DO WE UNDERSTAND THE PHYSICS IN THE CONSTITUTIVE EQUATION ?

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Summary

The failure of some careful attempts to provide numerical solutions of the equations for non-Newtonian flow suggests to us some inadequacies of the constitutive equations. (After all no one would doubt the validity of the conservation of mass and momentum.) To understand the physics in the constitutive equation, and thence to correct its undesirable features, it is helpful to look at a micro-structural model which leads to the constitutive equation. The bead-and-spring dumbbell model for a dilute polymer solution leads to an Oldroyd-like equation.

The simplest version of the bead-and-spring model has a linear spring and a constant friction coefficient for the beads. While this model is simple and usefully combines viscous and elastic behaviour, it has the very unphysical feature of blowing up in strong straining flows (i.e at a Deborah number in excess of unity), with the spring lengthening indefinitely in time and the steady extensional viscosity becoming unbounded at a critical flow strength. The hope that the corresponding large stresses would not occur in a flow calculation seems to have been misguided: some simple examples show that the large stresses may not act through the momentum equation to inhibit the flow.

To cure this unphysical behaviour one clearly needs to use a non-linear spring force which gives a finite limit to the extension. Incorporating this modification into the constitutive equation enables the numerical solution of (some) flow problems to proceed to large Deborah numbers. Care is of course still needed in the numerical calculations, for example in resolving thin layers of high stress. (A boundary layer theory needs to be developed for the nonlinearity introduced by the non-Newtonianness.)

A further modification of the bead-and-spring model may be necessary if agreement is sought between numerical calculations and experiments. Many

flows of interest subject the fluid to a sudden strong strain. In such circumstances the polymer chains will not be in thermodynamic equilibrium and so will not give the standard entropic spring. It may be possible to model this behaviour by a large temporary internal viscosity.

1. Introduction

Ten years ago it appeared to us that the problem experienced in computing non-Newtonian flows at Deborah numbers greater than unity was due to poor numerical techniques. But there have now been some very careful numerical studies (Crochet et al. [1]), all getting into trouble at a Deborah number of order one. There are also other disturbing signs. Phan-Thien and Walsh's study [2] of an Oldroyd-B fluid in a squeeze film has the (steady) solution breaking down at a finite Deborah number. Yeh et al.'s [3] numerical study of a two-dimensional 4:1 contraction shows limit points at a critical Deborah number. Hence in our opinion the governing equations themselves must be under suspicion.

Now no one is going to doubt the validity of the conservation of mass and of momentum. Thus the finger must point to a fundamental difficulty with the constitutive equation. The constitutive equation most commonly employed is an Oldroyd equation. This equation is simple, with just a few parameters and has the simplest combination of elastic and viscous effects. There is certainly no point in contemplating any more complicated constitutive equation until one can first compute flows with such a simple rheological equation.

Unfortunately the Oldroyd equation has problems in steady pure-straining flows. The extensional viscosity increases to infinity as a critical strain-rate is approached. It has been argued that this undesirable property will never cause a problem, because with a finite force available any real flow will adapt in order to avoid an infinite stress. These hopes are ill-founded. In a spinning problem, Hinch [4] has shown that the stress grows with no steady state. More intriguingly it is shown in Section 3 that an infinite stress can occur in the interior of a steady flow. This stress may have zero divergence in which case the flow is unaffected. Alternatively, the divergence may be infinite, but sufficiently limited in space that there is a negligible effect on the flow. These infinite stresses are unphysical, because they arise from infinitely stretched polymers in a region of flow with finite strain rate. Furthermore unless they can be smoothed appropriately they will inevitably give rise to computational difficulties.

Hence we need to understand the constitutive equation used in any flow calculation, its *limitations and merits*. Rather than studying the rheological performance and mathematical structure of the coupled flow equations, we prefer to retreat to some physical model of the microstructure which generates the constitutive equation. Here we consider bead-and-spring models of polymer solutions. We do not believe these simple models can represent a polymer solution perfectly, but on the other hand some aspects of the model will apply to other more sophisticated deformable microstructures. The aim is to understand to the physical behaviour of the model and thereby understand which desirable features have been included and which have been omitted in various versions. Hence the title of this paper.

2. The bead-and-spring dumbbell model

This model was originally introduced by Kramers [5] for *dilute* polymer solutions, i.e. no overlapping of the polymers $c < c* = 1/[\mu]$. A full discussion is given by Bird et al., [6]. The model represents only the gross distortion of the macromolecule by the vector R or its expectation $A = \langle RR \rangle$, so that the distorted macromolecule is effectively represented by its moment of inertia tensor.

The distorting effect of the imposed flow is incorporated by calculating the opposing viscous drag forces on the two halves of the macromolecule. Using the Stokes drag law, this force will be a friction coefficient $6\pi\mu a$ times the slip velocity of the end of the vector R relative to the imposed flow, i.e. $R \cdot \nabla u - \dot{R}$. Because hydrodynamic interactions between all parts of the polymer are strong, we use for the bead size a the radius of gyration of the undistorted macromolecule, $b \times (N/6)^{1/2}$, where b is the bond size of a single monomer and N is the number of monomers in the polymer (the degree of polymerisation). If the polymer is not in a theta solvent, then excluded volume effects increase the purely random walk $N^{1/2}$ to something nearer to $N^{0.6}$.

Under the action of rapid Brownian motions of the whole polymer chain, the randomly coiled macromolecule tries to have an isotropic spherical envelope. This is represented by a restoring spring force acting to reduce the distortion R. In the simplest model the force law is taken to be linear, proportional to the length of the vector, R with a spring constant $\kappa = 3kT/Nb^2$.

