Renormalization-group analysis of weak-flow effects on dilute polymer solutions

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A Gaussian polymer chain in the presence of hydrodynamic interactions and subjected to steady linear flows is investigated renormalization-group theoretically. To order ϵ ($=4-d$, d being the spatial dimensionality) and to the lowest nontrivial order in the flow strength, we consider the hydrodynamic effect on the mean-square end-to-end distance. From our general formula, we extract results for the physically interesting cases of shear and elongational flow. In the light of recent experimental results there is a possibility that the Gaussian model is of limited validity, even below the stretching transition.

I. INTRODUCTION

Renormalization-group approaches have enabled us to systematically study the universal properties of polymer solutions.[1–4] The static properties of both dilute and semidilute solutions have been studied successfully. However, truly time-dependent properties, even for dilute solutions, are relatively less studied. Some problems in dynamics which have been considered are the following: the relaxational spectrum;[5] properties of a chain in elongational flows;[6] time-dependent correlation functions of conformations;[7] and diffusion and complex intrinsic viscosities[8] by the Green-Kubo formalism.

The behavior of polymers in flow fields has attracted much interest both experimentally[9] and theoretically.[6,10] In a recent letter,[11] we have applied the renormalization-group approach to the problem of a polymer chain in a weak flow in the presence of hydrodynamic interactions. Notice that a major complication is introduced by the presence of the systematic flow which makes the problem a nonequilibrium one. In Ref. 11, we had calculated the mean-square end-to-end distance for a single polymer chain in the $t\rightarrow\infty$ limit. Although our results were correct, the arguments were a bit excessively simplified. A correct derivation of formulas will be given in the present paper.

The ordinary model used by us is that of a Gaussian polymer chain subjected to a solvent flow field whose average is a linear flow. The chain conformation and the solvent velocity field are governed by Langevin equations. The Langevin equation for the solvent velocity field is equivalent to the Oseen tensor model traditionally used in polymer dynamics to the lowest nontrivial order in the strength of hydrodynamic interactions[3,12] and in the flow strength.

In the present paper, we study the transient and asymptotic behaviors of the mean-square end-to-end distance of a Gaussian chain with hydrodynamic interactions. Our general conclusion, which can be understood easily by a dimensional analytic argument, is at variance with the recent experimental results of the Bristol group.[9] A possible grave consequence of this discrepancy is discussed. Those who are interested only in the relevant discussion may go directly to Sec. IV.

The outline of our paper is as follows. In Sec. II, we present the Langevin equations for our model and their formal solutions. In Sec. III we present details of our calculation. We end with formulas for the explicit time dependences of the mean-square end-to-end distance in the physically interesting cases of shear and elongational flows. In Sec. IV we discuss our results in the light of the experimental results of the Bristol group and consider the repercussions of this comparison. Finally, we present a brief summary of this paper.

II. LANGEVIN EQUATIONS FOR CHAIN-SOLVENT DYNAMICS

The Langevin equation for a single chain is[3]

$$\frac{\partial \mathbf{c}}{\partial t}(\tau,t)=\frac{1}{\zeta_0}\frac{\partial^2\mathbf{c}}{\partial\tau^2}(\tau,t)+\mathbf{v}(\mathbf{c}(\tau,t))+\mathbf{u}(\mathbf{c}(\tau,t),t)+\boldsymbol{\theta}(\tau,t)\ , \tag{2.1}$$

where $\{\mathbf{c}(\tau,t)\}_{\tau=0}^{\tau=N_0}$ is the instantaneous conformation of the chain at time t, ζ_0 is the bare translational friction constant for the chain unit, $\mathbf{u}$ is the fluctuating part of the solvent velocity field, $\mathbf{v}$ is the systematic part of the flow, and $\boldsymbol{\theta}$ is a Gaussian white noise with mean zero and with covariance given by

$$\langle\boldsymbol{\theta}(\tau,t)\boldsymbol{\theta}(\sigma,s)\rangle=2\zeta_0^{-1}\delta(\tau-\sigma)\delta(t-s)I\ , \tag{2.2}$$

with I being the $d\times d$ unit matrix. The fluctuating part of the solvent velocity field is described by the Langevin equation

$$\frac{\partial\mathbf{u}}{\partial t}(\mathbf{r},t)=\eta_0\Delta\mathbf{u}(\mathbf{r},t)-\mathbf{u}\cdot\nabla\mathbf{v}-\mathbf{v}\cdot\nabla\mathbf{u}-\mathbf{v}\cdot\nabla\mathbf{v}-\int d\tau\,\delta(\mathbf{r}-\mathbf{c}(\tau,t))\frac{\partial^2\mathbf{c}}{\partial\tau^2}(\tau,t)-\nabla p+\mathbf{f}(\mathbf{r},t)\ , \tag{2.3}$$

which is essentially the linearized Navier-Stokes equation around the systematic flow $\mathbf{v}$. The noise is added to maintain local equilibrium. This is valid only when the flow is microscopically weak (see below). In (2.3), p is the pressure, η_0 is the solvent viscosity (we will choose the system of units so that $\eta_0=1$ in the following), and $\mathbf{f}$ is a Gaussian white noise with mean zero and variance

$$\langle \mathbf{f}(\mathbf{r},t)\mathbf{f}(\mathbf{r}',s)\rangle = -2\Delta\delta(\mathbf{r}-\mathbf{r}')\delta(t-s)I \ . \quad (2.4)$$

We write the systematic flow, which is linear, in the form

$$\mathbf{v}(\mathbf{r}) = g\underline{A}\mathbf{r} \ , \quad (2.5)$$

where g measures the strength of the flow and $\underline{A}$ is a constant $d\times d$ matrix. For the simple shear flow $\underline{A}$ is

$$\begin{bmatrix} 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (2.6)$$

and for the uniaxial elongational flow $\underline{A}$ is

$$\begin{bmatrix} 1 & 0 & 0 & \cdots \\ 0 & -1 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} . \quad (2.7)$$

We assume that the initial ensemble is in equilibrium without flow, and that the systematic flow is switched on at $t=0$. We further assume that $\mathbf{c}(0,0)=\mathbf{0}$ without any loss of generality, as the flow is linear.

