

Mechanical models of dilute polymer solutions in strong flows

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In strong flows, such as turbulence, it is suggested that randomly coiled macromolecules might become nearly fully extended. To investigate this extended state, four models are considered which show the importance of the inextensibility of the polymer chain and the variation of the friction coefficient with the extension. The rheological consequences of these processes are then explored in an appropriately modified dumb-bell model. A dilute polymer solution is predicted to have a high extensional viscosity but a low shear viscosity, a stress hysteresis, and a slow stress relaxation. The action of the novel rheology is shown in two simple flows. Finally, speculations are made on the possible way dilute polymer solutions can modify turbulence.

I. STRESS LEVEL

Before attempting to explain the reduction of turbulent drag by very dilute polymer solutions, it is necessary to understand a little about both turbulent drag and dilute polymer solutions. This paper is concerned solely with the polymer side. Those features of the rheology of polymer solutions which I consider important in drag reduction will be reviewed. A complete historical review of the development of the subject has not been attempted.

For me the most amazing feature of drag reduction is that dramatic effects on the drag can be achieved with exceedingly small quantities of polymer additive, just a few parts per million by weight. How so little can be so effective is one question we can answer. Let me start by producing some estimates of the change in the levels of stress caused by suspending some small particles in a solvent.

A suspension of small particles can be treated as an effective continuum, albeit non-Newtonian and different from the solvent, as long as the particles are smaller than the smallest length scale of the flow. Often the length scale of the flow is simply the dimension of the apparatus, but in a turbulent boundary layer the required scale is the thickness of the viscous sublayer. A randomly coiled polymer is sufficiently small, typically being one hundredth the size of the smallest eddy. I should perhaps note here that this is not the situation in drag reduction by dusty gases and fiber suspensions. In these cases the relevant particle size, the stopping distance of the dust particles and the fiber length, usually exceeds the smallest eddy size by a large factor. Hence, dusty gases and fiber suspensions cannot be regarded as continua when studying turbulent drag reduction.

An immediate consequence of the ratio of the flow scale and the polymer size being large is that this non-dimensional group has no dynamical significance. By measuring the properties of a continuum, it is not possible to determine the size of its microstructure. Thus, the "length hypothesis" for the onset of drag reduction, however good it might appear as an experimental correlation, can have no physical basis.

When a suspension of particles acts as an effective continuum, the typical stress levels can often be estimated by applying Einstein's effective viscosity calculation. Einstein¹ showed that, for a dilute suspension of rigid inert spheres, the fractional change in the viscosity was two and a half times the volume fraction of the spheres. Before applying this result one needs to know that in low-Reynolds-number flows (the flow around the small polymers has a Reynolds number less than 10^{-4}) the effective hydrodynamic size of a particle is its largest linear dimension, e.g., the drag on a falling rod is crudely given by Stokes' law based on the half-length of the rod, with a very weak logarithmic dependence on the shape and thickness of the rod. Thus, to estimate the viscosity of dilute polymer solutions we use the volume fraction of those spheres which just enclose the separate polymer molecules.

Three things can go wrong with this procedure for estimating the stress levels in the suspension. First the particles can deform and thus not carry the same stress as a rigid particle which fully resists the straining. When polymers deform, however, they can avoid only a fraction of the rigid particle stress. Second, rod-like particles can sometimes align in a direction in which there is no component of strain, and this leads to a reduction in the apparent viscosity. This directionality effect occurs, however, only in simple shear flow which is not typical of turbulent motions. Finally, the effective hydrodynamic volume fraction can be large and thus break the diluteness restriction used in the Einstein calculation. In fact, this occurs in our application, even though the true volume fraction of the particles is minute. Fortunately, we are saved here by a recent theory of Batchelor² verified in some experiments by Mewis and Metzner³: in the case of fibrous particles the dilute formula still holds with very weak modifications.

As an illustration which will be continued through the paper, I will take a 100 ppm solution in water of Polyox of molecular weight 10^6 . The relevant dimensions are then $0.3 \mu\text{m}$ for the separation of the polymers in solution, $0.03 \mu\text{m}$ for the rms size of the coiled (equilibrium) polymer in which each monomer is joined to the preceding one at a random angle and the chain thus executes a random walk (in a θ solvent), and $7 \mu\text{m}$ for the length

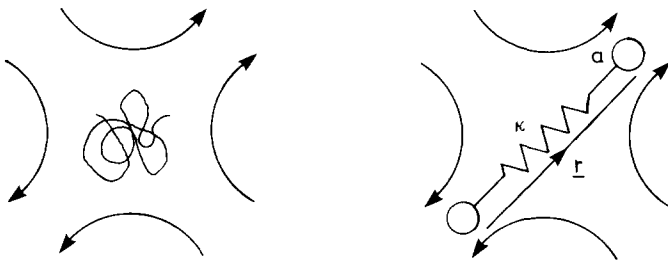


FIG. 1. The elastic dumb-bell model of a distorting polymer in the linear velocity field $\mathbf{u}(\mathbf{x}, t) = \mathbf{x} \cdot \nabla U(t)$.

of the chain when it is stretched straight. If the polymers are coiled, the viscosity is estimated to change by a few percent, which is consistent with observation, while if the polymers are fully stretched the procedure suggests the viscosity increases by a factor of ten thousand.

The preceding illustration shows that if the polymers were all fully stretched then large changes in the rheology of a dilute solution can be expected, changes sufficient to effect turbulent drag. Clearly, the polymers need not be fully extended; significant rheological changes occur when the polymer coil is extended by a factor of ten (a hundred being fully stretched). If one believes that turbulence is moderately robust and can only be modified by major dynamical changes, then one must conclude that in drag reduction the randomly coiled polymers are stretched substantially. How the polymers can become stretched is tackled in the next section.

Why drag reduction can be achieved with only a little polymer has now been answered. Weight is simply an inappropriate measure of the added polymer. A better measure is the effective hydrodynamic volume fraction, i. e., the volume fraction of spheres just enclosing the separate polymers, and this measure shows a large concentration if the polymers are highly stretched.

Finally, I would like to criticize the agglomeration theories of drag reduction for not producing estimates of the effectiveness of aggregates. In order to produce a large rheological effect in turbulence but a negligible effect in a viscometric flow, the effective size of the aggregates must be ten times larger in turbulence. I fear that the implied levels of stress within an extended aggregate far exceeds the weak binding forces.