Hence we have derived the governing equation for the vector R

$$\dot{R} = R \cdot \nabla u - \lambda R, \tag{1}$$

where $\lambda = 0.4kT/\mu b^3 N^{1.5}$ is the relaxation rate (for the gross distortion).

By adding Brownian motion for the beads we can form an equation for the second moment $A = \langle RR \rangle$, which can be thought of as the moment of inertia tensor of the molecule

$$\delta A / \delta t \equiv DA / Dt - A \cdot \nabla u - \nabla u^T \cdot A = -2\lambda [A - (a^2/3)I], \qquad (2)$$

where $\delta / \delta t$ is an Oldroyd time derivative (which is the rate of change seen by an observer advecting with the bulk flow and also rotating and deforming with the flow).

To complete the governing equations we need a relation between the stress and the deformed microstructure. This is obtained by counting the number of springs cutting a surface area element

$$\sigma = -pI + \mu (\nabla u + \nabla u^T) + \tau, \qquad (3)$$

with

$$\tau = n\kappa [A - (a^2/3)I], \qquad (4)$$

where n is the number of polymer molecules per unit volume.

Now it is possible to take the Oldroyd derivative of the stress and then use the microstructure equation to obtain a standard Oldroyd fluid

$$(\delta / \delta t + 2\lambda)\sigma' = (\delta / \delta t + 2\lambda_2)2\mu(1 + c)E,$$

where σ' differs from σ by an isotropic pressure, E is the strain-rate and

$\lambda_2 = \lambda / (1 + c)$ with $c = n\pi a^3$.

Here c is an effective volume concentration of the polymers, and for a dilute solution c is small. Although it is possible to eliminate the microstructure variable A and form a single standard constitutive equation as above, we prefer in what follows not to suppress a central feature of the problem by making this substitution.

The rheological behaviour of this Oldroyd equation is well-known. In steady simple shear flow, the effective viscosity is constant, the first-normal-stress difference increases quadratically with shear-rate, and there is no second-normal-stress difference. In steady pure straining motion, the extensional viscosity increases with strain-rate, becoming infinite at the finite critical strain-rate $E_c = \lambda$. While the shear flow response is not quite correct, the straining motion response is very unrealistic.

In order to understand the unacceptable rheological response, and hence see a cure, it is prudent to look at the microstructural behaviour. In steady simple shear the macromolecule stretches to a length proportional to the shear-rate becoming more and more aligned with the direction of the flow. In pure straining motion, the macromolecule stretches by a finite amount at sub-critical strain-rates, but stretches indefinitely in time at super-critical

strain-rates. From eqn. (1), it is obvious that the polymer length will extend indefinitely if $|\nabla u| > \lambda$. Note that the case of pure straining motion is typical of almost all flows—strictly, any flow whose velocity gradient has an eigenvalue which has a positive real part [7].

There are many possible refinements of the crude bead-and-spring dumb-bell model. The most urgent one is to stop the macromolecule stretching indefinitely. This is accomplished by making the spring law non-linear with some finite limit to the extension. Modifications to the friction law to reflect (a) the distortion of the polymer and (b) the distributed friction force will also be discussed. Other refinements which we mention in passing are (i) to take a polydisperse solution of polymer molecules each with different relaxation times, and (ii) to give the polymer some internal structure with N linearly connected beads-and-springs (this linear structure has the correct spectrum of relaxation times in a mono-disperse solution). These last two refinements may be necessary if flow computations are to predict accurately the flow of specific polymer solutions. For the present, however, they are clearly inessential. In the final section another modification, which is more tentative, but which may be even more important in understanding the flow of real materials, will be introduced.

2.1 Non-linear spring

The linear spring law used in the first crude model is appropriate for small distortions of the macromolecule. The 'correct' non-linear law, at least for a linear chain of freely-hinged bonds in a theta solvent, is the inverse Langevin force $F = kT/b\mathscr{L}^{-1}(R/Nb)$, where $\mathscr{L}(x) = \coth x - 1/x$ [8]. This law limits the extension to $R < L = Nb$. Given the complications of a real macromolecule, we adopt instead the simple non-linear law with a finite extension $F = R \times 3kT/Nb^2/(1 - R^2/L^2)$. An even simpler law would be the linear-locked law which takes the linear from up to $R = L$, at which point the restoring force becomes whatever is necessary to stop the extension exceeding L.

To implement our preferred non-linear spring law, λ should be replaced by $\lambda/(1 - R^2/L^2)$ in the microstructure eqn. (2) and the κ should be replaced by $\kappa/(1 - R^2/L^2)$ in the expression for the stress (4). Thus

$$\delta A/\delta t = -2\lambda \left[A - (a^2/3)I \right]/(1 - \mathrm{tr}(A)/L^2), \tag{5}$$

$$\tau = n\kappa \left[A - (a^2/3)I \right]/(1 - \mathrm{tr}(A)/L^2), \tag{6}$$

where tr is the trace.

With any of these spring laws the polymer behaves reasonably: its response at small distortions is virtually identical to the linear spring law

(because the undistorted size is much smaller than the full extended length, $a \ll L$), but there is now a limit to the large distortions.

The rheological consequence of the finite-extensibility is to make the extensional viscosity tend to a finite limit $\mu(1 + naL^2)$ at high strain-rates. Computations of strong flows can now proceed to high Deborah numbers (see e.g. Chilcott and Rallison [9]). In simple shear there is a small degree of shear-thinning, but only at very high shear-rates ($\lambda L/a$). The growth of the primary normal-stress-difference is also controlled at these high shear-rates.

