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Calculation of the effect of polymer additive in a converging flow

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The conical-channel flow of a dilute polymer solution is investigated theoretically. The stress field due to polymer additive is calculated using a new molecular model, based on the physical picture of the polymer molecules *unravelling* in strong flows and Batchelor's theory for the stress in a suspension of elongated particles. Good agreement is obtained with the experimental results of James & Saringer (1980). The absence of a significant polymer effect in a two-dimensional case (the wedge-channel flow), observed by the same authors (James & Saringer 1982*a*), is also explained. The fundamental differences between the proposed model and the elastic-dumbbell models are discussed.

1. Introduction

In an important recent work, James & Saringer (1980) performed careful measurements of the pressure drop in a flow of a dilute polymer solution through a conical channel (see figure 1). The Reynolds number was high enough that the velocity field inside the channel could be well approximated by the sink flow. James & Saringer (1980) noted that since 'the flow field downstream of the exit is uncertain..., the reservoir-to-reservoir pressure differential does not correspond to a known velocity field', and placed the downstream pressure port (A in figure 1) just before the exit. Their results therefore correspond to a flow with well-known, and simple, kinematics (the sink flow), which makes them suitable for a quantitative analysis.

James & Saringer (1980) did observe very large non-Newtonian effects in this flow; King & James (1983) later proposed that effects of such magnitude could be produced if the polymer chains 'froze', after some partial extension by the flow, due to intramolecular entanglements. However, the theory (Brochard & de Gennes 1977) predicts essentially no intramolecular entanglements ('self-knots') in dilute solutions for molecular weights below $O(10^8)$; also, the well-known experimental fact that the chain scission in shear (or extensional) degradation occurs almost precisely at the midpoint of the chain (see, for example, Odell & Keller 1985) appears to contradict the idea of intramolecular entanglements (if they existed, they would randomize the distribution of the chain segments subjected to extension, and thus of the locations of rupture).

No quantitative explanation exists at the moment of the observed large non-Newtonian effects in the conical-channel flow of James & Saringer (1980), nor of the virtual absence of such effects in the wedge-channel flow, also studied by James & Saringer (1982*a*). The purpose of the present paper is to give such explanation, based on a new molecular model. It should be noted that the experiments of James & Saringer (1980, 1982*a*) provide a unique opportunity for testing new (and old) models

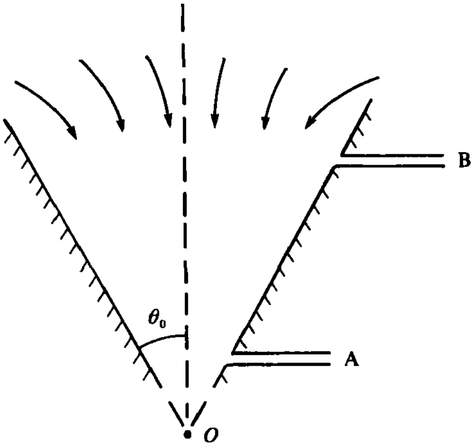

FIGURE 1. Sketch of the conical-channel flow. Pressure ports A and B are at distances r_A and r_B, respectively, from the apex O. In the experiment of James & Saringer (1980) the upstream reservoir served as port B.

of the hydrodynamics of dilute polymer solutions since the kinematics of the flow field is essentially independent of the polymer effect (see §3 below), which allows one to study the dynamical (stress) effect of the polymer without having to solve the highly nonlinear problem of flow modification.

2. The model

Let us first define some useful quantities. In the absence of flow, or in sufficiently weak flows, the macromolecules are in the coiled state and act hydrodynamically as spheres with some effective radius R_0, which in a dilute solution is directly connected with the intrinsic viscosity $[\eta]$, polymer concentration by weight c, number density of polymer molecules in the solution n, and the hydrodynamically effective volume concentration of polymer ϕ:

$$\tfrac{4}{3}\pi R_0^3 n = \phi = \tfrac{2}{5}c[\eta]. \tag{1}$$

Here the Einstein result for the effective viscosity of a dilute suspension of spheres was used. The conical-channel flow of a Newtonian fluid at high Reynolds number is well approximated by a sink flow outside the thin boundary layer, so that in the Lagrangian frame of a fluid particle the velocity field is a uniaxial extension, with zero vorticity, and the rate-of-strain tensor given by

$$\boldsymbol{E} = E \begin{vmatrix} 1 & 0 & 0 \\ 0 & -\tfrac{1}{2} & 0 \\ 0 & 0 & -\tfrac{1}{2} \end{vmatrix}, \tag{2}$$

where the principal direction 1 is along the streamline. The principal strain rate $E_{11} \equiv E_{rr} \equiv E$ is increasing along the path of a fluid particle (here r is a coordinate in a spherical coordinate system, centred at the apex of the cone).

We need therefore to consider the behaviour of a polymer molecule in an extensional flow. Apparently, the first to do this was Frenkel (1944); however, this important work remained virtually unknown outside research on the shear degradation of polymers. The current theoretical understanding derives from the works of Peterlin (1966), de Gennes (1974), Hinch (1974, 1977), Tanner (1975), and Rabin, Henyey & Pathria (1985). The physical picture emerging from these studies served as the motivation for the model to be proposed here.

This physical picture may be summarized as follows. At very small rates of strain the polymer chain preserves its undisturbed configuration (random coil, or its modification due to the excluded volume effects) and acts hydrodynamically as a sphere of radius R_0. As the rate of strain seen by the macromolecule increases, the macromolecule stretches somewhat till the entropic restoring force (which is due to Brownian motion) balances the increased viscous pull of the extensional flow. At small deformations the restoring force must be proportional to $(l-2R_0)$, where l is the hydrodynamically effective length of the elongated coil. On the other hand, the viscous pull at a given rate of strain E increases with l faster than linearly, say as l^{α}, where α approaches 2 as elongation grows (both the hydrodynamic size and the magnitude of the undisturbed velocity variation over the length of the macromolecule grow with l; see, for example, Hinch 1977). It is clear that for a rate of strain less than some critical value E_{cs} the partially elongated coil will be stable, while for $E > E_{cs}$ the balance between the restoring force and the viscous pull will become impossible, and the stretching will become a runaway process. Equating both forces and their derivatives at $E = E_{cs}$, one obtains the expression for the 'prestretching ratio' $\beta = l_{cs}/2R_0$ in the form $\beta = \alpha/(\alpha-1)$; here l_{cs} is the length of the elongated coil at $E = E_{cs}$, i.e. the maximum stable coil length. We may thus expect $\beta \approx 2$; this is close to the value $\beta = 1.8$ obtained by Rabin *et al.* (1985). No experimental information on β appears to exist at the moment.

