Notes

Chain Orientation and Extension in Steady Shear Flow

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1. Introduction

The stretching and orientation of linear polymer chains under shear has been investigated in recent experiments[1−4] and computer simulations.[5] Inclusion of finite-extensibility effects[6] within the free-draining Rouse model for chain dynamics[7] has been shown to permit semiquantitative agreement with measurements on fluorescently labelled DNA molecules.[1] The present work generalizes this approach to include hydrodynamic interactions within the preaveraged Zimm approximation.[7,8] Our results are compared with light scattering measurements[2−4] on polystyrene (PS) in dioctyl phthalate (DOP).

2. Theory

We incorporate finite extensibility in our bead−spring model by a self-consistent determination[6] of the effective spring constant k. The effective spring constant k is related to a shear-rate and chain conformation-independent spring constant k_0 through the function b, defined as

$$b \equiv \frac{1-\alpha}{1-z} \equiv \frac{k}{k_0} \tag{1}$$

where α and z are, respectively:

$$\alpha \equiv \langle R^2\rangle_0/\langle R^2\rangle_m, \text{ and } z \equiv \langle R^2\rangle/\langle R^2\rangle_m \tag{2}$$

In eq 2, $\langle R^2\rangle$ is the mean square end-to-end distance of the chain at 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 maximal value of the mean square end-to-end distance at high shear rates. The ansatz in eqs 1 and 2 is motivated by recent work within the Rouse model,[6] which reported semiquantitative agreement with experimental results[1] for sheared solutions of DNA. Θ conditions are assumed throughout this work; i.e., ideal chain statistics describe the shear-free state. This functional form for the effective spring constant is motivated by the finitely extensible nonlinear elastic (FENE) model[6,9] for linear polymers. Equations 1 and 2 relate the effective spring constant k self-consistently to the chain extension ratio under shear. The effective segment length, σ, is related to the segment length, σ_0, in the absence of shear by $\sigma^2 = \sigma_0^2/b$. N denotes the number of beads per chain. The parameter α introduced in eq 2 specifies the ratio of quiescent to maximal observed values of the mean square end-to-end distance. In the spirit of earlier work,[6] we treat α as an empirically adjusted fitting parameter, as opposed to calculating it directly from the contour length.[10] (Light-scattering experiments for extensional flows[11] suggest that, even at high shear rates, individual chains may not undergo full stretching up to the limit imposed by the contour length.) The usual, strictly harmonic, formulations of the Rouse and Zimm models are recovered by equating b to unity.

The overdamped Langevin equations describing the chain dynamics written in terms of the Rouse normal modes,[6,7,12] defined as

$$X_p(t) = \frac{1}{N}\int_0^N \mathrm{d}n \cos\left(\frac{pn\pi}{N}\right) R_n(t), \qquad p = 0, 1, 2, ..., (N-1) \tag{3}$$

where $R_n(t)$ are the instantaneous bead coordinates and p indexes the normal modes, take the form

$$\dot{X}_p + \frac{k_p}{\varsigma_p} X_p - \hat{\kappa}\cdot X_p = \frac{1}{\varsigma_p} f_p \tag{4}$$

where $\hat{\kappa}$ is the velocity gradient tensor, f_p is a random force, and k_p and ς_p and are force and friction constants associated with the pth normal mode, respectively. We employ the notation of ref 12. For simple shear flow, where $\hat{\kappa}_{ij} = \dot{\gamma}\delta_{ix}\delta_{jy}$, the steady-state normal mode correlations satisfy[12]

$$\langle X_{p\alpha}{}^2\rangle = \frac{k_B T}{k_p} + \frac{1}{2}\frac{k_B T}{k_p}\left(\frac{\varsigma_p\dot{\gamma}}{k_p}\right)^2 \delta_{\alpha x} \quad \text{and} \quad \langle X_{px}X_{py}\rangle = \frac{k_B T \varsigma_p \dot{\gamma}}{2k_p{}^2}$$

where

$$k_p = 2k_0\frac{\pi^2 p^2}{N}, \text{ and } k_0 = \frac{3k_B T}{\sigma_0{}^2} \tag{5}$$

