

Chain dynamics in steady shear flow

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Recent experimental measurements of the static and dynamic properties of single fluorescently labeled molecules of DNA in steady shear flow are compared with the predictions of a theoretical model of chain dynamics. The model is based on a set of coupled kinetic equations for the evolution of chain conformations and solvent fluctuations. The polymer is represented as a continuous curve with no excluded volume or hydrodynamic interactions, while the solvent is described by a time and space-varying velocity field. In the absence of constraints that enforce the finite extensibility of the chain at large shear rates, the calculated curves of the normalized dynamic autocorrelation function of the mean extension reproduce the qualitative features of the measured curves, but otherwise deviate significantly from them. We develop an analytically tractable finitely extensible model of the Gaussian chain that is more successful in reproducing the experimental data.

I. INTRODUCTION

Of the many descriptions of the unusual properties of polymer liquids in flow fields, few are as pithy as the limerick by Bird *et al.*¹ that opens the second chapter of their popular textbook on polymer dynamics. Had the authors also reflected on the behavior of single chains, their poetic musings may have taken the following form:

“A polymer chain can be queer,
Especially if subject to shear.
It tends to deform
Away from the norm,
Looking more like a rod than a sphere.”

But polymers apparently do much more than just stretch when sheared. They tumble, they fold, they curl up into dumbbells and half dumbbells, they send local defect structures traveling up and down the length of the backbone, they stand upright against the direction of flow. These are some of the findings of experiments on the direct optical imaging of single fluorescently labeled molecules of flexible DNA published this past year almost simultaneously by research groups at Stanford² and Johns Hopkins.³ The findings are a challenge to theoretical notions about polymers in flow, which have only just begun to recognize—largely through simulations—the richness of the conformational states that can be adopted by such systems.

Some of the effects now being directly visualized had been anticipated. For instance, de Gennes suggested as early as 1974 that extended states of polymers in strong flows, being inherently unstable, would suffer large fluctuations.⁴ The fluctuations certainly do exist, as the recent work on DNA dynamics demonstrates,^{2,3} but it is less clear that the reasons for their occurrence can be found in de Gennes’ analysis of the polymer-flow problem. The dumbbell model that is at the center of this analysis is very limited as a description of the collective many-body effects of real polymers. It can be especially unreliable, as pointed out by Wiest *et al.*,⁵ when used in conjunction with an approximation (the

Peterlin approximation⁶) that is known to give rise to spurious hysteresis loops of the kind that de Gennes identified with loci of chain instability. Some of the limitations of de Gennes’ approach were addressed by Wiest *et al.* themselves without seriously undermining the physical picture of polymers as objects prone to coil–stretch transitions under the action of strong flows.

Simulations have proved to be useful in discerning some of the finer details of this picture,^{7–10} particularly in regard to the nature of the conformations that chains assume at given instants of time when acted on by shear forces. An especially vivid illustration of the effects of ever larger shear rates on chain conformations can be found in the recent Brownian dynamics simulations of Lyulin *et al.*,¹⁰ which shows the gradual unfolding and refolding of a compact coil of 129 beads under shear. The different stages in this evolution share many of the conformational features of the intermediates in Smith *et al.*’s study of DNA.² Other simulated observables are in less satisfactory agreement with the results of experiment, however. For instance, the dependence on the shear rate of the stretching ratio z —defined as the quotient of the mean square end-to-end distance and the mean square maximum extension—is nonmonotonic for all but one of the models in the simulations of Ref. 10; the experimental curve, on the other hand, increases smoothly and then plateaus. For certain values of the imposed shear rate, the temporal decay of fluctuations in the end-to-end distance of a number of simulated chains is also nonmonotonic in regions where the experimental curves are not.

Differences of this kind seem to indicate the need for refinements to existing models of polymers in flow fields. Efforts in this direction have already been made. Oono and others have developed a description of chain dynamics in flow that begins with a set of coupled kinetic equations for the evolution of chain conformations and solvent fluctuations.¹¹ The formalism provides for the explicit treatment of hydrodynamic and excluded volume interactions by modern multiple scattering and renormalization group meth-

ods. The polymer is typically represented as a continuous Gaussian chain of fixed chain length, while the solvent is represented by a vector field that specifies its velocity at different times and places. This kinetic theory approach is rigorous, systematic and well-controlled, but appears not to have been sufficiently tested against the kind of real data that are now becoming available and that could conceivably expose the limitations of models that fail to allow for constraints of finite extensibility. It seems appropriate therefore to confront at least some of its predictions with the results of recent experiments. To this end we apply the method to two sets of measurements from the Stanford group² that seem most congenial to a statistical mechanical analysis: the variation of chain size with flow rate, and the time dependence of the decay of conformational fluctuations for different values of the flow rate.

Section II introduces the kinetic equations that define the model. The equations are solved for the time-dependent position of an arbitrary chain segment in the limit of no excluded volume and hydrodynamic interactions. Expressions for the appropriate physical variables are constructed from this solution, and compared with the results of experiment in the steady state limit. The comparison suggests the need for improvements to the Gaussian model of the chain, which are introduced in Sec. III through a constraint that limits the amount of chain stretching. As shown in Sec. IV, the extended model is seen to provide a better description of the experimental data at large shear rates. The implications of these results are discussed in Sec. V.

