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Dynamics of Complex Flow

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Problems of the flow of complex suspensions or melt materials and powders are classified according to the existence of exact formulations and of useful models. Regimes of interest are classified into dilute, entangled, and packed, and the difficulties and sucesses of the different types of objects and the different types of regimes are studied. Particular notice is taken of situations where a phase change is found between regimes.

KEY WORDS: Melt rheology; polymer dynamics; granular flow; powder rheology.

1. TYPES AND REGIMES

I will study three types of objects in a complex flow, and three regimes. The types are: (1) rods (liquid crystal molecules), (2) flexible (or semiflexible) polymers, and (3) shapes (soft and hard). The regimes are (1) dilute, i.e., each object is far away from every other compared to its own size and hydrodynamic influence; (2) entangled, i.e., objects do sense their neighbors, but still have substantial freedom to move; and (3) packed, i.e., each object is in permanent contact with others. To these one can add the solid version of regime 3, which is glass.

At first sight these regime divisions may seem arbitrary, but in several cases there is a phase change between the flows loosely defined as an abrupt change in behavior, and even when there is not, they define areas where effective approximations can be made. The following questions arise concerning the types and regimes:

(α) Is there a mathematically exact description available, and in particular, is here a useful exact description?

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(β) Is there a useful model, i.e., a simplification which contains enough of reality to answer question α?

(γ) Are there solutions to α and β?

(δ) Is it possible to simulate the systems so as to produce a check on theory, since experiment is often difficult to characterize clearly?

I will now give a commentary on the current state of affairs as I see it. (This is not a review paper—it is a personal view; the reader will find a much broader treatment in the other papers of this conference.)

2. RODS

(a) The dilute case has been solved long ago (see ref. 1, Chapter 8, for review).

(b) The entangled case seems adequately handled by assuming a tube model, i.e., representing the cage of neighboring rods as a cylinder from which a particular rod escapes by Browman motion and thus relaxes stress. The original constitutive equation coming from this model is reviewed in the book of Doi and Edwards.(1) It has been meticulously developed by Rallison(2) and is standing up well. The viscosity goes like rod length to the ninth power, and certainly very high viscosities are found.

An enormously more complex system is now emerging with modern chemical synthesis. For example, Aharoni and Edwards(3) synthesized hinged rods by the Yamazaki pathway and one can see intuitively that the viscoelasticity of the situation depicted in Fig. 1 is very different from that in Fig. 2 (the dots represent other rods passing through the plane, which are not easy to draw). The molecule in Fig. 1 is locked and is only released if the confining rods move. If they are rods, one can work it out, but if they also are flails, then the system locks. Remarkable new materials can be now envisaged.

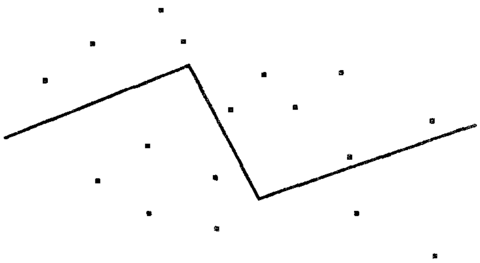

Fig. 1

Fig. 2

This discussion has ignored nematicity, and it is possible to find such regimes. In general, however, nematicity will arise and domains of parallel rods, in flow, offer a real challenge. New work by Marrucci(4) addresses this problem.

I feel sure that there will be a phase change between the dilute and entangled regimes, but there is no experimental study of this region, principally because of the competition of nematicity.

(c) The packed case of rods is not very accessible experimentally, but is of outstanding interest theoretically, for, since every rod is tightly enclosed by neighbors, it is possible to use mean field theory rigorously, and hence find a soluble model of the glass transition. The simplest approach has been studied by Edwards and Evans,(5) who solve the diffusion of a rod where motion is blocked by other rods. They find, on the assumption that the blocking rod is uncorrelated with the rod it is blocking, that

$$D = D_0(1-\alpha)$$

where α is T_g/T or V_g/V, etc. If cooperation is allowed, i.e., processes like those in Fig. 3, then one has

$$D = D_0 e^{\{A/(1-\alpha)\}}$$

which is Vogel–Fulcher–Dolittle law.

