MECHANICAL MODELS OF DILUTE POLYMER SOLUTIONS
FOR STRONG FLOWS WITH LARGE POLYMER DEFORMATIONS

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Abstract

A difference between strong and weak flows explains why viscometric measurements may be useless in some other engineering flows. Some useful rheological insights into the strong flows with large polymer deformations can be obtained from simple-minded models. The traditional models have overlooked the possibility of bead rotations and changes in size which are important when there are deformations of the polymer. The large difference in size between the nearly spherical and nearly fully extended configurations leads to large stresses in strong flows whereas there are no detectable rheological effects in weak flows. A new nonlinear dumb-bell model predicts that the polymer may be almost fully extended in drag reduction, these extensions being aided by a hysteresis phenomenon. The new model also allows predictions of the conditions in which mechanical degradation can occur.

Résumé

La différence entre les écoulements forts et faibles explique pourquoi les mesures viscométriques peuvent être inutiles dans quelques autres écoulements industriels. Quelques utiles aperçus rhéologiques sur les forts écoulements peuvent être obtenus à partir de modèles simples. Les modèles traditionnels ne tiennent pas compte de rotations et des changements de taille des grains qui sont importants quand il y a déformation du polymère. La grande différence de dimension entre les configurations presque sphérique et presque complètement étendue conduit à de fortes contraintes dans les écoulements forts alors qu'il n'y a pas d'effets rhéologiques décelables dans les écoulements faibles. Un nouveau modèle d'haltères non-linéaires prévoit que le polymère peut être presque complètement étendu en réduction de trainée, extension pouvant être facilitée par un phénomène d'hystérésis. Le nouveau modèle permet aussi de prévoir dans quelles conditions des dégradations mécaniques peuvent avoir lieu.

Introduction

The dynamics of long chain macromolecules in dilute solutions are complicated. A bulk flow deforms the polymer competing against a restoring mechanism from the thermal motions. In the undeformed state the statistics are determined by the random walk of the linear chain which is due to some arbitrariness in the siting of adjacent monomers. The random walk is subject to the constraints of an excluded volume of the monomers and an accompanying shell of solvent. Ionic polymers are also affected by charge repulsion between the ionic subgroups and possible free ions in electrolytic solvents. The discrete nature of the solvent leads to Brownian motions in the chain configuration. Long range interactions of the moving chain with itself and with the bulk flow can be calculated by treating the solvent as a continuum Newtonian fluid. An inflexibility in the siting of adjacent monomers can result in irreversible energy losses as the chain length changes, and this has suggested the chain possesses an internal viscosity.

The full problem as described above is so complicated
that the mathematics is quite intractable. In the last forty years physical chemists have made significant progress in producing simplified tractable models. Perhaps the most noteworthy group of models are the bead-and-spring variety following the ideas of Rouse and Zimm. These successfully predict the intrinsic viscosity at zero shear rate and the relaxation spectrum as displayed in the frequency dependence of the dynamic viscosity. Such predictions are an essential tool for polymer characterization in which gross properties like molecular weight, flexibility, overall shape and openness are related to easily measured bulk properties of a solution. It is pertinent to observe, however, that the physical chemist usually employs viscometric shear flows (because of their experimental simplicity) and often with shear rates less than the slowest polymer relaxation rate.

The use of polymer solutions by chemical engineers in technologically important problems such as turbulent drag reduction and lubrication has uncovered some disturbing deficiencies in the standard characterizations. From the measured minute changes in the viscosity of a solution of a few parts per million of a high molecular weight polymer, or the indetectable normal stress differences, who could have expected the dramatic reductions in skin friction? Note these unexpected phenomena usually occur in non-viscometric flows and with deformation rates exceeding the slowest polymer relaxation rate.

This paper attempts to provide an insight into the different behaviours observed by physical chemists and chemical engineers. It will be suggested that the difference is due to the chemist only probing the chain in a nearly spherical configuration whereas the engineer extends the chain almost fully. Some new simplified and tractable models will be introduced which help to build up an understanding of the mechanics of highly deformed polymers.