II. DYNAMICAL EQUATIONS FOR POLYMER AND SOLVENT

The kinetic theory formalism of Oono and others¹¹ is based on equations that are similar to those that describe the critical dynamics of binary liquids under shear.¹² Polymer and solvent are described by coupled stochastic equations that essentially account for the balance of forces in the medium. The polymer is modeled by a continuous curve, while the solvent is modeled by a continuous velocity field. The governing equations of this system are

$$\left(\frac{\partial}{\partial t} - \frac{1}{\zeta} \frac{\partial^2}{\partial \tau^2} - \dot{\gamma} A \cdot \right) \mathbf{c}(\tau, t) = \mathbf{v}(\mathbf{c}(\tau, t), t) + \boldsymbol{\theta}(\tau, t), \quad (1)$$

$$\begin{aligned} & \left(\rho \frac{\partial}{\partial t} - \eta \nabla^2 \right) \mathbf{v}(\mathbf{r}, t) + \nabla P \\ & = \int_0^N d\tau \delta[\mathbf{r} - \mathbf{c}(\tau, t)] \frac{\partial^2}{\partial \tau^2} \mathbf{c}(\tau, t) + \mathbf{f}(\mathbf{r}, t), \end{aligned} \quad (2)$$

where $\mathbf{c}(\tau, t)$ is the spatial location at time t of a monomer segment on the backbone that is a distance τ from one end of the chain, $\mathbf{v}(\mathbf{r}, t)$ is the velocity of the solvent at time t at the point \mathbf{r} , A is the velocity gradient tensor that contains the details of the applied flow, $\dot{\gamma}$ is the strain rate, ρ and η are, respectively, the number density and viscosity of the solvent, ζ is the monomer friction coefficient, and P is the hydrostatic pressure. The variables $\boldsymbol{\theta}$ and \mathbf{f} are stochastic variables with white noise statistics whose correlations satisfy

$$\langle \boldsymbol{\theta}(\tau, t) \boldsymbol{\theta}(\tau', t') \rangle = \frac{2}{\zeta} \delta(\tau - \tau') \delta(t - t') \mathbf{I}, \quad (3)$$

$$\langle \mathbf{f}(\mathbf{r}, t) \mathbf{f}(\mathbf{r}', t') \rangle = -2 \eta \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \mathbf{I}, \quad (4)$$

where \mathbf{I} is the unit tensor. The units of the spatial variable $\mathbf{c}(\tau, t)$ have been chosen to eliminate factors of the Kuhn length l , the dimension d , and the Boltzmann factor $k_B T$ from the expression for the Hamiltonian H of the chain, allowing it to be written in the compact form¹³

$$H = \frac{1}{2} \int_0^N d\tau \left| \frac{\partial \mathbf{c}(\tau, t)}{\partial \tau} \right|^2. \quad (5)$$

In writing H in this form, we are explicitly assuming that excluded volume interactions are absent.

The solutions to Eqs. (1) and (2), in component form, can be expressed in terms of a flow-modified Green's function and the static Oseen tensor,

$$\begin{aligned} c_i(\tau, t) &= c_i^0(\tau, t) + \sum_j \int_0^N d\tau_1 \int_0^t dt_1 G_{ij}(\tau, \tau_1 | t - t_1) \\ & \quad \times v_j(\mathbf{c}(\tau_1, t_1), t_1), \quad i = x, y, z \end{aligned} \quad (6)$$

and

$$\begin{aligned} v_i(\mathbf{r}, t) &= \sum_j \int d\mathbf{r}_1 T_{ij}(\mathbf{r} - \mathbf{r}_1) f_j(\mathbf{r}_1, t) \\ & \quad + \sum_j \int_0^N d\tau_1 T_{ij}[\mathbf{r} - \mathbf{c}(\tau_1, t)] \frac{\partial^2}{\partial \tau_1^2} c_j(\tau_1, t), \end{aligned} \quad (7)$$

with $c_i^0(\tau, t)$ given by

$$\begin{aligned} c_i^0(\tau, t) &= \sum_j \int_0^N d\tau_1 G_{ij}(\tau, \tau_1 | t) c_j(\tau_1) \\ & \quad + \sum_j \int_0^N d\tau_1 \int_0^t dt_1 G_{ij}(\tau, \tau_1 | t - t_1) \theta_j(\tau_1, t_1). \end{aligned} \quad (8)$$

In these equations, $\mathbf{c}(\tau)$ is the monomer segment position at time $t=0$, the instant of time at which the flow is imagined to be first turned on, while $T(\mathbf{r} - \mathbf{r}')$ is the static Oseen tensor. The Green's function G_{ij} is the solution to the following equation:

$$\begin{aligned} & \sum_j \left(\delta_{ij} \frac{\partial}{\partial t} - \frac{1}{\zeta} \delta_{ij} \frac{\partial^2}{\partial \tau^2} - \dot{\gamma} A_{ij} \right) G_{jk}(\tau, \tau_1 | t) \\ & = \delta_{ik} \delta(\tau - \tau_1) \delta(t). \end{aligned} \quad (9)$$

By inspection, it is seen to be given by

$$G_{jk}(\tau, \tau_1 | t) = [e^{\dot{\gamma} A t}]_{jk} G_0(\tau, \tau_1 | t), \quad (10)$$

where the unperturbed Green's function G_0 is the solution to

$$\left(\frac{\partial}{\partial t} - \frac{1}{\zeta} \frac{\partial^2}{\partial \tau^2} \right) G_0(\tau, \tau_1 | t) = \delta(\tau - \tau_1) \delta(t), \quad (11)$$

and is given by

$$G_0(\tau, \tau_1|t) = \frac{1}{N} \theta(t) \left[1 + 2 \sum_{p=1} \cos(p\pi\tau/N) \times \cos(p\pi\tau_1/N) e^{-\lambda_p^2 t/\xi} \right], \quad (12)$$

where $\lambda_p = p\pi/N$ and $\theta(t)$ is the step function.

Equations (6)–(8) provide the basic ingredients for calculating two of the measures of deformation derived from the experiments of Smith *et al.*² One is the dynamic autocorrelation function of the normalized chain extension, which we shall denote $C(s)$, and shall define as

$$C(s) = \langle \mathbf{R}(t) \cdot \mathbf{R}(t+s) \rangle / \langle \mathbf{R}(t) \cdot \mathbf{R}(t) \rangle, \quad (13)$$

where s is some arbitrary interval of time, $\mathbf{R}(t)$ is the extension—effectively the end-to-end distance—of the chain at time t , i.e.,

$$\mathbf{R}(t) \equiv \mathbf{c}(N, t) - \mathbf{c}(0, t), \quad (14)$$

and the angular brackets denote an average over the steady state distribution of the chain. The other measured quantity is the ratio of the mean extension of the chain at a given flow rate to the contour length of the chain.