Thus the essential singularity of the glass transition can be identified with the fact that as $T \rightarrow T_g$ only cooperative motion involving more and more molecules is permitted.

The simulation of rod systems is discussed in ref. 6.

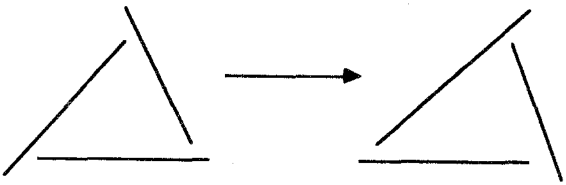

Fig. 3

3. POLYMERS

Already in the dilute case a single chain has a topological problem, for these two configurations can only be interchanged very slowly (see Fig. 4), but it appears from the vast amount of experimental data that this just renormalizes the constants which would obtain if the chain was considered to be invisible to itself, i.e., able to pass directly between, for example, the configurations sketched in Fig. 4.

Hydrodynamic effects are screened out in the entangled regime, so that the viscosity gradually changes from $M^{1/2}$ to CM, where M is the molecular weight and C the concentration. However, as the concentration further increases, there is a phase change up to $M^{3.4}$, where M^3 is easily explained by reptation down the tube, but the remaining 0.4 has varying explanations.

It is possible to write the exact equations for the Brownian motion of polymers, modeled as curves $R(s, t)$, s being the arc length. The distribution of chains P, in equilibrium, is

$$\exp\left[-\frac{3}{2l}\sum_i \int_0^L \mathbf{R}_i'^2(s)\,ds - \sum_{i,j}\int_0^L\int_0^L W(\mathbf{R}_i(s_i)-\mathbf{R}_j(s_j))\,ds_i\,ds_j\right]$$

and this is the equilibrium solution of

$$\left(\frac{\partial}{\partial t}-\sum_{ij}\iint\frac{\partial}{\partial r_i(s_i)}G([r_i][r_j])\left(\frac{\partial}{\partial r_j(s_j)}+\frac{3}{l}\frac{\partial^2 r_j}{\partial s_j^2}+\sum_k \nabla_j\int W\right)\right)P=0$$

where G is the Oseen hydrodynamic tensor and l the Kuhn length. Rather remarkably, this equation conserves topology and gives an exact basis of polymer hydrodynamics. However, it seems impossible to solve directly. If G is averaged, it gives Zimm's preaveraged equation, which is satisfactory below the transition, but cannot describe the tube model which is essential

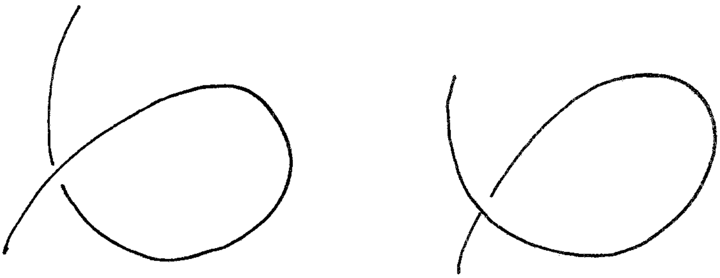

Fig. 4

above the transition to the 3:4 regime. Above the transition there are many effective applications of the idea that the polymer has to reptate by Brownian motion in a tube, and these are reviewed in ref. 1. There has not been much attention paid to the problem of the phase change between the M and $M^{3.4}$ regimes, probably because it is difficult to do convincing experiments right at the transition. However simple models can be offered(7) and the further transition to the glass regime has been much studied.(8 10)

Simulation of the packed polymer problem is bedevilled by the immense amount of computer time involved, and I find myself very skeptical of much work purporting to resolve this issue. There is no doubt that with a fixed background polymers reptate correctly, and the longest computations so far(11) support this.