II. STRONG FLOWS

About the simplest representation of a distorted polymer is the elastic dumb-bell, introduced by Kuhn and Kuhn.⁴ While, this limited model cannot answer many questions about macromolecular behavior, it does expose most clearly the key issues which determine how much distortion can be expected when the polymer is placed in a particular flow.

The gross distortion of the random walk of the chain, e. g., the separation of the monomers at the end of the chain, is represented by a single vector \mathbf{r} which becomes the extension of a spring separating two beads, see Fig. 1. Now Brownian fluctuations in the chain con-

figuration produce a relaxation of the distortion. This entropic desire to return to the most probable, spherically symmetric, randomly coiled state is modeled by the elasticity of the spring. The linearized spring constant κ is usually taken to be $3kT/Nb^2$, in which kT is the Boltzmann temperature, N is the number of monomers, and b is their length. This spring law corresponds to the force which must be applied at the opposite ends of a single independent bond in order to produce an expected alignment of \mathbf{r}/N , the calculation closely following the theory of magnetic susceptibility. When $r/N \ll b$ the (inverse Langevin) spring law can be linearized.

The polymer chain is distorted by a flow with a velocity gradient because there is a velocity difference between the two sides of the random walk. In the elastic dumb-bell model this stretching is represented by the hydrodynamic drag on the spherical beads, with friction constants $6\pi\mu a$, according to Stokes' law. As I noted in the preceding section, the effective hydrodynamic size of the polymer chain is its linear dimension and so in this gross model one should take $a = b(N/6)^{1/2}$ (known as the impermeable case).

To derive the evolution equation of the dumb-bell, a force balance is made on each bead, resulting in

$$\dot{\mathbf{r}} = \mathbf{r} \cdot \nabla U(t) - \lambda \mathbf{r} \quad (1)$$

where $\lambda = \kappa/6\pi\mu a$. Also, one concludes that the polymer is advected by the local bulk flow, so that the velocity gradient tensor should be evaluated as a function of time in a Lagrangian frame. The two terms on the right-hand side of (1) express, as any simple model of the microstructure of a fluid inevitably must, the flow-induced distortion and its relaxation, with only the relaxation rate depending on the details of the model. For the continuing illustration of the Polyox solution referred to earlier, the relaxation time is estimated to be a little shorter than a millisecond, which is consistent with observations of the dynamic viscosity.

The question of how much distortion can be expected when the polymer is placed in a particular flow can now be answered by solving (1). For simplicity, we consider flows with constant histories, i. e., the ∇U seen by the polymer advected by the bulk flow is independent of time. Under such circumstances the solution of the linear evolution equation (1) is the sum of three exponential functions of time. Denoting $|\nabla U|$ as the largest real part of an eigenvalue of the tensor ∇U , the behavior of the polymer can be divided into two classes. If $|\nabla U| < \lambda$ (a weak flow), the restoring force wins and the distortion decays. If $|\nabla U| \geq \lambda$ (a strong flow), the stretching flow wins, and within this crude model, the distortion increases in time without bound. The next section will examine the development of the very large distortions more carefully. For the present we only need the suggestion that large distortions exist in strong flows. The first indication of the existence of strong flows was Takserman-Krozer's⁵ study of the related Rouse-Zimm model in uni-axial straining motion.

From the discussion of the preceding section relating the levels of stress to the distortion of the polymers,

dramatic rheological effects are to be expected in strong flows. The condition that the flow is strong leads⁸ to the "time hypothesis" for the onset of drag reduction: that the turbulent wall strain rate u_*^2/ν , should exceed the principal polymer relaxation time $0.4 kT/\mu N^{3/2} b^3$. Experimentally, the two time scales are found to be of the same order of magnitude, but there is wide scatter in the data. I think the reason for the poor practical correlation is that both time scales need some refinement. It is becoming increasingly clear that the polymers respond more to the peak strain rate rather than the rms level represented by u_*^2/ν . The peak levels will have a weak Reynolds number dependence because of the intermittency within the turbulence. The molecular time scale employed can be faulted as depending too much on a poor theory, even when expressed in the less sensitive form $[\eta] \mu M/RT$. Direct observation of the relaxation time, e.g., from the dynamic viscosity, would be preferable. The influence of polydispersivity also needs to be understood.

Using the classification of flows into weak and strong, an unsatisfactory feature of viscometric testing is exposed. Simple shear flow has the property that $|\nabla\mathbf{U}|$ vanishes whatever the magnitude of the flow. Viscometric measurements may thus not be relevant to strong flows such as those found in turbulence.

The strange property of simple shear, that it is weak whatever the magnitude of the flow, is very rare in the class of all possible types of flow; in fact, those flows with this property have the zero measure of a point on a plane. Lumley's⁷ study of two-dimensional flows is misleading on this matter because two-dimensional flows are weak if the vorticity exceeds the strain rate. The trouble stems from his special orthogonality of the vorticity vector to the only two principal axes of strain. If the vorticity is sufficiently large, the polymer molecule spins roughly with the vorticity and this spinning averages out the oscillating strain-rate that it sees in the plane orthogonal to the vorticity. Thus, in two-dimensional flows the spinning molecule sees an average strain rate of zero once the vorticity is large enough. In three-dimensional flows, however, it is most unusual for the component of the straining in the direction of the vorticity to vanish, i.e., for the average strain rate in the orthogonal plane to vanish.

Before passing on to some models of polymers at large distortions, I should briefly mention some classical improvements in the crude elastic dumb-bell model. By adding Brownian motion to the beads, the undesirable feature of the distortion vanishing altogether in weak flows can be avoided; instead the distortion tends to a small nonzero equilibrium. With the polymer state now described by the expected second moment of the distortion $\langle \mathbf{r}\mathbf{r} \rangle$ the evolution equation becomes

$$\frac{D}{Dt} \langle \mathbf{r}\mathbf{r} \rangle = \langle \mathbf{r}\mathbf{r} \rangle \cdot \nabla\mathbf{U} + \nabla\mathbf{U}^T \cdot \langle \mathbf{r}\mathbf{r} \rangle - 2\lambda \left(\langle \mathbf{r}\mathbf{r} \rangle - \frac{r_0^2}{3} \mathbf{1} \right), \quad (2a)$$

in which r_0 is the equilibrium radius of gyration. The constitutive equations for the dilute polymer solution are completed (in this extension of the elastic dumb-bell) by an expression for the bulk stress,

$$\boldsymbol{\sigma} = -p\mathbf{1} + \mu(\nabla\mathbf{U} + \nabla\mathbf{U}^T) + nK\langle \mathbf{r}\mathbf{r} \rangle, \quad (2b)$$

in which n is the number density of the polymers. Adding the Brownian motions of the beads does not change the classification of strong and weak flows, for diffusion cannot produce very large distortions in weak flows or limit the growing distortions in strong flows.

