasi-properties themselves will be reproducible by widely different physical methods of measurements. At the other end of the scale will be quasi-properties of a low order which, although reproducible on replicate samples by some standard method, will neither be unique dimensionally for any appreciable range of materials nor equal quantitatively when derived from different types of test. Normally, one is faced with the choice of selecting a large number of true properties or a smaller number of quasi-properties, since it is nearly always possible to express rheological behaviour in terms of true properties provided enough constants are fitted.

It is hoped to show that the latter course is by no means always the best.
G. W. S. Blair, B. C. Veinoglou and J. E. Caffyn

Mathematical treatment of quasi-properties. The principle of intermediacy

In many industries, the firmness of materials is assessed by handling by experts, and psycho-physical studies have been made of the thresholds (i.e. smallest perceptible differences) for various systems (Blair & Coppen 1939, 1940, 1942, 1943). It has also been found that experts handling materials tend to judge firmness not as if the materials were mixtures of elastic and viscous components but rather as though the quality of firmness lay between those of elastic modulus and of viscosity. This principle of ranking complex entities as lying at a certain distance between the prototypes, which we call the ‘Principle of Intermediacy’, common in psychology, is rare in rheology—one of the few existing examples in the latter science is the ‘viscosity index’ of an oil.

It may be objected that any such treatment will preclude any simple relation between the stress and strain tensors and will involve an infinite series of tensors. This is true, but, as has already been pointed out, for the very large strains which have to be considered, and, in view of non-equilibrium conditions, the usual tensor theory would be inapplicable in any case. Whether it will be possible to develop a new tensor theory, relating drive to strains, we do not know.

In the meantime, however, there are several possible applications of the Principle of Intermediacy which will help, bearing in mind that the materials given are in quasi-equilibrium and that there being no Newtonian bodies concerned within the material, the use of the second as the uniform time unit is sure to involve motions which are neither velocities nor accelerations. It is clear that in order to define a quasi-property it is necessary to specify (a) numbers indicating the dimensions of the quasi-property and (b) quantities measuring its intensity.

The first attempt was made by Blair & Coppen (1939) for constant stress conditions and was based on the following argument:

The entity which is found to be constant for true fluids is given by \( \eta = S\sigma^{-1}t \); the entity which is found to be constant for elastic solids is given by \( n = S\sigma^{-1} \). It was therefore proposed that the entity which might well be expected to be constant for complex materials would be

\[
\psi = S\sigma^{-1}t^k,
\]

where, normally, \( 1 > k > 0 \).

This is a special case of a more general equation derived by intermediacy from the imaginary prototypes \( S^0\sigma^{-1}t \) and \( S^0\sigma^{-1}t^0 \), for which we will redefine

\[
\psi = S^\delta\sigma^{-1}t^k.
\]

This equation had been empirically proposed by Nutting (1921a, b) many years earlier.

A more general treatment (Blair 1944) is to consider viscosity as defined by the equation \( \eta = S \frac{d\sigma}{dt} \) and shear modulus as \( n = S \sigma \).
Limitations of the Newtonian time scale

A quasi-property $\chi_1$ is then defined by the Principle of Intermediacy:

$$\chi_1 = S + \sqrt{\frac{d^p\sigma}{dt^p}},$$

(3)

where $\int$ indicates a fractional differentiation. (We propose this convenient symbol since it reminds us of both fractions and $\Gamma$-functions.)

In our psycho-physical work we had already made use of the fractionally differentiated form of equation (2) for constant stress conditions:

$$\int \frac{\partial^p\sigma}{\partial t^p} = \frac{\Gamma(k+1)}{\Gamma(k-\nu+1)} t^k \psi^{-1} S,$$

(4)

Our psycho-physical experiments did not at the time justify us in equating $\nu$ and $k$, but Caffyn & Blair (1945) later showed that if one is prepared to equate $\nu$, $k$ and $\mu$ (in equation (3)), the equations can be combined, since (4) becomes

$$\int \frac{\partial^k\sigma}{\partial t^k} = \Gamma(k+1) \psi^{-1} S,$$

(4a)

from which it follows that

$$\frac{S}{\int \frac{\partial^k\sigma}{\partial t^k}} = \chi_1.$$  

(4b)

Hence

$$\psi = \Gamma(k+1) \psi^{-1} S.$$  

(5)

Since $\Gamma(k+1)$ is a number, in this special case when the Nutting equation holds, $\psi$ and $\chi_1$ measure the intensity of the same quasi-property.