Some interesting new results of Baumgartner and Muthukumar(12) suggest that under appropriate conditions, disordered background interaction can give the polymer localized states and a theoretical basis for this can be found.(13 16) The mathematics resembles that for the Anderson localization in semiconductors; it is too early to see whether this will prove an important issue in viscoelastic models.

4. SHAPES

4.1. Soft

Shapes can have complex internal structure, but the simplest model is to say that the energy is solely a function of surface area and that the blob of material is incompressible and of integrity. In this case an analogous exact equation is available for the evolution of the shape and movement of all the blobs given by

$$\psi(\mathbf{r}, t) = 0$$

The coupled equations in low-Reynolds-number flow with viscosity ν for a fluid velocity $v(r, t)$ and ψ are

$$\frac{\partial v}{\partial t} + (v \cdot \nabla) v = \frac{1}{m\rho} \frac{\partial}{\partial t} (\mu \nabla\psi) - \frac{1}{m\rho} \nabla\rho + \nu \nabla^2 v$$

where μ is a Lagrange multiplier satisfying

$$\frac{\partial \mu}{\partial t} + v \cdot \nabla\mu = -\lambda \nabla \cdot (\nabla\psi / |\nabla\psi|)$$

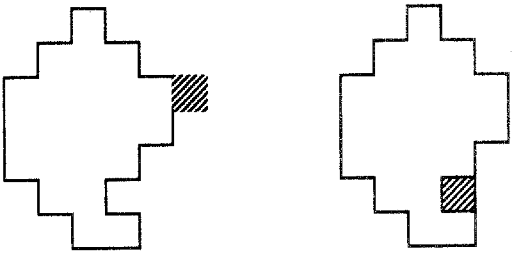

Fig. 5

and these equations can be checked to obtain Taylor's answer for the (near spherical) dilute case.(17) However, they suffer the same problem as the polymer equations in concentrated suspensions, in that approximations destroy the ability of the equations to preserve the integrity of the blobs of material when they collide. An alternative attack is to simulate blob flow, and this has some success by using a Monte Carlo method (e.g., see Fig. 5).

For highly concentrated blobs, which are the analogue of the polymer melt, the problem now resembles foams, in that the pattern of flow is dominated by changes in the number of faces of the closely packed polyhedra.

In Fig. 6, side a shrinks to zero and is replaced by a new side b.

The mathematics of this has not yet been resolved, principally because the intense correlations do not seem to point to any easy and convincing model.

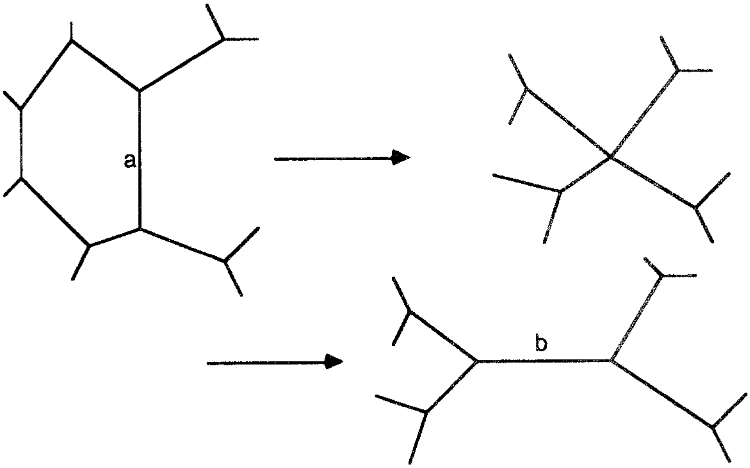

Fig. 6

4.2. Hard Shapes

Hard shapes are powders. This problem requires some development of the fundamental basis of its statistical mechanics before flow problems can be attempted. The key issue is that there must be an intensive quantity which describes how different powders partition a joint space available to them just as temperature partitions energy between materials in thermal contact. The dilatancy available to powders, i.e., the fact that a given amount of material can occupy a variable volume, means that volume for powders takes the role of energy in thermodynamic systems. A powder has an entropy, of course, being the logarithm of the number of ways the powder can be assembled to occupy a definite space. Thus, by exactly the arguments underlying statistical mechanics, we are led to the equivalent formula that the analogue of temperature, which I call the compactivity X, is given by