We can formally solve (2.1) by introducing the Green's-function matrix $\underline{G}(\tau,\sigma\mid t)$ satisfying

$$\frac{\partial \underline{G}}{\partial t}(\tau,\sigma\mid t) = \zeta_0^{-1}\frac{\partial^2 \underline{G}}{\partial \tau^2}(\tau,\sigma\mid t) + g\underline{A}\underline{G}(\tau,\sigma\mid t) + \delta(\tau-\sigma)\delta(t)I \ , \quad (2.8)$$

along with the free-end condition

$$\left.\frac{\partial \underline{G}}{\partial \tau}\right|_{\tau=0} = \left.\frac{\partial \underline{G}}{\partial \tau}\right|_{\tau=N_0} = \underline{0} \ .$$

Then we have

$$\underline{G}(\tau,\sigma\mid t) = e^{g\underline{A}t}G_0(\tau,\sigma\mid t) \ , \quad (2.9)$$

where $G_0(\tau,\sigma\mid t)$ is the Green's function for the case without flow given by

$$G_0(\tau,\sigma\mid t) = N_0^{-1}\left[1+2\sum_{p=1}^{\infty}\cos(\hat{p}_0\tau) \times \cos(\hat{p}_0\sigma)e^{-\hat{p}_0^2 t/\zeta_0}\right] , \quad (2.10)$$

with $\hat{p}_0=\pi p/N_0$. From (2.9) it follows that the systematic flow is taken into account to all orders in g.

We can write the formal solution to (2.1) as

$$\mathbf{c}(\tau,t) = \mathbf{c}_0(\tau,t) + \int_0^{N_0} d\alpha \int_0^t ds\, \underline{G}(\tau,\alpha\mid t-s)\mathbf{u}(\alpha,s) \ , \quad (2.11)$$

with

$$\mathbf{c}_0(\tau,t) = \int_0^{N_0} d\alpha\, \underline{G}(\tau,\alpha\mid t)\mathbf{c}(\alpha) + \int_0^{N_0} d\alpha \int_0^t ds\, \underline{G}(\tau,\alpha\mid t-s)\boldsymbol{\theta}(\alpha,s) \ , \quad (2.12)$$

where $\{\mathbf{c}(\alpha)\}_{\alpha=0}^{\alpha=N_0}$ is the initial conformation distributed in an equilibrium ensemble.

For the formal solution of (2.3), we have to make certain approximations. Equation (2.3), as pointed out above, is valid only when the flow is microscopically weak, i.e., $ga^2 \ll \eta_0$, where a is the typical bare monomer size. This condition means that systematic flow effects are locally dissipated quickly and the condition of local equilibrium can be maintained. Nevertheless, (2.3) still contains systematic flow terms and the usual Oseen tensor description is not valid [even to $O(\epsilon)$] contrary to Yamakawa's statement.[13] The Oseen tensor is modified by the terms linear in the systematic flow. However, to $O(g^2)$ and to $O(\epsilon)$ there are no extra terms resulting from this modification and we can still use the conventional Oseen tensor description. We show this to be true in Appendix B. Also, to $O(g^2)$, no further complication arises from the term quadratic in the systematic flow. (Actually, this is zero for the case of shear flow.) Solving (2.3) formally to $O(\epsilon)$ we obtain

$$\mathbf{u}(\mathbf{c}(\tau,t),t) = \int_0^{N_0} d\alpha\, \underline{T}(\mathbf{c}(\tau,t),\mathbf{c}(\alpha,t)) \times \frac{\partial^2 \mathbf{c}}{\partial \alpha^2}(\alpha,t) + \hat{\mathbf{u}}(\mathbf{c}(\tau,t),t) \ , \quad (2.13)$$

where $\underline{T}$ is the flow-modified Oseen tensor

$$\underline{T}(\mathbf{c}(\tau,t),\mathbf{c}(\alpha,t)) = \int_{\mathbf{k}} \underline{P}' e^{i\mathbf{k}\cdot[\mathbf{c}(\tau,t)-\mathbf{c}(\alpha,t)]} \ , \quad (2.14)$$

where

$$\underline{P}' = \left[1+\frac{g\underline{P}\underline{A}}{k^2} - \frac{g\underline{P}}{k^2}\left[\mathbf{k}\cdot\underline{A}\frac{\partial}{\partial \mathbf{k}}\right]\right]^{-1}\underline{P}k^{-2} \ ,$$

$$\underline{P} = I - \frac{\mathbf{k}\mathbf{k}}{k^2} \ ,$$

$$\int_{\mathbf{k}} \equiv \int \frac{d^dk}{(2\pi)^d} \ ,$$

$$\langle \hat{\mathbf{u}}(\mathbf{c}(\tau,t),t)\hat{\mathbf{u}}(\mathbf{c}(\alpha,s),s)\rangle = 2\delta(t-s)\underline{T}(\mathbf{c}(\tau,t),\mathbf{c}(\alpha,s)) \ , \quad (2.15)$$

with all averages being taken over the initial equilibrium distribution and noise. In the above we have assumed that the relaxation of the chain is slower than that of the solvent velocity field as in the case of critical dynamics and used the Markovian approximation. This can be justified only to the lowest nontrivial order as the Oseen tensor is reliable only to this order.[12]

III. CALCULATION OF MEAN-SQUARE END-TO-END DISTANCE

In this section we calculate

$$\langle \mathbf{R}^2(t)\rangle = \langle [\mathbf{c}(N_0,t)-\mathbf{c}(0,t)]^2\rangle \ .$$

To this end, we calculate the general correlation function

$$Q(\tau,t\mid\sigma,t)=\langle \mathbf{c}(\tau,t)\cdot\mathbf{c}(\sigma,t)\rangle$$

and use it to determine $\langle \mathbf{R}^2(t)\rangle$ from

$$\langle \mathbf{R}^2(t)\rangle = Q(N_0,t\mid N_0,t)+Q(0,t\mid 0,t) -2Q(N_0,t\mid 0,t) \ . \tag{3.1}$$

Using the formal solution for $\mathbf{c}(\tau,t)$ presented in (2.11), we have

$$\begin{aligned}
Q(\tau,t\mid\sigma,t)&=\langle \mathbf{c}(\tau,t)\cdot\mathbf{c}(\sigma,t)\rangle\\
&=\langle \mathbf{c}_0(\tau,t)\cdot\mathbf{c}_0(\sigma,t)\rangle+\left[\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^t ds\langle[\underline{G}(\tau,\alpha\mid t-s)\mathbf{u}(\mathbf{c}(\alpha,s),s)]^T\mathbf{c}_0(\sigma,t)\rangle+\tau\leftrightarrow\sigma\right]\\
&\quad+\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_0^t ds'\langle[\underline{G}(\tau,\alpha\mid t-s)\mathbf{u}(\mathbf{c}(\alpha,s),s)]^T[\underline{G}(\sigma,\beta\mid t-s')\mathbf{u}(\mathbf{c}(\beta,s'),s')]\rangle\\
&\equiv\langle \mathbf{c}_0(\tau,t)\cdot\mathbf{c}_0(\sigma,t)\rangle+Q^2+\overline{Q}^2+Q^3 \ ,
\end{aligned} \tag{3.2}$$

where Tr and the superscript T, respectively, denote the trace and transpose operations on their matrix arguments.