2.2 Non-linear friction

As the distortion of the polymer increases, the size of the object on which the flow exerts its frictional force grows [7]. For viscous flows (low Reynolds numbers) the frictional force grows with the largest linear dimension of the object. It should be noted that the frictional force on a long slender rod of length $2L$ and thickness d is the same as that on a sphere of radius $4L/3 \log(L/d)$. An alternative way of expressing this change in the friction factor is to say that the as the polymer becomes extended, the hydrodynamic shielding of the interior of the random coil is reduced, and so the hydrodynamics changes from Zimm-like towards Rouse-like. A simple way of modifying the friction factor, is to replace λ in the microstructure equation by $\lambda a/\mathrm{tr}(A)^{1/2}$.

The rheological consequences of the increasing friction factor are first to increase the high strain-rate extensional viscosity to $\mu(1 + nL^3)$. Second, a hysteresis in the extensional viscosity is introduced: a weaker flow is needed to maintain a highly stretched state than is required initially to stretch out the random coil. Strictly speaking this hysteresis is only an apparent one—in a true steady state there would be a steady distribution of dumbbells between the two stable equilibria, but the time taken to achieve the steady distribution can be too long to be of interest in practice.

In simple shear flow the change in the friction factor can lead to a shear-thickening viscosity. This unwanted behaviour reflects how odd simple shear flow is, and how sensitive predictions for simple shear are to the details of the model. The behaviour may be corrected by a further, minor modification.

2.3 Rotation of the beads

In the crude bead-and-spring model the distorting frictional force on the polymer is calculated from the relative slip of the single point at the end of the vector $\boldsymbol{R}$. In reality, the hydrodynamic force is distributed all over the polymer chain. This problem is exposed by the behaviour in simple shear,

where the dumbbell aligns with the flow and thereafter does not rotate (except Brownian motion). In simple shear there should still be a turning couple exerted on the thick polymer when it is aligned with the flow.

A cure for this defect is to consider not only the force exerted on the beads but also the couple [10]. The beads are not allowed to rotate independently, but are joined rigidly to the spring. A couple balance on the beads and spring together then yields the rotation rate. With this modification the bead-and-spring rotates with the vorticity in the bulk flow, but with only a fraction of the straining motion. The efficiency of the straining motion increases with the distortion, and as for the rotation of a long slender rod becomes nearly 100% efficient when the distortion is large.

To incorporate this change in the response of the dumbbell to straining motion, the Oldroyd derivative in the microstructure equation should be replaced by

$$\mathcal{D}A/\mathcal{D}t + \left[\operatorname{tr}(A)/(\beta a^2 + \operatorname{tr}(A))\right]\left[E \cdot A + A \cdot E\right],$$

where β is a numerical factor of order unity and $\mathcal{D}A/\mathcal{D}t = DA/Dt + \Omega \cdot A - A \cdot \Omega$ is the Jaumann derivative (which is the rate of change seen advected with the flow and rotating with the vorticity). The expression for the stress must also be modified by the inclusion of a term proportional to the inefficiency of the straining motion, i.e. an extra dissipation term

$$2\mu E\left[\beta a^2/(\beta a^2 + \operatorname{tr}(A))\right]n\left(\operatorname{tr}(A)\right)^{3/2}.$$

In simple shear flow the microstructure now tends at high shear-rates to a finite distortion which is comparable with the random coil size and not the fully extended size. This finite distortion aligns itself with the flow, effectively with the polymer itself rotating inside a stationary envelope. The material shear-thins by an $O(c)$ amount to a high shear-rate viscosity, thinning at shear-rates comparable with λ instead of the previous $\lambda L/a$. There is a new second normal-stress-difference, which is negative and about half the magnitude of the primary normal-stress-difference. At high shear-rates these normal-stress-differences tend to constant values. The rheological response is little changed in pure straining motion.

3. Problems with infinite extensibility

As mentioned in the introduction, it had been hoped in the past that the infinite extensional viscosity in the crude dumbbell model would never cause any problem in a computation of a flow because the flow would adapt to avoid the infinite stress. Some simple flow calculations show this not to be the case.

In a simplified calculation of the time-dependent behaviour of a dilute polymer solution in the spinning geometry, with a constant applied load, Hinch [4] found that although the extension rate was significantly reduced after a certain stage, the polymer molecules nevertheless continued to extend indefinitely. Initially the polymer molecules had no effect on the flow, because they were started from the undistorted state and the solution was assumed to be dilute. A little after the strain-rate exceeded λ, the polymers were sufficiently stretched to contribute to the stress significantly. At this point the strain-rate fell dramatically, because the polymer molecules would otherwise continue to stretch rapidly and thereby produce a stress larger than the fixed applied load divided by the local area. This magnitude of the sudden drop in the strain-rate was found to be inversely proportional to the the square of the diluteness. There then followed a slow evolution with the stress provided by the polymers which were prevented from relaxing by a weak strain-rate. As this strain-rate reduced the area, the stress increased and so the polymers stretched indefinitely.