A second equation can also be obtained by fractional differentiation of stress with respect to strain

$$\chi_2 = \int \frac{\partial^p\sigma}{\partial \sigma^p} t,$$

(6)

which, taken together with equation (3), leads to the general equation

$$X = \int \frac{d^p\sigma}{d\left(\frac{d^p\sigma}{dt^p}\right)^p}.$$  

(7)

At present we are not able to make use of equation (7), but Bosworth (1946), quite independently of us, has recently proposed a somewhat similar quasi-property as a criterion of plasticity.

So far, the gamma function has not been much used in rheology. Its relation to power-law treatments is discussed by Gemant (1936, 1944) who has used half-differentials, but, although in his earlier paper he suggests that at least for secondary differential equations [the fractional differential] may really occur in a physically realizable case, in his later paper he expresses the view that it ‘only occurs as a useful mathematical symbol, whereas the underlying elementary process, whatever it may be, will probably contain differential quotients of an integral order’. His
view of the matter is clearly very different from ours. Our own view of the physical meaning of the fractional differential is somewhat as follows:

If cylinders of Californian bitumen (which is very nearly a true fluid) are compressed under constant stress, the amount of deformation produced will depend equally on the stress and on the time of its application. In the case of rubber, which may be regarded as nearly Hookean, the strain will depend on the stress only and not at all on the time. In the case of a certain plastic, strain is found to depend on stress and a fifth as much on the time, i.e. the Nutting equation holds and $k = 0.2$. When this simple equation does not hold for constant-stress experiments, the next simplest hypothesis is that, just as there is a constant property for the bitumen (viscosity) which is given by the ratio of stress to the first differential of strain with respect to time, and a constant ratio (shear modulus) for the rubber given by the stress divided by the zero-differential of strain with respect to time, so the plastic has a quasi-property which is constant and given by the ratio of stress to the 0.2 differential of strain with respect to time. It must be remembered, of course, that if this plastic were the only physical system to be considered, it would be simpler to use a different rule for equating time intervals chosen so that the constant entity would have dimensions with whole-number exponents.

This view has strong experimental support (Blair & Coppen 1943), since it is found that in a statistical study of the compression of a large number of cylinders of a plastic in direct handling comparison with cylinders of rubber or bitumen, $k$, calculated from the relative importance of squeezing time, agrees (within experimental error limits) with $k$ derived from simple compressions on a machine at constant stress. We regard this experimental fact as strong evidence for the validity of our line of approach.

It is known that some materials show a simple power-law relation between stress and strain not involving time (Bach's law), though as Reiner (1933) points out this does not involve us in dimensional difficulties. There are, on the other hand, many systems for which $\beta$ (in equation (2)) is almost unity, though we have shown this to be, in some cases, a chance cancellation of the opposite effects of plasticity and a type of dilatancy (Blair & Veinoglou 1944a).

All these phenomena may not be found to be explainable in terms of the non-Newtonian time scale, but certainly many of the anomalies hitherto unexplained would seem to be clarified by it.

Although we have shown (and indeed so have many other authors) that a very large number of materials obey the simple Nutting law within the limits of experimental error, it is certainly worth while to consider what happens when the situation is not so simple.

Equation (4) can be integrated to give an equation of the type

$$\sigma = S^{\beta}(At^{\beta} + Bt^{\beta-1} + Ct^{\beta-2} \ldots),$$

and it is clear that the Nutting equation is a special case of this when $A \gg B, C, \ldots$, etc., and that the addition of subsequent terms would not only account for differences
Limitations of the Newtonian time scale

between \( k \) and \( \mu \) but might also express the quasi-properties of those of our materials whose agreement with the simple Nutting equation is unsatisfactory. In fact we will show in the experimental part that it is rarely necessary to go beyond the second term.

In the light of this introduction we would then summarize the purposes of our experiments as follows:

We believe that in the case of many complex colloidal materials, such processes as simple straining (under constant stress) and stress dissipation (under constant strain) are not equilibrium processes in the Newtonian sense, and that the time system which would most simply explain their behaviour is not Newtonian time. If Newtonian time is used, the entities which most simply describe their behaviour, which we call 'quasi-properties', will not have whole-number dimensions in \( MLT \), and their fractional dimensions will be more or less dependent on the nature of the material. We would ask ourselves: (1) With what accuracy can these 'quasi-properties' be measured in straining and relaxation and how will their values obtained by these two very different methods agree with one another? (2) Simple tensor theory is not applicable to these conditions, nor has the necessarily more complex non-linear tensor theory been developed; but we have proposed certain fractional differential equations from which the 'quasi-properties' associated with 'firmness' can be defined. How well do these equations fit the experimental data, and how does the fit and the simplicity of treatment compare with the classical methods of deriving true 'physical properties'?