We denote

$$Q_0(\tau,t\mid\sigma,t)=\langle \mathbf{c}_0(\tau,t)\cdot\mathbf{c}_0(\sigma,t)\rangle \ .$$

This represents the general correlation function in the absence of hydrodynamic interactions. To calculate it, we use the formal solution (2.12) for $\mathbf{c}_0(\tau,t)$ to write

$$\begin{aligned}
Q_0(\tau,t\mid\sigma,t)&=\mathrm{Tr}\int_0^{N_0}d\gamma\int_0^{N_0}d\gamma'\langle[\underline{G}(\tau,\gamma\mid t)\mathbf{c}(\gamma)]^T[\underline{G}(\sigma,\gamma'\mid t)\mathbf{c}(\gamma')]\rangle\\
&\quad+\mathrm{Tr}\int_0^{N_0}d\gamma\int_0^t ds\langle[\underline{G}(\tau,\gamma\mid t-s)\boldsymbol{\theta}(\gamma,s)]^T\int_0^{N_0}d\gamma'\int_0^t ds'[\underline{G}(\sigma,\gamma'\mid t-s')\boldsymbol{\theta}(\gamma',s')]\rangle \ .
\end{aligned} \tag{3.3}$$

Using (2.2) and $\langle \mathbf{c}(\gamma')[\mathbf{c}(\gamma)]^T\rangle=\min\{\gamma,\gamma'\}I$ (which is valid only in the absence of self-avoiding interactions) we obtain

$$Q_0(\tau,t\mid\sigma,t)=Q_0^1+Q_0^2 \ , \tag{3.4}$$

where

$$Q_0^1=\mathrm{Tr}\int_0^{N_0}d\gamma\int_0^{N_0}d\gamma'\,\underline{G}^T(\tau,\gamma\mid t)\underline{G}(\sigma,\gamma'\mid t)\min\{\gamma,\gamma'\} \ , \tag{3.5}$$

$$Q_0^2=2\zeta_0^{-1}\mathrm{Tr}\int_0^{N_0}d\gamma\int_0^t ds\,\underline{G}^T(\tau,\gamma\mid t-s)\underline{G}(\sigma,\gamma\mid t-s) \ . \tag{3.6}$$

Before proceeding to a calculation of the perturbation terms in (3.2), we calculate $\langle \mathbf{R}^2(t)\rangle_0$, the unperturbed contribution to $\langle \mathbf{R}^2(t)\rangle$. From (3.1), we have

$$\langle \mathbf{R}^2(t)\rangle_0=Q_0(N_0,t\mid N_0,t)+Q_0(0,t\mid 0,t)-2Q_0(N_0,t\mid 0,t) \ .$$

Recall that $\underline{G}(\tau,\sigma\mid t)=\underline{B}(t)G_0(\tau,\sigma\mid t)$ with $\underline{B}(t)=e^{g\underline{A}t}$. Then, the contribution of Q_0^1 to $\langle \mathbf{R}^2(t)\rangle_0$ is

$$Q_{0\,\mathrm{cont}}^1=\mathrm{Tr}[\underline{B}^T(t)\underline{B}(t)]\int_0^{N_0}d\gamma\int_0^{N_0}d\gamma'\min\{\gamma,\gamma'\}[G_0(N_0,\gamma'\mid t)-G_0(0,\gamma'\mid t)][G_0(N_0,\gamma\mid t)-G_0(0,\gamma\mid t)] \ . \tag{3.7}$$

A simple calculation proves the relation

$$8N_0\sum_{\substack{p=1\\p\ \mathrm{odd}}}^{\infty}\frac{1}{(\pi p)^2}e^{-2\hat{p}_0^2t/\zeta_0}=\int_0^{N_0}d\gamma\int_0^{N_0}d\gamma'\min\{\gamma,\gamma'\}[G_0(N_0,\gamma'\mid t)-G_0(0,\gamma'\mid t)][G_0(N_0,\gamma\mid t)-G_0(0,\gamma\mid t)] \ . \tag{3.8}$$

Thus

$$Q_{0\,\mathrm{cont}}^1=\mathrm{Tr}[\underline{B}^T(t)\underline{B}(t)]8N_0\sum_{\substack{p=1\\p\ \mathrm{odd}}}^{\infty}\frac{1}{(\pi p)^2}e^{-2\hat{p}_0^2t/\zeta_0} \ . \tag{3.9}$$

Correspondingly, the contribution of Q_0^2 to $\langle \mathbf{R}^2(t)\rangle_0$ is

$$Q^2_{0\,\mathrm{cont}}=4\zeta_0^{-1}\int_0^t ds\,\mathrm{Tr}[\underline{B}^T(t-s)\underline{B}(t-s)][G_0(0,0\,|\,2(t-s))-G_0(N_0,0\,|\,2(t-s))]\ , \tag{3.10}$$

where we have used a property of the Green's function

$$\int_0^{N_0} d\gamma\, G_0(\tau,\gamma\,|\,t)G_0(\gamma,\sigma\,|\,t)=G_0(\tau,\sigma\,|\,2t)\ . \tag{3.11}$$

Thus

$$\begin{aligned}\langle \mathbf{R}^2(t)\rangle_0&=Q^1_{0\,\mathrm{cont}}+Q^2_{0\,\mathrm{cont}}\\&=\mathrm{Tr}[\underline{B}^T(t)\underline{B}(t)]8N_0\\&\quad\times\sum_{\substack{p=1\\p\ \mathrm{odd}}}^{\infty}\frac{1}{(\pi p)^2}e^{-2\hat{p}_0^2t/\zeta_0}+4\zeta_0^{-1}\int_0^t ds\,\mathrm{Tr}[\underline{B}^T(t-s)\underline{B}(t-s)][G_0(0,0\,|\,2(t-s))-G_0(N_0,0\,|\,2(t-s))]\ .\end{aligned} \tag{3.12}$$

In the case of a simple shear flow

$$\mathrm{Tr}[\underline{B}^T(t)\underline{B}(t)]=d+(tg)^2\ .$$

Using the explicit form for the Green's function and performing the time integration we find for the shear flow

$$\frac{\langle \mathbf{R}^2(t)\rangle_0}{dN_0}=1+g^2N_0^4\zeta_0^2\sum_{\substack{p=1\\p\ \mathrm{odd}}}\frac{1}{(\pi p)^6}\left[1-e^{-2\hat{p}_0^2t/\zeta_0}-\frac{2t}{N_0^2\zeta_0}(\pi p)^2e^{-2\hat{p}_0^2t/\zeta_0}\right]\ . \tag{3.13}$$

The correct result (3.13) for $t\to\infty$ has been presented only recently by Bird *et al.*[14] This result is valid to all orders in the flow coupling g.