A second example is provided by the steady plane extensional flow generated at the centre of a 4-roller device, which has been investigated experimentally by Leal [11] and Dunlap and Leal [12] and others (see the references in Leal's paper). A flow field with similar elongational characteristics is also produced by a cross-slit device, see experiments of Gardner et al. [13], and also the low-D numerical solution of Perera et al. [14]. Consider first the simplified problem of homogeneous flow with constant strain-rate E so that, *if the flow were unperturbed by the polymer,* the fluid velocity would be

$$u = Ex, \qquad v = -Ey.$$

Suppose further that the polymers are unstretched at $y = y_0$ (notionally the point at which they enter the region of homogeneous flow in the 4-roller device). Then eqn. (1) gives

$$\dot{R} = (E - \lambda)R \text{ and } R = a \text{ at } y = y_0.$$

Now along the hyperbolic trajectories of the molecules $x = x_0 \, e^{Et}$, $y = y_0 \, e^{-Et}$ and so

$$R = a \, e^{(E-\lambda)t} = a(y/y_0)^{(\lambda/E-1)},$$

giving an elastic stress

$$\tau_{11} = na^2\kappa(y/y_0)^{(2\lambda/E-2)}.$$

Thus if the Deborah number $D = E/2\lambda$ exceeds $1/2$, then $\tau_{11} \to \infty$ as $y \to 0$. Now the equation of motion for the fluid can be written

$$\rho(\partial u/\partial t + u \cdot \nabla u) = -\nabla p + \mu\nabla^2 u + \nabla \cdot \tau,$$

where ρ is the fluid density, and so in calculating the extra flow generated by this elastic stress only $\nabla \cdot \tau = \partial \tau_{11}/\partial x$ appears, and for this problem $\partial \tau_{11}/\partial x \equiv 0$. Thus although infinite (and unphysical) stresses occur they cannot inhibit the straining motion which gave rise to them.

This calculation, though revealing, is an oversimplification in that the independence from x formally requires that the region of constant straining extends to infinity. In the 4-roller flow field however the constant strain region is finite. The strain-rate along the x-axis is now $E(x)$, where E is stationary at $x = 0$ and varies weakly. Thus, as may easily be verified by numerical solution, the elastic stress in the region near the origin becomes

$$\tau_{11} = na^2\kappa(y/y_0)^{(2\lambda/E(0)-2)} \times (\text{function of } x),$$

and so has the same singular behaviour as $y \to 0$ if $D = E(0)/2\lambda > 1/2$. Now this elastic stress distribution has a non-zero divergence and so gives rise to an additional flow. At low-Reynolds-numbers, the inertial terms in the equation of motion are negligible and a point force f at position x gives rise to a (planar) viscous fluid velocity at x' proportional to both f and $\log|x - x'|$, hence the total perturbation to the flow generated by these elastic forces is

$$u^{\mathrm{E}}(x') = \int\int J \cdot e_x \frac{\partial \tau_{11}}{\partial x} \mathrm{d}x \, \mathrm{d}y, \tag{7}$$

where $J(x - x') \propto \log|x - x'|$ and e_x is a unit vector in the x-direction.

Now if $1/2 < D < 1$, the integral in (7) is convergent and hence proportional to n, which in a dilute solution is small. Thus the flow field suffers only a small perturbation and the kinematics which give rise to the infinite polymer stress are unaffected. (For $D > 1$, the y-integral no longer converges and thus however small n the flow *is* affected.)

We have thus demonstrated for linear dumbbells at low concentration a range of values for D in which stress infinities can exist but over so small a region that the singularities are integrable and the fluid velocity is everywhere finite. In our opinion such stress infinities (which arise from infinitely extended molecules) are unphysical and inevitably lead to computation difficulties (e.g. Perera et al. [14]). Such a phenomenon is likely to occur in any flow for which the strain-rate at a stagnation point can become super-critical, e.g. at the stagnation points on a gas bubble, or at a re-entrant corner in a flow.

4. Dumbbells with finite extensibility

We have noted above that infinitely extensible dumbbells can give rise to infinite stresses in strong flows such as occur in the 4-roll mill. Can

experimental observations of such a flow be reproduced—at any rate qualitatively—by a non-linear dumbbell model? Following the suggested modification of Section 2 we have

$$\dot{R} = ER - \lambda R/(1 - R^2/L^2),$$

so that while $R \ll L$ and $E > \lambda$, $R = a(y/y_0)^{(\lambda/E-1)}$ as before. But now this behaviour must cease for sufficiently small y when R becomes comparable with L, i.e. when

$$y/y_0 = (L/a)^{E/(\lambda - E)}.$$

Since the exponent is negative, if L is large this value of y is small. Now when R becomes comparable with L, R is necessarily small and so the dominant balance in the equation gives

$$1/(1 - R^2/L^2) \approx E/\lambda,$$

and thus the stress eqn. (4) gives

$$\sigma_{11} \propto \mu naL^2 E.$$

The proportionality between σ and E indicates that the net effect of the polymers is to provide a thin region of fluid of high viscosity μnaL^2 along the outgoing stagnation streamline with negligible influence on the stress elsewhere in the flow. A suggestion of the same kind for a flow with inertia has been made by Rabin et al. [15]. For a low-Reynolds-number flow, this viscous region can be regarded as a distribution of Stokeslets along the x-axis of strength

$$(L/a)^{E/(\lambda - E)} \times \frac{\partial}{\partial x}(naL^2 E(x)).$$

In consequence, the fluid velocity along the x-axis satisfies the integral equation

$$u(x) = u_0(x) + c\int (L/a)^m J(x - \xi)u''(\xi)\,d\xi, \tag{8}$$

where u_0 is the unperturbed Stokes flow, $J(x - \xi) \propto \log|x - \xi|$ is the fluid velocity produced by a point force (neglecting boundary effects), and $m = (2\lambda - E)/(\lambda - E)$.