Experimental

Data of a kind suitable to test the theory outlined above are best obtained by holding either stress or strain constant and measuring the rate of change of the remaining variable with time. There are various ways of extending strips or rods in such a way that the load diminishes proportionally to the average change in cross-section of the test-piece (volume changes being ignored), but if a single instrument is to be used both for extensions and compressions, there is everything to be said for the bent lever type of compensator. The limitations and uses of this type of constant-stress device has been worked out fully by Caffyn (1944). Blair & Veinoglou (1944b) have already shown that many complex colloidal systems tested on machines of this type follow the Nutting equation with reasonable accuracy. In preliminary experiments a few materials were tested after rapid straining in relaxation at constant strain as well as by comparatively slow straining at constant stress.

Equation (2) can be partially differentiated for these two processes to give

\[
\frac{\partial S}{\partial t} = \frac{k}{\beta} \frac{S}{t} \quad \text{for relaxation and} \quad \frac{\partial \sigma}{\partial t} = k \frac{\sigma}{t} \quad \text{for straining.}
\]

Thus the slope of the relaxation curve plotting \( \log S/\log t \) is \( k/\beta \), and of the straining curve, plotting \( \log \sigma/\log t \) is \( k \). The constant \( \beta \) can be calculated from the position of a series of curves obtained at different strains and stresses respectively.
G. W. S. Blair, B. C. Veinoglou and J. E. Caffyn

For the few materials tested in this way it was found that the Nutting constants $k, \beta$ and $\psi$ were not only remarkably constant in each experiment but also their values obtained in relaxation and in straining were the same within the limits of experimental error.

But to make a thorough study of these materials an apparatus was made by which a strip or rod ($B$) could first be extended at constant stress, the load being compensated for average change in cross-section by means of a bent lever ($H$) passing from the horizontal downwards towards the vertical; or to compress cylinders ($A$) with correctly increasing load effected by a lever moving from the vertical towards the horizontal ($G$). The movement is checked at a preselected strain by means of collars set the correct distance apart (at $J$). The subsequent stress dissipation is measured by a strong spring ($C$) resting on knife-edges, serving as a base for the compressed cylinder or a ceiling to which the extended strip is attached. The movements of the spring are negligible by comparison with the deformations produced in the test-piece, and the load on the spring is measured by an optical lever ($D$) which magnifies some thousandfold.

![Diagram](http://rspa.royalsocietypublishing.org/)

**Figure 1.** Compensated straining and relaxation apparatus.

The deformations of the stretched strip are measured by a pointer on a scale ($F$), but those of the compressed cylinder are too small for this and are suitably magnified by a second optical lever ($E$) operating from the stirrup which loads the cylinder. The whole instrument, which is shown diagrammatically in figure 1, is operated in a constant-temperature room, some experiments being done at $15^\circ$ C and some at $18^\circ$ C.
Limitations of the Newtonian time scale

With this apparatus, test-pieces could be strained under high or low stress and to large or small preselected strains and the subsequent stress dissipations followed.

Since 'quasi-properties' refer to processes rather than to states, the question arises whether relaxation should be regarded as a separate process from straining, a new time zero being taken; or whether a single time scale should be used throughout the double experiment. For very rapid straining the difference between these two methods is negligible and the best relaxation data were obtained in this way, being compared with data from separate and slower straining experiments. For relaxation following very slow straining it is best to use a single time scale. If a new time zero is taken there will be an appreciable period before the new state of quasi-equilibrium is established and, on account of frictional effects, the instrument is not suited to very slow working. Finally, all our data were calculated by the two-process method, a small number of data from slow straining experiments being discarded.

As already pointed out, altogether apart from our treatment, the classical elasticity equations relating tensile to shear conditions are not valid for the large strains in which we are interested, nor do our materials generally remain isotropic on straining.

It would really have been better if, from tensile stresses and strains, 'tensile' constants had been derived even though shear modulus has more fundamental significance than Young's modulus; but, historically speaking, the constant $\psi$ in the Nutting equation has always been defined as analogous to viscosity and shear modulus rather than to coefficient of viscous traction and Young's modulus. For this reason, $\psi$ is calculated from a shear stress taken as $\frac{1}{3}$ of the tensile (or compressive stress). This is purely a matter of convention and has no theoretical meaning. The factor 3 could be replaced by $2(1 + \Pi)$, but $\Pi$ (Poisson's ratio) differs little from $\frac{1}{2}$ for these materials.