A second standard modification of the elastic dumb-bell is the model Rouse⁸ and Zimm⁹ in which the polymer chain is represented by a necklace of beads and springs, with some form of hydrodynamic interaction between the beads. The necklace allows some internal distribution of the distortion to be represented in addition to the gross distortion. This internal distribution shows itself in the dynamic viscosity, but only modifies the strong and weak flow classification by changing the critical flow strength, λ , to the relaxation rate of the slowest mode.

Finally, there are a number of complicated effects which make the radius of gyration of the equilibrium random walk differ from the ideal result $r_0 = b(N/6)^{1/2}$. These effects are the hindered rotation of the bond angle between monomers, the finite volume of the monomers and adjacent solvent molecules, and short and long range electrostatic interactions between subgroups. All these effects are usually lumped into a modified value of r_0 , sometimes ten times the ideal value. Changes in these effects with distortion are not normally considered.

III. LARGE DISTORTIONS

So far we have seen that large distortions of the polymer molecules are needed for dilute solutions to have dramatic flow properties and that the crude elastic dumb-bell model suggests such large distortions can be expected in strong flows. In this section the dynamics of polymers with large distortions are explored. Four models are presented which exhibit in a simple way different aspects of the dynamics. I think a full model incorporating all conceivable effects would not necessarily be an improvement because it would be intractable and cloud our understanding of the mechanics underlying the phenomena.

Two important effects enter when the distortion becomes large. As soon as the distortion becomes comparable with the radius of gyration, the hydrodynamic shielding of parts of the chain by other parts is altered. At very much larger distortions the finite extensibility of the polymer chain becomes relevant. I am going to concentrate on these two effects, even though in practice excluded volume, ionic charges and knotting of the chain may not be negligible. These other effects are, however, auxiliary factors in the essential competition between the bulk flow creating the distortion and the entropic restoring mechanism.

A. Elastic ellipsoid

The first nonlinear effect to be considered then is the dependence of the stretching by the bulk flow on the distortion. A suitable model to exemplify this effect is the elastic ellipsoid model, introduced by Cerf¹⁰ before the necklace generalization of the bead-and-springs and ex-

plored later by Roscoe.¹¹ In the model the deformed polymer is represented by an ellipsoidal shaped particle of constant volume. The solvent flow around the particle exerts distorting surface tractions. For the entropic restoring forces the particle is given a simple Hookean elasticity. Resistance to changes in shape due to the chain moving in a viscous solvent and also due to the chain entangling with itself is represented by an internal viscosity of the particle which exceeds the solvent value.

It should be noted that the elastic ellipsoid is again a gross distortion model; the internal distribution of the chain distortion is not represented. The model further suffers the use of an *ad hoc* relation between its elastic modulus and the molecular origin of the restoring force. The beauty of the model, however, is that if the particle starts as a homogeneously stressed ellipsoid, e. g., a sphere at rest, then it always remains an ellipsoid. The development of the distortion can therefore be tracked into the nonlinear regime using just five variables. Even so the mathematics is too complex to be presented here. From the details two new effects emerge.

The first and more important conclusion from the elastic ellipsoid model is that the frictional grip of the flow increases with the distortion. As pointed out in the first section of the paper, the effective hydrodynamic size of a particle is its maximum linear dimension. The detailed mathematics must therefore reflect this basic fact with a friction coefficient for the stretching motion increasing roughly in proportion to the distortion. A consequence of this increasing frictional grip is that large distortions can be maintained by some weak flows so long as the initial distortion is large enough. Because the nonlinear hydrodynamics only widens the difference between the stretching and restoring forces in strong flows, the growing distortion can only be limited by the finite extensibility of the polymer chain (or the finite duration of the strong flow). Finite extensibility will be taken up in the next model.

The second conclusion from the model, which is less important in dilute solutions, is that the particle spins with a sum of the full vorticity but only part of the straining motion. The inefficiency of the straining motion in spinning the particle is due to the "rigidity" of the particle provided by the internal viscosity. It appears that this internal rigidity leads to several rheological phenomena absent in the elastic dumb-bell, namely, a shear thinning viscosity, second normal stress differences, and, in flows starting from rest, a nonzero initial stress and oscillatory overshoots. None of these effects would have a large magnitude in a dilute solution.

B. Inextensible flexible thread

The preceding model has shown that in strong flows (of sufficient duration) the distortion will grow until it is limited by the finite extensibility of the polymer chain. To examine the combined effects of hydrodynamic stretching and the inextensibility, I have investigated a new flexible thread model.¹² For slender bodies such as

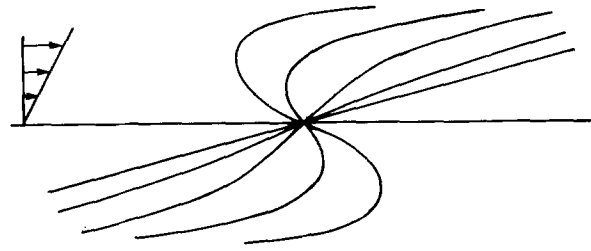


FIG. 2. The straightening of a flexible inextensible thread in a shear flow, starting from the S shape. The configuration $\mathbf{x}(s, t)$ is plotted as a function of s at $\gamma t = 0, 1, 2, 3, 4$.

a thread, there is an asymptotic theory for the flow of the solvent around a thread. With the thread described by a vector function of arc length s and time t , $\mathbf{x}(s, t)$, and with $\mathbf{T}(s, t)$ the tension in the thread, the governing equations can be found as

$$\dot{\mathbf{x}} = \mathbf{x} \cdot \nabla \mathbf{U} + \frac{\log}{2\pi\mu} (\mathbf{T}' \mathbf{x}' + \frac{1}{2} \mathbf{T} \mathbf{x}'') \quad (3a)$$

$$\mathbf{T}'' - \frac{1}{2} (\mathbf{x}'')^2 \mathbf{T} = - (2\pi\mu / \log) \mathbf{x}' \cdot \nabla \mathbf{U} \cdot \mathbf{x}', \quad (3b)$$

where the primes denote differentiation with respect to arc length and the argument of the logarithm is the ratio of the length to the breadth of the thread. These equations can be solved by perturbation methods for nearly straight threads, and more generally on a computer. Figure 2 is an example of a numerical solution for simple shear flow starting from an initial S shape.

