

## **RHEOLOGY SERIES**

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**Vol. 1 Numerical Simulation of Non-Newtonian Flow (Crochet, Davies and Walters)**

**Vol. 2 Rheology of Materials and Engineering Structures (Sobotka)**

**Vol. 3 An Introduction to Rheology (Barnes, Hutton and Walters)**

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The photograph used on the cover shows an extreme example of the Weissenberg effect. It illustrates one of the most important non-linear effects in rheology, namely, the existence of normal stresses. The effect is produced, quite simply, by rotating a rod in a dish of viscoelastic liquid. The liquid in the photograph was prepared by dissolving a high molecular-weight polyisobutylene (Opanol B200) in a low molecular-weight solvent of the same chemical nature (Hyvis 07, polybutene). As the rod rotates, the liquid climbs up it, whereas a Newtonian liquid would move towards the rim of the dish under the influence of inertia forces.

This particular experiment was set up and photographed at the Thornton Research Centre of Shell Research Ltd., and is published by their kind permission.

#### 7.1.4 Flow-induced structures

We shall consider first, relatively unaggregated systems in which the Brownian forces dominate. When a concentrated suspension of this type flows at very low shear rates, the particles necessarily have to move around each other or "bounce off" each other for overall flow to occur. This involves a large resistance and the resulting viscosity is high. On the other hand, the distribution of particles remains essentially undisturbed because the effect of Brownian motion dominates the shear motion and restores the randomness of the rest-state distribution. The viscosity remains essentially constant. At slightly higher shear rates, the imposed velocity gradient induces an orientation of the particle structure, which is not restored by the Brownian motion. However this orientation enables particles to move past each other more freely than at very low shear rates and hence the viscosity is lower. At even higher shear rates, the structure is so grossly orientated that the particles form layers separated by clear layers of the continuous phase. The viscosity is then at its minimum value. The suspension is shear-thinning. The existence of particle layers has been confirmed by light diffraction. When shearing is stopped the flow-induced layered structure gradually disappears.

If the shear stress is increased above a critical value, the layers disrupt and gradually disappear. Hence, the viscosity begins to rise again and it also increases with time of shearing.

Flow-induced structures can also be formed by the more complicated clay and soap suspensions mentioned earlier. In these cases, flow causes the plates and ribbons to align in the direction of flow. This orientation can be detected by optical techniques.

Examples of increased flocculation caused by flow are also known (see, for example, Cheng 1973).

## 7.2 The viscosity of suspensions of solid particles in Newtonian liquids

### 7.2.1 Dilute dispersed suspensions

A considerable amount of progress has been made in predicting the viscosity of dilute suspensions (10% and less phase volume). All studies essentially extend the work of Einstein (1906, 1911) on spheres, so that particle shape, charge and the small amount of hydrodynamic interaction arising when any one particle comes into the vicinity of another can all be taken into account.

Einstein showed that single particles increased the viscosity of a liquid as a simple function of their phase volume, according to the formula

$$\eta = \eta_s(1 + 2.5\phi), \quad (7.2)$$

where  $\eta$  is the viscosity of the suspension and  $\eta_s$  is the viscosity of the suspending medium.

We notice immediately that in eqn. (7.2) there is no effect of particle size, nor of

particle position, because the theory neglects the effects of other particles. When interactions between particles are included, the situation becomes more complicated. The presence of other particles is accounted for by higher-order terms in  $\phi$ . However the only tractable theory is for extensional flow, because only in this type of flow can the relative position of the particles be accounted for analytically. Batchelor (1977) gives the viscosity in this case as

$$\eta = \eta_s(1 + 2.5\phi + 6.2\phi^2), \quad (7.3)$$

where the viscosities must now be interpreted as extensional viscosities (Chapter 5).

A number of experimental determinations of the term multiplying  $\phi^2$  for *shear flows* have been made, but the range of values so obtained is large (varying from about 5 to 15).

A great deal of work has been done and many reviews written (see, for example, Barnes 1981) on dilute suspensions, but almost all conclude that, apart from providing some limiting condition for the concentrated case, the work is of little relevance to suspensions of industrial importance. Dilute suspension theory covers the range below 10% phase volume, and this accounts for no more than a 40% increase in viscosity over the continuous phase.

### 7.2.2 Maximum packing fraction

The influence of particle concentration on the viscosity of the concentrated suspensions is best determined in relation to the maximum packing fraction. There must come a time, as more and more particles are added, when suspensions "jam up", giving continuous three-dimensional contact throughout the suspension, thus making flow impossible, i.e. the viscosity tends to infinity. The particular phase volume at which this happens is called the maximum packing fraction  $\phi_m$ , and its value will depend on the arrangement of the particles. Examples are given in Table 7.1. Maximum packing fractions thus range from approximately 0.5 to 0.75 even for monodisperse spheres.

The maximum packing fraction, as well as being controlled by the type of packing, is very sensitive to particle-size distribution and particle shape (see, for

TABLE 7.1  
The maximum packing fraction of various arrangements of monodisperse spheres

Arrangement	Maximum packing fraction
Simple cubic	0.52
Minimum thermodynamically stable configuration	0.548
Hexagonally packed sheets just touching	0.605
Random close packing	0.637
Body-centred cubic packing	0.68
Face-centred cubic/ hexagonal close packed	0.74

example, Wakeman 1975). Broader particle-size distributions have higher values of  $\phi_m$  because the smaller particles fit into the gaps between the bigger ones. On the other hand, nonspherical particles lead to poorer space-filling and hence lower  $\phi_m$ . Particle flocculation can also lead to a low maximum packing fraction because, in general, the flocs themselves are not close-packed.