Now in the dynamically important part of the flow the variation of E is small, and $E > 2\lambda$. In consequence as a first approximation the variation with x of the exponent m is negligible compared with the u'' term retained (especially if $E \gg 2\lambda$). We may then put

$$m = (2 - 2D)/(1 - 2D) \text{ where } D = E(0)/2\lambda,$$

and hence on integrating by parts

$$u(x) = u_0(x) - \alpha\int_{-\infty}^{\infty} \frac{1}{x - \xi}u'(\xi)\,d\xi,$$

where $\alpha = c(L/a)^m$ and $\int$ denotes the Cauchy principal value. Now taking Fourier transforms, we have by the convolution theorem

$$\tilde{u}(k) = \tilde{u}_0(k) - |k|\pi\alpha\tilde{u},$$

and so, since $u(x)$ is odd,

$$u(x) = -\frac{i}{\pi}\int_0^\infty \frac{\tilde{u}_0(k)\sin kx}{1+\pi\alpha|k|}\,dk.$$

Now Leal (1985) [11] has measured the strain-rate along the axis of his 4-roller apparatus for a Stokes flow and, as shown in Fig. 1, the velocity distribution is well-approximated for a suitable scaling of x by the (mathematically convenient) representation

$$u_0 = (x+x^3)\,e^{-x^2/2}.$$

The result above for $u(x)$ then predicts that the strain-rate is modified by the polymers to

$$u'(x) = \sqrt{\frac{2}{\pi}}\int_0^\infty e^{-k^2/2}\frac{4k^2-k^4}{1+\pi\alpha k}\cos kx\,dk. \tag{9}$$

If α is small, the perturbation to the stagnation point strain-rate $u'(0)$ is small and thus our solution is self-consistent. If α is of order unity, the prediction is that the value of $u'(0)$ is changed by a numerical factor. If D/α is sufficiently large however, the local kinematics near the stagnation point are unaffected, the degree of polymer extension is unaltered, and the solution should still be appropriate. If however $\alpha \gg 1$, the flow near the stagnation point is changed and then eqn. (9) ceases to apply. In the Leal [11] experiments it appears that α is always small (though in the cross-slit experiments of Gardner et al. [13] larger values are achieved). We now compare our results with Leal's observation.

First Leal observes a sudden onset of birefringence along the x-axis at a critical roller speed. In our terms this onset corresponds to the critical Deborah number $(1/2)$ at which polymers first become extended, and, as noted above, the region of high extension coincides with the outgoing stagnation streamline.

Second, as shown on Fig. 2 the strain-rate in the flow is not modified by the polymer when the birefringence first appears, but requires a higher Deborah number (approximately twice as large) before dynamic effects appear. This flow regime $1/2 < D < 1$ is that for which the integral (7) converges to give a small $O(c)$ perturbation to the flow.

Third, as shown in Fig. 1 the region in which the strain-rate is most significantly reduced by polymer is surprisingly not at the stagnation point
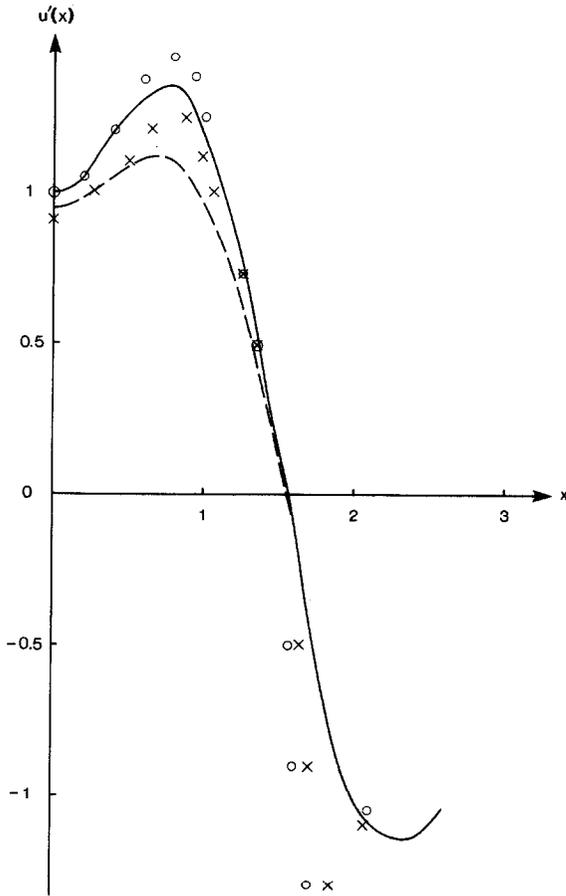
Fig. 1. Flow in a 4-roll-mill. Strain-rate versus distance from the stagnation point. ○ measurements of Leal [11] for a Newtonian fluid (no polymers); — strain-rate for the approximate velocity $u = (x + x^3) e^{-x^2/2}$, $\alpha = 0$; × measurements of Leal [11] with polymer; - - - - - - calculated distribution with $\alpha = 0.05$. Measured strain-rates are normalized so that $u'(0) = 1$ for the Newtonian case; distances are scaled to give agreement for the value where u' has its maximum.