In the present model, the shear-rate independent spring constant k_0 is replaced by the effective spring constant k as described above. Consequently, k_p becomes

$$k_p = \frac{6k_B T b\pi^2 p^2}{\sigma_0{}^2 N} \tag{6}$$

For the free-draining Rouse model, the transformed friction coefficient ζ_p is[7,8,12]

$$\varsigma_p = 2N\varsigma \tag{7}$$

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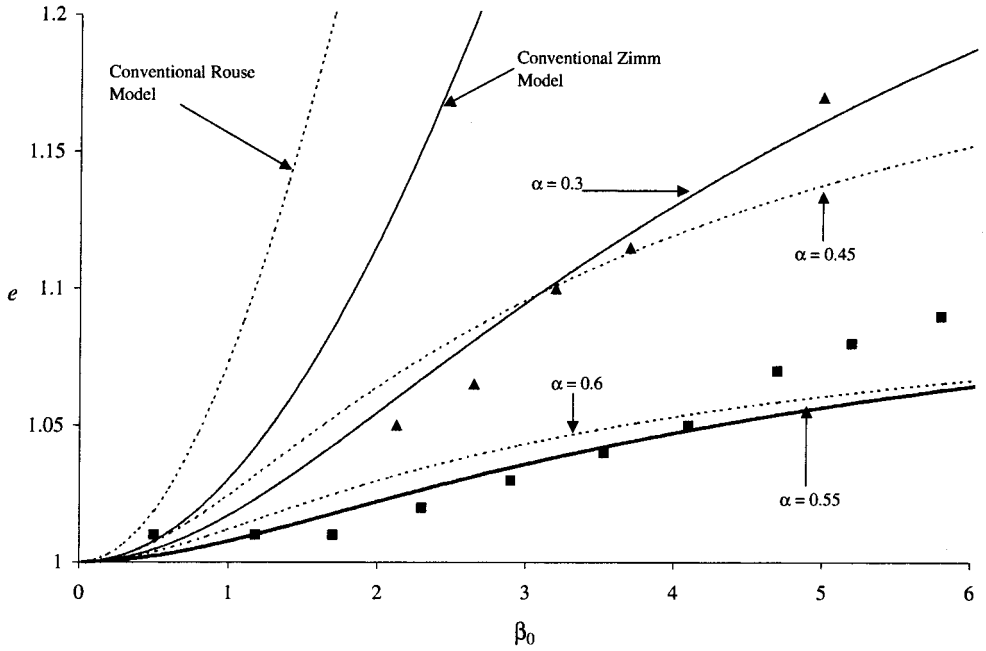

Figure 1. Coil extension ratio under shear, e (eq 4), as a function of dimensionless shear rate β_0. The broken and solid lines show results from the Rouse and Zimm hydrodynamic models, respectively, with and without the finite chain extensibility accounted for. Calculations within the Rouse model employ the strictly harmonic model, and $\alpha = 0.45$ and 0.6. Calculations within the Zimm model likewise employ the strictly harmonic model, and $\alpha = 0.3$ and 0.55. The filled triangles and squares represent flow light scattering measurements[2−4] on solutions of PS of molecular weights 3×10^6 and 10^7, respectively, in DOP.

where ζ is the friction coefficient for a single bead. For the Zimm model, in which hydrodynamic interactions are accounted for in a preaveraged sense,[7,8,12] ζ_p is

$$\zeta_p = \eta_s\sqrt{\frac{12\pi^3 N\sigma_0^2 p}{b}} \tag{8}$$

where η_s is the solvent viscosity. The components of the mean-square end-to-end vector and mean-square radius-of-gyration tensors are, respectively[7,12]

$$\langle R_\alpha R_\beta\rangle = 16\sum_{p=1,3,5\ldots}\langle X_{p\alpha}X_{p\beta}\rangle, \quad \text{and}$$

$$\langle S_\alpha S_\beta\rangle = 2\sum_{p=1}^{\infty}\langle X_{p\alpha}X_{p\beta}\rangle \tag{9}$$