From the above considerations, we see that the ratio  $\phi/\phi_m$  is a relevant normalized concentration.

### 7.2.3 Concentrated Newtonian suspensions

The situation for concentrated suspensions, where we expect higher-order terms than  $\phi^2$  to be important, is even more difficult to analyse from a theoretical point of view. The only methods available to tackle the problem are to introduce a technique for averaging the influence of neighbouring particles or alternatively to simulate the situation using computer modelling.

One recent development, based on an averaging technique, is that of Ball and Richmond (1980) who essentially start from the assumption that the effect of all the particles in a concentrated suspension is the sum of the effects of particles added sequentially. Hence the Einstein equation can be written in a differential form

$$d\eta = (5\eta/2) d\phi, \quad (7.4)$$

where  $d\eta$  is the increment of viscosity on the addition of a small increment of phase volume  $d\phi$  to a suspension of viscosity  $\eta$ . The viscosity of the final suspension is then obtained by integrating the phase volume between 0 and  $\phi$ , for which the viscosity is  $\eta_s$  and  $\eta$ , respectively. Then

$$\eta = \eta_s \exp(5\phi/2). \quad (7.5)$$

Ball and Richmond point out that this omits the correlations between spheres due to their finite size. This means that when a particle is added to a relatively concentrated suspension it requires more space than its volume  $d\phi$ , due to packing difficulties. Therefore  $d\phi$  has to be replaced by  $d\phi/(1 - K\phi)$ , where  $K$  accounts for the so-called "crowding" effect. Integration now yields

$$\eta = \eta_s (1 - K\phi)^{-5/(2K)}. \quad (7.6)$$

From this equation we see that the viscosity becomes infinite when  $\phi = 1/K$ . Therefore, we can identify  $1/K$  with the maximum packing fraction  $\phi_m$ . Ball and Richmond's expression is effectively identical to that of Krieger and Dougherty (1959). Krieger and Dougherty's theory also states that, in the general case, the 5/2 factor could be replaced by the intrinsic viscosity  $[\eta]$ .\* The value of 5/2 is the

\* Note: in suspension rheology  $[\eta]$  is dimensionless, since the phase volume is also dimensionless (see eqn. (7.2)); whereas in polymer rheology the concentration is usually expressed as a mass per unit volume, thereby giving  $[\eta]$  the dimensions of a reciprocal concentration (see § 6.5).

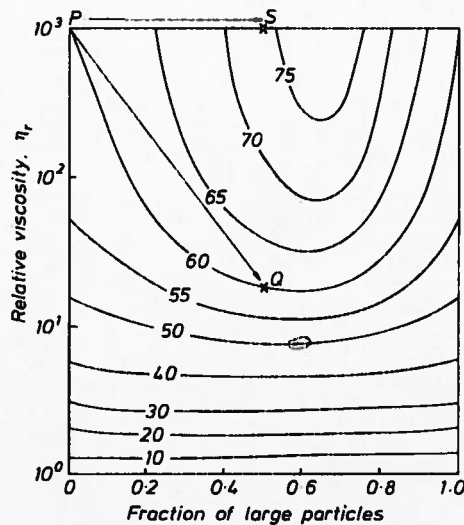


Fig. 7.4 Effect of binary particle-size fraction on suspension viscosity, with total % phase volume as parameter. The particle-size ratio is 5:1. P → Q illustrates the fiftyfold reduction in viscosity when a 60% v/v suspension is changed from a mono- to a bimodal (50/50) mixture. P → S illustrates the 15% increase in phase volume possible for the same viscosity when a suspension is changed from mono- to bimodal.

intrinsic viscosity for an ideal dilute suspension of spherical particles. Replacing it by  $[\eta]$  allows particles of any shape to be accounted for.

The Krieger–Dougherty equation is

$$\eta = \eta_s (1 - \phi/\phi_m)^{-[\eta]\phi_m} \quad (7.7)$$

Equations 7.6 and 7.7 both reduce to the Einstein equation (eqn. (7.2)) when  $\phi$  is small.

The values of  $\phi_m$  obtained from the empirical use of eqn. (7.7) are strongly dependent on the particle-size distribution. Thus,  $\phi_m$  increases with increasing polydispersity (i.e. the spread of sizes). This is illustrated by Fig. 7.4 where the viscosities of mixtures of large and small particles are plotted as a function of the total phase volume. The large reduction in viscosity seen near a fraction of 0.6 of large particles is known as the Farris effect. The effect is very large at a total phase volume of more than 50%. Mixing particle sizes thus allows the viscosity to be reduced whilst maintaining the same phase volume, or alternatively, the phase volume to be increased whilst maintaining the same viscosity. Similar effects can also be shown for tertiary mixtures (cf. Fig. 7.5). In the example shown in Fig. 7.5 the minimum relative viscosity is approximately 25 for the optimum tertiary mixture and is over 30 for the binary mixture. All these effects can be predicted using eqn. (7.7) by assuming, for instance, that the small particles thicken the continuous phase