The main conclusion of the study of the flexible thread is that nearly always the thread rapidly straightens as shown in Fig. 2. First, the thread tends to an orientation in which it is in tension. This tension then snaps the thread straight. An exceptional flow is simple shear in which the tension vanishes in the eventual orientation, but here the bends of the thread are found to decay more rapidly than the approach to the final orientation, so that a straight thread still results.

From this model something can be said about the possibility of mechanical degradation of polymers in drag reduction. If one accepts the premise that some polymers may be fully stretched in the turbulence, then (3b) enables the tension at the center of the chain to be estimated as $2\pi\mu |\nabla \mathbf{U}| N^2 b^2 / \log N$. If our standard illustration of Polyox is placed in a flow with $|\nabla \mathbf{U}| = 10^5 \text{ sec}^{-1}$, corresponding to a friction velocity of 0.3 m/sec this tension is 10^{-8} N . To estimate the binding force of the carbon atoms along the backbone, I have taken the binding energy of $\mathcal{E} = 120 \text{ kcal/mol}$ and divided this by the atomic separation of 3 Å. The resulting estimate of the binding force is 10^{-8} N . Thus, one would expect the polymer to break into two in a flow with a strain rate as strong as 10^5 sec^{-1} . This prediction is consistent with general experience of degradation. It is interesting to note the variation with molecular weight of the onset point for drag reduction $|\nabla \mathbf{U}| \gtrsim kT / \mu N^{3/2} b^3$, and the onset point for mechanical degradation $|\nabla \mathbf{U}| \gtrsim \mathcal{E} / \mu N^2 b^3$. Making the degree of polymerization, N , larger may insure an earlier onset of drag reduction, but my modeling suggests that it may be more effective at lowering the start of degradation. Crudely speaking, I

would expect degradation to occur with drag reduction whenever $N > 10^5$. Perhaps the best way to improve drag reduction is not to look to very high molecular weights but to consider improving the solvation.

C. Transversely diffusing thread

The preceding model examined the interplay of hydrodynamic stretching and finite extensibility. When these two effects dominate, I concluded that the polymer chain would be stretched out almost straight. A question now naturally arises as to how strong the flow need be for these two effects to dominate. To answer this question the Brownian motion of the chain must be reintroduced, so that the conditions under which the Brownian coiling of the stretched chain is ineffective can be found.

In a second thread model,¹³ I have included some weak Brownian motions. Weak Brownian motions acting on a straight thread cause small transverse distortions which can be described by a diffusion process in the deformation space. So that the continuum thread represents the small but finite bonds of the polymer backbone, the degrees of freedom of the transverse distortions must be truncated. This truncation also avoids an "ultraviolet catastrophe."

Some straightforward analysis yields the probability distribution of the distortions. There is less transverse displacement at the center compared with the ends of the thread, because there the tension is largest and it is the tension which snaps out the Brownian distortions. The rms transverse displacement is $0.2 (kT \log(kT \log N / \mu N b |\nabla U|)^{1/2})$, a result insensitive to the truncation. Associated with the transverse distortions is a small coiling effect; the ends of an inextensible thread must come closer when the thread is not straight. This shortening is found to have a magnitude $kT \log N / \mu N b^2 |\nabla U|$, with a precise value which depends critically on the truncation. In some sense each degree of freedom of the transverse distortions brings $\frac{1}{2} kT$ potential energy; energy stored as the tension multiplied by the shortening. Thus, the shortening is roughly proportional to the number of degrees of freedom, i.e., dependent on the truncation. Also note that the shortening varies as the small strength of the weak Brownian motion multiplied by the large number of degrees of freedom, a result exploited in the following model.

For the Brownian motions to have a small effect, it is necessary that the transverse distortions and the associated shortening should both be small compared with the length of the thread, Nb . The second condition is the more stringent, $|\nabla U| \gtrsim kT \log N / \mu N^2 b^3$. Note that the flow strength needed to maintain the stretched polymer is $N^{-1/2}$ times weaker than the flow required to produce the initial large distortion of the random coil. This result simply reflects the increased frictional grip on the polymer.

D. Elastic rod

In the transversely diffusing thread model we saw that, except in extremely strong flows, the shortening is an order of magnitude larger than the transverse dis-

placements, although both were restricted to be small in the analysis. This result opens the possibility of a further regime for less strong flows, in which it is envisaged that the thread executes a noticeable random walk contained within a long slender envelope. To examine this regime, I present my final model of an elastic rod. The distorting forces of the bulk flow are still calculated using the slender-body theory for Stokes' flow, but are now applied to the envelope rather than directly to the thread. The Brownian motions of the polymer chain are included by treating the envelope as an elastic rod with an entropic longitudinal elasticity related to the local coiling of the thread.

To describe the coiling of the polymer chain in the elastic rod, the position r along the straight rod is specified as a function of the arc length s along the thread, i.e., $r(s, t)$. The local stretching of the random walk is thus $\partial r / \partial s$. Using similar arguments as for the elastic dumb-bell, the longitudinal tension \mathbf{T} in the elastic rod is related to this local stretching by the Langevin spring law,

$$\mathbf{T} = (kT/b) \mathcal{L}^{-1}(\partial r / \partial s) .$$

The drag of the bulk flow on the stretching rod yields

$$\frac{\partial r}{\partial t} = r |\nabla \mathbf{U}| + \frac{\log}{2\pi\mu} \frac{\partial \mathbf{T}}{\partial s} \frac{\partial r}{\partial s} .$$

Careful consideration must be given to the moving ends of the rod where the tension vanishes. There are many similarities between my elastic rod model and the fully nonlinear Rouse-Zimm model.