We turn first to a consideration of the quantity $C(s)$. A few remarks here about its physical content will help motivate some of the steps that are used later in treating it. Initially, the chain is unperturbed. At some instant, which defines the zero of time, the flow is turned on. Thereafter, the chain conformation evolves, and at some later time t , it attains a steady stretched state. In the steady state, the chain extension fluctuates around a mean. The fluctuations tend to regress over an interval of time s . The projection of the extension at s on the initial extension at t averaged over the allowed states of the chain in the steady state is proportional to $C(s)$. $C(s)$ will be independent of t if the chain had indeed been in equilibrium at t . In general, for the chain to be in equilibrium at t , t must be very long.

The extension of the chain at any arbitrary time can be calculated from Eqs. (6)–(8). This calculation can be simplified considerably if hydrodynamic interactions are neglected. Under these conditions,

$$\mathbf{c}(\tau, t) = \mathbf{c}^0(\tau, t), \quad (15)$$

with $\mathbf{c}^0(\tau, t)$ given by Eq. (8). The neglect of hydrodynamic interactions, though serious, is not too restrictive. For one thing, such interactions are expected to become less important as the flow increases,⁴ and for another, they are easily reintroduced into the formalism if they need to be. However, the calculations become fairly complicated when hydrodynamic interactions are included. A recent multiple scattering-renormalization group calculation of the friction coefficient of Gaussian chains at the theta point illustrates the kind of approach that would be required to go beyond the present zeroth order approximation.¹⁴

At time $t+s$, then, the position of the monomer segment at τ is given by

$$c_i(\tau, t+s) = \sum_j \int_0^N d\tau_1 G_{ij}(\tau, \tau_1|t+s, 0) c_j(\tau_1) + \sum_j \int_0^N d\tau_1 \int_0^{t+s} dt_1 G_{ij}(\tau, \tau_1|t+s-t_1) \times \theta_j(\tau_1, t_1). \quad (16)$$

Were we to use this expression to calculate $C(s)$, we would have to calculate averages of the form $\langle c_i(\tau_1) c_j(\tau_2) \rangle$, where, as indicated earlier, the angular brackets denote an average with respect to the steady state distribution of the chain. But $c_i(\tau_1)$ and $c_j(\tau_2)$ refer to segment positions at the zero of time, when the flow has just been turned on, and the chain has not yet attained equilibrium. According to the remarks above, the steady state is reached only at some much later time t . So averages like $\langle c_i(\tau_1) c_j(\tau_2) \rangle$ do not have a very convenient operational meaning. However, the position $c_j(\tau, t+s)$ can also, presumably, be reached by evolving it from some position, say, $\mathbf{c}(\tau, t)$, at time t , where the chain is in the steady state. It should then follow that

$$c_i(\tau, t+s) = \sum_j \int_0^N d\tau_1 G_{ij}(\tau, \tau_1|t+s, t) c_j(\tau_1, t) + \sum_j \int_0^N d\tau_1 \int_t^{t+s} dt_1 G_{ij}(\tau, \tau_1|t+s-t_1) \times \theta_j(\tau_1, t_1). \quad (17)$$

If the above reasoning is correct, Eqs. (16) and (17) should be the same. It is easily verified that they are by substituting Eq. (6) into Eq. (17), and carrying out a few steps of algebra using the relation $\exp(A)\exp(B) = \exp(A+B)$ for commuting operators A and B , and the relation

$$\int_0^N d\tau_1 G_0(\tau, \tau_1|a) G_0(\tau_1, \tau'|b) = G_0(\tau, \tau'|a+b) \quad (18)$$

for the Green's function of the unperturbed chain.

The coordinate averages that would result from using Eq. (17) in the definitions of $\mathbf{R}(t)$ and $C(s)$ are in a form that renders the meaning of the steady state averages transparent. When Eq. (17) is thus used, one finds, after averaging over the Gaussian random variable $\theta(\tau, t)$, that $C(s)$ can be written as

$$C(s) = C_1 - C_2 - C_3 + C_4, \quad (19)$$

where

$$C_1 = \sum_{ij} \int_0^N d\tau_1 G_{ij}(N, \tau_1|s) \langle c_j(\tau_1, t) c_i(N, t) \rangle, \quad (20)$$

$$C_2 = \sum_{ij} \int_0^N d\tau_1 G_{ij}(N, \tau_1|s) \langle c_j(\tau_1, t) c_i(0, t) \rangle, \quad (21)$$

$$C_3 = \sum_{ij} \int_0^N d\tau_1 G_{ij}(0, \tau_1|s) \langle c_j(\tau_1, t) c_i(N, t) \rangle, \quad (22)$$

$$C_4 = \sum_{ij} \int_0^N d\tau_1 G_{ij}(0, \tau_1|s) \langle c_j(\tau_1, t) c_i(0, t) \rangle. \quad (23)$$

To calculate the averages that appear on the right-hand sides of these equations we shall use the Smoluchowski equation for the evolution of the probability distribution $P(\{\mathbf{c}(\tau, t)\})$ of the chain,¹⁵

$$\begin{aligned} \frac{\partial P}{\partial t} &= \frac{1}{\zeta} \sum_i \int_0^N d\tau \frac{\delta^2 P}{\delta c_i(\tau)^2} + \frac{1}{\zeta} \sum_i \int_0^N d\tau \frac{\delta}{\delta c_i(\tau)} \\ &\times P \frac{\delta H}{\delta c_i(\tau)} - \sum_{ij} \int_0^N d\tau \frac{\delta}{\delta c_i(\tau)} A_{ij} c_j(\tau) P. \end{aligned} \quad (24)$$