There are various ways of defining large strains. Like Bridgman (1945) we prefer the natural strain, $\log_e (l/l_0)$ and have used this formula throughout. It has the great advantage of being additive.

When possible, straining curves were obtained at some six constant stresses and relaxation curves starting from about four different initial strains for each of these stresses. A complete test on a material thus comprised about twenty-four curves, though in many cases such a complete experiment was not possible owing to shortage of materials.

Curves from part of a typical experiment with a thiokol are given in figure 2. On the left-hand side of the figure, $\log \sigma / \log t$ curves are given for seven different constant stresses; and above is the derived curve plotting $S$ against $\log \sigma_{10}$ where $\sigma_{10}$ is the strain after 10 sec. The slope of this curve, by the method of least squares, gives $\beta$.

The part of the relaxation experiment shown on the right of the figure corresponds to six different constant strains, all the samples being submitted to the same initial stress ($\log \delta_0 = 6.07$). There were other curves at other stresses, but to show more in a single figure would be confusing. Above are plotted the six corresponding points.
logσ/logS_{10}, where S_{10} is the stress after 10 sec. dissipation. The slope of the lower curves gives k/β and that of the upper curve, though of course with many more points, gives β in relaxation. (We are not the first to apply power-laws to relaxation of stress. Prache (1930) gets excellent curves for unvulcanized rubber.)

**Figure 2.** Compression and relaxation curves for a typical thiokol. 
S is in dynes/cm², t is in sec.

**Figure 3.** Nutting plots for compression and relaxation of highly anomalous materials.

**Compression**
- ○ S = 17.8 × 10⁴
- △ S = 21.9 × 10⁴
- + S = 30.2 × 10⁴

**Relaxation**
- × σ = 0.0624
- ▽ σ = 0.146
- + σ = 0.263
Limitations of the Newtonian time scale

These curves are shown as being reasonably typical. The Nutting treatment (without addition of a second term) in this case is not particularly satisfactory in relaxation.

Unless the discrepancies are exceptionally large it is not possible to show clearly the effects of fitting the second term graphically or even in tabular form. A rather extreme case of a butyl rubber is given in table 1, the Nutting plots of which are shown in figure 3. To economize space, only three stresses are shown.

**Table 1. Comparison of equations (2) and (8) with experimental data for compression and relaxation for a highly anomalous butyl rubber**

<table>
<thead>
<tr>
<th>$S \times 10^4 \ldots$</th>
<th>17.8</th>
<th>21.9</th>
<th>30.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$\sigma_{exp.}$</td>
</tr>
<tr>
<td>10</td>
<td>0.1016</td>
<td>0.0984</td>
<td>0.1012</td>
</tr>
<tr>
<td>13</td>
<td>0.1057</td>
<td>0.1046</td>
<td>0.1059</td>
</tr>
<tr>
<td>16</td>
<td>0.1107</td>
<td>0.1111</td>
<td>0.1109</td>
</tr>
<tr>
<td>20</td>
<td>0.1165</td>
<td>0.1180</td>
<td>0.1175</td>
</tr>
<tr>
<td>25</td>
<td>0.1233</td>
<td>0.1254</td>
<td>0.1245</td>
</tr>
<tr>
<td>32</td>
<td>0.1308</td>
<td>0.1332</td>
<td>0.1303</td>
</tr>
<tr>
<td>40</td>
<td>0.1401</td>
<td>0.1417</td>
<td>0.1387</td>
</tr>
<tr>
<td>50</td>
<td>0.1486</td>
<td>0.1505</td>
<td>0.1497</td>
</tr>
<tr>
<td>63</td>
<td>0.1589</td>
<td>0.1599</td>
<td>0.1585</td>
</tr>
<tr>
<td>79</td>
<td>0.1701</td>
<td>0.1699</td>
<td>0.1718</td>
</tr>
<tr>
<td>100</td>
<td>0.1823</td>
<td>0.1805</td>
<td>0.1820</td>
</tr>
<tr>
<td>126</td>
<td>0.1955</td>
<td>0.1918</td>
<td>0.1972</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\sigma = 0.0624$</th>
<th>$\sigma = 0.146$</th>
<th>$\sigma = 0.263$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$</td>
<td>$S_1$</td>
<td>$S_2$</td>
</tr>
<tr>
<td>316</td>
<td>2.431</td>
<td>2.592</td>
</tr>
</tbody>
</table>

$\sigma_s$ is strain and $S_s$ is stress ($\times 10^4$) calculated from two terms of equation (8).