We express our results in terms of the dimensionless shear rate β, defined as[2−4]

$$\beta \equiv \frac{[\eta]\eta_s M\dot\gamma}{N_A k_B T} \tag{10}$$

where $[\eta]$ is the intrinsic viscosity, M the polymer molecular weight, and N_A Avogadro's number. Within the present linear bead−spring model, the intrinsic viscosity is[7]

$$[\eta]^{Rouse} = \frac{N_A N^2 \zeta\sigma_0^2}{36M\eta_s b}, \quad \text{and}$$

$$[\eta]^{\text{Zimm}} = \frac{0.425N_A}{M}\left(\frac{N\sigma_0^2}{b}\right)^{3/2} \tag{11}$$

where the factor b modifying the effective spring constant is yet to be determined. Equation 11 reveals the following relationships between the values of the dimensionless shear-rate variable β and β_0, calculated respectively with and without the present adjustment for finite chain extensibility:

$$\beta^{\text{Rouse}} = \beta_0 b^{-1} \text{ and } \beta^{\text{Zimm}} = \beta_0 b^{-3/2} \tag{12}$$

Self-consistent determination of the factor b modifying the effective spring constant follows from eqs 1, 2, 5, and 9, and leads to the following equations for determining b in terms of the dimensionless shear rate variable β_0 and the extensibility parameter α:

$$b^3 - b^2 - 0.2\beta_0^2\alpha = 0, \quad \text{Rouse model}$$

and

$$b^4 - b^3 - 0.0797\beta_0^2\alpha = 0, \quad \text{Zimm model} \tag{13}$$

3. Results

We define the chain extension ratio, e, as

$$e = \sqrt{\frac{\langle R_g^2\rangle_\beta}{\langle R_g^2\rangle_0}} \tag{14}$$

where $\langle R_g^2\rangle_\beta$ is the mean-square radius of gyration under shear flow. Recent flow light scattering experiments[2−4] on solutions of PS in DOP have shown that the simple Rouse and Zimm models without correction for finite chain extensibility significantly over-predict the degree of chain extension. Equations 1, 2, 5, 9, 13, and 14 show that the chain extension is given by

$$e_{\text{Rouse}}^2 = \frac{1}{b}\left[1 + 0.152\left(\frac{\beta_0}{b}\right)^2\right]$$

and

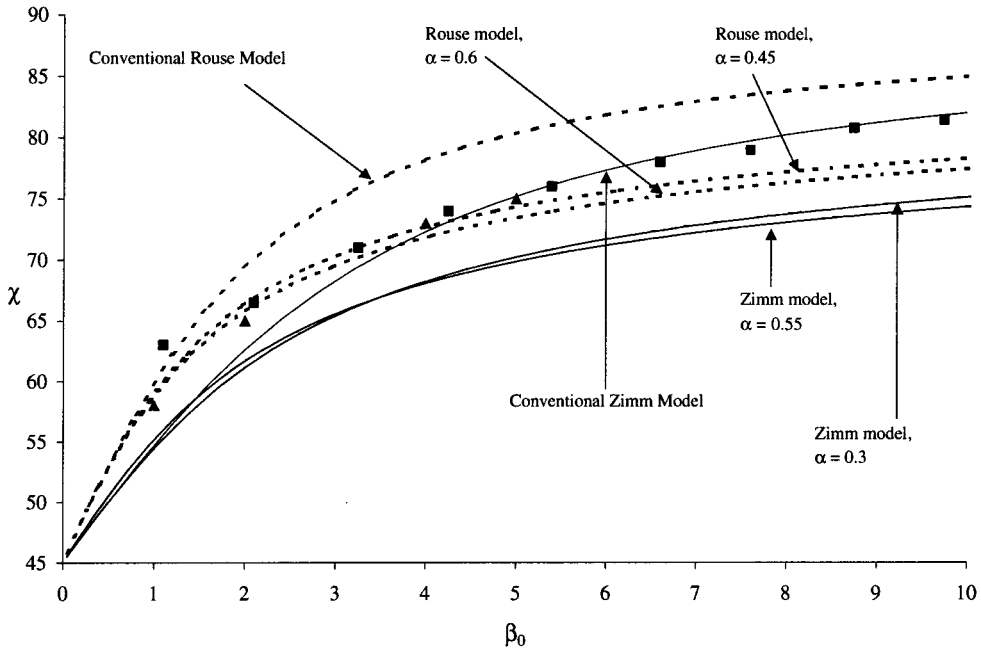

Figure 2. Coil orientation angle χ as a function of dimensionless shear rate β_0. All symbols have the same significance as in Figure 1.

