

# THE CHANGING RHEOLOGY OF CHANGING SYSTEMS\*

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Rheology, "the study of the deformation and flow of matter", is a branch of physics and, as in other branches of physics, the first consideration is to find *invariants*. These invariants are generally *physical properties* which can be precisely defined in terms of whole-number (or occasionally half) powers of Mass, Length and Time (MLT). Units other than MLT may be used: indeed there need not even be three; but MLT are the most convenient.

Except in quantum physics, with which we are not concerned, it is a basic requirement of a "physical property" that it should not be changed by the process of measuring it. Such a condition cannot always be fulfilled and it is usual to define *basic equations* representing true physical properties, and then to modify them when necessary.

In rheology, the two principle basic equations are those of Hooke for elastic solids: stress ( $\tau$ ) is proportional to strain\*\* ( $\gamma$ ) and of Newton for viscous liquids,  $\tau$  is proportional to rate of shear ( $\dot{\gamma}$ ) ("Newton's dot" indicates differentiation with respect to time). It happens that quite a large number of materials obey these equations with considerable accuracy but of course there are many that do not. Some follow simple combinations of the two equations (equations of Maxwell for relaxation and of Kelvin-Voigt for retardation), while others are far more complex. The present lecture is concerned with those all-too-common cases, to be found in Industry, in which there are changes in the rheological characteristics of the material during the testing process, caused either by the process of testing itself, or by chemical changes taking place during the test. The importance of these "changing" systems in industrial rheology requires corresponding changes in our rheological theories.

In this lecture, two processes will be discussed: first, the behaviour of a suspension (or emulsion) whose structure is broken down by the shearing needed to test it, but in which the rate of recovery is so great that there is a unique relation between  $\tau$  and  $\dot{\gamma}$  and secondly, the process of polymerization as exemplified by the clotting of blood.

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\*\* Hooke's law is more often expressed in terms of extensions but it is here more convenient to consider shears.

The equations proposed will be basic equations, in the sense that they are the simplest equations that will fit the situation. In real systems, as with other basic equations, they may well require modification.

In connection with the first problem, when a structured suspension is sheared, as stress is increased, so the structure will tend to be broken down and the apparent viscosity falls. Although there is a unique relation at any time between stress and shear-rate, the effect of the latter will be independent of that of the former. We know that the attractive forces between the particles will cause the structure to be re-formed as quickly as possible but the rate of this re-forming will depend on the rate of shear which tends to prevent it. The simplest assumption is that these two processes are both exponential, and I have shown [1] that a simple combination of these two equations leads to a power equation of the form

$$\left. \begin{array}{l} \ln \tau = \ln K + a \ln \dot{\gamma} \\ \text{or} \\ \tau = K \dot{\gamma}^a \end{array} \right\} \text{where } K \text{ and } a \text{ are parameters of the material (1)}$$

This equation has been found to hold, in practice, for many suspensions often over too wide a range of shear-rate for it to be likely that the double logarithmic plot is no more than an empirical straightening device (see especially PRENTICE [2] for cream). The idea that the prevalence of such power equations might well be a result of the combination of two exponential equations was derived from two sources: HUXLEY [3], who discussed the relative value of growth of the great claw of the lobster to its body size and BERTALANFFY [4] who treated the problem from the purely theoretical angle.

Double logarithmic equations have been criticized on dimensional grounds. While they are not, as has sometimes been alleged [5] "inhomogeneous", since in equation (1) the dimensions of  $K$  are defined by a magnitude of  $a$ , the situation is complex, since for each value of  $a$ ,  $K$  will have different dimensions.