Steady equilibria are found if the flow is strong enough, $|\nabla \mathbf{U}| \gtrsim kT \log^2 N / 4\pi\mu N^2 b^3$. In such an equilibrium the chain is at least half fully stretched. The model shows that in the central region the chain is more fully stretched. An asymptotic concentration of the coiling in regions near the ends never dominates in practice because of its mere logarithmic dependence.

The elastic rod model shows two effects in time dependent flows: Depending on the circumstances, the polymer can respond much slower or much faster than the relaxation time of the randomly coiled polymer. If the flow is strong, say strong enough to create the large distortions of the random coil, then in equilibrium the polymer is virtually fully extended, hard against the stops of the nonlinear spring. The polymer then responds very quickly and often almost as a rigid rod. If little of the polymer is fully stretched, then its response time is much longer, $N^{1/2} \lambda^{-1} / \log^2 N$, which is longer than that of random coil. Here, the nonlinearity of the spring is unimportant and it is the second effect of the \sqrt{N} enhanced friction which is significant. At large distortions the polymer relaxes slowly against the large frictional resistance.

IV. RHEOLOGICAL FUNCTIONS

Large distortions were examined in the preceding section. In strong flows of sufficient duration the polymer was found to become virtually fully extended. The simple models also revealed two basic physical processes; a frictional grip increasing with the distortion and a

rate of coiling rapidly increasing as the distortion is limited by the finite extensibility of the chain. These basic results now need more careful study by refined models. Experimental testing of some of the associated predictions is also necessary.

Instead of considering more refined models here, we now turn to the other direction for development, namely, the rheological response of a dilute solution of polymers with large distortions. If complex flows, such as those thought to be present in turbulence are to be analyzed using a rheology representing polymer solutions, then the rheological constitutive equations employed must be simple. The constitutive equations describing any of the partial models of the preceding section are far too complicated for such purposes. A realistic approach to interesting flows, I think, must involve highly simplified constitutive equations which symbolically represent, rather than accurately describe, the microstructural dynamics. I therefore propose to modify the simple elastic dumb-bell constitutive equations (2) so as to incorporate, at least at some crude level, the two basic physical processes revealed in Sec. III. In this section the modification will be made and the standard rheological functions evaluated. In the following section we will see how the rheology affects some flows. As first suggested by Peterlin,¹⁴ the finite extensibility can be incorporated into the elastic dumb-bell model by changing the spring constant κ of the linear spring to $\kappa/(1-r/Nb)$, where the length of the spring r is extracted from $\langle \mathbf{r}\mathbf{r} \rangle$ by $r^2 = \text{Tr}\langle \mathbf{r}\mathbf{r} \rangle$. While some arguments can be put forward for using the inverse Langevin spring, I prefer the above nonlinear elastic law for its simplicity. In addition, the bonds are not in reality fully independent as required for the Langevin law. My elastic law shares with the correct one, whatever it is, three general features; a linear region vanishing at zero deformation, an infinite force restricting extensions to $r < Nb$, and variations on a length scale of Nb rather than $N^{1/2}b$. If the ignored effects of excluded volume and charge repulsion were taken into account, then there might be variations in the details of the elastic law on the length scale of $N^{1/2}b$.

The improved frictional grip at large distortions can be included by making the bead size, a , change with r . Perhaps the most appropriate dependence for the bead size, and certainly the simplest, is just to replace a by r so that the friction coefficient was the largest linear dimension. This modification of the elastic dumb-bell was introduced by de Gennes¹⁵ and independently by Hinch.¹⁶ Slender-body theory for Stokes' flow suggests that the linear increase with r should be reduced by a weak logarithmic factor, $\log(r/N^{1/2}b)$, but we shall ignore this possible refinement.

In addition to the two basic physical processes in large distortions, I wish to include further the rigidity effect found in the elastic ellipsoid model. This third effect has little influence on genuinely large distortions, but apparently it is essential in insuring an acceptable behavior in simple shear flow, which probably stretches the random coil at most by a factor of three. The rigidity effect modifies the constitutive equations in two

places. In the evolution equation for $\langle \mathbf{r}\mathbf{r} \rangle$, the velocity gradient $\nabla \mathbf{U}$ is first split into the antisymmetric part, $\mathbf{\Omega}$ the vorticity tensor, and the symmetric part, \mathbf{E} the strain rate tensor. Then, the symmetric part is multiplied by an "inefficiency factor" $r^2/(3r_0^2+r^2)$. Note at large distortions the efficiency increases to unity. The second part of the rigidity modification is to include an additional term in the bulk stress $10\mu nr_0^3 \mathbf{E} r^2/(3r_0^2+r^2)$. Without an adequate study of polymer behavior in simple shear flow, there is necessarily an arbitrariness in my modification and this is unsatisfactory. Thus, the detailed predictions for simple shear should not be trusted.

The constitutive equations for the elastic dumb-bell with the modifications noted herein are

$$\begin{aligned} \frac{D}{Dt} \langle \mathbf{r}\mathbf{r} \rangle = & \langle \langle \mathbf{r}\mathbf{r} \rangle \cdot \mathbf{\Omega} - \mathbf{\Omega} \cdot \langle \mathbf{r}\mathbf{r} \rangle \rangle \\ & + \frac{r^2}{3r_0^2+r^2} \langle \langle \mathbf{r}\mathbf{r} \rangle \cdot \mathbf{E} + \mathbf{E} \cdot \langle \mathbf{r}\mathbf{r} \rangle \rangle \\ & - 2\lambda \frac{aNb}{r(Nb-r)} \left(\langle \mathbf{r}\mathbf{r} \rangle - \frac{r_0^2}{3} \mathbf{1} \right), \\ \sigma = & -p\mathbf{1} + 2\mu \left(1 + 5nr_0^3 \frac{r^2}{3r_0^2+r^2} \right) \mathbf{E} + n\kappa \frac{Nb}{Nb-r} \langle \mathbf{r}\mathbf{r} \rangle, \end{aligned}$$

with $r = \text{Tr}\langle \mathbf{r}\mathbf{r} \rangle^{1/2}$. (Note that these constitutive equations are not in the familiar form in which stress is given as a functional of the strain rate; instead stress depends on the strain rate and the microstructural dynamics. To display the rheological response of this pair of constitutive equations, in this section I will take $N=10^4$, $a=r_0=N^{1/2}b$ and $nr_0^3=10^{-3}$, values corresponding very roughly to the 10^6 Polyox at 100 ppm.