We have defined the critical strain rate E_{cs} as such that at $E > E_{cs}$ the macromolecule cannot exist in a coiled state (i.e. E_{cs} defines the stability limit of the coil). This value is, probably, somewhat higher than the value corresponding to the so-called 'coil-stretch transition' (de Gennes 1974); the latter, however, is relevant only in the thermodynamic (infinite time) limit, while flows in hydrodynamic experiments are normally transient in the Lagrangian sense. Incidentally, in such flows the extension of the chain should exhibit hysteresis effects, that is, once extended, the chain can be maintained for a long time in the extended state by a strain rate which is much smaller than E_{cs} (de Gennes 1974; Hinch 1974, 1977; Tanner 1975; Rabin *et al.* 1985); eventually, the chain will be able to retract into a coiled state due to Brownian fluctuations, unless, of course, the strain rate has increased again above E_{cs}. The value of the critical strain rate is expected to satisfy the relation

$$E_{cs}\tau_1 = O(1),$$

where τ_1 is the longest relaxation time of the macromolecule.

The fast increase of the viscous pull with the chain length means that, upon onset of the supercritical (runaway) regime, the elongation of the chain will essentially follow the elongation of the fluid element until the chain is nearly fully stretched (Daoudi 1976; Hinch 1977; de Gennes 1979, p. 192). This is usually described by saying that 'the polymer molecule stretches (deforms) affinely with the fluid', and connotes the image of something like a piece of very soft rubber, deforming the same way as the fluid in its place would deform.

A different physical picture of the supercritical regime will be proposed here, with important consequences for the calculation of the stress field due to polymer additive. This picture was motivated by the description of the terminal equilibrium configuration of a macromolecule stretched by a strong flow, first given by Frenkel (1944); recently, the same description was arrived at, independently of Frenkel's work, by de Gennes (1974, p. 5041), by Hinch (1977, p. S26), and, in the framework of a detailed analysis based on the rotational isomeric state theory, by Rabin *et al.* (1985, p. 49). Let us quote from the abstract of Frenkel's (1944) paper: '...the central portion of the molecule becomes straightened out along the direction of flow, as soon as [the critical velocity gradient] is reached, while the two end portions remain curled in the usual way'. In other words, in the terminal equilibrium configuration the macromolecule is not stretched uniformly, but may be divided heuristically into a taut central portion, straightened out along the axis of extension, and two randomly coiled end portions (in reality, of course, the transitions between the portions are gradual), for the simple reason that the viscous pull due to extensional flow is not uniform along the length of the chain, but roughly parabolic, being zero at the ends and maximum in the middle (which is why the chains break in the middle in the shear degradation experiments; this was also predicted by Frenkel 1944).

Let us now postulate that the above 'coil–string–coil' picture is also a good description of the configuration of the macromolecule *during the transient process of the supercritical stretching*, from some moment soon after its onset and till the stretching is complete. That is, unlike in the case of the subcritical ($E < E_{cs}$) stretching, when the Brownian motion ensures that the instantaneous configurations of the chain are randomized within its hydrodynamically effective 'envelope', the supercritical stage should be described by the word *unravelling*, whereby the central portion is straightened out first and then remains taut and grows in length at the expense of the two coiled portions at the ends; these end portions move apart in a symmetrical fashion under the influence of the flow, simultaneously diminishing in size. If the flow later becomes weak, the chain will curl back into a coil. In other words, each half of the chain unravels (in a strong flow) and curls back (in a weak flow) just like the string in the well-known children's toy, the 'yo-yo', unravels and curls back when the yo-yo is played. The term 'yo-yo model' may be used to designate the present approach.

We are now in a position to discuss the polymer effect on the macroscopic stress field. It is obvious that the end coils, moving apart with the flow, will not add substantial energy dissipation (the relative increase in 'viscosity' due to the end coils should be of the same order as that due to the undisturbed coil in a weak flow, i.e. $O(c[\eta])$, which is small by definition of a dilute solution). On the other hand, the central portion of the chain, whose length at higher elongations will constitute essentially the entire hydrodynamically effective length of the macromolecule l, acts hydrodynamically as a taut string; such a string is completely equivalent to a rigid rod in terms of the additional stress generated in a pure straining motion. We can thus use the theory for the stress in a suspension of rigid rods, developed by Batchelor (1971) with the express purpose of providing a rigorous basis for modelling polymer solutions.

The symmetry of the uniaxial extension (2) implies that the additional deviatoric stress due to polymer molecules $\boldsymbol{\sigma}'$ will have the same tensorial structure as the rate-of-strain tensor $\boldsymbol{E}$ and so may be written as

$$\boldsymbol{\sigma}' = 2\zeta\eta_s \boldsymbol{E}, \tag{3}$$

where η_s is the viscosity of the solvent, and ζ is the ratio of the contributions to the bulk deviatoric stress due to the presence of the macromolecules and due to the pure solvent. This does not mean, of course, that the rheology of the polymer solution can be described by (3) in general – it certainly cannot. It is only due to the particular structure of the flow under discussion that (3) is valid. Roughly speaking, this equation describes not a certain fluid but a certain flow; it is, however, completely rigorous within this task, and does not imply any additional assumptions. Note that ζ is not a constant but a function of the extension of the macromolecules, and thus of the history of motion. According to Batchelor (1971, equation (5.2)), this function is given by

$$\zeta = \frac{\pi}{9}\frac{nl^3}{\log(\pi/\phi)}, \tag{4}$$

where ϕ is the hydrodynamically effective volume concentration, i.e. the number density n multiplied by the volume of a rigid rod which has the same length l as the macromolecule and produces the same perturbation in the flow.

It is important to write the expression for ζ in the above form, and not in the form $\zeta = \frac{4}{9}(\phi/\log(\pi/\phi))\,(l^2/d^2)$, where d is the diameter of the rod, as originally given by Batchelor (1971). The two forms are, of course, completely equivalent for the rigid rods considered by Batchelor (1971); however, using the second form in the context of modelling polymer solutions may lead to serious errors. This is so because the values of both d (i.e. the hydrodynamically effective cross-sectional diameter of a polymer chain) and ϕ are highly uncertain. In particular, it is quite probable that, as the chain unravels, its hydrodynamically effective volume changes (probably decreases due to decreasing hydrodynamic screening); however, there appears to be no simple way to take this into account. The variation of d is equally hard to predict. It is therefore important to use the form given in (4), so that the poorly defined ϕ appears only under the logarithm sign, and its exact value is thus of little significance, while d does not appear at all. If, on the other hand, one were to use the second form, one could be tempted to estimate d as the size of the monomer, or of the Kuhn statistical element, etc., in other words to assign to d some constant value. This would result in ζ growing with l quadratically at most, or even much slower if the decrease in ϕ with unravelling were taken into account, in contrast to the correct nearly cubic dependence displayed in (4).