In the case of an elongational flow

$$\mathrm{Tr}[\underline{B}^T(t)\underline{B}(t)]=d+2(tg)^2\ ,$$

correct to $O(g^2)$. Thus, for the elongational flow to $O(g^2)$

$$\frac{\langle \mathbf{R}^2(t)\rangle_0}{dN_0}=1+4g^2N^4\zeta_0^2\sum_{\substack{p=1\\p\ \mathrm{odd}}}^{\infty}\frac{1}{(\pi p)^6}\left[1-e^{-2\hat{p}_0^2t/\zeta_0}-\frac{2t}{N_0^2\zeta_0}(\pi p)^2e^{-2\hat{p}_0^2t/\zeta_0}\right]\ . \tag{3.14}$$

(The result correct to all orders in g is also easy to obtain.) Next, we calculate the perturbation terms in (3.2). First, consider Q^2:

$$\begin{aligned}Q^2&=\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^t ds\langle \mathbf{c}_0(\sigma,t)\mathbf{u}^T(\mathbf{c}(\alpha,s),s)\rangle\underline{G}^T(\tau,\alpha\,|\,t-s)\\&=\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^t ds\left\langle \mathbf{c}_0(\sigma,t)\left[\int_0^{N_0}d\beta\,\underline{T}(\mathbf{c}_0(\alpha,s),\mathbf{c}_0(\beta,s))\frac{\partial^2\mathbf{c}_0}{\partial\beta^2}(\beta,s)\right]^T\right\rangle\underline{G}^T(\tau,\alpha\,|\,t-s)\ ,\end{aligned} \tag{3.15}$$

where we have used (2.13), replacing $\mathbf{c}$ by $\mathbf{c}_0$ to get results correct to $O(\epsilon)$. Writing the explicit form of the Oseen tensor from (2.14), and using the preaveraging approximation

$$Q^2=\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\frac{\partial^2}{\partial\beta^2}\langle \mathbf{c}_0(\sigma,t)\mathbf{c}_0^T(\beta,s)\rangle\underline{P}'\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle\underline{G}^T(\tau,\alpha\,|\,t-s)\ . \tag{3.16}$$

Notice that the preaveraging result is *identical* to the exact result in the elongational flow case. For the case of the shear flow, the extra term can be readily computed. It is similar to the term discussed in Appendix A, and is negligible as explained in Appendix A. Thus, we do not expect the preaveraging approximation to introduce a large error. Let us first calculate $(\partial^2/\partial\beta^2)\langle \mathbf{c}_0(\sigma,t)\mathbf{c}_0^T(\beta,s)\rangle$. Using (3.5) and (3.6) this can be written as

$$\begin{aligned}\frac{\partial^2}{\partial\beta^2}\langle \mathbf{c}_0(\sigma,t)\mathbf{c}_0^T(\beta,s)\rangle&=\frac{\partial^2}{\partial\beta^2}\left[\int_0^{N_0}d\lambda\int_0^{N_0}d\lambda'\,G(\sigma,\lambda\,|\,t)\min\{\lambda,\lambda'\}\underline{G}^T(\beta,\lambda'\,|\,s)\right.\\&\qquad\left.+2\zeta_0^{-1}\int_0^{N_0}d\lambda\int_0^s ds'\underline{G}(\sigma,\lambda\,|\,t-s')\underline{G}^T(\beta,\lambda\,|\,s-s')\right]\\&\equiv 1+2\ .\end{aligned} \tag{3.17}$$

Using

$$\frac{\partial^2}{\partial\beta^2}\underline{G}(\beta,\lambda'\,|\,s)=\frac{\partial^2}{\partial\lambda'^2}\underline{G}(\beta,\lambda'\,|\,s)$$

and integrating by parts we get

$$\begin{aligned}1&=\underline{B}(t)\underline{G}^T(\beta,0\,|\,s)-\int_0^{N_0}d\lambda\,\underline{G}(\sigma,\lambda\,|\,t)\underline{G}^T(\beta,\lambda\,|\,s)\\&=\underline{B}(t)\underline{B}^T(s)G_0(\beta,0\,|\,s)-\underline{B}(t)\underline{B}^T(s)G_0(\sigma,\beta\,|\,t+s)\ .\end{aligned}\tag{3.18}$$

Term 2 can be simplified by using

$$\frac{\partial^2}{\partial\beta^2}\underline{G}^T(\beta,\lambda\,|\,s-s')=\underline{B}^T(s-s')\zeta_0\frac{\partial}{\partial s}G_0(\beta,\lambda\,|\,s-s')\ ,\tag{3.19}$$

and we obtain

$$2=-\int_0^s ds'\,\underline{B}(t-s')\underline{B}^T(s-s')\frac{\partial}{\partial s'}G_0(\sigma,\beta\,|\,t+s-2s')\ .\tag{3.20}$$

Integrating by parts we get

$$2=\underline{B}(t)\underline{B}^T(s)G_0(\sigma,\beta\,|\,t+s)-\underline{B}(t-s)G_0(\sigma,\beta\,|\,t-s)+\int_0^s ds'\frac{\partial}{\partial s'}[\underline{B}(t-s')\underline{B}^T(s-s')]G_0(\sigma,\beta\,|\,t+s-2s')\ .\tag{3.21}$$

Combining this with term 1, we obtain the expression for Q^2 as

$$\begin{aligned}Q^2=\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\Big[&\underline{B}(t)\underline{B}^T(s)G_0(\beta,0\,|\,s)-\underline{\underline{B}(t-s)G_0(\sigma,\beta\,|\,t-s)}\\&+\int_0^s ds'\frac{\partial}{\partial s'}[\underline{B}(t-s')\underline{B}^T(s-s')]G_0(\sigma,\beta\,|\,t+s-2s')\Big]\\&\times\underline{P}'\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle\underline{B}^T(t-s)G_0(\tau,\alpha\,|\,t-s)\ .\end{aligned}\tag{3.22}$$

Notice that $\overline{Q}^2$ is the same as Q^2 with τ and σ interchanged. For Q^3 we obtain, using (2.15)

$$Q^3=2\,\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\underline{B}(t-s)G_0(\sigma,\beta\,|\,t-s)\underline{P}'\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle\underline{B}^T(t-s)G_0(\tau,\alpha\,|\,t-s)\ .\tag{3.23}$$

We find that Q^3 cancels the underlined term in (3.22) combined with the corresponding term from $\overline{Q}^2=Q^2$ $(\tau\leftrightarrow\sigma)$. Therefore the correlation function can be written as

$$\begin{aligned}Q(\tau,t\,|\,\sigma,t)&=\langle\mathbf{c}_0(\tau,t)\cdot\mathbf{c}_0(\sigma,t)\rangle\\&+\Bigg\{\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\Bigg[\underline{\underline{B}(t)\underline{B}^T(s)G_0(\beta,0\,|\,s)}\\&\qquad+\int_0^s ds'\left[\frac{\partial}{\partial s'}[\underline{B}(t-s')\underline{B}^T(s-s')]\right]G_0(\sigma,\beta\,|\,t+s-2s')\Bigg]\\&\qquad\times\underline{P}'\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle\underline{B}^T(t-s)G_0(\tau,\alpha\,|\,t-s)+\tau\leftrightarrow\sigma\Bigg\}\ .\end{aligned}\tag{3.24}$$