Most rheological tests are performed with simple shear flow. As discussed earlier, the constitutive equations were not carefully designed for this weak flow which probably does not produce large distortions. Only the most qualitative features of the response in shear flows are therefore worth noting. The viscosity of the dilute solution differs little from that of the solvent; there is an undetectable shear thinning between a zero shear rate viscosity 0.2% above the solvent value and a high shear rate limit 0.13% above the solvent value, half the thinning occurring by $\gamma=2\lambda$. The second normal stress difference is negative and about half the magnitude of the primary difference, although both are less than one thousandth of the shear stress. At low shear rates the normal stress differences vary quadratically in the shear rate, while at high shear rates they level off to constant values as the polymer tends to a small finite distortion aligned with the flow.

The prototype strong flow is axisymmetric straining motion. Plotted in Fig. 3 as a function of strain rate is the polymer contribution to the viscosity for this flow in steady state conditions. Most striking is the high value, $6 \times 10^3 \mu$, of the extensional viscosity in the stronger flows which stretch out the polymer; a good illustration of the discussion of the levels of stress in Sec. I. In the simplified constitutive equations this high value of the extensional viscosity is $2\pi\mu nN^{3/2}b^3$. Refinements from a slender-body analysis would reduce this

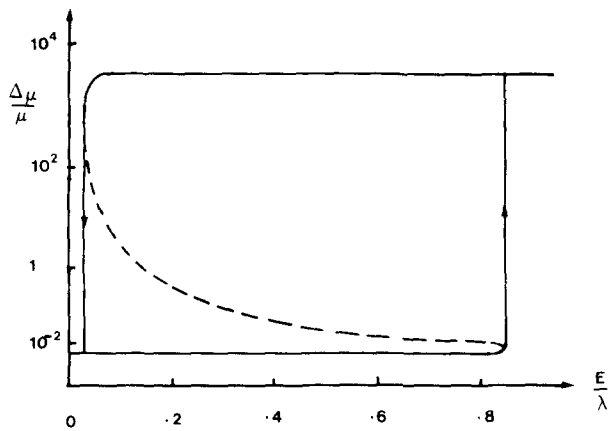


FIG. 3. The polymer contribution to the viscosity as a function of the axisymmetric strain rate.

by $18 \log(nN^2b^3)$. The solution viscosity does not differ significantly from that of the solvent until $r > 6r_0$.

The extensional viscosity exhibits a hysteresis in the range $0.02\lambda < E < 0.84\lambda$, the dotted part of the curve corresponding to unstable equilibria. At $E = 0.84\lambda$ the polymer extension jumps from $r = 1.2r_0$ up to $r = 0.99Nb$, if E is increased, while at $E = 0.02\lambda$ the extension drops from $r = 0.5Nb$ down to $r = 1.00003r_0$ if E is decreased. The hysteresis occurs because the frictional grip increases with the distortion and thus a weaker flow, $2\lambda N^{-1/2}$, is required to maintain a large distortion once it has been created. Tanner¹⁷ noted that most phenomenological theories of constitutive equations are unable to represent a hysteresis.

Steady state conditions in axisymmetric straining motions are difficult to achieve experimentally. It is therefore pertinent to consider the transient problem. This also reveals some further rheological properties. Plotted in Fig. 4 is the polymer contribution to the time dependent stress in an axisymmetric straining motion which is suddenly applied and later removed. A flow strength of $E = 2\lambda$ was used, and this exceeds the critical value of 0.84λ necessary to create large extensions. Initially, the stretching is retarded by the restoring force, an extension of only $r = 2.7r_0$ being produced by $\lambda t = 1.5$. Then follows a phase of duration $\log N/4E$ in which the polymer is stretched like a fluid element with virtually no elastic resistance. During this phase, at $\lambda t = 2.1$, the polymer contribution to the stress becomes comparable with, and then very quickly dominates, the solvent stress. Finally, the nonlinear elasticity abruptly arrests the stretching $r_0 E/8$ short of the full extension on a time scale of $\lambda/N^{1/2}E^2$. When the flow is removed, there is a very fast initial decay on the time scale $\lambda/N^{1/2}E^2$ in which the nonlinear elasticity factor $1/(1 - r/Nb)$ drops from $N^{1/2}E/\lambda$ to $O(1)$, thus reducing the stress by a similar amount. There then follows a long relaxation of duration $N^{1/2}/\lambda$ which is made slow by the high friction associated with the large distortions.

The transient response illustrates several important rheological features. Time is needed for the polymers to become sufficiently stretched for them to contribute to bulk stress. Before this happens the solution differs

imperceptibly from the pure solvent, but once the polymers begin to contribute they soon overwhelm the solvent (assuming that the straining motion can be maintained in the presence of the very large stresses). The transients also exhibit a fast relaxation process accelerated by the highly nonlinear elasticity, and also a slow relaxation process retarded by the enhanced friction.

V. TWO FLOW STUDIES

The high extensional viscosity must clearly be relevant to drag reduction, especially when potentially assisted in intermittent conditions by the hysteresis. Before continuing to more detailed comments on drag reduction, I wish to present two flow phenomena associated with the rheology of the preceding section. The first phenomenon is an anisotropy involving only polymers which are fully extended, and the second is the inhibition of a stretching flow by the large stresses which would occur if the flow were not checked.

In the first study we suppose the flow is strong everywhere and remains so. Therefore, after a short time the polymers are virtually fully extended and in a regime where the nonlinear elasticity produces a fast response to changes. Under these conditions the polymer solution behaves much the same as a suspension of rigid rods, with some useful simplification of the constitutive equations. Evans¹⁶ has studied the flow of a dilute suspension of rigid rods in several simple geometries, solving the constitutive equations and the momentum equation together. (Note the constitutive equations include one for the reorientation of the rods, an effect omitted from papers about similar problems presented at this Symposium on Structure of Turbulence and Drag Reduction).