itself but some way downstream. The same effect is seen for non-zero values of α in eqn. (9). The explanation is that in a Stokes flow the strain-rate has a weak *minimum* at the stagnation point (see Fig. 1). The polymers are most stretched however where the strain-rate is highest, here downstream of the origin ($x \approx 0.7$). The body force exerted by the nearby polymers therefore acts to *increase* the strain-rate at the stagnation point. More distant polymers are relatively unstretched however, and these exert a net body force that acts to decrease the central strain-rate. These two effects tend to cancel
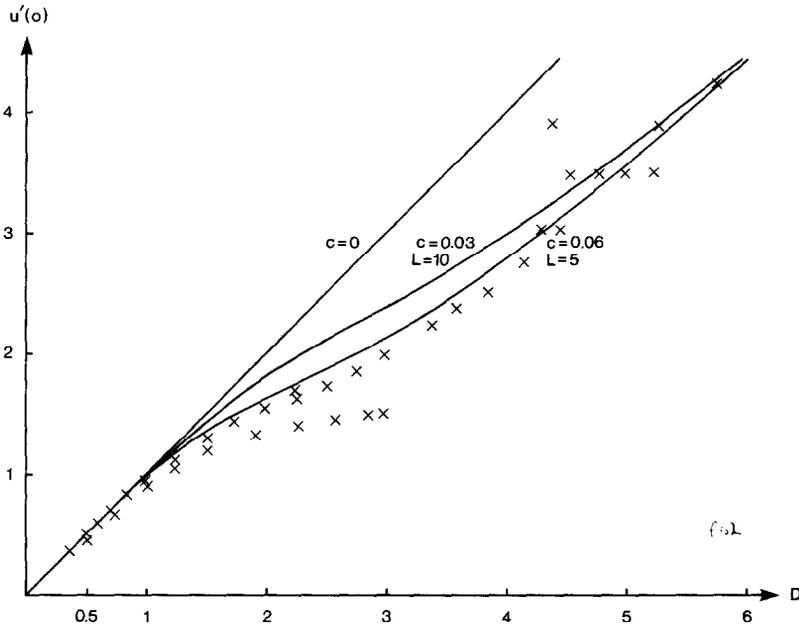
Fig. 2. Flow in a 4-roll-mill. Strain-rate at the stagnation point versus Deborah number. The onset of optical birefringence is taken to define $D = 1/2$. The continuous curves are predicted values; x measured values from Leal [11].

at the origin, but reinforce at the strain-rate maximum. Indeed for small α eqn. (9) gives

$$u'(x) = u_0'(x) - \alpha\sqrt{2\pi} \int_0^\infty e^{-k^2/2}(4k^3 - k^5) \cos kx \, \mathrm{d}k + O(\alpha^2),$$

and at $x = 0$ the $O(\alpha)$ term vanishes, but is negative for other values of x, having a minimum near $x = 1$.

Fourth, for large values of D the dynamic effect of the polymer appears (Fig. 2) to saturate, in that the measured strain-rate at the origin increases linearly with D (but with a different slope than for small D). Again this effect is predicted by theory: as D rises so the flow field is affected only weakly through

$$\alpha = c(L/a)^{(2-2D)/(1-2D)},$$

and as $D \to \infty$, $\alpha \to$ constant. The physical reason is that for $D \to \infty$ the region of strongly stretched polymers is asymptotically of thickness a/L (independent of D) and behaves like a viscous fluid. Thus for creeping flows the fluid velocity everywhere is linearly proportional to the roller speed.

Finally, Leal [11] noted that the magnitude of the polymer perturbation to the flow is smaller than might be expected if the polymers were regarded as fully uncoiled rigid rods. A partial reason for this is simply that the region of extended polymers is so thin (a/L) that their dynamic effect is reduced. But additionally attempts to fit the dynamic flow data by suitable choice of c and L/a (see Fig. 1) suggest that a *small* value of L/a (≤ 5) may in fact do better than a large value. The same conclusion is reached by Chilcott and Rallison [9] in the context of flow past an obstacle. On the other hand, the peak birefringence data appears to require a much larger value of L/a (Dunlap and Leal [12]). The likely implication is that the thickness of the zone in which the polymers contribute significantly to the stress is much broader than the strongly birefringent region (see also the discussion in Rabin et al. [15]), and a microstructural explanation is advanced in the following section.

5. Sudden strong strains

5.1. The problem

Most experiments on dilute polymer solutions that show a large non-Newtonian effect subject the moving fluid particles to a sudden transient strong strain. In contrast experiments using simple shear flows subject the fluid particles to a near-constant strain history (and show comparatively few non-Newtonian effects). Standard constitutive equations may not adequately describe the fluid response to the transient conditions as described below.

The problem is clearly revealed in the thesis of A. Ambari (1986) [16]. Ambari used the *same* dilute solution of 'Polyox coagulant' in a series of experiments with different flow geometries, and thereby exposed a discrepancy between the experiments and theory which had not been apparent when the various experiments had been performed separately.

In a flow past a cylinder, Ambari found that the mass transfer changed from the water value when the strain-rate exceeded 50 s^{-1}, which is consistent with the relaxation-rate of the polyox (molecular weight about 5×10^6, concentration 150 ppm.) being 10 ms. In flow through a circular orifice in a wall, the pressure drop changed from the water value at a strain-rate of 2×10^3 s^{-1}, i.e. 40 times the critical value for flow past a cylinder. Finally in two-dimensional flow through a long slot in a wall, the pressure drop changed from the water value at a strain-rate of 2×10^4 s^{-1}, i.e. 10 times the critical value for the axisymmetric hole.

Previous workers had found that the onset of non-Newtonian effects was characterized by a critical strain-rate (which varied a little with concentration), and that this critical strain-rate was similar to the molecular relaxa-

tion-rate. The difference between the precise value of the relaxation rate and the critical strain-rate has always been blamed on the polydispersity of polymer solutions. That excuse is not available to explain the differences between the different flows of the same solution prepared by the same person in the same way.