We shall now neglect the variation of ϕ with the chain extension and assume that ϕ is always given by (1). For the James & Saringer (1980) solution $c = 2.0\times10^{-5}$ g/cm^3 and $[\eta] = 2.5\times10^3$ cm^3/g, so (1) gives $\phi = 0.02$ and $\log(\pi/\phi) = 5.06$. The lowest conceivable limit for ϕ, which, in all probability, underestimates the true value by orders of magnitude, can be found as the 'pure' (i.e. not hydrodynamically effective) volume concentration of the polymer molecules, i.e. c/ρ_{p}, where $\rho_{\mathrm{p}} \approx 1$ g/cm^3 is the density of the polymer in its pure (not dissolved) state. This gives the value of 2.0×10^{-5}, i.e. 10^3 times less than ϕ from (1). However, even with this value the logarithm in (4) would change only by a factor of about 2, which should be compared to a possible $O(10^6)$ increase in ζ upon extension due to the l^3 term. Clearly, the variation of ϕ can be safely neglected.

Strictly speaking, (4) becomes valid only after the macromolecules are stretched so strongly that they begin to interact hydrodynamically. At the initial stage of the supercritical stretching this is certainly not the case; moreover, modelling the macromolecule as a taut string between two coils, approximating the length of this string as the total effective length l, etc., are also hardly justifiable at this initial stage. Thus, (4) must be seriously in error there, and would need to be modified. (The error is in the direction of underestimating the polymer effect.) However, the largest and most important contribution of the additional stress due to macromolecules takes place, of course, where the macromolecules *are* strongly elongated (l is large), and so the above modification would not change the overall result substantially. In other words, where the prediction of (4) is substantially different from the true value of ζ as defined in (3), both the true value and the prediction are so small (in a dilute solution!) as to be entirely negligible. We will therefore use (4) for all l upon onset of the supercritical stretching.

Then, combining (1), (4), and the definition of the prestretching ratio β, we obtain

$$\left.\begin{aligned} &\zeta = \frac{4}{15}\frac{\beta^3 c[\eta]}{\log(5\pi/2c[\eta])}\left(\frac{l}{l_{\mathrm{cs}}}\right)^3 \\ \text{or}\qquad &\zeta = \kappa\xi^3; \\ \text{where}\qquad &\kappa \equiv \frac{4}{15}\frac{\beta^3 c[\eta]}{\log(5\pi/2c[\eta])}; \quad \xi \equiv \frac{l}{l_{\mathrm{cs}}}. \end{aligned}\right\} \tag{5}$$

Let us briefly discuss the two dimensionless quantities involved, the 'polymer parameter' κ and the variable ξ. Since β is likely to be about the same for all flexible polymers, while the log factor is not likely to change by more than a factor of 2 (in either direction) within the realm of dilute solutions, we can say that κ is roughly proportional to $c[\eta]$, with the numerical coefficient that is about 0.3 for the polymer solution used by James & Saringer (1980) if we use $\beta = 1.8$ as calculated by Rabin *et al.* (1985). Generally, κ is mainly determined by the easily measurable quantities c and $[\eta]$, which makes it convenient to use.

The variable ξ, though defined in terms of the effective length of the polymer molecule, is essentially a kinematical quantity, namely, it is the relative elongation (i.e. the current length divided by the initial length) of a material line element, lying along the principal axis of extension, from the critical point where $E = E_{\mathrm{cs}}$. It is thus a function of the history of the motion, and of the critical strain rate E_{cs} as a parameter. The actual polymer size has been scaled out of the problem.

Obviously, ξ is limited from above by the maximum possible elongation of the chain. For a typical polymer with the number of the Kuhn statistical elements $N = O(10^4)$ the maximum value of ξ is thus $O(100)$; such elongations are not reached in the James & Saringer (1980) experiment before the downstream pressure port A (see §4 below). Rupture of the chains will also change ξ (and n).

This essentially completes the formulation of the 'yo-yo' model.† If we had a general flow field, this formulation would not be sufficient, of course. We would need generalized criteria for both the onset of the supercritical stretching and the return to the coiled state, as well as a more complete constitutive relation for the 'stretched-polymer' fluid, which cannot be described by (3) in a general case. These questions are the subject of current research; the sink flow allows us to test the viability of the yo-yo model in the simplest form given above.

3. Calculation of the stress field

The unravelling of the macromolecules strongly increases the 'viscosity' of the fluid, and this may, in principle, change the kinematics of the flow (a highly viscous Newtonian fluid would not form boundary layers, for example). James & Saringer (1980) excluded the cases when the change in kinematics was obvious (i.e. when a large-scale vortex ring appeared in the channel), but this does not guarantee that the flow field in which they made their measurements can, in fact, be represented as an

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† The model, in a brief preliminary form, was first presented in Ryskin (1985).

irrotational sink flow in the core plus a thin boundary layer. We will nevertheless assume that it can, for the following reasons.

The macromolecules that are carried along the streamlines passing through the irrotational core (the sink flow part) are subjected to a strong extensional flow and thus begin to stretch, as described in the preceding section. On the other hand, the macromolecules carried through the boundary-layer region are subjected to a weak shear flow (where they rotate with vorticity and are therefore pulled apart and compressed in an alternating manner) and thus are not likely to stretch appreciably. Note that in the conical-channel flow the thickness of the boundary layer quickly diminishes downstream, and so the macromolecules already stretched by the extensional flow in the core do not enter the boundary layer (if they did, they could remain stretched even in a comparatively weak flow). These considerations suggest that the 'coiled-polymer' fluid (C-fluid) in the boundary layer retains its low viscosity, nearly equal to that of the solvent, while the fluid in the core has its 'viscosity' increased owing to the stretched macromolecules. The velocity fields in these two regions are connected only through the velocity and pressure at the outer edge of the boundary layer. If the boundary layer is thin, the change in the pressure at its outer edge due to the polymer effect in the core, while causing some changes in the velocity distribution within the boundary layer, will not produce a sizable back effect on the velocity field in the irrotational core (but see §5). This means that if a sink flow is dynamically possible for the 'stretched-polymer' fluid (S-fluid) in the core, the kinematics of the whole flow field in the conical channel may remain essentially the same as for the pure solvent, though the stress field will be different.

The velocity field for the three-dimensional sink flow follows immediately from the continuity equation $\nabla \cdot \mathbf{u} = 0$ alone (where $\mathbf{u}$ is the velocity), if one can assume that $\mathbf{u}$ depends only on the distance from the apex r and is independent of both angular coordinates in the corresponding spherical coordinate system. Consequently, this velocity field is dynamically possible in any fluid whose rheology does not contradict the above assumption, that is, does not produce angular dependence in the stress field where none is present in the kinematics. The S-fluid is obviously of such type (see (3)). The core of the entire flow field is therefore the sink flow of the S-fluid, with the 'viscosity' which is rapidly increasing downstream; this core is shielded from the no-slip boundaries by the thin boundary layer of the C-fluid with constant low viscosity.