The calculation proceeds by first rewriting this equation in terms of a set of normal or Rouse modes $\{\xi_p\}$, which are related to the original coordinate variables $\{\mathbf{c}(\tau)\}$ by

$$\mathbf{c}(\tau) = \sqrt{\frac{2}{N}} \sum_{p=1}^{N-1} \xi_p \cos(p\pi\tau/N) \quad (25)$$

and by

$$\xi_p = \sqrt{\frac{2}{N}} \int_0^N d\tau \mathbf{c}(\tau) \cos(p\pi\tau/N). \quad (26)$$

(For convenience, we are ignoring a $p=0$ mode that corresponds to the center-of-mass motion of the chain.) The transformed Smoluchowski equation is easily shown to be

$$\begin{aligned} \frac{\partial P}{\partial t} &= \frac{1}{\zeta} \sum_p \sum_i \frac{\delta^2 P}{\delta \xi_{pi}^2} + \frac{1}{\zeta} \sum_p \sum_i \frac{\delta}{\delta \xi_{pi}} P \frac{\delta H}{\delta \xi_{pi}} \\ &- \sum_p \sum_{ij} \frac{\delta}{\delta \xi_{pi}} A_{ij} \xi_{pj} P. \end{aligned} \quad (27)$$

If this expression is multiplied by $\xi_{pi}\xi_{qj}$ and then integrated over all $\{\xi_p\}$, one can derive the the following rate equation for $\xi_{pi}\xi_{qj}$ averaged over the distribution P (the average being denoted by an overbar),

$$\begin{aligned} \frac{\partial \overline{\xi_{pi}\xi_{qj}}}{\partial t} &= \frac{2}{\zeta} \delta_{pq} \delta_{ij} - \frac{1}{\zeta} (\lambda_p^2 + \lambda_q^2) \overline{\xi_{pi}\xi_{qj}} \\ &+ \sum_k A_{jk} \overline{\xi_{qk}\xi_{pi}} + \sum_k A_{ik} \overline{\xi_{pk}\xi_{qj}}, \end{aligned} \quad (28)$$

where $\lambda_p \equiv p\pi/N$. In the steady state limit, $\partial \overline{\xi_{pi}\xi_{qj}}/\partial t = 0$, from which it follows that

$$\begin{aligned} \langle \xi_{pi}\xi_{qj} \rangle &= \frac{\zeta}{\lambda_p^2 + \lambda_q^2} \left[\frac{2}{\zeta} \delta_{pq} \delta_{ij} + \sum_k A_{jk} \langle \xi_{qk}\xi_{pi} \rangle \right. \\ &\left. + \sum_k A_{ik} \langle \xi_{pk}\xi_{qj} \rangle \right]. \end{aligned} \quad (29)$$

When A describes steady shear flow, i.e., when A is given by¹

$$A = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (30)$$

the dyadic $\langle \xi_p \xi_q \rangle$ is easily constructed. It is given by

$$\langle \xi_p \xi_q \rangle = \frac{2}{\zeta} \delta_{pq} D_{pq} \begin{pmatrix} 1 + 2\dot{\gamma}^2 D_{pq}^2 & \dot{\gamma} D_{pq} & 0 \\ \dot{\gamma} D_{pq} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (31)$$

where $D_{pq} = \zeta/(\lambda_p^2 + \lambda_q^2)$. The analogous dyadic $\langle \mathbf{c}(\tau, t) \mathbf{c}(\tau', t) \rangle$ in the original variables can be written in terms of the matrix elements of Eq. (31) using Eq. (25). When the matrix elements of $\langle \mathbf{c}(\tau, t) \mathbf{c}(\tau', t) \rangle$ are used in Eqs. (20)–(23) along with the definition of the Green's function G_{ij} , and the simple integrals over the contour variables are carried out, one finds, for example, that

$$C_1 = \frac{2}{N} \sum_{pq} \sum_{ij} [e^{\dot{\gamma} A s}]_{ij} (-1)^{p+q} \langle \xi_{pi} \xi_{qj} \rangle e^{-\lambda_p^2 s/\zeta}, \quad (32)$$

similar relations being obtained for the functions C_2 , C_3 , and C_4 . These relations are substituted into Eq. (19) defining $C(s)$ together with Eq. (31) and the relation

$$e^{\dot{\gamma} A s} = \begin{pmatrix} 1 & \dot{\gamma} s & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (33)$$

for the case of steady shear flow to produce, finally

$$\begin{aligned} C(s) &= \frac{24N}{\pi^2} \sum_{p=1,3,5,\dots} \frac{1}{p^2} e^{-p^2 s/(N^2 \zeta/\pi^2)} \left[1 + \frac{\dot{\gamma}^2 s (N^2 \zeta/\pi^2)}{6p^2} \right. \\ &\left. + \frac{\dot{\gamma}^2 (N^2 \zeta/\pi^2)^2}{6p^4} \right]. \end{aligned} \quad (34)$$

This is the sought for expression for the dynamical correlation function of the chain extension, but to compare it to experiment we shall do two additional things; the first is to retain only the lowest $p=1$ mode (corrections from the higher modes can be shown numerically and analytically¹⁶ to be small), and the other is to introduce dimensionless parameters. The combination of variables $\dot{\gamma} s$ is naturally dimensionless, and will be left as such. The combination of variables $N^2 \zeta/\pi^2$ is proportional to the longest relaxation time of the polymer;¹⁵ the product of this relaxation time with $\dot{\gamma}$ is a dimensionless number that we shall identify with the Weissenberg number Wi introduced in the measurements of Smith *et al.*² In terms of these dimensionless parameters, the normalized $C(s)$ becomes

$$\frac{C(s)}{C(0)} = e^{-\dot{\gamma} s/Wi} \left[1 + \frac{\dot{\gamma} s Wi/6}{1 + Wi^2/6} \right], \quad (35)$$

which is one of the key results of this paper.