5.2. Theory for flow through a hole

We start the investigation by considering the flow in n ($=2$ or 3) dimensions through a hole in a wall. Let the prescribed velocity of the fluid through the hole be U, the diameter of the hole d and call the radial distance from the centre of the hole r. Then the velocity of the fluid approaching the hole will be $u = U(d/r)^{n-1}$. The strain-rate has a magnitude $\nabla u = Ud^{n-1}/r^n$.

Now moving with speed u the polymer molecule sees a rapidly increasing strain-rate. It will be distorted little until it reaches the position where the strain-rate first exceeds the molecular relaxation-rate, i.e. at r_* given by $Ud^{n-1}/r_*^n = \lambda$. Thereafter, according to the dumbbell model presented in Section 2, it will be stretched like a fluid line element (unless it becomes fully extended), because its relaxation is soon dominated by the rapidly increasing strain-rate. Hence the polymer distortion R is given up to a numerical constant (near to 1) by $a(r_*/r)^{n-1}$ as it approaches the hole.

We can now estimate the magnitude of the elastic contribution to the stress from the polymers as $\tau = O(c\mu\lambda(R/a)^2) = O(c\mu\lambda(r_*/r)^{2n-2})$ and compare this with the Newtonian solvent stress $2\mu e = O(\mu Ud^{n-1}/r^n) = O(\mu\lambda(r_*/r)^n)$. In the two-dimensional case, both the elastic stress and the solvent stress increase towards the hole like r^{-2} but the elastic stress is always smaller by the diluteness factor c. Hence the dumbbell model of Section 2 predicts that a dilute polymer solution should not exhibit any non-Newtonian effect. Others have found this same problem when examining the response of an Oldroyd fluid through a two-dimensional hole, e.g. see Tanner [17]. In the axisymmetric case $n = 3$, the elastic stress grows like r^{-4} and so can dominate the solvent stress which grows like r^{-3} if the Deborah number is sufficiently large for the extra factor r_*/r to dominate the small c, i.e. if $U/d\lambda > c^{-3}$. Unfortunately although the experiments show some variation of the onset strain-rate with concentration, the dependence does not scale with c^{-3}, but is closer to $c^{-1/2}$.

Now the estimates above supposed that when the molecular relaxation is weak the dumbbells are deformed by the strong flow like a fluid element, and that they just exert an elastic stress. Suppose instead that the dumbbells were unable to stretch quite so fast; suppose that they could only deform with some proportion, 80% say, of the strain of the fluid. Then while the

above estimates of the size of the deformation stand unaltered (except for the numerical 80%), there would be an additional viscous stress to reflect the dissipation in the 20% slip of the dumbbell relative to the fluid, with magnitude $O(c\mu\nabla u(R/a)^3)$. Now in the two dimensions, this stress increases like r^{-5} and could dominate the solvent stress if the Deborah number is sufficiently large $U/d\lambda > c^{-2/3}$. In the flow through the axisymmetric hole, the additional viscous stress increases like r^{-9}, and this exceeds the solvent stress if $U/d\lambda > c^{-1/2}$. Thus by incorporating the additional viscous stress (i) a non-Newtonian effect can now be anticipated in the two-dimensional case, and (ii) (because $c^{-2/3} > c^{-1/2}$ when $c \ll 1$) a larger Deborah number is predicted for the two-dimensional case (as seen in Ambari's experiments [16]). A further bonus is that the $c^{-1/2}$ dependence of the strain-rate was found by James and McLaren [18] in examining flow through a porous medium, which might be considered to look like a succession of roughly axisymmetric holes. The idea of introducing this additional viscous stress can be found in King and James [19] and Ryskin [20].

5.3. Molecular basis

There remains the problem of identifying a molecular basis for the additional viscous stress. To address this question we have performed some simple computer simulations of a polymer molecule in a sudden strong strain. Bonds of fixed length were joined in a linear chain by free hinges. This was placed in an axisymmetric straining motion with a viscous drag force applied at each hinge proportional to its slip relative to the flow, i.e. hydrodynamic interactions were neglected for simplicity. No Brownian motion relaxation was included because the flow was taken to be strong. Under these circumstances the time-dependence of the straining motion is irrelevant, the configuration depends only on the total strain.