The principal rheological property of a suspension of rigid rods is a high viscous resistance to any extensional motion in the direction of the rods, and a low resistance to other motions, i.e., a high extensional viscosity with a low shear viscosity. This anisotropy of the suspension influences the structure of flows which are combinations of straining and shear. Such a combination occurs in flow in a tapered channel or flow through an orifice. Simple similarity solutions show that the material anisotropy reduces the transverse length scale of the flow relative to the scale in the stream direction

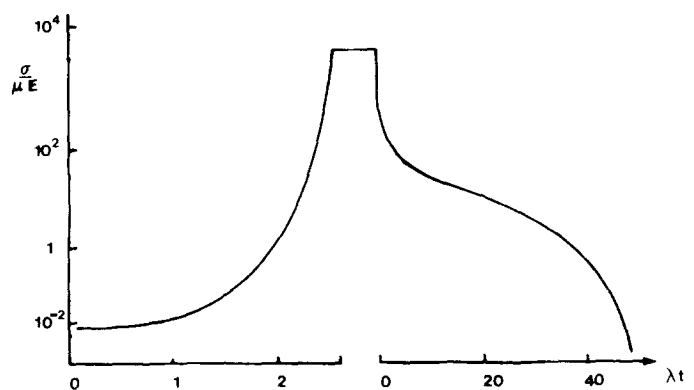


FIG. 4. The build up and relaxation of the polymer contribution to the stress.

(the direction of the rods), the ratio of the length scales becoming the square root of the ratio of the extensional and shear viscosities. The compression of the transverse scale in the two converging flows has the effect of introducing backflow regions at smaller angles of convergence than occur in the isotropic Newtonian case. Evans has taken these simple ideas generated from the similarity solution and looked at the more realistic flow in the contraction between two channels. Figure 5 shows that the suspension has larger recirculating eddies and a convergence with a slightly greater streamwise extent.

While considering the rheological functions in Sec. IV and also in the first flow study, I have implicitly assumed that the strong flow can be maintained when the polymers have been greatly extended and thus are producing large stresses. The second flow study examines the conflict between these large stresses resisting the very flow which creates them. A flow with a limited stretching effort, and which can easily be analyzed, is the time dependent stretching of a column of the polymer solution under a constant tension and neglecting inertia. This is an oversimplification of the nylon spinning problem. Figure 6 shows typically how the thickness of the column changes in time. Initially, the polymers contribute little to the bulk stress and the thickness follows the Newtonian curve. Just before the moment when the Newtonian column would have zero thickness the polymers become sufficiently stretched for their contribution to the bulk stress to be important. A new dynamical regime is then entered, with the unsupportably large stresses being avoided by a sudden drop in the strain rate. This drop in the strain rate leaves

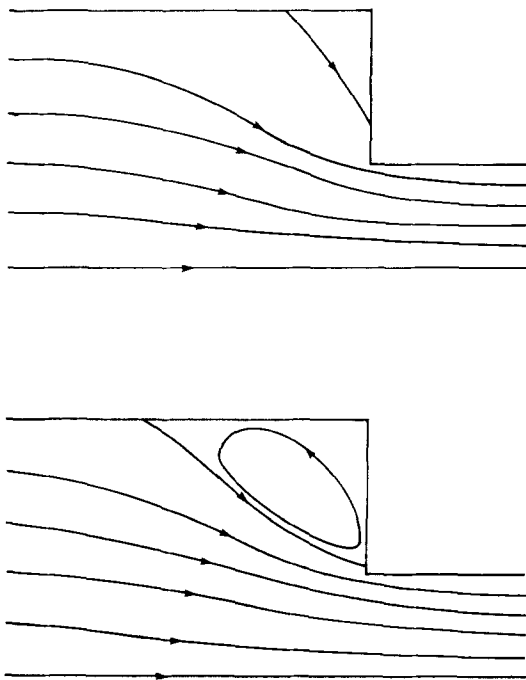


FIG. 5. The converging flow from a channel to one a third of the width, upper for a Newtonian fluid and lower for a suspension of rigid rods with an extensional viscosity fifty times the shear viscosity.

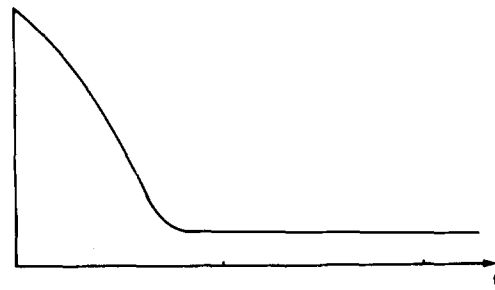


FIG. 6. The thickness as a function of time of a column of polymer solution under constant tension.

the bulk stress dominated by the polymer contribution. To stop the polymers collapsing some stretching is required, but the necessary strain rate is just the polymer relaxation rate for large distortions $\lambda/N^{1/2}$. Thus, the new regime lasts a long time, and the "saturation" dynamics are independent of the magnitude of the tension. This latter feature may be relevant to the well-known persistence of polymer threads and the good stability in spinning. The regime eventually ends, with the polymers fully extended and the column thickness simultaneously vanishing. For the related nylon spinning problem, Petrie¹⁹ found that several phenomenological constitutive equations show a similar limitation of the strain rate.

VI. DRAG REDUCTION

I wish to conclude the paper with a few speculative comments on drag reduction. There is no doubt in my mind that the high extensional viscosity in strong flows is the principal instrument in reducing the drag, but I do not find such a plain statement a satisfactory level of explanation. The phenomenological theories of turbulence, which can sometimes predict drag reduction by tampering with a length scale or with the turbulence intensities (in conflict with observed intensity changes?), may not, I fear, be able to provide a satisfactory link between the change in rheology and the change in drag. Fortunately, the improving picture of the detailed structures in shear flow turbulence reported at the Symposium does offer an opportunity to contemplate the mechanisms of drag reduction, although certainly more understanding of the turbulence is required before a complete explanation can be presented. With the present picture of turbulence there appear to me to be four different ways the polymers might affect the turbulence, each an aspect of the high extensional viscosity.