Figure 1 shows a plot of $C(s)/C(0)$ vs $\dot{\gamma} s$ for different values of Wi . Also shown in the figure are actual experimental data points from Ref. 2. As is evident, the theoretical curves do a reasonable job of reproducing the overall trends in the experimental data, but they are quantitatively inaccurate, especially at high shear rates. We believe that at least one of the reasons for the discrepancies has to do with using a Gaussian model for the chain, thus neglecting the constraints on real polymers that prevent them from being stretched indefinitely. In the next section, we test this idea by modifying the above formalism to include, rather crudely, the effects of finite extensibility.

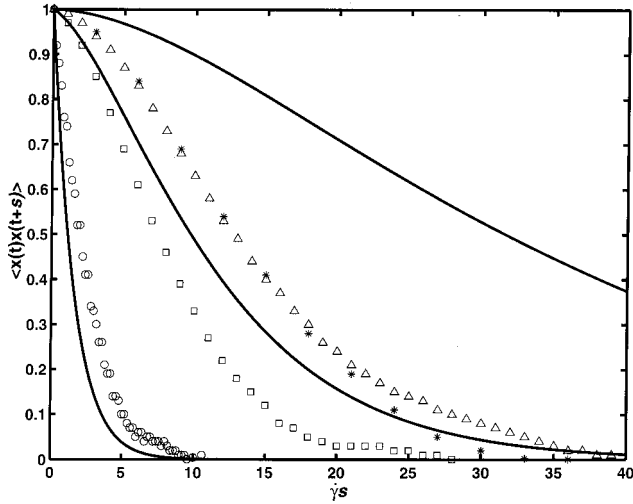


FIG. 1. The normalized dynamic autocorrelation function of the chain extension vs the dimensionless shear rate $\dot{\gamma}s$ for the Gaussian model of the chain as calculated from Eq. (35). The full lines are the theoretical curves, while the symbols denote the experimental data points of Ref. 2; \circ , $Wi = 1.3$, $\dot{\gamma} = 0.2$; \square , $Wi = 6.3$, $\dot{\gamma} = 1.0$; $*$, $Wi = 19$, $\dot{\gamma} = 3.0$; \triangle , $Wi = 19$, $\dot{\gamma} = 1.0$. From left to right, the theoretical curves correspond to Wi values of 1.3, 6.3, and 19, respectively.

A final remark before proceeding further. Exactly the same expression for $C(s)$ as derived in Eq. (35) can be obtained if the operation defined by $\langle\langle \cdot \cdot \rangle\rangle$ is identified with the average over the initial unperturbed distribution of the chain and the limit $t \rightarrow \infty$ is taken at the end of the calculations. The approach we have taken here seems more closely to correspond to the sequence of operations that define the actual experimental measurements; it also appears to be more easily adapted to include the kinds of effects that are discussed in the next section.

III. A FINITELY EXTENSIBLE CHAIN MODEL

The Gaussian chain model we have been using up to this point can be thought of as an elastic spring obeying Hooke's Law for all values of an applied force. This effectively means that the spring can be stretched indefinitely without breakage. Real polymers do not, of course, behave this way, although for small extensions of the chain, they do indeed show Hookean response. In this linear regime, the spring constant b of the chain can be identified with the coefficient of the connectivity term in the Hamiltonian H of Eq. (5); b is thus $3k_B T/l^2$ in original units, or unity in the present, redefined units. If H is more faithfully to describe the behavior of real chains, it should allow for the effects of local inextensibility. Continuum models of chain conformations that do this (essentially by introducing delta function constraints on the magnitudes of the tangent vectors at each point along the chain backbone) are well-known,¹⁷ but they are difficult to treat rigorously under conditions of imposed flow. A physically plausible alternative to this approach is the use of a flow-dependent spring constant b in the chain Hamiltonian. For a polymer model employing discrete extendable bonds, one modification to b that accounts for non-Hookean response is the following so-called FENE ansatz,¹

$$b = \frac{1}{1 - l_i^2/l_m^2}, \quad (36)$$

where l_i is the bond length of the i th bond at the prevailing kinematic conditions and l_m is the maximum extension of the bond. Clearly, l_i can never achieve its full extension unless the applied force is infinitely large. By imposing such a penalty on stretching, the chain is effectively prevented from assuming configurations that extend it unphysically.

As a practical matter, b in Eq. (36) is often replaced by the more tractable

$$b = \frac{1}{1 - \langle l_i^2 \rangle / l_m^2}, \quad (37)$$

which *preaverages* the instantaneous bond extension.⁶

The above considerations suggest the following simple generalization of the earlier Gaussian model as a means of introducing size constraints into the problem,

$$H = \frac{b}{2} \int_0^N d\tau \left| \frac{\partial \mathbf{c}(\tau)}{\partial \tau} \right|^2 \quad (38)$$

with b defined by

$$b \equiv \frac{1 - \langle R^2 \rangle_0 / \langle R^2 \rangle_m}{1 - \langle R^2 \rangle / \langle R^2 \rangle_m}, \quad (39)$$

where $\langle R^2 \rangle$ is the mean square end-to-end distance of the *chain* (not bond) in the steady state for a given shear rate, $\langle R^2 \rangle_0$ is the mean square end-to-end distance in the absence of shear, and $\langle R^2 \rangle_m$ is the maximum *observed* value of the mean square end-to-end distance under shear. ($\langle R^2 \rangle_m^{1/2}$ is therefore *not* simply the contour length L , which is the maximum *theoretical* extension of the chain. In defining $\langle R^2 \rangle_m$ in this way, we are taking note of experimental data—that show that even under very high rates of shear, the chain is far from being fully extended.)