Strong and weak flows

About the simplest representation of a distorted polymer is the elastic dumb-bell. While this limited model can not answer many questions about macromolecular behaviour, it does expose most clearly the key issues in how much distortion of the chain can be expected when it is subjected to a particular flow history.

The gross distortion of the random walk of the chain, e.g. the expected end-to-end separation, is represented by a single vector \( \mathbf{r} \) which becomes the extension of a spring separating two beads. The desire to remain in the most probable undistorted spherical shape, through the Brownian fluctuations in the chain configuration, give the spring its elasticity. The linearized (Gaussian) spring constant \( K \) is usually taken to be \( 3kT/Nb^2 \) for \( N \) bonds with a persistence length \( b \). A bulk flow \( \mathbf{u}(x,t) = x \cdot \nabla \mathbf{u}(t) \) distorts the polymer by exerting a different hydrodynamic drag on the spherical beads with friction constants \( 6\pi \mu a \). For free draining conditions \( a \propto Nb \), but for the more realistic conditions including unsuppressible hydrodynamic interactions \( a \propto N^{1/2}b \). The relative force balance for the beads yields an evolution equation for the distortion

\[
\dot{r} = r \cdot \nabla \mathbf{u} - \lambda r
\]

where \( \lambda = K/6\pi \mu a \). In more sophisticated bead-and-spring necklaces which can depict some internal structure of the distortion, the gross magnitude of the distortion relaxes with the longest relaxation time for \( \lambda \).

For simplicity consider flows with constant histories, i.e. the \( \nabla \mathbf{u} \) seen by an advected particle is independent of time. In such circumstances the linear evolution equation is solved in terms of exponential function of time. Denote by \( |\nabla \mathbf{u}| \) the largest real part of an eigenvalue of the tensor \( \nabla \mathbf{u} \). The behaviour of the solution can then be divided into two classes. If \( |\nabla \mathbf{u}| \leq \lambda \) (a weak flow), the restoring force wins and the distortion decays. If \( |\nabla \mathbf{u}| > \lambda \) (a strong flow) the distorting flows and, within this crude model, the distortion grows in time without bound. Because the stress is related to the distortion, more dramatic rheological effects must be expected in strong flows than in weak flows. The first indication of the existence of strong flows was Takserman-Krozer's study of the Rouse-Zimm model in elongational flow.

The unsatisfactory feature of viscometric testing is now exposed. Simple shear has the property that \( |\nabla \mathbf{u}| \) identically vanishes whatever the magnitude of the shear rate. Flows with this strange property are very rare in the class of all possible types of flow; in fact they have the zero measure of a point in a plane. The elastic dumb-bell model does demonstrate that viscometric measurements do have a restricted application. They will be useful in viscometric engineering flows and in a partial polymer characterization, but they might have little relevance to non-viscometric flows, i.e. most engineering flows.

The clear classification of flows by their strength helps one understand turbulent drag reduction. In shear flow turbulence the drag by the walls on the core is exerted mainly by an irregular ejection of low momentum wall fluid into the core with an associated return circulation. These bursts and sweeps are typified by jet-like elongational flows in contradistinction to simple shear flows. Thus this part of the turbulence giving rise to drag is intrinsically of a strong flow type, \( |\nabla \mathbf{u}| \neq 0 \). At the onset of drag reduction it is conjectured that the magnitude of the flow strength \( |\nabla \mathbf{u}| \) (where \( \mathbf{u} \) is the local bulk velocity in the active regions and not the mean velocity) reaches the critical value of \( \lambda \), and that this heralds the changeover to a strong flow rheology which differs greatly from the rheology
of weak flows. The point of onset being determined by such a critical flow strength is commonly known as the time hypothesis. The hypothesis is experimentally supported by \( U^2/\nu \) being of the same order of magnitude as \( k T/\mu N^{1/2} b^3 \). Both these two time scales need refinements before a good correlation will be given by the time hypothesis.

Nonlinearities

The elastic dumb-bell model is an oversimplification. An ultracautious person might admit that it only suggests classes of strong and weak flows in which the polymer is significantly and is hardly distorted. Now the suggestion of highly distorted polymers must be considered further.