$\sigma_2$ and $S_2$ are stress ($\times 10^4$) calculated from equation (2) (Nutting's law).

$\sigma_{exp.}$ and $S_{exp.}$ are experimental values.

$t$ is time in sec. Initial stress in relaxation (all three curves) = 39.3 $\times 10^4$ dynes/cm.$^2$.

The relaxation data illustrate one of those rare cases where even the addition of a second term, although effecting a great improvement, still leaves something to be
desired. The addition of a third term from equation (8) improves the fit still further, but this improvement would not normally justify the large amount of labour involved in the calculation.

In introducing a second or even a third term of equation (8), it is important to bear in mind their significance over different parts of the time scale. For very short times when $A$ and $B$ have the same sign, the two-term plot goes through a minimum in straining or a maximum in relaxation since the second term with a negative exponent preponderates. This has no more physical significance than the minimum in the well-known Buckingham-Reiner equation if it is applied to stresses below the yield-value (see Blair 1938). The condition of quasi-equilibrium which the treatment postulates has not been reached at such small values of $t$.

But it is curvature in the Nutting curves for comparatively short times that is most effectively corrected by introducing the second term.

A good Nutting curve which deteriorates only after long times is not easy to deal with by means of equation (8). Downward curvature of this type is rare, and upward curvature suggests an examination of the test-piece for signs of rupture or, in the case of extensions, slipping at the grips.

In relaxation, where deviations from simple Nutting behaviour are on the whole more serious, curvature is almost invariably found in the short-time part of the curves.

There are a number of cases where the log $\sigma$/log $t$ plot for a series of constant stress experiments gives curves which superficially appear to be linear, but it is found that the slope, $k$, increases or decreases progressively with increasing stress. It is thought likely that this is due to the fact that the Nutting equation is only the first term of the series equation (equation (8)), and that even though the second term correction might be small, the value of $k$, determined over the experimental range, might differ significantly from the true slope, i.e. the slope at large strains. If this is the explanation, then any slight upward curvature of the log $\sigma$/log $t$ curve should lead to an apparent increase in $k$ with increasing stress, whereas downward curvature would lead to the reverse. Curvature is easily checked by comparing the magnitude of $k$ from the Nutting equation and $k'$ from the two-term fit, and it was found in the great majority of cases that any tendency for $k$ to vary with stress was in the sense predicted on this hypothesis. Evidence is, however, not adequate to state categorically that all apparent variations of $k$ with stress are due to this cause.

As well as the problem of fixing a time zero, there is also the question of the strain zero. For simple elastic systems this is easy, but for complex systems zero strain means no more than the shape of the test-piece at the start of the experiment, assuming that the material is then in the normal rest condition with which the test is required to deal. As Love (1906) puts it: ‘The unstrained state…is, as it were, an arbitrary zero of reckoning, and the choice of it is in our power.’

The presence of undissipated internal stresses, which would lead to the fixing of a zero of strain different from that selected if the material were devoid of internal stresses, would produce a curvature in the log $\sigma$/log $t$ curves assuming a
Limitations of the Newtonian time scale

normal Nutting behaviour for the unstressed system. Furthermore, the source of ‘error’ would lead to a modification of the Nutting equation precisely the same as equation (8).

This suggests that the presence of a significant second term in equation (8) may, at least in some cases, be indicative of undissipated internal stresses, a point which, if verified, would be of considerable practical importance.

Unfortunately, we have neither time nor suitable materials to test this hypothesis adequately, though preliminary experiments are sufficiently encouraging to warrant further investigation.

Alternative treatments

As pointed out in the introduction, it is possible, by postulating enough exponential terms, to obtain an adequate fit to almost any $S/t$ curve. In order to get accuracy comparable to that derived from the two-term form of equation (8), either two or three exponential terms are generally required. The equations, which were calculated by Whitehead’s (1935) method, are of the form $S = pe^{-t\tau_1} + qe^{-t\tau_2} + r$ which means that a two-term exponential involves five parameters (‘properties’) and a three-term involves seven. The work involved depends on the method used. With Whitehead’s graphical method, the calculation takes less time than that for the two-term equation (8), but it must be remembered that the latter calculation gives a statistical fit whereas the former does not give the errors in the fitted parameters.