The above modification of the chain Hamiltonian is entirely ad hoc, but in the same way as Eq. (37), it is designed to recover the Gaussian value of the spring constant at zero shear rates and to ensure the finiteness of the chain at very large shear rates.

b is initially unknown because it contains the unknown parameter $\langle R^2 \rangle$. However, $\langle R^2 \rangle$ itself can be separately expressed in terms of b (as we shall see), thereby allowing $\langle R^2 \rangle$ (and by extension b) to be calculated self-consistently. It is this circumstance that motivates the use of the mean size of the chain in b rather than the more traditional mean size of the bond. This new model of the chain is identical to the old except for the added presence of an as yet unknown numerical coefficient in the chain Hamiltonian. (The coefficient does not merely rescale the Gaussian chain results, since b depends nonlinearly on the flow through $\langle R^2 \rangle$.) In terms of the other variables in the theory, however, the only effect of this coefficient is to change G_0 [Eq. (12)] to

$$G_0(\tau, \tau' | t) = \frac{1}{N} \theta(t) \left[1 + 2 \sum_{p=1}^N \cos(p\pi\tau/N) \times \cos(p\pi\tau'/N) e^{-\lambda_p^2 t / (\zeta/b)} \right] \quad (40)$$

and—if the algebra that leads from Eq. (24) to Eq. (31) is repeated—to change the factor D_{pq} to

$$D_{pq} = \frac{\zeta}{b(\lambda_p^2 + \lambda_q^2)}. \quad (41)$$

The new expression for $C(s)$ can therefore be summarily constructed; in dimensionless variables and with neglect of all but the lowest Rouse mode, it is

$$\frac{C(s)}{C(0)} = e^{-\gamma b s / \text{Wi}} \left[1 + \frac{\gamma s \text{Wi} / 6b}{1 + \text{Wi}^2 / 6b^2} \right]. \quad (42)$$

It remains to determine the unknown spring constant b . We do so by calculating the mean square steady state end-to-end distance of the chain, $\langle R^2 \rangle$, (which in the terminology we have been using before is simply the mean square extension of the chain) using the Hamiltonian of Eq. (38). $\langle R^2 \rangle$ is calculated from the expression,

$$\begin{aligned} \langle R^2 \rangle &= \langle (\mathbf{c}(N, t) - \mathbf{c}(0, t))^2 \rangle \\ &= \langle \mathbf{c}(N, t)^2 + \mathbf{c}(0, t)^2 - 2\mathbf{c}(N, t) \cdot \mathbf{c}(0, t) \rangle. \end{aligned} \quad (43)$$

As before, the coordinate correlation functions in this expression can be derived from the corresponding correlation functions involving the Rouse modes $\{\xi_j\}$, which in turn can be obtained from the matrix elements of Eq. (31) by amending them to incorporate the factor of b coming from the Hamiltonian H of the finitely extensible chain [Eq. (38)]. In this way, it is easily shown that

$$\langle R^2 \rangle = \frac{8}{Nb} \sum_{p=1,3,5,\dots} \left[\frac{3}{\lambda_p^2} + \frac{\gamma^2 \zeta^2}{2b^2 \lambda_p^6} \right]. \quad (44)$$

Had the spring constant in this expression been unity, as in our original Gaussian model, the steady end-to-end distance R would have a correction to the leading Gaussian result that scaled as N^5 , which is unphysical. (A similar unphysical limit is encountered in Schulman and Gaveau's investigation of charged polymers.¹⁸)

When b is given by Eq. (39), we find instead that $\langle R^2 \rangle$ is given implicitly by the equation

$$\frac{z}{\alpha} = \frac{1-z}{1-\alpha} + A \text{Wi}^2 \frac{(1-z)^3}{(1-\alpha)^3}, \quad (45)$$

where $z = \langle R^2 \rangle / \langle R^2 \rangle_m$, $\alpha = \langle R^2 \rangle_0 / \langle R^2 \rangle_m$, and $A = \pi^4 / 720$. In deriving this expression, we have made use of the results $\sum_{p=1}^{\infty} (2p-1)^{-2} = \pi^2 / 8$ and $\sum_{p=1}^{\infty} (2p-1)^{-6} = \pi^6 / 960$. Equation (45) is a cubic equation in z , and its coefficients are such that it has one real root and a pair of complex conjugate roots. If only the real root is retained as being physically meaningful, one can show that¹⁹

$$\begin{aligned} z = \frac{\langle R^2 \rangle}{\langle R^2 \rangle_m} &= 1 - \frac{1-\alpha}{(2A \text{Wi}^2 \alpha)^{1/3}} \left\{ [1 - \sqrt{1 + 4/27A \text{Wi}^2 \alpha}]^{1/3} \right. \\ &\quad \left. + [1 + \sqrt{1 + 4/27A \text{Wi}^2 \alpha}]^{1/3} \right\}. \end{aligned} \quad (46)$$

The spring constant thus becomes

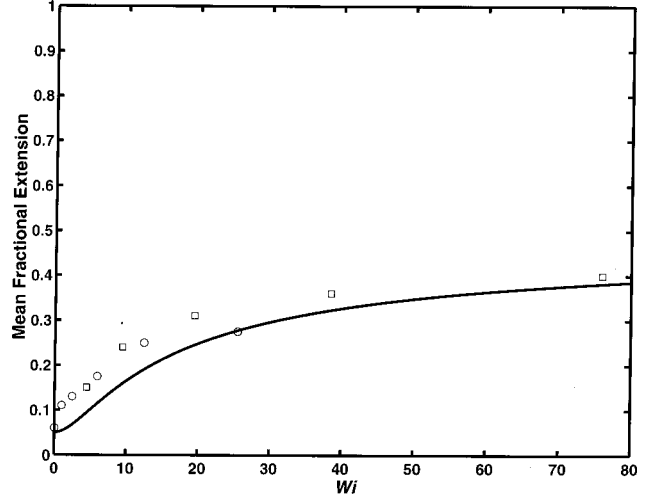


FIG. 2. The mean fractional extension of the chain vs Wi as calculated from Eq. (46) using $\langle R^2 \rangle_m^{1/2} / L = 0.5$ and $\alpha = 0.01$. The symbols denote the experimental data points of Ref. 2; \circ , viscosity $\eta = 60$ cP, \square , $\eta = 220$ cP.

$$b = \frac{(2A \text{Wi}^2 \alpha)^{1/3}}{[1 - \sqrt{1 + 4/27A \text{Wi}^2 \alpha}]^{1/3} + [1 + \sqrt{1 + 4/27A \text{Wi}^2 \alpha}]^{1/3}}. \quad (47)$$

It is easily verified that $\langle R^2 \rangle \rightarrow \langle R^2 \rangle_0$ as $\text{Wi} \rightarrow 0$, and that $\langle R^2 \rangle \rightarrow \langle R^2 \rangle_m$ as $\text{Wi} \rightarrow \infty$. Similarly, $b \rightarrow 1$ as $\text{Wi} \rightarrow 0$, and $b \rightarrow \infty$ as $\text{Wi} \rightarrow \infty$.