The above considerations are obviously not too rigorous, and a careful analysis of the boundary-layer structure would be highly desirable, especially of its outer region where the flow character changes gradually from weak to strong. These interesting questions are, however, beyond the scope of the present work.

Before proceeding with the calculation of the stress, it is important to consider carefully what is actually measured by a pressure gauge connected to the pressure port A. In Newtonian fluid mechanics it is well known that the pressure is uniform across a boundary layer; a slight reformulation of the usual argument shows that it is equally correct to assert the uniformity of the normal stress across a boundary layer. In the Newtonian case the two differ, besides the sign, by only a negligible amount; the difference, i.e. the viscous normal stress, is exactly zero on the rigid surface due to the incompressibility condition, while its variation along the surface in the effectively inviscid (high-Reynolds-number) flow just outside the boundary layer is negligible in comparison with the inertia forces, and thus the pressure variation.

The situation is quite different in the present problem. The fluid just outside the boundary layer has high 'viscosity', so the normal stress does not reduce to minus pressure there, though it does on the rigid surface. Therefore, the pressure at the wall p_w, measured by the pressure gauge, is equal to minus the total normal stress in the sink flow just outside the boundary layer, i.e.

without the polymer (for the pure solvent)

$$p_w = p_s - 2\eta_s E_{\theta\theta},$$

while for the polymer solution

$$p_w = p_s + p' - 2\eta_s E_{\theta\theta} - \sigma'_{\theta\theta}.$$

The right-hand side in the above expressions is evaluated on the irrotational sink flow in the core; here p_s is the pressure in the pure solvent flow, $(p_s + p')$ is the pressure in the polymer solution flow with the same flow rate, θ is the angular coordinate normal to the wall of the channel. The term $2\eta_s\, E_{\theta\theta}$ can be neglected in both cases as explained above.

We are only interested in the polymer-induced change Δ in the pressure differential between the ports B and A (i.e. pressure at B minus pressure at A). Clearly

$$\Delta = (p' - \sigma'_{\theta\theta})_{\mathrm{A}}^{\mathrm{B}}$$

From the structure of the tensor $\boldsymbol{\sigma}'$ (see (2) and (3)) we see that

$$\sigma'_{\theta\theta} = -\tfrac{1}{2}\sigma'_{rr} = -\zeta\eta_s E_{rr}.$$

The additional pressure field p' arises exclusively in order to balance the force from the additional deviatoric stress $\boldsymbol{\sigma}'$ (other terms in the equation of motion for the polymer solution coincide with the ones for the pure solvent and thus balance each other). We thus obtain

$$-\nabla p' + \nabla \cdot \boldsymbol{\sigma}' = 0$$

and then
$$\nabla p' = 2\eta_s \nabla \cdot (\zeta \boldsymbol{E}) = 2\eta_s \boldsymbol{E} \cdot \nabla \zeta = 2\eta_s E_{rr} \frac{\mathrm{d}\zeta}{\mathrm{d}r} \hat{\boldsymbol{r}},$$

where $\hat{\boldsymbol{r}}$ is a unit vector in the radial direction. Here we used the facts that $\nabla \cdot \boldsymbol{E} = 0$ in an irrotational flow of an incompressible fluid, that $\zeta = \zeta(r)$, and that $\hat{\boldsymbol{r}}$ is one of the principal directions of $\boldsymbol{E}$ in the sink flow.

Thus

$$p'|_{\mathrm{A}}^{\mathrm{B}} = 2\eta_s \int_{r_{\mathrm{A}}}^{r_{\mathrm{B}}} E \frac{\mathrm{d}\zeta}{\mathrm{d}r} \mathrm{d}r$$

and so
$$\Delta = \eta_s \left\{ \zeta E|_{\mathrm{A}}^{\mathrm{B}} + 2 \int_{r_{\mathrm{A}}}^{r_{\mathrm{B}}} E \frac{\mathrm{d}\zeta}{\mathrm{d}r} \mathrm{d}r \right\}. \tag{6}$$

So far we have used only the symmetry of the sink flow and the assumption of the polymer effect being negligible in the boundary layer. To proceed further, we need the particular form of ζ as a function of r, which depends on the model and the kinematics of the flow. As is evident from (5), we need to know the dependence on r of ξ, the elongation of a material line element from the critical point r_{cs} (where $E = E_{cs}$). Consider a spherical shell of fluid, centred at the apex: as it moves in a sink flow, its area decreases as r^2, and thus its thickness must increase as r^{-2}. This means that $\xi \propto r^{-2}$, since we are interested in the elongation of a material line element directed along r. One thus obtains (see, for example, de Gennes 1979, p. 192)

$$\xi = \left(\frac{r_{\mathrm{cs}}}{r}\right)^2.$$

To determine r_{cs}, we recall that in sink flow

$$u \equiv u_r = -\frac{q}{r^2}; \quad E \equiv E_{rr} = \frac{2q}{r^3};$$

where
$$q \equiv \frac{Q}{2\pi(1-\cos\theta_0)},$$

Q is the total flow rate, and θ_0 is the half-angle of the cone. Therefore

$$r_{\mathrm{cs}} = \left(\frac{2q}{E_{\mathrm{cs}}}\right)^{\frac{1}{3}}$$

and we obtain
$$\zeta = \frac{4\kappa q^2}{E_{\mathrm{cs}}^2}\frac{1}{r^6}. \tag{7}$$

Equation (7) obviously applies only until the molecule is 'fully stretched'; afterwards ξ will be constant. However, in the experiment of James & Saringer (1980) this may be shown *a posteriori* to happen after the downstream pressure port A and hence is of no consequence for the measurements (see §4). Thus, for the analysis of this experiment, (7) can be used without modification.

Returning now to (6) for the polymer-induced change in the pressure drop, we see that it can be written as

$$\Delta = \eta_s\left\{-(\zeta E)_{r=r_{\mathrm{A}}} + 2\int_{r_{\mathrm{A}}}^{\infty} E\frac{\mathrm{d}\zeta}{\mathrm{d}r}\,\mathrm{d}r\right\}.$$

Here we took into account that $r_{\mathrm{A}} < r_{\mathrm{cs}} < r_{\mathrm{B}}$ (in the experiment of James & Saringer 1980 the upstream reservoir served as the port B) and neglected the polymer contribution to the stress at $r > r_{\mathrm{cs}}$, where the macromolecules are still coiled; also, since the integrand in (6) tends to zero very rapidly with the increase in r, viz. as r^{-10}, the integration can be formally extended to infinity, with the error thus introduced being small (ζ is then formally defined by (7) for all r).