From the last expression and (3.1) we can determine the mean-square end-to-end distance under preaveraging[4]

$$\begin{aligned}\langle\mathbf{R}^2(t)\rangle=\langle\mathbf{R}^2(t)\rangle_0+2\,\mathrm{Tr}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\int_0^s ds'&\left[\frac{\partial}{\partial s'}[\underline{B}(t-s')\underline{B}^T(s-s')]\right]\underline{P}'\underline{B}^T(t-s)\\&\times\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle[G_0(N_0,\alpha\,|\,t-s)-G_0(0,\alpha\,|\,t-s)]\\&\times[G_0(N_0,\beta\,|\,t+s-2s')-G_0(0,\beta\,|\,t+s-2s')]\ .\end{aligned}\tag{3.25}$$

Notice that the underlined term in (3.24) does not contribute to (3.25). Result (3.25) is valid for any linear flow within the preaveraging approximation. As pointed out in the discussion after (2.12), to $O(g^2)$ and to $O(\epsilon)$ there are no extra terms resulting from the modification of the Oseen tensor. Thus, in the subsequent calculation we use the usual form of the Oseen tensor. Inserting the matrix $\underline{B}$ for the shear flow into (3.25) and performing the Tr operation we obtain

$$\langle \mathbf{R}^2(t)\rangle = \langle \mathbf{R}^2(t)\rangle_0 + 2\int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_0^t ds \int_{\mathbf{k}} \int_0^s ds' \left[2g\frac{k_1k_2}{k^2} - \left[1-\frac{k_1^2}{k^2}\right] g^2(t+s-2s') - \left[1-\frac{k_2^2}{k^2}\right] g^2(t-s)\right] \langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle \times [G_0(N_0,\beta\,|\,t+s-2s')-G_0(0,\beta\,|\,t+s-2s')] \times [G_0(N_0,\alpha\,|\,t-s)-G_0(0,\alpha\,|\,t-s)] \; . \tag{3.26}$$

Now,

$$\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle = e^{-k^2|\alpha-\beta|/2} + O(g) \; . \tag{3.27}$$

As we are interested in terms to $O(g^2)$ only, we can discard the $O(g)$ contribution in (3.27) except for the first perturbation correction term in (3.26). For this term the necessary calculation is done in Appendix A. The resulting term is numerically small (see below) and does not affect any asymptotic results. Hence we discard it in the following.

Performing the momentum integration in the terms of $O(g^2)$ and inserting the explicit forms of the Green's function, we obtain for the shear flow

$$\frac{\langle \mathbf{R}^2(t)\rangle}{dN_0} = \frac{\langle \mathbf{R}^2(t)\rangle_0}{dN_0} + 16\frac{g^2(d-1)}{d(d-2)}(2\pi)^{-d/2}\frac{1}{dN_0^3} \times \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_0^t ds \sum_{\substack{p,p'=1\\ p,p\ \mathrm{odd}}}^{\infty} \cos(\hat{p}_0\beta)\cos(\hat{p}'_0\alpha)\,|\alpha-\beta|^{-1+\epsilon/2} e^{-(\hat{p}_0^2+\hat{p}_0'^2)(t-s)/\zeta_0} \times \left[\left[\frac{N_0^2\zeta_0}{(\pi p)^2}(s-t) - \frac{N_0^4\zeta_0^2}{2(\pi p)^4} + \frac{N_0^4\zeta_0^2}{2(\pi p)^4} e^{-2\hat{p}_0^2 s/\zeta_0} + \frac{tN_0^2\zeta_0}{(\pi p)^2} e^{-2\hat{p}_0^2 s/\zeta_0}\right] + p \leftrightarrow p'\right] . \tag{3.28}$$

The contour integrals to be performed in (3.28) are frequently encountered in these calculations. Pole terms in ϵ arise from the diagonal ($p=p'$) terms in the sum. We quote the final result for the contour integral I in the case $p=p'$:

$$I(p=p') = N_0\left[2\epsilon^{-1} + \ln N_0 + \mathrm{ci}(\pi p) - \hat{\gamma} - \ln(\pi p) - \frac{1}{\pi p}[\mathrm{si}(\pi p) + \pi/2]\right] ,$$

correct to $O(1)$. Here we have used the definitions

$$\mathrm{si}(x) = -\int_x^\infty dt\,\sin t/t \; ,$$
$$\mathrm{ci}(x) = -\int_x^\infty dt\,\cos t/t \; ,$$

and $\hat{\gamma}$ is Euler's constant ($\simeq 0.577$). For $p\neq p'$, the answer is somewhat more involved. There are no pole terms arising from the $p\neq p'$ terms.

The presence of pole terms necessitates a renormalization. We use the standard prescription[3]

$$N = Z_N N_0 \; ,$$
$$\zeta = Z_\zeta \zeta_0 \tag{3.29}$$

to introduce the renormalized couplings and the renormalization constants, viz., Z_N and Z_ζ. We introduce a length scale L and define dimensionless parameters as usual

$$\xi_0 = \zeta_0 L^{\epsilon/2} \; ,$$
$$\xi = \zeta L^{\epsilon/2} \; . \tag{3.30}$$

In the absence of self-avoiding interactions $Z_N=1$ and $Z_\zeta = 1-(3/8\pi^2\epsilon)\xi$ to lowest nontrivial order.[7] After the renormalization has been performed, we insert the fixed point value $\xi=\xi^*=8\pi^2\epsilon/3$ which follows from the β function in the one-loop terms. Recall that the dimensionless coupling occurring in $\langle \mathbf{R}^2(t)\rangle$ was of the form $g^2N_0^4\zeta_0^2$. We find the same dimensionless form here, but as logarithmic corrections of the form $\ln(2\pi N)$ appear multiplied with terms of $O(\epsilon)$. We have to introduce an fective exponentiated coupling of the form $w=g/(2\pi)^2\xi(2\pi N)^{z\nu}$, where $\nu=\frac{1}{2}$ is the Flory exponent in the absence of self-avoiding interactions and $z=d\,(=4-\epsilon)$ is the dynamical critical exponent. Besides, in order to obtain a result which is uniformly reliable in time, we have to perform an exponentiation in the $p=p'$ terms giving a corrected eigenvalue $\lambda(p)$ (Ref. 7) to $O(\epsilon)$. Our exponentiated result is

$$\frac{\langle \mathbf{R}^2(\bar{t})\rangle}{dN}=1+w^2\left[\sum_{\substack{p=1\\p\text{ odd}}}^{\infty}\frac{1}{(\pi p)^6}e^{-\epsilon\bar{C}(p)}-\sum_{\substack{p=1\\p\text{ odd}}}^{\infty}\frac{1}{(\pi p)^6}e^{-2\bar{\lambda}(p)\bar{t}}e^{-\epsilon\bar{C}(p)}-2\sum_{\substack{p=1\\p\text{ odd}}}^{\infty}\frac{1}{(\pi p)^4}e^{-2\bar{\lambda}(p)\bar{t}}\frac{\bar{t}}{\pi^2}\right]+2\epsilon w^2\sum_{\substack{p,p'=1\\p,p'\text{ odd}\\p\neq p'}}^{\infty}D(p,p')T(p,p',t)\ . \tag{3.31}$$