It appears, however, that in certain systems where changes are not directly connected with the testing process, the dimensional situation can be simplified. NEDONCHELLE and SCHUTZ [6] studied the gradual "thickening" of starch pastes under certain conditions (known as "retrogradation") and obtained a series of double-logarithmic curves following equation (1). They also found that a plot of  $K$  against  $a$  gave a straight line and this means that, on extrapolation, all the double logarithmic curves would meet at a singular point corresponding to definite stress ( $\tau'$ ) and strain-rate ( $\dot{\gamma}'$ ) values. This implies that the equation may be written in the dimensionless form

$$\frac{\tau}{\tau'} = \left( \frac{\dot{\gamma}}{\dot{\gamma}'} \right)^a \quad (2)$$

Later, TUSZYŃSKI and SCOTT BLAIR [7] found that a similar equation could be applied to milk, treated in the cold with rennet and, after some hours, raised to a temperature at which it would coagulate only very slowly. It is not known to how many other coagulating or "thickening" systems this equation applies.

The second case to be considered is the process of coagulation itself, as produced by the polymerization of a protein. The treatment has been applied to blood (fibrin) and milk (casein). Such systems are generally studied by means of a forced sinusoidal strain oscillation in a coneplate or cone-cone viscometer (or, less efficiently between coaxial cylinders).

If the induced stress-wave is found to be sinusoidal, then the system must be either Hookean (if the curves are in phase), Newtonian (if exactly out-of-phase), or either Maxwellian or Kelvin if there is a finite phase-angle. The tangent of the phase angle gives the proportion of the viscous (energy dissipated) to elastic (energy stored) parts of a complex modulus.

In the earlier stages of coagulation, the complex modulus will increase at an accelerating rate because, when any two molecular chains join at one point, this will make for a rapid junction of these chains at other points. By quite a different process, towards the end of the coagulation, the number of unattached junction points will rapidly decrease and the process must decelerate. This means that the modulus-time curve ( $G/t$ ) must be sigmoid and almost certainly not symmetrical, which would seem to rule out the application of the most obvious autocatalytic equation

$$\dot{G} = aG + bG^2 \quad (3)$$

Experimentally, this equation certainly does not apply to blood. Earlier work seemed to indicate that it did not apply to milk, though the question is again under discussion (TUSZYŃSKI — private communication).

Some years ago, a treatment analogous to that given above for the "shear-thinning" of suspensions\* was proposed for coagulation. This work is best summarized in more recent papers [8, 9]. To recapitulate briefly the argument, it is clear that the simplest equation, the exponential, is not applicable, since the curve is sigmoid. Likewise two combined exponentials giving a power equation, would be inapplicable. These equations may be written:

$$\dot{G} = n_0 Gt^0 \text{ exponential}$$

$$\dot{G} = n_1 Gt^{-1} \text{ power}$$

These equations constitute the first two terms of a series, of which the third term is:

$$\dot{G} = n_2 Gt^{-2} \quad (4)$$

\* A similar treatment can also be applied to shear-thickening systems: see ref. [1].

which may be written:

$$\dot{G} = \frac{\Theta}{t} \cdot G^{-1} \quad (4a)$$

It will be seen that this is the same as the power equation, except that the power ( $\Theta/t$ ) is steadily decreasing with increasing time. If the power were constant ( $n_1$ ) the curve would slope either upwards or downwards, depending on whether  $n$  is greater or less than unity. It has therefore been replaced by a time variable in which time must be the denominator and, for dimensional reasons, the numerator must be also a time-characteristic of the material. Equation (4) has been found to hold reasonably well for coagulating milk and extremely well for coagulating blood (up to a time when softening processes start to counteract the coagulation effects).

That there is now some slight doubt about milk may well be due to the fact that, whereas in coagulating blood, the monomer fibrin is being continually replaced during the process of coagulation, with milk, the amount of substrate (casein) is virtually constant.

It will be noticed that equation (4) bears a close analogy to the equations of Maxwell and Kelvin. The importance of the ratio of a time characteristic of the material to the experimental time (which REINER [10] has called "The Deborah number" in the case of relaxation) is again striking.  $\Theta$  is the time taken for the  $G$  to reach a value of  $1/e$  of its theoretically ultimate value.

In conclusion, the writer feels that, in these complex situations of changing conditions, what is really required is an extended theory of dimensions which would specify behaviour not in terms of single magnitudes ("properties") but of inseparable groups of magnitudes. An attempt was made many years ago to inaugurate such a system in terms of fractional differential equations [11, 12], but this was not followed up.

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