The final result for the polymer-induced change in the pressure differential is as follows:

$$\begin{aligned}\Delta &= -\frac{7}{3}\frac{\kappa\eta_s Q^3}{\pi^3(1-\cos\theta_0)^3 E_{\mathrm{cs}}^2 r_{\mathrm{A}}^9}\\ &= -\frac{28}{45}\frac{\beta^3 c[\eta]\eta_s Q^3}{\pi^3(1-\cos\theta_0)^3 \log(5\pi/2c[\eta])\, E_{\mathrm{cs}}^2 r_{\mathrm{A}}^9}.\end{aligned} \tag{8}$$

4. Comparison with experiment

In the James & Saringer (1980) experiment, the requisite values were: $\theta_0 = 29°$, so that r_{A} can be estimated (see their figure 4) as 0.021 cm; $\eta_s \approx 0.01$ g/cm s; $[\eta] = 2.5\times 10^3$ cm^3/g; $c = 2.0\times 10^{-5}$ g/cm^3. Taking the acceleration due to gravity as 980 cm/s^2, we obtain

$$\Delta = -1.29\times 10^9\,(\beta^3 E_{\mathrm{cs}}^{-2})\,Q^3, \tag{9}$$

where E_{cs} is in s^{-1}, Q in cm^3/s, and Δ in cm of water head differential.

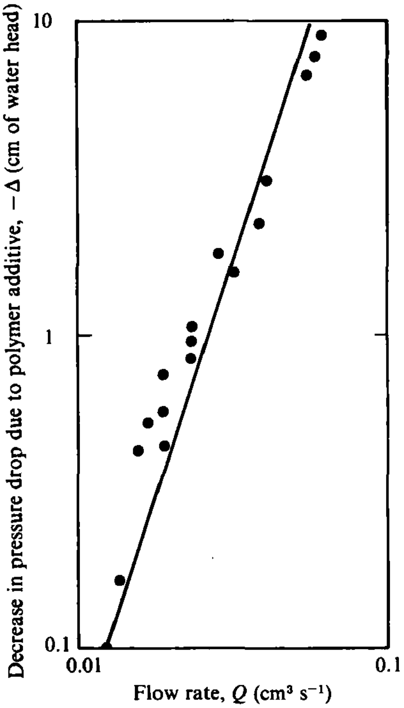

FIGURE 2. Comparison of the scaling law for the polymer-induced change in the pressure drop between ports B and A with the experimental data of James & Saringer (1980). Solid line, the scaling law $-\Delta \propto Q^3$, see (9); points, the experimental data, taken from figure 6 of James & Saringer (1980).

Figure 2 presents the experimental data for Δ, taken from figure 6 of James & Saringer (1980), as the difference between the head differentials for water and for polymer solution at the same flow rate. Since β and E_{cs} are not known precisely, we represent the scaling $-\Delta \propto Q^3$ on the log–log plot by drawing a straight line through the experimental points, whose slope corresponds to the scaling. It can be seen that the data are in good agreement with the scaling; comparing now the equation of the line, viz.

$$\Delta = -5.3 \times 10^4 Q^3,$$

with (9), we obtain an estimate for $\beta^{\frac{3}{2}} E_{\mathrm{cs}}^{-1}$ of

$$\beta^{\frac{3}{2}} E_{\mathrm{cs}}^{-1} \approx 6.4 \times 10^{-3}\ \mathrm{s}. \tag{10}$$

We can now check the consistency of our assumption (see (7)) that the macromolecule is not yet 'fully stretched' when it passes the pressure port A. To see this, we find the degree of elongation at the port A, where the effective chain length will be denoted as l_{A}, from the formula

$$\frac{l_{\mathrm{A}}}{2R_0} = \left(\frac{Q}{\pi(1-\cos\theta_0)}\right)^{\frac{2}{3}} \frac{(\beta^{\frac{3}{2}} E_{\mathrm{cs}}^{-1})^{\frac{2}{3}}}{r_{\mathrm{A}}^2},$$

which gives about 23 for the highest flow rate in figure 2, and about 8 for the lowest. The 'full' extension of the macromolecule would correspond to a degree of elongation of order 100; our solution is therefore self-consistent. It is of interest to note that the supercritical stretching begins at the distance from the apex r_{cs} which is about $3.6r_{\text{A}}$ for the highest flow rate in figure 2, and about $2.1r_{\text{A}}$ for the lowest (the actual exit is located at about $0.7r_{\text{A}}$, see figure 4 of James & Saringer 1980).

The parameters β and E_{cs} in (10) are of a different nature: the first is expected to be nearly the same for all flexible polymers, while the second must be characteristic of a particular polymer–solvent pair. If we use the value $\beta = 1.8$ calculated by Rabin *et al.* (1985), we obtain from (10)

$$E_{\text{cs}}^{-1} \approx 2.7 \times 10^{-3}\ \text{s}. \tag{11}$$

As mentioned in §2, molecular theories predict $E_{\text{cs}}^{-1} \approx \tau_1$, where τ_1 is the longest relaxation time of the polymer molecule. An expression for τ_1 can be written in a form involving only easily measurable quantities and thus nearly independent of the underlying molecular theory (except for a numerical factor; see Ferry 1980, pp. 190 and 195). Choosing the numerical factor for the non-free-draining (Zimm) case, one obtains

$$\tau_1 = 0.42\,\frac{[\eta]\,\eta_s M}{RT}, \tag{12}$$

where R is the gas constant, T the temperature, and M the molecular weight of the polymer (for the free-draining Rouse case one would have 0.61 instead of 0.42). James & Saringer (1980) used Polyox with $M = 8 \times 10^6$ g/mol at $T = 295$ K, as mentioned in their later paper (James & Saringer 1982*a*). This gives

$$\tau_1 = 3.5 \times 10^{-3}\ \text{s}.$$

The agreement with (11) is much better than could be expected, taking into account the many uncertainties in the theory, imprecise knowledge of the position of the pressure port A, etc. Indeed, such agreement should probably be considered fortuitous until more experimental data become available.

5. Speculations on the abrupt appearance of a vortex ring in the conical channel

Experiments (James & Saringer 1980) show that at sufficiently large flow rates a large unsteady vortex ring suddenly appears in the flow. A tentative explanation of this phenomenon may be attempted as follows.

In the Newtonian flow through a conical channel the pressure at the outer edge of the boundary layer (called the external pressure hereinafter) is decreasing downstream, and thus there is no tendency for the boundary layer to separate. The polymer effect is to increase the external pressure by the amount $-\Delta$, which is zero at the critical point r_{cs}, but is rapidly increasing downstream after that point. The new external pressure may thus have a minimum at some point downstream of r_{cs}, creating conditions for the boundary layer to separate; the separation point being, presumably, not far downstream from the point of minimum pressure. Since the polymer effect is greatest near the exit, the separation point will first appear there and will be moving upstream as the flow rate is increased. Finally, when the size of the separated region becomes comparable with the exit opening, the latter will be sufficiently obstructed, and this will lead to an increase in flow velocity and strain rate, with the resulting further increase in polymer pressure and backflow. This positive feedback is likely to result in the abrupt creation of a large-scale backflow, i.e. a vortex ring, as is indeed observed.