Implicit within the modelling of the elastic dumb-bell, and also of the bead-and-spring necklace, are two linearizations which are applicable to low distortion conditions but not to large distortions. First a linear spring was taken instead of one like the full inverse Langevin function which incorporates a finite extensibility. This is only permissible if the distortion is much less than the full extension, \( r \ll N b \). Second and more subtly the hydrodynamics was linearized by taking a constant friction factor for the beads. This corresponds to taking a preaveraged hydrodynamic interaction in the Rouse-Zimm theory. As soon as the distortion is comparable with the radius of gyration the hydrodynamic shielding of parts of the chain by other parts is altered. Thus the second linearization requires the more restrictive condition \( r \ll N^{1/2} b \). The first non-linearity to be investigated is therefore the hydrodynamics, and only if this predicts larger distortions need the elasticity be made non-linear.

The restrictions of the linearizations are often overlooked; only certain deductions are valid. The linear Rouse-Zimm theories are limited to the Newtonian regime of the rheology. Thus two undesirable properties of such theories, that the viscosity is independent of shear rate and that there is no second normal stress difference, are properties which are strictly speaking outside the scope of the theories.

In this paper I wish to examine the consequence of nonlinearities in the hydrodynamics and the spring law. I choose to ignore the important effects of excluded volume, ionic charge and knotting of the chain. While these effects may not be negligible in practice, they are auxiliary factors in the essential competition between the bulk flow creating the distortion and the entropic restoring mechanism. The study will proceed using alternative simple models which isolate individual effects and clearly illustrate the main issues. A full nonlinear model incorporating all conceivable effects is not necessarily good, because it will be intractable and will cloud the mechanics underlying the phenomena.

Elastic sphere model

Before the introduction of the necklace of beads and springs, Cerf proposed this alternative to the elastic dumb-bell which treats very well the solvent flow around the distorting polymer. As in the elastic dumbbell only the gross distortion with no internal structure is considered.

The deformed polymer is represented by an ellipsoidal shaped particle of constant volume. The solvent flow around the particle exerts distortions and tactions. For the entropic restoring forces the particle is given an elasticity which I will take to be linear at non-infinitesimal deformations, i.e. neo-Hookean. The resistance to changes in shape due to the chain moving in a viscous solvent and also entangling with itself gives the particle an internal viscosity which will exceed the pure solvent viscosity.

The beauty of the model 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 independent variables. Even so the detailed mathematics is too complex to be presented here. Two important results can however be summarized. In the familiar bead-and-spring language these can be described as the hydrodynamics implications that the beads should rotate and change size.

Rotation of beads

When the spin of the ellipsoidal particle in a bulk flow \( \nabla U \) is examined, two independent contributions are found arising separately from the vorticity and the strain rate (the antisymmetric and symmetric parts of \( \nabla U \)). If there were no strains motion, the particle would rotate exactly with the vorticity. The strain-motion is however not so completely successful due to hydrodynamic shielding and the rigidity of the particle. The particle spins, and also deforms, with a reduced fraction of the strain rate. Only when the ellipsoid is greatly stretched is the particle virtually advected by the bulk flow.

The failure of the standard treatment of the bead-and-spring models to display this reduced efficiency is due to the hidden assumption that allows the beads to rotate freely with the local vorticity alone. Unnoticed in the model the beads are usually held in universal joints.
If the beads are to represent the hydrodynamic interaction of the chain with the solvent, then they should assume the rotation as well as the translation of that chain, a rotation which may well differ from the local vorticity. The remedy is to prescribe the rotation of the beads to be the same as the connecting spring and to calculate this angular velocity from a couple balance. The extension of the spring is still to be calculated from a relative force balance. The result of the suggested modification is to change the time derivative from the convected Oldroyd derivative to something partway between this and the Jaumann derivative. As the spring extends the Oldroyd part of the mixture dominates.

The consequences of the reduced efficiency of the straining motions are not perceptible in the linear Newtonian regime of the rheology. Thus a physical chemist interested in the dynamic viscosity need not bother with the rotation of the beads. In the non-Newtonian regime, however, the two undesirable properties of the Rouse-Zimm models referred to earlier are eliminated. With the reduced efficiency of the straining motions the viscosity shows a shear-thinning and a negative second normal stress difference appears. These important rheological features are also possessed by the bead-and-spring models with the above modification of the time derivative.