IV. COMPARISON WITH EXPERIMENT

The two sets of experimental data from the Smith *et al.* study² that we shall compare with our analytical results are the mean fractional extension of the chain as a function of Wi and the dynamical correlation function of the chain extension as a function of time.

A. The static chain extension

The authors of Ref. 2 have determined the mean extension x of single DNA molecules for different values of the Weissenberg number Wi . The results have been expressed in terms of the mean fractional extension x/L , where L is the contour length of the chain. The graph of x/L vs Wi is found to be a smoothly increasing function of Wi that saturates around 0.4–0.5 for Wi in the vicinity of 100. The chain therefore never achieves its full extension L no matter how high the shear. If $\langle R^2 \rangle^{1/2}$ in Eq. (46) is identified with the experimentally measured mean extension x , Eq. (46) effectively describes the variation of x/L with Wi once the left-hand side of the expression is multiplied and divided by L^2 . When re-expressed in terms of x/L , Eq. (46) contains two unknown parameters, $\langle R^2 \rangle_m^{1/2} / L$ and $\langle R^2 \rangle_0^{1/2} / L$ (or equivalently, $\langle R^2 \rangle_m^{1/2} / L$ and α). From Fig. 4 of Ref. 2, we estimate that $\langle R^2 \rangle_m^{1/2} / L \approx 0.5$, and that $\langle R^2 \rangle_0^{1/2} / L \approx 0.05$. Using these values in Eq. (46), we can determine x/L vs Wi , which is shown in Fig. 2 along with experimental data points taken from Ref. 2.

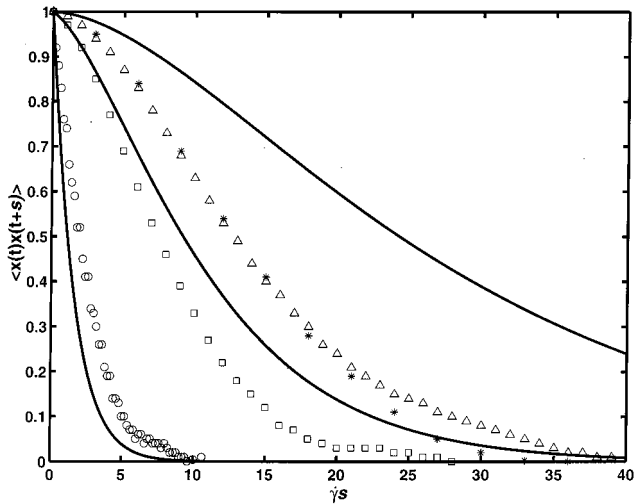


FIG. 3. The normalized dynamic autocorrelation function of the chain extension vs the dimensionless shear rate $\dot{\gamma}s$ for the finitely extensible Gaussian chain as calculated from Eq. (42) with the spring constant b determined from Eq. (47). The parameter $\langle R^2 \rangle_m^{1/2}/L$ is set to 0.5, while α is set to 0.01. The symbols represent the same set of experimental data points as shown in Fig. 1. The theoretical curves are calculated for the same Wi values used in Fig. 1, with Wi increasing from left to right.

B. The dynamic chain extension

Figure 3 shows the normalized autocorrelation function of the chain extension, $C(s)/C(0)$, as calculated from Eq. (42) using Eq. (47) for b with α set to 0.01 [$\alpha = \langle R^2 \rangle_0 / \langle R^2 \rangle_m \approx (0.05/0.5)^2$]. The calculated curves (full lines) are overlaid on the experimental curves of Ref. 2. As is evident, the introduction of finite extensibility into the Gaussian model of the polymer does provide some improvements over the purely Gaussian model, but there still remain non-negligible differences between the experimental and theoretical curves. However, the theoretical curve is sensitive to the value chosen for the parameter α , which we have currently estimated from experiment, and which is therefore subject to some degree of uncertainty. For instance, it is not entirely clear if the value of 0.05 that we have read off from Fig. 4 of Ref. 2 is indeed the best estimate of the parameter $\langle R^2 \rangle_0^{1/2}/L$. The estimate is certainly consistent with the reported values of the chain's contour length and unperturbed end-to-end distance ($22 \mu\text{m}$ and $1 \mu\text{m}$, respectively). But the end-to-end distance itself is not entirely consistent with an earlier measurement of the unperturbed radius of gyration, which was found to be $0.73 \mu\text{m}$,²⁰ a figure that would predict a value of $1.8 \mu\text{m}$ for the end-to-end distance. The figure of $22 \mu\text{m}$ for the contour length is also approximate, though to what extent is not clear. If the DNA were unlabeled, for instance, it would be $16.3 \mu\text{m}$.²¹ With this value of L , and an end-to-end distance of $1.8 \mu\text{m}$, the parameter $\langle R^2 \rangle_0^{1/2}/L$ could be as high as 0.1. If, further, $\langle R^2 \rangle_m^{1/2}/L$ were estimated to be 0.4 rather than 0.5 (both figures have been suggested by Smith *et al.*), α could potentially be in the region of 0.1, although this would likely represent an upper limit. With this value of α , the calculated decay curve of the autocorrelation of the chain extension is more nearly in agreement with the measured curves, as shown in Fig. 4. These latter values of