An approximate condition for the flow separation to be located at a given point can be derived as follows. The external pressure can be written as (neglecting Newtonian viscosity)

$$-\tfrac{1}{2}\rho u^2 - \Delta + \text{const},$$

while the pressure differential between the upstream reservoir and the given point is

$$\tfrac{1}{2}\rho u^2 + \Delta.$$

Since u^2 varies with r as r^{-4} and Δ as r^{-9}, taking derivative of the external pressure with respect to r and equating it to zero yields (after multiplication by r)

$$\tfrac{4}{2}\rho u^2 + 9\Delta = 0.$$

Thus at the separation point $\Delta \approx -\tfrac{2}{9}\rho u^2$ and the pressure differential is about half of its water value. The maximum polymer effect reported by James & Saringer (1980, figure 6) for the port A is of just about this magnitude, and one might guess that the data stop at this point because some flow instability appeared; this is indeed the case (D. F. James 1986, private communication).

Since $\Delta \propto cQ^3$ while $u^2 \propto Q^2$, one may expect that the flow rate necessary for the vortex creation should scale as c^{-1}. This does not explain, however, why more concentrated solutions ($c = 80$ p.p.m.) exhibit abrupt vortex creation before any appreciable change in the pressure drop (see figure 3 of James & Saringer 1980). Part of the explanation may lie in the fact that at low flow rates the boundary layer is very thick, so that the effective exit opening is narrow and may be sufficiently obstructed by a rather small flow separation. A simple test of this view and the above estimates would be to increase the polymer concentration from zero while running the experiment at a constant flow rate. If the above picture is correct, one should observe stable flows (without a large-scale vortex) at much higher flow rates and concentrations, and the transition to the vortex flow should follow the estimates given above.

6. Resolution of the two-dimensional-sink paradox

In a later publication, James & Saringer (1982*a*) reported some experiments with a two-dimensional sink flow in a wedge-shaped channel. They measured the reservoir-to-reservoir pressure drop and found that its relative increase upon addition of polymer was very much smaller than in the conical channel, viz. about 10–15 % compared with 300 %, for the same exit strain rate. It is difficult to analyse the reservoir-to-reservoir data quantitatively since they may reflect complicated changes in the flow kinematics upon passing the exit. The best that can be done here is to estimate the polymer-induced change in the pressure drop between the upstream reservoir and the exit itself. For convenience, we shall present in parallel the results for the conical-channel flow (i.e. three-dimensional sink), some of which are equivalent to those derived in §3, but are written in an alternative form, and the new results for the wedge-channel flow (two-dimensional sink). It should be noted that in the latter case the additional stress due to the polymer does not have the same tensorial form as the rate-of-strain tensor (see Batchelor 1971); this does not, however, complicate the calculations seriously.

One obtains (here r belongs to different coordinate systems – spherical and cylindrical – in three and two dimensions)

Conical channel (three-dimensional) | Wedge channel (two-dimensional)

$$u = -\frac{q}{r^2}; \quad E = \frac{2q}{r^3}; \qquad\Bigg|\qquad u = -\frac{q}{r}; \quad E = \frac{q}{r^2};$$

$$r_{\mathrm{cs}} = \frac{(2q)^{\frac{1}{3}}}{E_{\mathrm{cs}}^{\frac{1}{3}}}; \quad \xi = \left(\frac{r_{\mathrm{cs}}}{r}\right)^2; \qquad\Bigg|\qquad r_{\mathrm{cs}} = \frac{q^{\frac{1}{2}}}{E_{\mathrm{cs}}^{\frac{1}{2}}}; \quad \xi = \frac{r_{\mathrm{cs}}}{r};$$

where q depends on the total flow rate differently in three and two dimensions.

The polymer-induced change in the pressure drop between the upstream reservoir and a pressure port A in the channel wall near the exit is

$$\Delta_{\theta\theta}^{(3)} = 3\eta_{\mathrm{s}}\left[2\int_{r_{\mathrm{A}}}^{\infty} \frac{\zeta E}{r}\,\mathrm{d}r - (\zeta E)_{r=r_{\mathrm{A}}}\right], \qquad\Bigg|\qquad \Delta_{\theta\theta}^{(2)} = 3\eta_{\mathrm{s}}\left[\int_{r_{\mathrm{A}}}^{\infty} \frac{\zeta E}{r}\,\mathrm{d}r - (\zeta E)_{r=r_{\mathrm{A}}}\right],$$

which yields the decrease

$$\Delta_{\theta\theta}^{(3)} = -\tfrac{7}{3}\kappa\eta_{\mathrm{s}}\frac{(2q)^3}{r_{\mathrm{A}}^9\,E_{\mathrm{cs}}^2} = -\tfrac{7}{3}\kappa\eta_{\mathrm{s}}\frac{E_{\mathrm{A}}^3}{E_{\mathrm{cs}}^2}, \qquad\Bigg|\qquad \Delta_{\theta\theta}^{(2)} = -\tfrac{12}{5}\kappa\eta_{\mathrm{s}}\frac{q^{\frac{5}{2}}}{r_{\mathrm{A}}^5\,E_{\mathrm{cs}}^{\frac{3}{2}}} = -\tfrac{12}{5}\kappa\eta_{\mathrm{s}}\frac{E_{\mathrm{A}}^{\frac{5}{2}}}{E_{\mathrm{cs}}^{\frac{3}{2}}},$$

where $E_{\mathrm{A}} \equiv E\,|_{r=r_{\mathrm{A}}}$.