Related to the rheological property of a shear-thinning viscosity is the behaviour of the macromolecule at high shear rates. In the standard treatment with its constant shear viscosity the expected length of the polymer increases with the shear rate. Although simple shear was classified as an intrinsically weak flow ($|\nabla U| = 0$) in the elastic dumb-bell model study, in fact it is a marginal case. The effect of the neglected configurational diffusion on a marginal case leads to an expansion in size with shear rate; albeit an algebraic growth as opposed to the exponential growth in non-marginal cases. Mathematically, shear flow has a critical flow strength which is infinity. In the elastic sphere model, as well as in the bead-and-spring models with the rotational modification, the macromolecular size tends to a definite finite limit at high shear rates. Thus in reality simple shear flow is not a marginal case as appears in the standard elastic dumb-bell but is strictly weak.

**Size of beads**

In a strong flow, $|\nabla U| > \lambda$, the linearized bead-and-spring models indicate there is no stable equilibrium state which is near the spherical undeformed shape. The polymer must start to deform indefinitely in time, which of course takes it outside the linearizations of those models. The elastic sphere model enables the deformation to be followed into the regime where the hydrodynamics is nonlinear.

The simplest flow in which to consider the development of a large deformation is elongational motion (axisymmetric straining). Here the ellipsoid of Cerf is coaxial with the flow and can be specified by the length of its longest semi-diameter, $r$. A detailed calculation yields two contributions to the rate of deformation, $\dot{r}$, one proportional to the flow strength $|\nabla U| = E$ = the elongation rate, and one proportional to the elastic relaxation rate $\lambda$. The variation of these two contributions with deformation is indicated in figure 1, in which $r = 1$ represents a sphere.

The flow makes the sphere distort at a rate less than $E$. Here the deforming inefficiency of straining motion is due to the internal viscosity. At large deformations the flow simply advects the particle with a distort rate $E r$. The relaxation rate initially increases linearly with the distortion like $\lambda (r - 1)$.

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**Figure 1.** The contributions to the rate of deformation of the ellipsoid.
deformations the relaxation rate reaches a maximum and then drops like $\lambda r^{-1}$. The drop is the result of three active effects. In a neo-Hookean material as the distortion $r$ increases the elastic restoring stress increases proportional to $\lambda (r - r^{-1/2})$. But the cross-sectional area is decreasing like $1/r$, so that the restoring force exerted by one half of the ellipsoid on the other remains roughly constant. To obtain the relaxation rate from the restoring force it is necessary to divide by the appropriate drag factor. The detailed calculation of the viscous flow around a deforming ellipsoid shows the drag factor increases virtually proportional to the largest linear dimension of the particle, $r$. The drop in the relaxation rate is a feature of the neo-Hookean assumption which is not exhibited by more realistic models of the elasticity.

Subtracting off the relaxation rate from the distortion rate yields the evolution of the ellipsoidal particle. There are two possibilities, according to $E \gtrless \lambda$ (with a number of order unity suppressed as shown in figure 2.

The nonlinear hydrodynamics do not lead to a steady equilibrium where none existed in the linear regime. On the contrary the gap between the restoring and flow forces is widened. The underlying mechanism of this runaway is the increasing friction factor, the drag increases like the length of the distorted polymer. The larger the distortion the longer the length provided which the flow can grasp. A basic result for Stokes flow is that the viscous resistance to translation, rotation (not about the axis of a thin straight particle) and extension is almost entirely determined by the largest linear dimension and is not greatly influenced by shape, surface area or volume. This fact is central in the slender-body theory for Stokes flow which relates the drag per unit length of the body to the local slip velocity.

The standard bead-and-spring models can be modified to include the nonlinear effect of increasing drag by making the bead size change with the linear dimension of the chain which it hydrodynamically represents. To some extent the increasing drag is already incorporated in those necklace models with dominant hydrodynamic interactions which are not preaveraged.

