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REVIEW

Rheology. Theory and Applications. Vol. IV. Edited by F. R. EIRICH. Academic Press, 1967. 522 pp. 192*s*.

This volume contains nine assorted chapters on various aspects of rheology and its applications. Of these, the longest and the most impressive is a detailed and extended account of the microrheology of dispersions by H. L. Goldsmith and S. G. Mason. In it, the reader is taken carefully and methodically along certain logically connected steps (conceptual, theoretical and experimental) that the authors obviously believe are necessary to a full understanding of the rheology of dispersions. They restrict their attention largely to dispersions of uniformly sized particles or droplets in a Newtonian fluid, subject to slow simple shear. First the solutions for creeping flow around isolated solid spheroids in an unbounded fluid are given with emphasis placed on the co-ordinate systems employed and the role of the orbit constant; the connexion between these solutions and those for isolated rods and disks is made. The effect of electric fields is considered. Then the case of isolated fluid droplets showing internal circulation is treated, including the question of deformation in simple shear and in hyperbolic flow. Poiseuille flow is used to introduce the effect both of non-uniform shear and of walls; migration effects are discussed.

Next collisions, i.e. strong 2-particle interactions, are carefully analysed; here the elegance of the experimental observations made first shows itself, while full use is made of analytic studies into expected flow patterns. Statistical aspects are introduced here, concerning collision frequency and the distribution of doublet lives. The phenomenon of non-separating doublets is explained. Extensions to Poiseuille flow, to rods and disks, to deformable drops and to electrical effects are given. Up to this point theoretical predictions prove to be remarkably accurate. Then the behaviour of concentrated suspensions is described, with particular attention paid to steady-state orientation distributions for rods and disks.

The relation between observed suspension viscosities and the effects described earlier is considered, particular attention being paid to creeping flow migration effects in measuring equipment. Inertial effects are then considered; here theory is less able to predict observed effects, though clearly advances are currently being made. The chapter ends with a stimulating description of blood rheology, meticulous attention being paid to describing the formation of rouleaux (strings of red cells) and the deformation of single red cells in narrow capillaries.

The whole chapter is a gem. Written with great care, it is far more than a review. It has coherence and unity of style, and displays a profound understanding of the field covered. There are almost no gaps and no ambiguities in the treatment given, although it is clear at the end that there are still many directions to explore. It is surely no coincidence that recent developments in the subject have come largely from Professor Mason's own department; in effect, we are treated to an interim though considered verdict on some fifteen years' carefully organized work.

A. Bondi contributes a long chapter on viscosity and molecular structure. This is concerned with non-polymeric materials, and so the simple Newtonian concept of viscosity suffices. The variation of viscosity with temperature is the observable effect under consideration. It is interpreted in terms of molecular motions, details of which can be gleaned either by "direct observation, i.e. through the measurement of the relaxation times of nuclear magnetic resonance absorption and of electric dipole orientation" or by "analysis of equilibrium properties, such as density and heat capacity, by means of molecular theory". The author's aim is to bring up to date the earlier review given in volume I (published in 1956). Theories are considered largely from the chemist's point of view; the functions or quantities that are introduced are the radial distribution function of molecules, the potential function determining the forces between molecules, the deformation factor (for the pair correlation function) due to the flow field, various activation energies and standard thermodynamic variables. The object is to bring order into the mass of data available, so separate consideration is given to rigid non-polar molecules, rigid polar molecules, large ring compounds and flexible molecules. Though not of immediate importance to most fluid mechanicists, the account seems exhaustive and carefully written and could be used as an introduction to molecular effects in fluid flow.

The third substantial chapter is on non-linear steady-flow behaviour by H. Markovitz. This covers, to a large extent, ground already covered in many other texts and articles, three of which have previously been reviewed in this *Journal* (**16**, 313; **25**, 638; **28**, 205). The mathematical foundations of a general continuum theory of fluids are briefly described, but using Cartesian tensors for simplicity: the basic principles of co-ordinate invariance, isotropy and material indifference, as they apply to the formulation of constitutive equations; some simple examples, including the simple or memory fluid and the approximations that follows for slow flows and small deformation flows. The special case of viscometric flows is then considered in detail both theoretically and experimentally, with greatest emphasis on the measurement of normal stress differences using couette and cone-and-plate apparatus. Most of the results quoted are for polyisobutylene in cetane or decalin. Attention is given to sources of error in measurement, such as alignment error or rim effects. There is no consideration of extensional flows and little of more general shear flows. The term steady-state in the chapter title has been interpreted in a strictly rheological sense (i.e. as constant stretch history) rather than in the fluid-mechanical sense of 'Eulerian' steadiness. Given its objects, the chapter is well written and well laid out.