As a second alternative, Alexandrov & Lazurkin’s (1940) method was tried, though in the majority of cases the assumptions that there is an easily recognizable ‘immediate’ elastic reaction $\sigma_0$ and that, under constant stress, the strain approaches asymptotically to an equilibrium (maximum) value ($\sigma_\infty$), are so wide of the mark for most of the materials tested by us that it is rarely possible to get any fair measure of $\sigma_0$ or $\sigma_\infty$. For elastic bitumen, for which these constants could be determined with some confidence, the fit of the Alexandrov-Lazurkin equation was definitely bad.

Apart from the earlier work already published, we had some 173 straining and 455 relaxation curves suitable for a complete statistical treatment using equation (8). These data cover some thirty-eight ‘materials’, counting characteristically different members of the same family of polymers as distinct ‘materials’.

Statistical treatment

Under constant stress conditions, equation (2) gives linear $\log \sigma/\log t$ curves, and under constant strain conditions linear $\log S/\log t$ curves. The constants of these equations have been determined by fitting a straight line to the data by the method of least squares. It was assumed that the $\log t$ values were known accurately in both cases and the error was in $\log \sigma$ and $\log S$ respectively.
The constants of equation (8), (for tension) using the first two terms, were determined by transforming it to

$$\log \sigma = \beta \log S + \log A + k' \log t + \log [1 + B/At]$$
or

$$\log \sigma = \beta \log S + \log A + k' \log t + BM/At$$
to the first approximation, provided $BM/A < 1$, $t > 1$ and $M = \log e \times 10$. This equation can be written

$$y = a + bx + c \times 10^{-x},$$

where $y = \log \sigma$, $x = \log t$, $a = \log S + \log A$, $b = k'$, $c = BM/A$.

The values of $a$, $b$ and $c$ were determined by the method of least squares, assuming $x$ to be known exactly.

A similar transformation can be made for constant-strain conditions (relaxation) and the constants determined in the same way.

The summarized results of this analysis are given in table 2.

**DISCUSSION OF RESULTS**

In the case of the simple Nutting equation, the constant $k$ is directly derived from the rate of straining of a single test-piece under constant stress, and the rate of dissipation of the same test-piece gives $k/\beta$. The calculation of $\beta$, on the other hand, involves data obtained from a number of test-pieces, and there is no doubt that the very much higher standard error in $\beta$ is due to the fact that lack of homogeneity of the samples from which the test-pieces were taken is very much the limiting factor in defining the accuracy of comparison between different materials. For this reason it can hardly be over-emphasized that when it is stated that the introduction of a second term significantly improves the fit for a given curve, that does not mean that the unmodified Nutting equation would be inadequate if the purpose of the tests is to compare one material with another. The adequacy of any equation for this purpose depends on the homogeneity of particular materials. If two strips from the same sheet of plastic differ appreciably, as is often the case, there will be little point in improving on the Nutting plot in order to get effective constants for the material unless the second term is very much larger than that which would necessitate its use if only individual curves were considered.

Having given this warning it is now possible to proceed to discuss the proportion of cases in which individual curves can be improved by the use of a second term.

In the straining experiments (tension and compression) 66 curves out of 173 (38%) show significant improvement on fitting a second term. In terms of materials

47% of materials are significantly improved in less than 25% cases,

24% of materials are significantly improved in 25 to 75% cases,

29% of materials are significantly improved in more than 75% cases.