$$e_{\text{Zimm}}{}^2 = \frac{1}{b}\left[1 + 0.0617\left(\frac{\beta_0{}^2}{b^3}\right)\right] \tag{15}$$

where b is determined from eq 13 as a function of shear rate and the parameter α. Existing results[8,12] are recovered by equating b to unity in eqs 11 and 15.

Results based on the present treatment of the chain extension ratio calculated using both the Rouse and Zimm hydrodynamic models are compared with experimental measurements[2−4] on PS in DOP in Figure 1. The extensibility parameter α has been treated as anadjustable fitting parameter for the purpose of these calculations. The dimensionless shear rate variable β_0 used as the horizontal axis variable has been calculated using the intrinsic viscosity at zero shear rate, when $b \rightarrow 1$. Predictions based on the usual formulation of the strictly harmonic Rouse and Zimm models[7,12] substantially over-predict the chain deformation, consistent with previous findings.[2−4] However, accounting for the finite chain extensibility leads to improved agreement with the experiments, particularly when the hydrodynamic interactions are accounted for, albeit within the preaveraging approximation. It is believed that, at higher shear rates, the impact of hydrodynamic interactions is weakened[13] and the chain dynamics become more closely "Rouse-like". Such a crossover from Zimm to Rouse model-like dynamics may partially explain remaining discrepancies in the comparison shown in Figure 1, and is under current investigation.

In the present work, α has been treated as an adjustable parameter to obtain the best fit to experimental data for PS in DOP at relatively low shear rates. Our values for α are about 3−6 times larger (corresponding to weaker maximal chain distortion) than those found appropriate in an earlier work[6] which examined the stretching of DNA molecules at higher dimensionless shear rates. It is conceivable that extension of our results to treat experiments over a wider range of β_0 could lead to a fitted value for α which would correspond more closely to full extension toward the contour length under high shear conditions.

The orientation angle χ of the coils under flow is calculated from[8]

$$\tan 2\chi = \frac{2G_{21}}{G_{11} - G_{22}} \tag{16}$$

where G_{ij} are elements of the mean-squared radius-of-gyration tensor. Equations 5, 9, 13, and 16 lead to the following expressions for the orientation angle χ

$$\chi = \frac{\pi}{4} + \frac{1}{2}\arctan\left(\frac{\beta}{1.7454}\right) = \frac{\pi}{4} + \frac{1}{2}\arctan\left(\frac{\beta_0}{1.7454b}\right), \quad \text{Rouse model}$$

$$= \frac{\pi}{4} + \frac{1}{2}\arctan\left(\frac{\beta}{2.8363}\right) = \frac{\pi}{4} + \frac{1}{2}\arctan\left(\frac{\beta_0}{2.8363b^{3/2}}\right), \quad \text{Zimm model} \tag{17}$$

where b is determined from eq 13. Calculations of the orientation angle as a function of applied shear-rate from eqs 13 and 17 are compared with experimental measurements[2−4] on PS in DOP in Figure 2. The values of the parameter α used in these calculations are the same as those employed for the chain extension ratio calculations shown in Figure 1. This comparison reveals that the improved description of the coil extension ratio which is made possible by accounting for finite chain extensibility comes at the expense of a less accurate, though still qualitatively correct, prediction for the coil orientation. Nevertheless, a more accurate, semiquantitative description of the coil extension under shear is of interest in understanding the thermodynamics of flowing polymer solutions and blends, as the number of near-neighbor contacts and cohesive energy are intimately related to the coil geometry.[14]

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