High shear viscometry, a topic of great current interest and industrial importance, is dealt with rather cursorily and a little erratically by A. Ram. He stresses the concept of ultimate Newtonian viscosity (a limit attained at sufficiently high shear rates) while pointing out that attempts to achieve such shear rates experimentally lead to various forms of unsteady behaviour: high Reynolds number turbulence (including drag reduction), structural turbulence (noted in the twenties by various workers using polymer solutions) and elastic turbulence, or melt fracture (a more recently investigated phenomenon characteristic of high viscosity melts or concentrated solution). Although he quotes many references, I found his account lacked cohesion and insight.

J. T. Bergen contributes a chapter on the mixing of plastics compounds. This represents a rather specialized line of approach developed by plastics technologists, and is rather elementary. Readers familiar with G. I. Taylor's and G. K. Batchelor's contributions to the fundamentals of the subject—ideas taken up by P. V. Danckwerts (to whom reference is made)—will find the treatment a little disappointing, because it is primarily restricted to steady laminar flows. Equally specialized is the short chapter by H. F. Mark on melt spinning, which is unique in that it barely makes any use of references.

The rheology of liquid crystals, a subject only now being systematically treated by continuum mechanical methods, is described by R. S. Porter and J. F. Johnson. They start by attempting a definition of liquid crystals (which can occur in either pure materials or solutions) and distinguish diagrammatically between three main types: nematic, smectic and cholesteric. Then they turn to a review of past work that is concerned largely with viscosities (measured either in rotational or capillary instruments) and their interpretation in purely molecular terms. Flow theories referred to are those of Kirkwood, Kuhn & Kuhn, Zimm. They conclude "An adequate, complete rheological theory of mesophase types has yet to be developed. Even the mechanism responsible for non-Newtonian flow of cholesteric and smectic mesophases is yet to be defined. Our understanding of the nematic mesophase is on a considerably sounder foundation." Readers of this *Journal* may find the emphasis of the chapter rather too biased towards chemical structure from their point of view.

The last two chapters can be considered together. W. H. Bauer and E. A. Collins give a very readable and unmathematical survey of thixotropy and dilatancy. Clearly they have sympathy for the straightforward physical descriptions, given by earlier workers, of the interesting changes of state that take place when various dispersions are strained; in particular of the gel–sol reversible transition. They incline towards a historical (i.e. chronological) treatment, noting the elaboration in concepts that were required. Material behaviour is expressed by means of simple plots of shear stress *vs* shear rate, the curves obtained being parametric functions of time and thereby being functions of the strain and rate of strain history. Those familiar with modern continuum mechanics, e.g. as described by Markovitz, may deduce—if they are so minded—an almost historical inevitability in the development of 'hard' mathematical theories for the 'softer' experimental observations. I found it a pleasing chapter, firmly bedded in the observed behaviour of real materials, inclusive rather than narrowly selective, yet with an eye to later more formal developments. In particular, the authors deal firmly with the question of terminology: where the same term has been used by many earlier workers to describe quite different effects (each supposing his definition to be uniquely precise, of course!), then they point this out, neither in sorrow nor in anger; where a reasonably consistent interpretation can be put on a term, then they say so and adopt it; above all, they adopt a pragmatic approach seeking enlightenment wherever and however it can be found.

