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On the Use of Power Equations to Relate Shear-Rate to Stress in Non-Newtonian Liquids

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Since the early work of *de Waele* (1) and *Ostwald* (2) many workers have found it convenient to plot logarithms of shear rates ($\dot{\gamma}$) against logarithms of stresses (τ) to get straight lines giving two parameters by which materials may be classified. The relationships between parabolas and other functions were discussed by *Reiner* (3) and many log-log plots are to be found in a book by *Philippoff* (4).

Scott Blair (5) in a discussion with *Ostwald* (6) long ago showed that it is often hard to say, without statistical analysis, whether, for systems showing a yield-value, the log-log or the linear plot better describes the data; but the present paper is concerned only with non-Newtonian liquids which show no observable yield-value; nor will thixotropic systems be considered. A single-valued relation will be assumed between $\dot{\gamma}$ and τ .

The use of the log-log plot has generally been considered to be theoretically meaningless. It is sometimes said that any slightly curvilinear graph is likely to give a straight line when the data are plotted on log-log paper: in other words, all slightly non-linear curves are power laws. This is clearly quite incorrect; although, if approximate linearity of the log-log curves were limited to a short range, it would be true. In fact, log-log curves are often remarkably linear over several decades of shear-rate (4) and the aim of the present paper is to see whether, under the conditions considered, some quite simple and likely assumptions about the behaviour of non-Newtonian liquids will not lead to a power law relation.

The treatment is frankly copied from that proposed by *Huxley* (7) who pointed out that if the size of a specific organ of an animal's body, say a lobster's claw, increases in an exponential manner with time; and if the rate of growth of the rest of the body is also exponential, having a different rate constant, the relative rate of growth of the organ to that of the body as a whole will follow a log-log relation. There is, of course, a unique value for the size of the claw corresponding to each value for the total size of the body.

Shear thinning liquids

Consider the case of a liquid which, at rest, has a very high viscosity by reason of linkages between particles, solid or liquid, dispersed therein. The word "linkage" is preferred to "bond" as having a wider connotation.

When this system is sheared in a viscometer at a series of increasing constant rates of shear, there is for each rate of shear a constant equilibrium stress. But the physical effects of the stress and of the shear-rate on the linkages will be very different. The stress will tend to break the linkages, and the simplest physical hypothesis would be that the number (n) of linkages per unit volume will be linearly related to the logarithm of the stress. It is clear that this assumption cannot hold at the lowest stresses, since when τ becomes zero, $-dn/d\tau$ would be infinite. But, once the structure has begun to break down, it is reasonable to suppose that the rate of breakdown will diminish

exponentially as the number in linkages is reduced.

Hence we write $\ln \tau = \text{const.} - a n$, the value of the first constant being unknown. This is equivalent to:

$$-\frac{dn}{d\tau} = \frac{a}{\tau}, \quad [1]$$

where a is a constant. The effect of increasing rate of shear, on the other hand, is to prevent the particles from remaining long enough in close contact for the restoring forces, making for an increase in n , to be effective. Again, the simplest assumption would be that the number of linkages which can remain in spite of the shear-rate will be a linear function of the logarithm of the shear-rate or

$$-\frac{dn}{d\dot{\gamma}} = \frac{b}{\dot{\gamma}}, \quad [2]$$

where b is a constant.

The hypothesis leading to equation [1] concerns the behaviour of the linkages under static forces, while that leading to equation [2] is a reasonable additional hypothesis concerning their kinetic properties.

This means that n , the number of linkages per unit volume, is proportional to the logarithms of both τ and $\dot{\gamma}$, hence we can combine equations [1] and [2] to get

$$\frac{d\dot{\gamma}}{d\tau} = \frac{a}{b} \frac{\dot{\gamma}}{\tau}$$

or

$$\ln \dot{\gamma} = \frac{a}{b} \ln \tau + C, \quad [3]$$

where C is an integration constant. This is the commonly used "empirical" equation.

It has already been pointed out that this equation cannot hold over the whole range of shear-rates. At very high rates of shear, it may well be that all linkages are broken down and, as *Ostwald* predicted, there may be a "Laminarast" or straight portion of the $\dot{\gamma}/\tau$ curve, aiming at the origin, in which case a/b would reduce to unity. But the simplifying assumptions made in deriving equations [1] and [2] will only apply over a limited, albeit quite a wide, range of $\dot{\gamma}$.