In all cases where there was no significant ‘improvement’ it is implied that the Nutting fit was adequate within the limits of experimental error. There were no
<table>
<thead>
<tr>
<th>Material</th>
<th>number of curves showing significant curvature</th>
<th>percentage</th>
<th>straining</th>
<th>relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>showing significant curvature</td>
<td></td>
<td>k</td>
<td>k</td>
</tr>
<tr>
<td>polyvinyl chloride (1)</td>
<td>8</td>
<td>2</td>
<td>80</td>
<td>0.116</td>
</tr>
<tr>
<td>polyvinyl chloride (2)</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.108</td>
</tr>
<tr>
<td>polyvinyl chloride (3)</td>
<td>1</td>
<td>0</td>
<td>100</td>
<td>0.119</td>
</tr>
<tr>
<td>polyvinyl chloride (4)</td>
<td>2</td>
<td>1</td>
<td>66</td>
<td>0.037</td>
</tr>
<tr>
<td>polyvinyl chloride (5)</td>
<td>2</td>
<td>1</td>
<td>66</td>
<td>0.111</td>
</tr>
<tr>
<td>polyvinyl chloride (6)</td>
<td>1</td>
<td>1</td>
<td>50</td>
<td>0.008</td>
</tr>
<tr>
<td>polyvinyl chloride (7)</td>
<td>2</td>
<td>1</td>
<td>66</td>
<td>0.380</td>
</tr>
<tr>
<td>polyvinyl chloride (8)</td>
<td>3</td>
<td>7</td>
<td>30</td>
<td>0.075</td>
</tr>
<tr>
<td>polyvinyl chloride (9)</td>
<td>2</td>
<td>7</td>
<td>22</td>
<td>0.096</td>
</tr>
<tr>
<td>plastic (unspecified 1)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>plastic (unspecified 2)</td>
<td>2</td>
<td>0</td>
<td>100</td>
<td>0.289</td>
</tr>
<tr>
<td>plastic (unspecified 3)</td>
<td>2</td>
<td>0</td>
<td>100</td>
<td>0.275</td>
</tr>
<tr>
<td>plastic (unspecified 4)</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>0.266</td>
</tr>
<tr>
<td>plastic (unspecified 5)</td>
<td>1</td>
<td>2</td>
<td>33</td>
<td>0.737</td>
</tr>
<tr>
<td>cellulose acetate + phthalate</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.436</td>
</tr>
<tr>
<td>rubber—unvarnished (1)</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>0.118</td>
</tr>
<tr>
<td>rubber—unvarnished (2)</td>
<td>5</td>
<td>0</td>
<td>100</td>
<td>0.223</td>
</tr>
<tr>
<td>rubber—sulphur-free (3)</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0.022</td>
</tr>
<tr>
<td>elastic bitumen (1)</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0.164</td>
</tr>
<tr>
<td>elastic bitumen (2)</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0.121</td>
</tr>
<tr>
<td>bitumen (1)</td>
<td>7</td>
<td>1</td>
<td>88</td>
<td>0.037</td>
</tr>
<tr>
<td>bitumen (2)</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>0.429</td>
</tr>
<tr>
<td>chewing-gum</td>
<td>4</td>
<td>0</td>
<td>100</td>
<td>0.676</td>
</tr>
<tr>
<td>chewing-gum base</td>
<td>1</td>
<td>2</td>
<td>33</td>
<td>0.373</td>
</tr>
<tr>
<td>rye-flour toffee</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.962</td>
</tr>
<tr>
<td>milk toffee (gelatin base)</td>
<td>2</td>
<td>0</td>
<td>100</td>
<td>0.737</td>
</tr>
<tr>
<td>'Hyco'</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0.082</td>
</tr>
<tr>
<td>'butyl' (1)</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0.037</td>
</tr>
<tr>
<td>'butyl' (2)</td>
<td>6</td>
<td>0</td>
<td>100</td>
<td>0.275</td>
</tr>
<tr>
<td>neoprene A</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.034</td>
</tr>
<tr>
<td>neoprene B</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0.021</td>
</tr>
<tr>
<td>neoprene E</td>
<td>1</td>
<td>3</td>
<td>25</td>
<td>0.036</td>
</tr>
<tr>
<td>neoprene F</td>
<td>2</td>
<td>4</td>
<td>33</td>
<td>0.029</td>
</tr>
<tr>
<td>thiokol F.A.</td>
<td>0</td>
<td>16</td>
<td>0</td>
<td>0.065</td>
</tr>
<tr>
<td>thiokol A.Z.</td>
<td>3</td>
<td>4</td>
<td>42</td>
<td>0.134</td>
</tr>
<tr>
<td>polyisobutylene</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>0.134</td>
</tr>
<tr>
<td>G.R.S. (synthetic rubber)</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0.085</td>
</tr>
<tr>
<td>Cheddar cheese</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0.190</td>
</tr>
<tr>
<td>skim-milk cheese</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>0.190</td>
</tr>
</tbody>
</table>

**Limitations of the Newtonian time scale**

---

**Table 2. Mean Nutting Constants of Materials and Significance of Addition of a Second Term**

- Straining: The table provides data on the number of curves showing significant and insignificant curvature, standard error of $k \times 10^2$, and % error of $k$.
- Relaxation: The table includes the number of curves showing significant and insignificant curvature, standard error of $k \beta \times 10^2$, and % error of $k \beta$.
cases of bad Nutting fit where the introduction of a second term did not effect an improvement and only a very few (and then only in relaxation, e.g. see table 1) where the fitting of one further term did not give a statistically satisfactory fit.