However, a better estimate for the reservoir-to-reservoir 'pressure' effect is obtained if one calculates the polymer-induced change in the rr-component of the full stress tensor, since it is this component that can be viewed as transmitting the normal force between the fluid in the channel and the fluid in the downstream reservoir. This change is given by (here r_{ex} is the radial position of the exit)

$$\Delta_{rr}^{(3)} = 6\eta_{\mathrm{s}}\int_{r_{\mathrm{ex}}}^{\infty} \frac{\zeta E}{r}\,\mathrm{d}r, \qquad\Bigg|\qquad \Delta_{rr}^{(2)} = 3\eta_{\mathrm{s}}\int_{r_{\mathrm{ex}}}^{\infty} \frac{\zeta E}{r}\,\mathrm{d}r,$$

which yields an *increase* of magnitude

$$\Delta_{rr}^{(3)} = \tfrac{2}{3}\kappa\eta_{\mathrm{s}}\frac{(2q)^3}{r_{\mathrm{ex}}^9\,E_{\mathrm{cs}}^2} = \tfrac{2}{3}\kappa\eta_{\mathrm{s}}\frac{E_{\mathrm{ex}}^3}{E_{\mathrm{cs}}^2}. \qquad\Bigg|\qquad \Delta_{rr}^{(2)} = \tfrac{3}{5}\kappa\eta_{\mathrm{s}}\frac{q^{\frac{5}{2}}}{r_{\mathrm{ex}}^5\,E_{\mathrm{cs}}^{\frac{3}{2}}} = \tfrac{3}{5}\kappa\eta_{\mathrm{s}}\frac{E_{\mathrm{ex}}^{\frac{5}{2}}}{E_{\mathrm{cs}}^{\frac{3}{2}}}.$$

For the same exit strain rate E_{ex} the ratio of this increase in the conical channel to that in the wedge channel is

$$\frac{\Delta_{rr}^{(3)}}{\Delta_{rr}^{(2)}} = \frac{10}{9}\left(\frac{E_{\mathrm{ex}}}{E_{\mathrm{cs}}}\right)^{\frac{1}{2}}.$$

Since $E_{\mathrm{cs}} \approx 3\times10^2\ \mathrm{s}^{-1}$ and the highest exit strain rate in the James & Saringer (1980, 1982*a*) experiments was about $3\times10^4\ \mathrm{s}^{-1}$ (see figure 2 of the second paper), this ratio could easily reach $O(10)$. Moreover, James & Saringer (1982*a*) actually compared the *relative* increases in the pressure drop over the values for water and found these to be about 10–15 % in the wedge flow compared with up to 300 % in the cone flow. The pressure drop for water can be estimated as $\frac{1}{2}\rho u_{\mathrm{ex}}^2$, which can be rewritten as

$$\tfrac{1}{2}\rho\,\frac{E_{\mathrm{ex}}^2\,r_{\mathrm{ex}}^2}{4}. \qquad\Bigg|\qquad \tfrac{1}{2}\rho E_{\mathrm{ex}}^2\,r_{\mathrm{ex}}^2.$$

Then we obtain (see figure 2 of James & Saringer 1982*a* for the geometrical measurements of the channels):

$$\frac{\text{relative pressure drop increase in cone flow}}{\text{relative pressure drop increase in wedge flow}} = 4\left(\frac{r_{\mathrm{ex}}^{(2)}}{r_{\mathrm{ex}}^{(3)}}\right)^2 \frac{\Delta_{rr}^{(3)}}{\Delta_{rr}^{(2)}} \approx 2.6\left(\frac{E_{\mathrm{ex}}}{E_{\mathrm{cs}}}\right)^{\frac{1}{2}},$$

which is about 26 at the highest exit strain rates, in agreement with the experimental observations.

Qualitatively, the reason for the polymer effect being much smaller in the two-dimensional sink is the smaller degree of elongation reached before the exit. Even though the path of the supercritical stretching is longer in two dimensions for the same exit radius and strain rate (the critical radius can be written as $r_{\mathrm{ex}}\,(E_{\mathrm{ex}}/E_{\mathrm{cs}})^{\frac{1}{3}}$ in three dimensions and $r_{\mathrm{ex}}\,(E_{\mathrm{ex}}/E_{\mathrm{cs}})^{\frac{1}{2}}$ in two dimensions), the total elongation reached by the exit ξ_{ex} is still greater in three dimensions, viz. $(E_{\mathrm{ex}}/E_{\mathrm{cs}})^{\frac{2}{3}}$ in three dimensions compared with $(E_{\mathrm{ex}}/E_{\mathrm{cs}})^{\frac{1}{2}}$ in two dimensions. For $E_{\mathrm{ex}}/E_{\mathrm{cs}} = O(100)$ this means that the two-dimensional elongation is less than half of that in three dimensions, and thus the polymer effect is smaller in two dimensions by an order of magnitude (recall that $\zeta = \kappa\xi^3$).

A very different analysis of the 'paradox' discussed in this section has just been published by Chakraborty & Metzner (1986), who utilized Maxwell–Oldroyd rheological models in order to explain the large differences between the polymer effects in three- and two-dimensional sink flows. (The two-dimensional sink flow of the Maxwell fluid has also been analysed by Tanner 1985, pp. 277–282.) It should be noted that some of the predictions of Chakraborty & Metzner (1986) are substantially different from ours. For example, they predict that the relative increase in the pressure drop due to polymer, plotted *vs.* the exit strain rate, will exhibit a maximum, while our results indicate monotonic growth, at least until the strain rates are so high that the chain reaches a nearly full extension before the exit. The experiment with a conical channel does show a maximum at $E_{\mathrm{ex}} \approx 4\times10^4\ \mathrm{s}^{-1}$ (see figure 2 of James & Saringer 1982*a*); however, the decrease of the relative polymer effect beyond this point may be due to degradation of polymer, which becomes significant at these high strain rates (see James & Saringer 1982*b*, pp. 330–331). Further experiments are clearly needed to elucidate these phenomena.

7. Discussion

A thorough experimental testing of the present results is, of course, highly desirable. Using a conical channel and varying the flow rate and the position of the pressure port, one could test the prediction $\Delta \propto Q^3/r_{\mathrm{A}}^9$; if the channel shape is different from conical, a new analysis along the lines of §3 will be necessary (for the two-dimensional sink flow the results of §6 can be used; however, the polymer effect is small in this flow). If mass transfer measurements (e.g. using electrochemical technique – see Ambari, Deslouis & Tribollet 1984) were feasible, the detailed analysis of the boundary layer could become worthwhile.

Using a conical channel with fixed pressure port and flow rate, one can check the prediction

$$\Delta \propto [\eta]\,\eta_{\mathrm{s}}\,\tau_1^2,$$

where the onset condition $E_{\mathrm{cs}}\,\tau_1 = O(1)$ was assumed to hold.

The relaxation time τ_1 could be obtained from independent experiments; alternatively one can substitute for it using (12) to obtain

$$\Delta \propto \frac{[\eta]^3 \eta_s^3 M^2}{T^2}. \tag{13}$$

The last relation predicts a strong decrease of the polymer effect with temperature, in general agreement with observations (James & Saringer 1982*b*). It would be important, however, to separate experimentally the direct influence of temperature (via the T^2 term) from its indirect influence through η_s and $[\eta]$.

The molecular-weight dependence in (13) is very strong if $[\eta]$ is taken into account, viz. $M^{3.5}$–$M^{4.4}$, depending on the solvent power. The contribution of the high-molecular-weight tail of the polymer sample is thus disproportionately large; a narrow molecular-weight distribution is highly desirable in future experiments.