Shear thickening liquids

Such systems are less common than their shear-thinning counterparts. At rest, there is little or no structure and the effect of applying a shearing stress is to press the dispersed particles together to form aggregates. There must be an upper limit to the increase in apparent viscosity produced by

this process; but, over a limited range of stress, an equation exactly analogous to equation [1] would apply, only with a positive sign. As shear rate increased, the number of collisions between particles would increase and hence, by an entirely different mechanism, there would also be an increase in n (coagulation) and equation [2] would hold, but with a positive sign. The only difference in equation [3] would be that, whereas for shear thinning, $a > b$ and for a *Newtonian* fluid, $a = b$; for a thickening system, $a < b$. Both a and b will have the same dimensions as n , i. e. $[L^{-3}]$ and their ratio will depend on the relative importance of stress and of shear rate in defining changes in the apparent viscosity. Whether the system thins or thickens will depend on the shape of the potential energy curves [see *Sherman* (8)].

Comparison with Huxley's treatment

The author has discussed the subject matter of this paper with many kind friends. Some rheologists, while accepting *Huxley's* equations, have felt that it is not justifiable to apply an analogous treatment to the rheological problem. It would, therefore, be as well to list the differences which exist between the two situations.

1. The eliminated variable in *Huxley's* case is time, which must directly enter into the experiment and can be measured. The corresponding number of linkages per unit volume does not enter into the experiments. It would be very difficult in practice, but not on principle, to count n under the microscope.

2. Since time flows continuously, *Huxley* could not directly repeat individual measurements on any given animals. Repeat points at any required shear-rate can be obtained within reason as often as is desired.

3. In *Huxley's* case, his uncanceled variables are dimensionally similar (both weighs): in the rheological case, $\dot{\gamma}$ has different dimensions from τ .

4. If the claw of a lobster is removed, the rest of the body can continue to grow. Although this is not true in practice of all organs (e. g. the heart) there is no doubt that his variables are, in a certain sense, more independent than are $\dot{\gamma}$ and τ . It is impossible to remove a stress in the systems considered while retaining a rate of shear.

Of these four differences, only the last might possibly seem to raise doubts as to

whether the rheological analogy is a fair one. Indeed points 2 and 3 might seem to make the independence of equations [1] and [2] all the more evident.

It has further been suggested that partial differential equations should have been used. This would not be possible, since an expression such as $(\partial n/\partial \tau)_\dot{\gamma}$ would be meaningless. If $\dot{\gamma}$ is constant, τ cannot vary.

Finally, it should be pointed out that the assumptions underlying equations [1] and [2] are arbitrary: for instance, some powers of τ and $\dot{\gamma}$ might have been introduced. This is true but the assumptions used are the simplest physical assumptions and that is why they are made.

Many highly complex theories of viscosity of dispersions have been proposed (8) but, even so, these involve simplifying assumptions which are often not justified in dealing with industrial dispersions such as dairy creams, which interest the present author.

The author is indebted to too many kind friends whose advice he has asked about this work to mention them all by name. But, in view of a number of verbal criticisms, he has asked a Mathematician, Professor *J. N. Hunt*, to add a short note on the mathematical validity of the treatment, for which help he is deeply grateful.

Addendum (J. N. H.)

The author has derived equations [1] and [2] by analogy with the work of *Huxley*. The validity of equation [3] however does not depend on the strength or weakness of this analogy but rather on the existence of a single valued relation between stress and rate of shear. Thus in the absence of hysteresis

$$\dot{\gamma} = \dot{\gamma}(\tau) \tag{4}$$

If we suppose n to be a function only of τ such as to lead to equation [1] for $dn/d\tau$,

then the existence of [4] immediately gives

$$-\frac{a}{\tau} = \frac{dn}{d\tau} = \frac{dn}{d\dot{\gamma}} \frac{d\dot{\gamma}}{d\tau}$$

which, if [4] happens to be of the form

$$\dot{\gamma} = \tau^\alpha \tag{4'}$$

gives, on substituting for τ and $d\dot{\gamma}/d\tau$

$$-\frac{a}{\dot{\gamma}^{1+\alpha}} = \frac{dn}{d\dot{\gamma}} \propto \tau^{\alpha-1} = \frac{dn}{d\dot{\gamma}} \propto \dot{\gamma}^{\left(1-\frac{1}{\alpha}\right)}$$

or

$$\frac{dn}{d\dot{\gamma}} = -\frac{a}{\alpha} \frac{1}{\dot{\gamma}}$$

which is precisely of the form of equation [2]. Therefore, just as equations [1] and [4'] lead to equation [2], so [1] and [2] are consistent assumptions and lead to the existence of a relation of the form [4], or more precisely to [4'].

Summary

It is shown that some quite simple assumptions about the nature of the flow of non-Newtonian liquids lead to the use of the well-known power relation between shear-rate and stress, hitherto regarded as entirely empirical. The treatment is applicable both to thinning and to thickening liquids provided there is no hysteresis.

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