Figure 3 shows the evolution in time of a chain of 100 bonds, starting from a random configuration. Note that the initial random configuration is quite different from the free-hand sketches one often draws of a random chain. The real random walk dithers in one region and then advances before dithering again—the walk is not uniformly distributed throughout its envelope. Until $t = 0.8$ s, i.e. a total strain of 5 (logarithmic strain of 1.6), the chain seems to stretch with the flow, and the viscous dissipation is relatively low. But thereafter the chain stretches much more slowly than the flow (at roughly 35% of the flow rate), and this is accompanied by a large viscous stress (corresponding to the 65% slip), see Fig. 4. This later motion of the chain is characterized by the slow unfolding of *back-loops*. Similar back-loops were seen by Acierno et al. [21]. The difficulty in removing the unstable
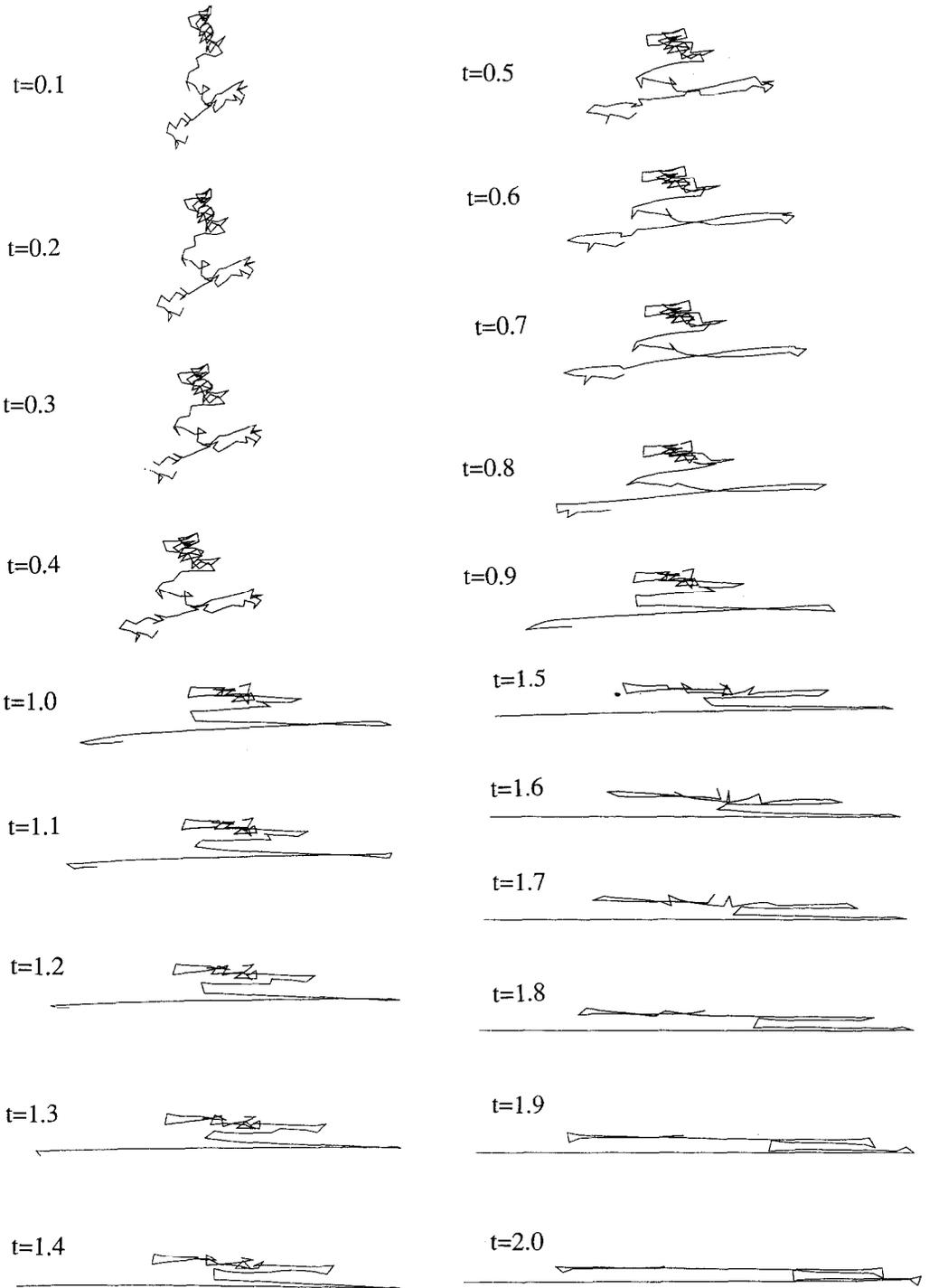
Fig. 3. Configurations at different time(s) of a freely-jointed chain of $N = 100$ fixed-length bonds in the axisymmetric straining flow $u = (2x, -y, -z)$.
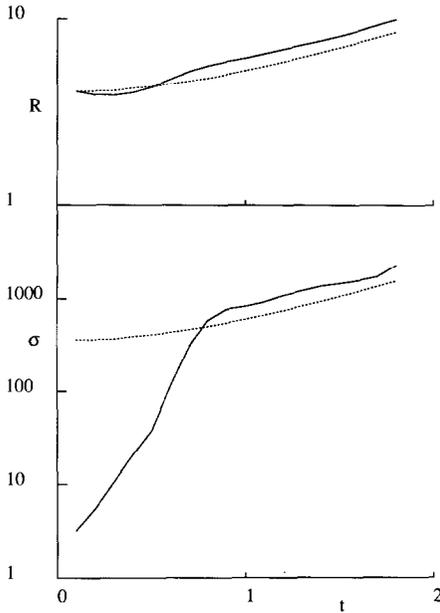
Fig. 4. The radius of gyration and the additional viscous stress and as a function of time for the freely-jointed chain in the strong straining motion. The broken curve would arise if the chain moved affinely with the flow $\mathbf{u} = \theta(2x, -y, -z)$ and $\theta = 0.35$, $R = a\sqrt{(e^{4\theta t}/3 + 2e^{-2\theta t}/3)}$ and $\sigma = (1-\theta)NR^2/3$.

back-loops comes from the compressional part of the flow in the direction perpendicular to the stretching part [22]. The results obtained in the simulation may be sensitive to the amount of hindered rotation included (here none), which would stop the back-loops being collapsed so awkwardly. Note that the back-loop configurations have a high degree of alignment of the bonds, and so would give a high birefringence without the chain being fully extended.

Further computer simulations are required, in particular for flows that are less strong. One interesting line to consider would be the effect of pre-shearing the polymer chains before subjecting them to the sudden strong straining. In experiments James et al. [23] have shown that pre-shearing can enhance the response in the flow through a hole of some types of polymers. The important outstanding problem, however, is to characterize this transient non-equilibrium behaviour of the polymers in a way which can easily be incorporated into the dumbbell model. One can speculate that this might be done by saying that beyond strains of 5 the polymer will behave as if it has an internal viscosity roughly twice that of the solvent, which makes the polymer stretch at 1/3 the flow rate.

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