M. Reiner and G. W. Scott Blair, no doubt after years of frustration, adopt a different solution to what is basically the same problem. They attempt a dictionary-style treatment of rheological terminology. For as they not unreasonably point out, "nothing can cause more misunderstanding and confusion in scientific communications than a lack of agreement over the use of technical terms". Splendid sentiment and here, I thought, was the opportunity to find my way through the intricacies of thixotropy, dilatancy, structural viscosity, shear thinning and so on. So, first I turned to the preliminary discussion (§ II), where I had noted a paragraph devoted to *structural viscosity*. It read:

> This term requires some explanation. It has been our policy throughout the making of our dictionary to choose definitions that define phenomena without implication of any theories about their origins. When Ostwald introduced the term *Strukturviskositaet*, he certainly thought in terms of a postulated breaking down of structures within a material. Moreover, at first sight it might seem that the English equivalent, 'structural viscosity', is no more than a synonym for *shear thinning*. There are occasions, however, when the latter term, although strictly correct, would be misleading such as in an experiment in which the rate of shear of, say, a damped pendulum is progressively falling and the consistency correspondingly rising. We base our retention of 'structural viscosity' on the fact that it is the viscosity, and not necessarily the material, that has a structure and would support this by quoting the *Shorter Oxford Dictionary's* third definition of *structural*: 'Of or pertaining to the arrangement and mutual relation of the parts of any complex unity.'

In the dictionary, however, we read

> *structural viscosity* the property of an Ostwald curve (see *Shear thinning, shear thickening*, § II);

following on I discovered

> *Ostwald curve* the consistency curve of an inelastic shear thinning, non-Newtonian liquid approaching a straight line, which extrapolates to the origin at high rates of shear

> *consistency curve* a curve of rate of shear versus shearing stress in a deformation.

I decided to settle for

> *shear thinning* a univalued reduction of the viscosity or consistency with increasing rate of shear (see *Shear thinning* (sic), *shear thickening* and *Thixotropy, rheopexy*, § II)

but remained unconvinced from this and other examples I met that agreement on the use of technical terms in rheology was thereby likely to be furthered.

The most important overall impressions that are given by all five volumes in this series are of the vast range of topics studied under the title of rheology and of the disappointing disconnectedness of the many contributions. One is forced to conclude either that the subject is now too wide to be treated as a whole or that it still lacks a unifying theme. Both conclusions are to some extent justified: on the one hand, it is clear that some rather specialized industrial applications of deformation theory, important as they were in kindling interest in the subject, should no longer be central preoccupations of rheologists as a group; on the other, it is equally clear that neither the proponents of formal mathematical continuum theories nor the molecular determinists nor even the pragmatic phenomenologists have succeeded in providing, on their own, a conceptual framework that is adequate for understanding gross material behaviour.

Can any unifying characteristic be discerned in real examples of complex rheological behaviour? It is not unreasonable to suggest two- (or multi-) phase effects as the most important common factor; if the material is a fluid and departures from Newtonian behaviour are to be pronounced, then we may expect the 'dispersed' phase to possess a structure. This definition need only eliminate pure liquids of low molecular weight and dry granular media. It could, however, include: (i) suspensions of solids, particularly where the particle concentration is high enough for some order (i.e. a structure) to be imposed on the particulate dispersion under shear; (ii) suspensions of liquid droplets, where surface tension is the source of structure; (iii) gels, where short-range forces between dissolved molecules suffice to introduce a matrix-like structure; (iv) colloids, where electrical forces are significant; (v) polymer networks, whether molten or rubbery, where crystallinity, cross-linking, aggregation and entanglement are all forms of structure. An alternative way of looking at the situation is to suppose that a hierarchy of structures exists. There exist already many theories, put forward to cover such situations: continuum theories of mixtures, of polar fluids, of orientable fluids; statistical theories of suspensions based on individual particle dynamics, or of polymer solutions based on chain segment dynamics. At present these tend to be regarded as peripheral outgrowths of basic rheology, the centre of the stage being held by the Oldroyd–Rivlin–Ericksen–Noll concept of the memory fluid (as discussed by Markovitz in chapter 6) and by the simpler but related one-dimensional mechanical models (given pride of place by Reiner and Scott Blair in chapter 9). The weakness of the latter, presently dominant, group of theories is that they avoid, deliberately, any detailed consideration of the way the stress within a deforming material is distributed between and within the *diverse* elements constituting the material. It is surely the interactions between the various elements that are the key to complex rheological behaviour, and so the most effective mathematical models are likely to be those that make use of this. I should like to think that later volumes of Rheology will contain accounts of progress made in this direction.

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