**A nonlinear dumb-bell model**

Because the nonlinear hydrodynamics leads to an indefinite extension of the polymer in strong flows, a nonlinear elasticity which reflects the finite extensibility must be considered. The correct nonlinear elastic law for freely hinged bonds is that described by the inverse Langevin function. In reality the bonds are far from freely hinged and the Langevin spring does not apply. The effect of hindered rotation is to reduce the initial linearity constant for the same fully extended length. For the purposes of exposition I will use an elastic law proportional to $r L/(L - r)$. This shares with the correct nonlinear law, whatever it be, three general features: — a linear region vanishing at zero deformation $r = 0$, an infinite force restricting extensions to $r < L$, and variations on a length scale of the full extension L rather than the radius of gyration of the undeformed macromolecule. If the ignored effects of excluded volume and charge repulsion were taken into account, then there would be variations in the details of the elastic law on the scale of the radius of gyration.

In this section I wish to study the way in which the non-linear elasticity brings an equilibrium in strong flows. This is most simply understood in the case of elongational flow. Of the two nonlinear hydrodynamic effects only the changing bead size enters this distortion problem with a single degree of freedom. The full tensorial system including the modification to the bead rotation is not required. The bead size nonlinearity
will be approximated by taking a friction constant $6 \pi \mu (a + r)$, where $a$ is the undeformed size and $r$ is the deformation. This approximation, like that chosen for the elasticity, is not the correct form but it retains the important feature of always using the largest linear dimension.

Combining the nonlinear bead size and nonlinear elasticity in the relative force balance yields an evolution equation

$$\dot{r} = E r - \lambda r \frac{a}{a + r} \frac{L}{L - r}$$

The first term represents the flow distortion while the second represents the entropic restoring mechanism. Care is needed in making deductions from the above equation which depend only on its general features and not on the incorrect details. Consistent with this caution all results will be presented with constants of order unity suppressed, because these constants must be sought from better detailed models.

To understand the nonlinear equilibration of a strong flow it is useful to consider the same graphs as in the elastic sphere model, plotting as functions of the deformation the contributions to the deformation rate from the flow and elastic forces. There is a new critical flow strength $\lambda a/L$, which together with the old critical strength $\lambda$ divide the flows into three classes as indicated in figure 3. If the flow is strong in the linear theory, then the flow forces build up to such large magnitudes by the time they are balanced by the nonlinear elasticity that the equilibrium has to have very nearly full extension, $r = L - a \lambda/E$. When the flow is moderately weak in the linear theory, the equilibrium can be either extended $r > 1/2 L$ or little deformed $r < 2 a$. As shown in the second graph, the choice of the equilibrium depends on the initial conditions, whether it is larger or smaller than the unstable middle equilibrium. Only when the flow is very weak $E < \lambda a/L$ does the extended equilibrium leaving a nearly spherical equilibrium to which all initial conditions must tend.

**Hysteresis**

There is an interesting consequence of the manner in which one of the stable equilibria of the moderately weak flow disappears at the critical flow strengths. Variations of the flow strength in time can give rise to a hysteresis. A strong flow is needed to crack open the undeformed random coil, but once extended into a long fibre the macromolecule can be maintained there by a much reduced flow strength because of the increased size on while the distorting flow can grasp.

The clarity of the hysteresis mechanics seen in the new dumb-bell model is slightly misleading. When diffusion in the configuration of the dumb-bell is added, the hysteresis apparently disappears. Regrettably there is a unique steady solution for the probability density function which prescribes a distribution between the two stable equilibria. This steady distribution is only established, however, after sufficient time for the equilibria to have leaked information to one another about their populations, leaking via very improbable intermediate states. By an analogy from statistical mechanics, the rate of settling down to the equilibrium distribution is $-\exp \{ - (E/\lambda - a/L) L^3/a^3 \}$ which can be expected to be exceptionally slow. A typical (transient) experiment operating on time scales of the order of $E^{-1}$ would observe therefore an effectively steady state exhibiting the hysteresis, and would not notice the much slower drift to the real steady state which has no hysteresis.