The exponentiation scheme is explained briefly in Ref. 7 and at length in Ref. 8. In Eq. (3.31)

$$C(p)=\tfrac{5}{6}+\mathrm{ci}(\pi p)-\hat{\gamma}-\frac{1}{\pi p}[\mathrm{si}(\pi p)+\pi/2]\ ,$$
$$\bar{C}(p)=C(p)-\ln(\pi p)\ . \tag{3.32}$$

We have introduced a new time unit in (3.31) as $\bar{t}=\lambda(1)t$ where

$$\lambda(p)=\left[\frac{\pi p}{N}\right]^{2-\epsilon/2}\frac{1}{\xi}e^{\epsilon C(p)/2}\ . \tag{3.33}$$

Finally, we have introduced normalized eigenvalues $\bar{\lambda}(p)$ as

$$\bar{\lambda}(p)=\lambda(p)/\lambda(1)\ .$$

The terms in the double sum of (3.32) are

$$T(p,p',t)=\left[\frac{1}{(\pi p')^2-(\pi p)^2}\left(e^{-2\bar{\lambda}(p)\bar{t}}-e^{-[\bar{\lambda}(p)+\bar{\lambda}(p')]\bar{t}}\right)\frac{1}{2(\pi p)^4}\left[1+2(\pi p)^2\frac{\bar{t}}{\pi^2}\right]+\frac{1}{(\pi p)^2[(\pi p)^2+(\pi p')^2]}e^{-[\bar{\lambda}(p)+\bar{\lambda}(p')]\bar{t}}\left[\frac{1}{2(\pi p)^2}+\frac{\bar{t}}{\pi^2}+\frac{1}{(\pi p)^2+(\pi p')^2}\right]+\frac{1}{(\pi p)^2[(\pi p)^2+(\pi p')^2]^2}-\frac{1}{2(\pi p)^4[(\pi p)^2+(\pi p')^2]}+p\leftrightarrow p'\right] \tag{3.34}$$

and

$$D(p,p')=\left[\frac{S(p,p')}{(\pi p'-\pi p)}+\frac{R(p,p')}{(\pi p'+\pi p)}\right], \tag{3.35}$$

with

$$S(p,p')=\left[\frac{\pi}{2}+\mathrm{si}(\pi p)\right]-(-1)^{p+p'}\left[\frac{\pi}{2}+\mathrm{si}(\pi p')\right] \tag{3.36}$$

and

$$R(p,p')=-\left[\frac{\pi}{2}+\mathrm{si}(\pi p)\right]-(-1)^{p+p'}\left[\frac{\pi}{2}+\mathrm{si}(\pi p')\right]. \tag{3.37}$$

In Fig. 1 we show $\Delta(\bar{t})$ as a function of $\bar{t}$ where

$$\Delta(\bar{t})=w^{-2}\left[\frac{\langle \mathbf{R}^2(\bar{t})\rangle}{dN}-1\right]\times 10^2\ .$$

From the general expression (3.25) we can also derive $\langle \mathbf{R}^2(t)\rangle$ for the elongational flow as

$$\frac{\langle \mathbf{R}^2(t)\rangle}{dN_0}=\frac{\langle \mathbf{R}^2(t)\rangle_0}{dN_0}+\frac{32}{dN_0^3}\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\sum_{\substack{p,p'=1\\ p,p'\text{ odd}\\ p\neq p'}}\cos(\hat{p}_0\alpha)\cos(\hat{p}'_0\beta)\,|\alpha-\beta|^{-1+\epsilon/2}e^{-\hat{p}_0^2(t+s)/\zeta_0}e^{-\hat{p}_0'^2(t-s)/\zeta_0}$$

$$\times\left\{\left[1-\left[\frac{k_2}{k}\right]^2\right]\frac{g}{\zeta_0^{-1}\hat{p}_0^2+g}\left(e^{2\hat{p}_0^2s/\zeta_0}e^{-2g(t-s)}-e^{-2gt}\right)\right.$$

$$\left.-\left[1-\left[\frac{k_1}{k}\right]^2\right]\frac{g}{\zeta_0^{-1}\hat{p}_0^2-g}\left(e^{2\hat{p}_0^2s/\zeta_0}e^{2g(t-s)}-e^{2gt}\right)\right\}\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle\,. \tag{3.38}$$

In the curly braces, we expand to $O(g^2)$. The expansion of exponential terms like e^{2gt} for arbitrary t is justified because of the rapidly time-decaying exponential prefactors. Again, as in the case of shear flow, there is a small term of $O(g^2)$ arising from the $O(g)$ contribution to $\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle$. For the same reasons as in the case of shear flow, this term is negligible. After performing the $\mathbf{k}$ integration, (3.38) gives

$$\frac{\langle \mathbf{R}^2(t)\rangle}{dN_0}=\frac{\langle \mathbf{R}^2(t)\rangle_0}{dN_0}+64\frac{g^2(d-1)}{d(d-2)}(2\pi)^{-d/2}\frac{1}{dN_0^3}$$

$$\times\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\sum_{\substack{p,p'=1\\ p,'\text{ odd}}}^{\infty}\cos(\hat{p}_0\alpha)\cos(\hat{p}'_0\beta)\,|\alpha-\beta|^{-1+\epsilon/2}$$

$$\times\left[e^{-\hat{p}_0^2(t+s)/\zeta_0}e^{-\hat{p}_0'^2(t+s)/\zeta_0}\frac{1}{(\pi p)^2}(s-t)\zeta_0N_0^2e^{2\hat{p}_0^2s/\zeta_0}+t\zeta_0N_0^2\right.$$

$$\left.-\tfrac{1}{2}N_0^4\zeta_0^2\frac{1}{(\pi p)^2}\left(e^{2\hat{p}_0^2s/\zeta_0}-1\right)\right]+p\leftrightarrow p'\Bigg]\,. \tag{3.39}$$