A simple mechanism for drag reduction, suggested several years ago, supposes that turbulent shear flows are comprised of many flow structures. The high extensional viscosity then selectively dissipates some of these structures, and it happens that the eliminated structures are more efficient than average at transporting momentum (producing drag). While many different features have been observed in turbulence, evidence is emerging, particularly at this Symposium, that perhaps the different features are organized as parts of a single grand structure. There seems to be little support for the availability of several unrelated transport processes

especially within the buffer region. A salient idea in this first mechanism, however, is the selective action of the polymers: a general increase in the viscosity must just increase the drag.

It is a small move from the first mechanism to the second and third which invoke the high extensional viscosity to stabilize the viscous sublayer. The low shear viscosity leaves unaffected the quiet shear-like parts of the sublayer, but selectively dissipates perturbations which must have an extensional component. Using the constitutive equations for a suspension of rigid rods, Bark²⁰ found that inflectional velocity profiles could be strongly stabilized, and at the Symposium, Tiederman's films convincingly show signs of a stabilized sublayer. There are two ways of completing the mechanism and relating the stabilization to drag reduction. For the second mechanism one argues that larger perturbations would be needed for the sublayer to break down, and this might just mean waiting longer before a burst which can transport momentum (assuming the transport by a single burst changes little). Less frequent bursting is usually observed in drag reduction. For the third mechanism one argues that the scales of the successful instability might adjust, with adjustments possible both in the overall scale and in the interal ratio of the scales such as shown in the first flow study, and these changes lead to less efficient transport. Observations of drag reduction always show increases in length scales, while it is not yet clear whether the ratio of the spanwise, streamwise and perpendicular lengths change. A variation on the third mechanism omits the stabilization of the sublayer and just changes the length scales of the bursts. The violence of the bursts may, however, mean that they are inertially controlled and thus beyond the influence of the rheology.

The fourth way the polymer could affect the turbulence is to limit the strain rate,²¹ as in the second flow study of Sec. V. If this were the only mechanism, I would expect it to be found in the later stages of the bursts after the polymers had been stretched in the earlier stages. Strain rate limitations within the bursts would reduce the rate they transport momentum. Unfortunately, there are no observations of the effect of polymers on the strain rate within bursts. The only relevant observation is that the duration of the bursts appears to be unchanged in drag reduction. This would contradict the fourth mechanism if one supposed that the strain rate limitation terminated the bursts early.

My discussion of possible drag reduction mechanisms raises many questions for further consideration, both experimental and theoretical. Two other questions are worth listing. Almost all rheologists share the view put forward in this paper that the polymers are highly stretched in drag reduction. Yet no direction observation has been made of the extension of the polymers in turbulence. Light scattering measurements in some laminar flows have shown polymers extending, although the extensions found are small because laminar flows cannot maintain high strain rates for long in the Lagrangian frame. Despite the severe technical difficulties of light scattering in a turbulent boundary layer, the ab-

sence of such an observation can only become increasingly embarrassing. Once a suitable experimental technique is available many points could be examined: Are the distortions just moderately large or are the polymers virtually fully extended, do the stretched polymers exist everywhere or just in the buffer region, is it the bursts which stretch the polymers, does the hysteresis and slow relaxation help to maintain the large distortions? While waiting for this experimental breakthrough, theoreticians can contribute by assessing the important flow variables in the polymer stretching processes, thereby avoiding the need to measure all nine components of the velocity gradient as functions of (Lagrangian) time.

The second outstanding problem concerns the onset of drag reduction. Verification of the "time hypothesis" would be improved with better monodisperse polymers and a direct measurement of the polymer relaxation time, e.g., by the dynamic viscosity. In view of practical applications a systematic study of polydispersity would also be useful. We should now, however, be turning to the challenging regime just beyond onset. Theoreticians can contemplate how the stretching of the polymers varies with the distance from the onset: Are the polymers stretched more, do the stretched polymers exist in a larger part of the flow, and does the flow adapt so the strain rate is limited by the value at onset? Experiments which find the appropriate molecular variables beyond onset can provide useful insights: Is the polymer concentration best nondimensionalized as $[\eta]c$ or $nN^{3/2}b^3$ (based on the coiled and stretched sizes, respectively), is the ratio of the coiled to stretched size important in addition to the concentration and the relaxation rate, and do all the changes in the turbulence depend on the same variables and thus scale with the drag reduction?

¹A. Einstein, *Ann. Phys. (Leipz.)* **19**, 289 (1906).

²G. K. Batchelor, *J. Fluid Mech.* **46**, 813 (1971).

³J. Mewis and A. B. Metzner, *J. Fluid Mech.* **62**, 593 (1975).

⁴W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **28**, 1533 (1945).

⁵R. Takserman-Krazer, *J. Polym. Sci. A* **1**, 2477 (1963).

⁶J. L. Lumley, in *Annual Review of Fluid Mechanics*, edited by M. Van Dyke (Annual Reviews, Palo Alto, Calif., 1969), Vol. 1, p. 367.

⁷J. L. Lumley, *Symp. Mathematica* **9**, 315 (1972).

⁸P. E. Rouse, *J. Chem. Phys.* **21**, 1272 (1953).

⁹B. M. Zimm, *J. Chem. Phys.* **24**, 169 (1956).

¹⁰R. Cerf, *J. Chim. Phys.* **48**, 59 (1951).

¹¹R. Roscoe, *J. Fluid Mech.* **28**, 273 (1967).

¹²E. J. Hinch, *J. Fluid Mech.* **74**, 317 (1976).

¹³E. J. Hinch, *J. Fluid Mech.* **75**, 765 (1976).

¹⁴A. Peterlin, *Pure Appl. Chem.* **12**, 273 (1966).

¹⁵P. G. de Gennes, *J. Chem. Phys.* **60**, 5030 (1974).

¹⁶E. J. Hinch, in *Proceedings of Colloques Internationaux du Centre de la Recherche Scientifique* (Editions du Centre National de la Recherche Scientifique, Paris, France, 1974), No. 233, p. 241.

¹⁷R. I. Tanner, *Trans. Soc. Rheol.* **19**, 557 (1975).

¹⁸J. G. V. Evans, Ph.D. thesis, Cambridge University (1975).

¹⁹C. J. S. Petrie, *J. Non-Newtonian Fluid Mech.* **2**, 221 (1977).

²⁰F. H. Bark, Ph.D. thesis, Kungl. Tekniska Högskolan, Stockholm (1975).

²¹F. A. Seyer and A. B. Metzner, *AIChE J.* **15**, 424 (1969).