In the relaxation experiments, the simple Nutting equation was less adequate than in straining. Thus, of 455 relaxation curves analysed, 270 (59%) were significantly improved by the addition of a second term.

Only 9% of materials tested required a second term in less than 25% cases,
54% of materials tested required a second term in 25 to 75% cases,
and 37% of materials tested required a second term in more than 75% cases.

It will be recalled that in the preliminary relaxation experiments in which the initial straining was very rapid, for the few materials tested, values of $\psi$, $k$ and $\beta$ were strikingly similar when obtained by straining at constant stress and by relaxation. With the slow controlled pre-straining of the later experiments, there were, in general, greater divergencies. Confining our comparisons only to materials for which the unmodified Nutting equation holds adequately, some results are given in table 3.

<table>
<thead>
<tr>
<th>Material</th>
<th>Straining log $\psi$</th>
<th>Relaxation log $\psi$</th>
<th>Straining $k$</th>
<th>Relaxation $k$</th>
<th>Straining $\beta$</th>
<th>Relaxation $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur-free rubber</td>
<td>7.76</td>
<td>8.56</td>
<td>0.022</td>
<td>0.046</td>
<td>1.07</td>
<td>1.19</td>
</tr>
<tr>
<td>Elastic bitumen</td>
<td>5.82</td>
<td>6.46</td>
<td>0.121</td>
<td>0.112</td>
<td>0.82</td>
<td>0.89</td>
</tr>
<tr>
<td>Butyl rubber</td>
<td>9.44</td>
<td>11.65</td>
<td>0.037</td>
<td>0.062</td>
<td>1.37</td>
<td>1.70</td>
</tr>
<tr>
<td>Neoprene A.</td>
<td>8.24</td>
<td>8.88</td>
<td>0.034</td>
<td>0.056</td>
<td>1.13</td>
<td>1.22</td>
</tr>
<tr>
<td>Thiokol F.A.</td>
<td>6.05</td>
<td>5.44</td>
<td>0.095</td>
<td>0.067</td>
<td>0.88</td>
<td>0.75</td>
</tr>
<tr>
<td>G.R.S. (synthetic rubber)</td>
<td>9.49</td>
<td>10.40</td>
<td>0.085</td>
<td>0.105</td>
<td>1.29</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Conclusions

We conclude that for the practical comparison of the rheological behaviour of many materials of the kind which we have studied, the Nutting treatment is not only adequate and relatively simple, but expresses those quasi-properties of materials which are often important in industry and are certainly used extensively for assessing their quality.

The limiting factor at present is lack of homogeneity of samples, and, in some cases, latent internal stresses. Where these difficulties can be overcome, it is worth while in a fair proportion of cases to extend the Nutting treatment by introducing the second term in the series equation of which it forms a part. Even then, the properties of the material are described by only four constants, i.e. less than the five constants required for even a two-term exponential treatment.

On the theoretical side much remains to be done, but we are convinced that a sound start has been made in approaching the problem in terms of the fundamental definition of the equality of time intervals.
Limitations of the Newtonian time scale

The use of constant-strain relaxation as a method of studying the rheology of plasctics is open to various objections. It is likely that the method will always be secondary to direct straining methods, but we feel that it has its uses, especially when it is desirable to measure properties or quasi-properties by two quite independent methods.

We would express our best thanks to the British Electrical and Allied Industries Research Association for permission to publish this work and to many friends, too numerous to mention by name, who have supplied us with materials and helpful advice. But we would especially thank Dr S. Whitehead, Dr P. White and Professor H. Dingle for their help and encouragement, and Miss M. Baron, Mr W. Lethersich and Miss J. Hazeldan for carrying out many statistical calculations.

References

British Rheologists’ Club (Committee) 1946 Essays in Rheology. London: Sir Isaac Pitman and Sons.
Dingle, H. 1942 Phil. Mag. 33, 321.
Dingle, H. 1944 Phil. Mag. 35, 499.
Gemant, A. 1936 Physics, 7, 311.
Gemant, A. 1944 Phil. Mag. 25, 540.
Mooney, M. 1940 J. Appl. Phys. 11, 582.
Piéron, H. 1945 Presidential Address to French Ass. for Advancement of Science, Paris.
Reiner, M. 1933 Naturwissenschaften, 21, 294.