The hysteresis is particularly relevant to the in-
mittent conditions in turbulence. Only the active parts of the turbulence need be strong enough to stretch the spherical coil out into the very extended fibre. Thereafter the quieter regions could still maintain the extended state. The ratio of the two critical flow strengths is $L/a$ which is roughly 100 for synthetic polymers like PEO at a molecular weight of $10^6$.

The modes of extension and collapse are also helpful in intermittent conditions. The extension is exponential taking a time $8/E$ to change size by the above factor of 100. The collapse is algebraic thereby taking $100/\lambda$ to change the same size. Thus the macromolecule need only be in the active regions for $8\lambda/E$ % of the time (and note $E > \lambda$ beyond onset) in order that the extension be maintained without any help from the quieter regions.

**Stress levels**

An understanding is now possible into how very dilute polymer solutions which show no change in shear viscosity can have a drastic effect on turbulence. However high the shear rate, simple shear is an intrinsically weak flow, $|\nabla U| = 0$, in which the macromolecule remains nearly spherical. In such a configuration the fractional change in the viscosity is $n a^4$, where $n$ is the number density of macromolecules and $a$ the undeformed size. For 100 ppm $10^6$ PEO this is $10^{-8}$, i.e. not measurable. On the other hand turbulence contains some strong flows as discussed earlier. Beyond the onset point I expect a substantial number of the macromolecules to be nearly fully extended. For this configuration the fractional change in the viscosity (a concept with a limited use in a strictly anisotropic material) is increased to $n L^2$, which would be $10^8$ rather than the weak flow $10^{-3}$ above. Such large changes in the rheology can be expected to modify the flow dramatically.

Of interest for drag reduction, a final prediction from the new nonlinear dumb-bell concerns mechanical degradation. The tension in the dumb-bell spring, i.e. in the monomer chain, is $\mu |\nabla U| L^2$ in the extended states. In water with a deformation rate in the active turbulent regions of $10^6$ sec$^{-1}$ (corresponding to a friction velocity of 30 cm$^{-1}$ in $u_2^* / \nu$), this estimate for $10^6$ PEO is $10^{-8}$ Newtons. This compares with the C-C bond strength. If the 120 kcal/mol is reduced to a binding energy per bond and then divided by the bond length, the typical binding force is $6 \cdot 10^{-8}$ Newtons. Thus strong turbulence can be expected to cause mechanical degradation of high molecular weight synthetic polymers.

**Conclusions**

The difference between strong and weak flows explains why viscometric measurements may be useless in some other engineering flows. Some useful rheological insights into the strong flows with large polymer deformations can be obtained from simpliminded models. The traditional models have overlooked the possibility of bead rotations and changes in size which are important when there are large deformations of the polymer. The large difference in size between the nearly spherical and the nearly fully extended configurations leads to large stresses in strong flows whereas there are no detectable rheological effects in weak flows. A new nonlinear dumb-bell model predicts that the polymers may be almost fully extended in drag reduction, these extensions being aided by a hysteresis phenomenon. The new model also allows predictions of the conditions in which mechanical degradation can occur.

This paper reports only some first results for the highly deformed regime. Work in progress involves investigations into the hysteresis phenomenon in shear flow, the non-Newtonian fluid mechanics of the new constitutive equations in simple geometries, and further models which improve on the details.

**Discussion**

M. Zakin: Conditioned sampling measurements by Kline's group at Stanford and by Willmarth and Lee show instantaneous values of $u'v'$ which are an order of magnitude or more greater than average values of $u'v'$ near the wall. These instantaneous effects may provide the "strong" shear effects you called for.

Auteur: The existence of large instantaneous values of local wall strain rate compared with the rms value, i.e. intermittency, make well explain some of the wild scatter in the time hypothesis correlations for onset, because the intermittency does change with Reynolds number.

M. Harnoy: Your molecular models are anisotropic so that the stress tensor cannot be calculated from one component to the stress. Are the models materially frame indifferent?

Auteur: 1) All molecular models are automatically material frame indifferent. They are based only on the laws of physics which of course are independent of the frame of the observer.

2) In the non-Newtonian regime molecular models are anisotropic, and hence knowing one stress component it is not possible to predict the full stress tensor (by the Newtonian law).