Integration of the force distribution along the unravelling chain (see equation (4.8) of Batchelor 1971) yields the magnitude of the stretching force at the midpoint of the chain

$$\tfrac{1}{2}\pi \frac{\eta_s E l^2}{\log(5\pi/2c[\eta])};$$

the rupture of the chain should occur when this force becomes comparable to the bond strength.

It is worth emphasizing that the importance of a thorough experimental check of the present theoretical results reaches beyond the conical-channel flow; in particular, it will have a direct bearing on the question of choice among different models of the polymer behaviour in a flowing solution. Let us now discuss briefly the issues involved.

It is generally understood that the bead–spring models of the Rouse or Zimm types are not suitable for describing the polymer behaviour in strong flows since these models are based on the linear Gaussian springs which are inadequate at large elongations. The (non-linear) elastic dumbbell is therefore usually advocated as the basic molecular model for the fluid dynamics of polymer solutions.

In my opinion, the elastic-dumbbell model (originated by Kuhn & Kuhn 1943 and Hermans 1943), with any kind of an entropic spring law (i.e. Gaussian, inverse-Langevin or its approximations, etc.), is not likely to give an acceptable description of the polymer-chain dynamics and contribution to the stress during the transient supercritical stretching, for the simple reason that any entropic spring law is an essentially equilibrium concept, applicable only when the corresponding relaxation time (i.e. τ_1) is much smaller than the timescale of the imposed process. In supercritical stretching the imposed time-scale is $E_{cs}^{-1} \approx \tau_1$. Using an entropic spring in such rapid motion would be akin to calculating the pressure on a piston, moving in a gas-filled cylinder, from the ideal-gas law and the instantaneous volume of the gas, even when the piston moves with a velocity equal to the speed of sound.

In essence, this was already understood by Kuhn & Kuhn (1945), who introduced the concept of 'internal viscosity' (see de Gennes 1979, pp. 198–203; Stockmayer 1979). However, no reliable way to predict this quantity from the first principles exists; moreover, the concept is likely to be inadequate in the supercritical regime anyway, since, as its name implies, it gives essentially a first-order (linear in the deformation rate) correction. Such a correction could be sufficient only if the implied expansion parameter (say, the relaxation time of the chain divided by the timescale of the imposed deformation) were small; in the supercritical regime it is $O(1)$ or higher.

It is then obvious that in the supercritical regime the elastic dumbbell models are likely to underestimate the additional stress due to the polymer by a large margin. It is worth emphasizing that this includes models with the nonlinear spring laws that produce finite extension, such as the inverse-Langevin spring (which is derived on the basis of equilibrium statistical mechanics and is therefore as much entropic as the Gaussian spring), or its empirical approximations – the Warner nonlinear spring, etc.

The second, equally fundamental, problem with the elastic-dumbbell models is that the associated physical picture of the supercritical regime, i.e. the affine (or nearly so) 'stretching', is misleading. It implies the image of a rubber band or a similar extensible object, held at the ends and stretched, and this naturally leads to the entropic elasticity, etc. The non-uniform character of the distribution of the viscous pull along the chain span is ignored. This should be acceptable during the subcritical (non-affine) stretching, when the chain fluctuates rapidly inside its hydrodynamically effective envelope, which is somewhat elongated, but remains nearly steady on the chain timescale τ_1. (Incidentally, the Gaussian spring should be sufficient in this regime since it provides a good approximation to the exact law up to very large extensions, of order 50 % of the total contour length of the chain; see Flory 1969, pp. 313–326). In the supercritical regime, on the other hand, Brownian rearrangements of large chain segments (comparable in length with the chain itself, i.e. the first-mode motions) occur on the same timescale τ_1 as the imposed deformation, and therefore are unable to alter the relative configuration of these segments, created by the flow. This means, first, that thermodynamic concepts such as the entropic elasticity of the chain are no longer applicable since different configurations of the chain are no longer equally probable (the same conclusion as the one reached above from a slightly different point of view). Secondly, this means that as soon as the high viscous pull in the centre creates a highly stretched portion there, the identity of this portion will be maintained; we are thus led to the 'unravelling coil–string–coil' picture of the yo-yo model.

In all probability, the yo-yo model oversimplifies the actual dynamics of the supercritical stretching. For example, one can easily imagine that at the initial stages of the supercritical regime several segments of the chain are unravelling in parallel, so we have the chain folded into a 'bundle' of coil–string–coil systems. However, these details of the chain dynamics are not likely to have a significant influence on the resulting stress field, for the following reasons. First, the extensional flow is likely to straighten the chain, i.e. to unfold the bundle into a single coil–string–coil configuration, by the time the chain is sufficiently long to begin to interact hydrodynamically with other chains and to generate large stress. Secondly, even when we are dealing with a bundle of strings, the contribution to the stress should be about the same as that due to a single string of the same length since the cross-dimension is essentially of no importance (see (4) and the accompanying discussion); the length will be determined by the elongation of a material line element in all cases. In fact, all that is needed for the yo-yo model to work is the existence within the unravelling polymer chain, from some moment soon after the onset of the supercritical regime, of *at least* one taut chain segment spanning nearly the entire extent of the chain in the direction of stretching.

We may conclude that the onset of the supercritical stretching signals the limit of usefulness of the elastic-dumbbell models (with any conceivable spring law). In the yo-yo model, the entropic elasticity plays no direct role in the description of the supercritical regime; thus all potential problems with the application of this equilibrium concept in a non-equilibrium situation are avoided.

The two major consequences for fluid dynamics are the following. First, the yo-yo model predicts much higher stress levels than the elastic-dumbbell models. Secondly, and perhaps even more importantly, the stress in the supercritical regime is produced via a different physical mechanism. The additional stress due to the elastic dumbbells originates in entropic elasticity; as such it should be proportional to kT (for a given instantaneous chain length; note that τ_1 and thus the onset of the supercritical regime are also functions of T), and the external mechanical energy spent on working against this stress should transform entirely into the elastic energy of stretched chains. The yo-yo model, on the other hand, produces the additional stress via a purely dissipative process; the stress is proportional to the solvent viscosity (again for a given instantaneous chain length) and thus decreases with a temperature increase, and no elastic energy storage is predicted. The latter prediction is, of course, valid only approximately: some elastic energy is always stored in a stretched chain; however, this stored energy is insignificant in comparison with the amount of energy dissipated during the supercritical regime.

The flows of engineering interest that are strong enough to induce the supercritical stretching of the polymer chains are usually unsteady in the Lagrangian frame. Thus the terminal equilibrium stretched configuration is not expected to occur often, and the polymer contribution to the stress during the supercritical regime is likely to represent the most prominent dynamical effect of polymer additive. We have seen that the predictions of the elastic-dumbbell models and of the present yo-yo model for this contribution are drastically different. The need for reliable experimental data, obtained in the fluid-dynamical context, is thus quite obvious.

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