$$X = \partial V / \partial S$$

$$S = \lambda \log \Omega, \qquad \Omega = \int \delta(V - W)$$

where W is the function which gives the volume in terms of the coordinates and orientation of the powder grains and λ an analogue of Boltzmann's constant which converts entropy into volume. As usual, it is more convenient to go to the canonical ensemble and introduce an effective volume Y which is the analogue of free energy,

$$\exp(-Y/\lambda X) = \int e^{\quad W/\lambda X} \, d(\mathrm{all})$$

$$V = Y - X \frac{\partial Y}{\partial X}$$

As an example,(18) suppose we have a mixture of two powders A and B and make the very simplest assumption that a contribution to the final volume is made by every pair of powder particles according to whether the pair is AA, AB, or BB. Then W has the form of the Bragg–Williams theory of alloys with the crucial quantity

$$v = v_{\mathrm{AA}} + v_{\mathrm{BB}} - 2v_{\mathrm{AB}}$$

If this is negative, the powders A and B are miscible, but is if $v > 0$, then there will be a surplus of A over B, ϕ say, where the Bragg–Williams mean field equation is

$$\phi = \tanh v\phi / \lambda X$$

The mixture is critical at $X = v/\lambda$, where ϕ commences becoming nonvanishing. At this level of compactivity the powder generates A-rich or B-rich domains, until ultimately it will separate at $X = 0$ into pure A and pure B. Another example of the use of these concepts is to calculate v in terms of X using a variety of models, using material in the statistical mechanical literature.(18, 19)

One can now attempt phenomenological equations for powder flow. Just as a liquid is determined by the equations of continuity, fluid velocity, and temperature, one can aim at equations for ρ, v, and X. Powders flow like liquids, so there ought to be a family resemblance.

The first two equations, continuity and Navier–Stokes, look just the same, with a constitutive equation for the stress tensor which one can argue will be dependent on X, i.e.,

$$p_{ij} = \frac{\partial}{\partial x_i} = \mu_1(X) v_j + \frac{\partial}{\partial x_j} \mu_2(X) v_i$$

Here the viscosities μ can be expected to look something like $1/X$, because $X = \infty$ corresponds to the powder breaking up at the minimum density, where μ is zero, whereas $X = 0$ is the maximum random close packing, where μ is infinite. The equation for X will have a form like

$$\frac{\partial X}{\partial t} + v \cdot \nabla X + A(X) = \alpha \dot{\gamma}_{ii} + \beta \dot{\gamma}_{ii} \dot{\gamma}_{jj} + \varepsilon \dot{\gamma}_{ij} \dot{\gamma}_{ji} + \cdots$$

where $\dot{\gamma}_{ij}$ is the strain rate $\frac{1}{2}(\partial v_i/\partial x_j + \partial u_j/\partial x_i)$ and $A(X)$ an appropriate function to return X to a steady value when γ is zero. The simplest argument would give $A(X)$ equal to aX, thus assuming the powder would become close packed when forces were removed (it would not of course, but I do not have space here to discuss more realistic statements). The terms in $\dot{\gamma}$ and $\dot{\gamma}\dot{\gamma}$ represent the extent to which the powder is "frothed" by shear and by compression.

Such equations show very interesting descriptions of, for example, the transition to plug flow from a nonmonotonic stress/strain rate relationship. Thus, the equations above predict where plug flow commences. I feel a microscopic, as against phenomenological, derivation of them will produce new features.

Finally, simulation of powders is producing very interesting new results(18 20) which offer a challenge for the analytic theories to explain.

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