The rest of the calculation is the same as in the case of shear flow. Our final renormalized and exponentiated result is

$$\frac{\langle \mathbf{R}^2(\bar{t})\rangle}{dN}=1+4w^2\left[\sum_{\substack{p=1\\ p\text{ odd}}}^{\infty}\frac{1}{(\pi p)^6}e^{-\epsilon\bar{C}(p)}-\sum_{\substack{p=1\\ p\text{ odd}}}^{\infty}\frac{1}{(\pi p)^6}e^{-2\bar{\lambda}(p)\bar{t}}e^{-\epsilon\bar{C}(p)}-2\sum_{\substack{p=1\\ p\text{ odd}}}^{\infty}\frac{1}{(\pi p)^4}e^{-2\bar{\lambda}(p)\bar{t}}\frac{\bar{t}}{\pi^2}\right]$$

$$+\epsilon w^2\sum_{\substack{p,p'=1\\ p,p'\text{ odd}\\ p\neq p'}}^{\infty}D(p,p')T(p,p',t)\,, \tag{3.40}$$

with the same functional definitions as in (3.31). Notice that the result for elongational flow is quite similar to that for the shear flow, to within a multiplicative factor of 4. Thus, we do not present the graphical result here.

IV. DISCUSSION

The calculations by Yamazaki and Ohta[6] and by us show that the natural parameter occurring in linear flow problems is $w \sim gN^{z\nu}$. This can be understood by a scaling argument. Since g has the dimension of reciprocal time, the natural parameter in the problem is the product of g and the representative time scale of the polymer chain, denoted by τ. If the dynamical exponent is denoted by z then $\tau \sim N^{z\nu}$. Thus $w \sim gN^{z\nu}$ must be the natural parameter. The renormalization-group calculation confirms this. There is good reason to believe that, near criticality, the chain is stretched to not more than 5 (probably about 2) times its equilibrium size.[15] An estimate of g_c may be obtained by use of the weak-flow time scales. (We will shortly return to discussion of the reliability of dynamical scaling.) From this, we conclude that the critical flow strength g_c for the stretching transition must scale as $N^{-z\nu}$. With hydrodynamic interactions, $z=d$, and without it $z=2+1/\nu$. The former is the consequence of kinematics of the Oseen tensor model,[12] so that, to $O(\epsilon^2)$, z need not be identical to d. But our experience with the binary critical fluid[16] tells us that this deviation will be at most of order 5%. The result $z=2+1/\nu$ is a purely kinematic result, so it is exact. Of course, our minimal model cannot describe the region beyond the stretching

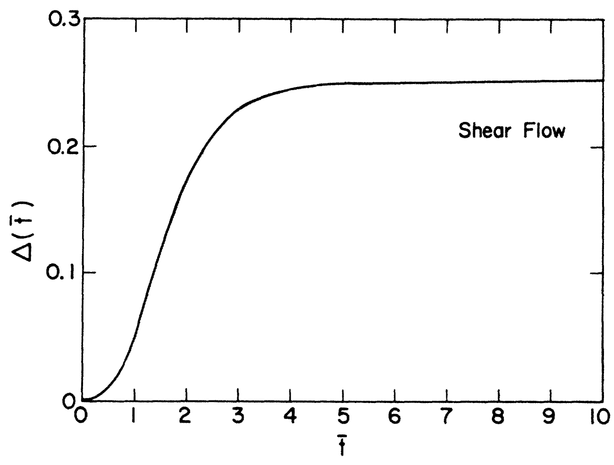

FIG. 1. Normalized deviation $\Delta(\bar{t})$ $(=w^{-2}[\langle \mathbf{R}^2(\bar{t})\rangle /Nd-1])\times 10^2$ of mean-square end-to-end distance from quiescent value, plotted as a function of $\bar{t}$ for the case of shear flow.

transition. It gives $\langle \mathbf{R}^2(t)\rangle \sim N^5$, which is wrong (at large flow strengths) because $\langle \mathbf{R}^2(t)\rangle$ cannot be larger than N^2. This discrepancy arises because we neglect the nonlinearity in the bonds which prevents excessive stretching.

According to recent experimental results by the Bristol group,[9] the critical flow strength for the stretching transition (denoted g_c) scales as $N^{-1.5}$ *irrespective* of the solvent quality. They claim that $N^{-1.76}$ can be definitely excluded. Thus, we must always use $z=d=3$, $\nu=\frac{1}{2}$, independent of the actual value of ν. One may argue that the discrepancy is due to the magnitude of w being outside the validity of our calculational scheme, even though the minimal model is correct. For sufficiently large N, $N^{-1.76}$ is significantly smaller than $N^{-1.5}$, so that at the critical flow strength $w\sim N^{-1.5}N^{1.76}\sim N^{0.26}$ becomes very big, invalidating the weak-flow argument we have been using. It is true that our results which are truncated to w^2 become unreliable. However, our formal results are more general. The general result (3.26) for $\langle \mathbf{R}^2(t)\rangle$ under the preaveraging approximation is correct for any flow strength [to $O(\epsilon)$ even if there exists a self-avoiding interaction] so long as we can ignore the nonlinearity of the backbone. Furthermore, we know that the preaveraging approximation affects only prefactors.[8] To calculate (3.27) for any g, we need $\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle$, which is time independent in the stationary state. Since the chain is not deformed strongly up to the stretching threshold, the length scale which is relevant to this quantity must be N^{ν}. Hence, the time scale is still given by $\tau\sim N^{z\nu}$. Therefore, the scaling argument should be reliable up to the threshold flow, if we can rely on our minimal model. Thus, we must take the discrepancy seriously.

One might conceive the following argument to explain this result: Just before the stretching transition, the chain has been stretched sufficiently to justify neglecting the self-avoiding interaction. Thus, $g_c\sim N^{-1.5}$ always. However, we know theoretically[17] that the self-avoiding interaction becomes negligible only when the chain has been stretched to about 10 times its equilibrium size. But, as mentioned before, the chain is not stretched extensively at the stretching threshold, so that the previous argument is untenable and cannot rescue our model in the vicinity of the stretching transition, if we believe the Bristol results to be conclusive.

We must stress that the crossover effect is very severe for dynamic quantities and that ν in g_c is not the static but the hydrodynamic ν. It may stay rather close to 0.5 even though the static ν is almost 0.6. (See, for example, the theoretical study of the crossover regime in Ref. 18.) Nevertheless, we would expect some variation of g_c with the solvent quality. Hence again the crossover effect seems insufficient to resolve the contradiction.

Thus we conclude that, if we rely on our minimal model, which is the best starting point so far proposed for dilute solution dynamics, theoretical results and the Bristol experiments are significantly at variance.