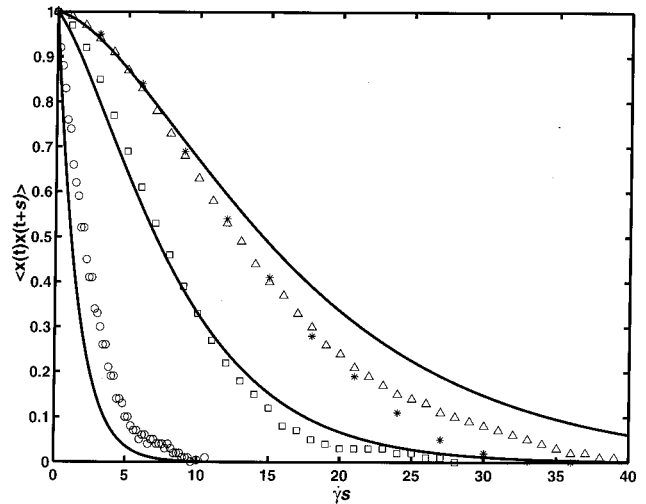


FIG. 4. The curves shown here have been determined in the same way as those in Fig. 3, the only difference being that $\langle R^2 \rangle_m^{1/2}/L$ has the value 0.4 and α has the value 0.1. The symbols have the same significance as the symbols in Figs. 1 and 3. Wi values for the theoretical curves are the same as those in Figs. 1 and 3, the direction of increase also being the same.

$\langle R^2 \rangle_m^{1/2}/L$ and α also improve the agreement between the calculated and experimental curves of x/L vs Wi, as shown in Fig. 5.

V. DISCUSSION

Advances in experimental and numerical techniques have added several new wrinkles to what had been for some time the fairly quiescent field of polymer-flow interactions. Among other things, fresh measurements of the behavior of *single* chains in different kinds of flow at flow rates that greatly surpass the limits achieved earlier reveal a plethora of novel conformational changes to the chain as it uncoils under the action of shear forces. Numerical simulations of related systems are beginning to see evidence of many of the same changes, as well as others that do not as yet echo the results

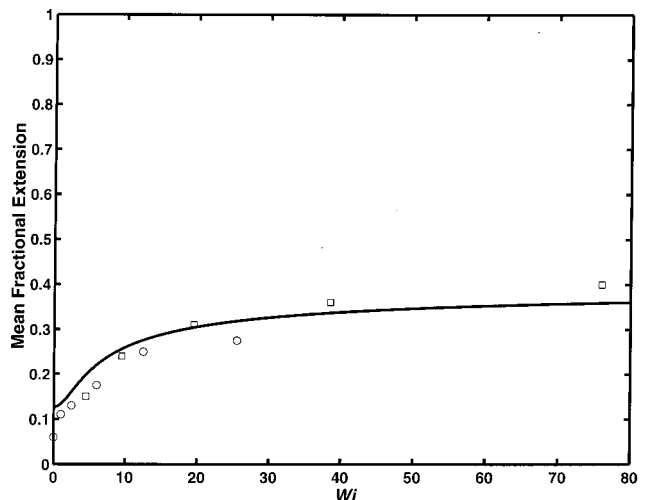


FIG. 5. The mean fractional extension of the chain vs Wi as calculated from Eq. (46) using $\langle R^2 \rangle_m^{1/2}/L = 0.4$ and $\alpha = 0.1$. The symbols represent the same set of experimental data points as shown in Fig. 2.

of experiments. As a way of addressing some of the issues raised by such behavior, we have attempted here to develop an analytical description of polymers in flow. Our approach is not new, based as it is on the coupled kinetic equation approach of Oono and others, but it is newly tested against experimental data that were unavailable before.

The approach uses a continuum Gaussian model of the chain and a linearized Navier–Stokes model of the solvent, and while it provides a satisfactory description of some rheological problems,¹¹ for at least two others it appears to be largely inadequate. For instance, it predicts an unphysical chain length dependence of the end-to-end distance [as can be seen from Eq. (44)], and it predicts a too slow fall-off of the temporal fluctuations of the chain size in the steady state (Fig. 1).

These deficiencies are at least in part due to the absence of an extensibility constraint on the chain size. A modified Gaussian model [Eq. (38)] that incorporates finite extensibility along the lines of the so-called FENE bead–spring models¹ is far more successful in reproducing the experimental trends in the variation of the steady state extension with the Weissenberg number (Fig. 2). In particular, it correctly predicts the asymptotic limit (~ 0.5) of the mean fractional extension at large values of Wi . This agreement is not achieved by construction; the modification to the Gaussian model of the chain merely ensures that the spring constant b is infinitely large at $Wi = \infty$. Other analytical calculations of steady state extension vs shear rate predict significantly larger values for the asymptotic limit, ranging from 0.75 to 0.90.²²

The finitely extensible Gaussian model is less successful as a description of the steady state regression of chain size fluctuations (Fig. 3), but its predictions are significantly improved (Fig. 4) if a certain amount of latitude is allowed in the interpretation of certain experimental parameters that enter the expression for the decay rate. [Similar improvement is noticed in the calculated values of x/L as a function of Wi under these conditions (Fig. 5).] The improvement is most conspicuous at the largest values of the shear rate. At smaller values of Wi , the finitely extensible model does only about as well as the Gaussian model itself. The reasons for this are not clear, but may have something to do with the neglect of hydrodynamic and excluded volume interactions. Such interactions are unlikely to be important at much higher shear rates where the chain is significantly stretched.⁴ In general, however, because the decay of fluctuations in the present model is driven by thermal noise alone, differences between the calculated and experimental curves may persist even if constraints on stretching or the effects of hydrodynamic and excluded volume interactions are properly accounted for; in real systems, rotational components of the shear flow (which

are not accounted for here) appear to be responsible for tumbling and other kinds of motions that may be effective in relaxing extended states of the chain.

Although clearly useful as a zeroth order description of polymers in flow, the finitely extensible Gaussian chain model suffers somewhat from its ad hoc treatment of the extensibility constraint. Refinements to this approach are presently being studied.

ACKNOWLEDGMENTS

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