There is an even more serious consequence of the previous discussion. If the harmonic chain model is reliable in the quiescent fluid, we would expect it to be reliable also just before stretching as the chain has not been strongly stretched at flow strengths less than g_c. But we have seen that this is not true. Thus, we are forced to discard our minimal model consisting of the Edward's Hamiltonian and the fluctuating solvent hydrodynamics. This model is theoretically nice and has so far given results in reasonable agreement with experiment for solution dynamics.[3] Of course, agreement with experiment does not necessarily justify a model but it seems difficult to modify our minimal model while keeping all the results for the quiescent fluid intact.

To summarize, we have calculated renormalization-group theoretically the mean-square end-to-end distance for a Gaussian chain in a weak systematic linear flow. The results strongly suggest a scaling form for g_c which does not agree with the experiments of the Bristol group. This leads to the grave conclusion that the minimal model currently in use is incorrect. The Bristol experiments, if conclusive, destroy the existing theoretical framework. We hope that experimentalists recognize the extreme importance of the molecular weight dependence of g_c.

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APPENDIX A

Here, we calculate the terms of $O(g)$ which appear in the calculation for the shear flow using the general expression (3.25) obtained within the preaveraging approximation. From (3.26) we have an extra $O(g)$ term T_g as

$$T_g=4g\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\int_{\mathbf{k}}\int_0^s ds'\frac{k_1k_2}{k^2}\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle[G_0(N_0,\beta\,|\,t+s-2s')-G_0(0,\beta\,|\,t+s-2s')]$$

$$\times[G_0(N_0,\alpha\,|\,t-s)-G_0(0,\alpha\,|\,t-s)]\ . \tag{A1}$$

We evaluate

$$\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle=\exp\left[-\tfrac{1}{2}\sum_i k_i^2\langle[c_{0i}(\alpha,s)-c_{0i}(\beta,s)]^2\rangle\right]$$

in the presence of shear flow. A simple calculation yields

$$\sum_i k_i^2\langle[c_{0i}(\alpha,s)-c_{0i}(\beta,s)]^2\rangle=k^2|\alpha-\beta|+\frac{2g}{N_0}\zeta_0k_1k_2\sum_{p=1}^{\infty}\frac{[\cos(\hat{p}_0\alpha)-\cos(\hat{p}_0\beta)]^2}{\hat{p}^4}(1-e^{-2\hat{p}_0^2s/\zeta_0})\ . \tag{A2}$$

Thus, to $O(g)$

$$\langle e^{i\mathbf{k}\cdot[\mathbf{c}_0(\alpha,s)-\mathbf{c}_0(\beta,s)]}\rangle=e^{-k^2|\alpha-\beta|/2}\frac{g}{N_0}\zeta_0k_1k_2\sum_{p=1}^{\infty}\frac{[\cos(\hat{p}_0\alpha)-\cos(\hat{p}_0\beta)]^2}{\hat{p}^4}(1-e^{-2\hat{p}_0^2s/\zeta_0})e^{-k^2|\alpha-\beta|/2}\ . \tag{A3}$$

The $\mathbf{k}$ integration reduces to zero terms of $O(g)$ in our expression for T_g. This conforms with our intuitive expectation that $\langle\mathbf{R}^2(t)\rangle$ should not contain terms of $O(g)$ because the stretching should be independent of the flow direction and depend only upon its magnitude. Replacing (A3) in (A1) and performing the $\mathbf{k},s'$ integrations, we have

$$T_g=\frac{g^2}{6(2\pi)^2}N_0^2\zeta_0^2\int_0^{N_0}d\alpha\int_0^{N_0}d\beta\int_0^t ds\sum_{\substack{p,p',p''=1\\ p,p',p''\ \mathrm{odd}}}^{\infty}|\alpha-\beta|^{-2}\cos(\hat{p}_0'\alpha)\cos(\hat{p}_0''\beta)\frac{[\cos(\hat{p}_0\alpha)-\cos(\hat{p}_0\beta)]^2}{(\pi p)^4}$$

$$\times\left[e^{-(\hat{p}_0'^2+\hat{p}_0''^2)(t-s)/\zeta_0}(e^{-2\hat{p}_0^2s/\zeta_0}-1)(e^{-2\hat{p}_0^2s/\zeta_0}-1)\frac{1}{(\pi p'')^2}+p'\leftrightarrow p''\right]\ . \tag{A4}$$

In (A4) we have put $d=4$ (or $\epsilon=0$), as this expression does not contain any pole terms.

A numerical evaluation of these terms was conducted by us. It gave a negligible contribution to $\langle\mathbf{R}^2(t)\rangle/(Nd)$. Thus, we are justified in neglecting these terms.

APPENDIX B

Here we show that, to $O(g^2)$ and $O(\epsilon)$, there are no extra terms resulting from the modification of the Oseen tensor by systematic flow terms. A simple calculation yields the modified form of the Oseen tensor to $O(g)$ for the linearized Navier-Stokes equation (2.3) as

$$\underline{T}(\mathbf{r},\mathbf{r}')=\int\frac{d^dk}{(2\pi)^d}\left[1-\frac{g\underline{P}\underline{A}}{k^2}+\frac{g\underline{P}}{k^2}\left[\mathbf{k}\cdot\underline{A}\frac{\partial}{\partial\mathbf{k}}\right]\right]$$

$$\times\underline{P}k^{-2}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\ , \tag{B1}$$

where $\underline{P}\equiv I-\mathbf{k}\mathbf{k}/k^2$ and $\underline{A}$ is the flow matrix. Extra terms of $O(g^2)$ are expected to arise from the $O(g)$ terms in (B1). However, if we insert the modified projection operator

$$\underline{P}'=\left[1-\frac{g\underline{P}\underline{A}}{k^2}+\frac{g\underline{P}}{k^2}\left[\mathbf{k}\cdot\underline{A}\frac{\partial}{\partial\mathbf{k}}\right]\right]\frac{\underline{P}}{k^2} \tag{B2}$$

in (3.25), the $\mathbf{k}$ integration takes the form

$$\int\frac{dk}{(2\pi)^d}k^{-4}e^{-k^2|\alpha-\beta|/2}\propto|\alpha-\beta|^{\epsilon/2}\ . \tag{B3}$$

Thus, the extra terms do not have poles in ϵ. Furthermore, to $O(\epsilon)$ we can immediately put $\epsilon=0$ in the extra terms. The α,β integrations then decouple out and are of the form

$$\int_0^{N_0}d\alpha[G_0(N_0,\alpha\,|\,t-s)-G_0(0,\alpha\,|\,t-s)]=0\ . \tag{B4}$$

Hence, there are no extra terms in $\langle\mathbf{R}^2(t)\rangle$ to $O(g^2)$ and to $O(\epsilon)$.

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