Suppression of Excluded-Volume Exponents in Shear Flow of Dilute Polymer Solutions

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The analogy between polymer and binary critical fluid dynamics in simple shear flow is used to construct a renormalization-group analysis of the scaling exponent v for the end-to-end distance of an isolated long polymer chain in a good solvent undergoing strong shear flow. The shear flow induces a crossover from the usual fixed point with the good-solvent Flory exponent v to a new, strong-shear fixed point with the classical exponent $v = \frac{1}{2}$. Based on the blob picture we argue that the dynamic exponent z is not affected by the flow and remains at its zero-shear value $z = 3$. Experimentally observable consequences of this result are also discussed.

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Experimentally observable properties $\{A\}$ of high-molecular-weight polymers in dilute solution such as radius of gyration, diffusion constant, intrinsic viscosity, etc., obey scaling relations of the form

$$A \sim M^a, \tag{1}$$

where M is the molecular weight and a is a scaling exponent that is independent of the local structure of the polymer chain and its molecular weight but depends on the quality of solvent. This dependence reflects the variation in the strength of the excluded-volume interaction with solvent quality such that the exponent varies between its excluded-volume and ideal (phantom) chain limits when the solvent changes from good to θ solvent.[1]

Are polymer scaling exponents modified by externally applied flow? Experimentally, such modification was reported for polymers in elongational flow, where it was observed that, independent of the quality of solvent, the critical strain rate for the coil-stretch (CS) transition scales with the inverse relaxation time of an ideal polymer.[2] In other words, it appears that the excluded-volume effect is suppressed at the CS transition. Although there were several attempts to explain this observation based on the suppression of excluded volume by the stretching of the chain[3,4] (blob model) and on the role of inelastic effects at the transition point,[5] the *ad hoc* character of the explanations cannot be considered satisfactory. Unfortunately, a more systematic analysis of the phenomenon appears to be prohibitively difficult since all fundamental theories which capture the universal features of high-molecular-weight polymers (this excludes dumbbell-type models) are based on the Edwards Hamiltonian, e.g., modeling the polymer as an elastic chain, an approximation that breaks down at the coil-stretch transition. This problem does not occur in simple shear (planar Couette) flow where the coil-stretch transition is not expected to take place.[6] Indeed, from the exact solution,[7] $R^2/N^2 \propto (1 + \gamma^2 N^4)/N$, for the rms end-to-end distance R of a Gaussian chain (in the absence of excluded-volume and hydrodynamic interactions) in sim-

ple shear flow (SF), one concludes that in the range $N^{-1/2} \gg \gamma T_T \gg 1$, where N is proportional to the polymerization index, γ is the velocity gradient, and $T_R \propto N^2$ is the Rouse relaxation time of the polymer chain, one can expect strong flow effects on the global conformation and dynamics of the polymer, well within the domain of the validity of the elastic model. We emphasize that inelastic effects become important only when the velocity gradients are large enough to affect the local conformations of the chains or, in other words, when the end-to-end distance becomes comparable to the total length of a fully stretched chain. In the following, we shall limit our discussion to the elastic (Gaussian) regime, i.e., to chain deformations well below full extension, for which the entropic restoring forces of the polymer can be derived from the Edwards Hamiltonian [Eq. (4)].

A renormalization-group (RG) analysis of SF effects on the polymer conformation (end-to-end distance), based on the coupled Langevin equations for the polymer and solvent system (CLEPS) and including both hydrodynamic interactions and excluded-volume effects, was carried out in Ref. 8. Based upon a perturbative calculation, to first order in $\epsilon = 4 - d$, where d is the spatial dimensionality, and to second order in the velocity gradient γ, combined with an estimate of some higher-order (in γ) contributions, the authors concluded that polymer exponents (e.g., the excluded-volume exponent v and the dynamic exponent z) are not affected by the flow. Using the RG terminology, this means that the fixed points of the RG equations are not affected by shear and that one can use the zero-shear fixed-point values of the excluded-volume coupling constant and of the friction coefficient even in the presence of large velocity gradients. Similar conclusions were reported for the elongational-flow case, for strain rates in the range where the Gaussian model can still be applied.[8,9] To the best of our knowledge, there is no direct experimental evidence that supports or refutes the above predictions in the case of SF. The previously mentioned indirect evidence against them in the elongational-flow case[2] cannot

be considered conclusive since the elastic-chain model breaks down at the coil-stretch transition.

From a purely theoretical point of view, the conclusion of Ref. 8 is rather surprising since, as is often the case in polymer physics, the CLEPS model was constructed[10,11] using the analogy with dynamical critical phenomena and one expects the dynamics of a polymer in SF to be related to the problem of critical dynamics of a scalar order-parameter field in SF. However, in the latter case, it is known[12] that the presence of shear has a strong effect on the critical fluctuations of the order-parameter field and that in the high shear limit the upper critical dimension is reduced from 4 to below 3, leading to the appearance of classical exponents in 3D. Since the analysis of Ref. 12 is valid to all orders in the velocity gradient γ and since the examination of the deviation of the new, strong-shear, fixed point leads to the conclusion that it cannot be obtained by perturbative arguments, the question of the modification of polymer exponents cannot be resolved by a perturbative calculation in powers of γ. It should be emphasized, however, that the analogy between polymer dynamics and critical dynamics in shear should not be taken too far; the main

difference between the two problems is that because of chain connectivity the polymer cannot be represented by a scalar density field and furthermore, unlike the order-parameter field, the polymer is not passively advected by the flow. Thus, arguments based on the model of Ref. 12 cannot be directly applied to the polymer problem and can only be used as guiding principles. With this in mind we now proceed to analyze the question of polymer exponents in strong SF.

Consider a polymer in good solvent subjected to externally imposed SF with velocity gradient tensor $\Gamma^T = \gamma \hat{y} \hat{x}$, where the superscript T denotes the transpose of a matrix. Neglecting the hydrodynamic interactions, the polymer dynamics is described by the stochastic equation,[9,10]

$$\frac{\partial c(\tau,t)}{\partial t} = -\zeta_0^{-1} \frac{\delta H}{\delta c(\tau,t)} + \Gamma \cdot c(\tau,t) + \theta(\tau,t) , \qquad (2)$$

where $c(\tau,t)$ is the position of the τth monomer at time t, ζ_0 is the bare monomer friction coefficient, and θ is a Gaussian random noise with zero mean and correlator

$$\langle \theta(\tau,t)\theta(\tau',t') \rangle = 2\zeta_0^{-1}\delta(t-t')\delta(\tau-\tau')\mathbf{1} . \qquad (3)$$

The Edwards Hamiltonian H is given by

$$H = \frac{1}{2} \int_0^{N_0} d\tau \left[\frac{dc(\tau)}{d\tau} \right]^2 + \frac{1}{2} v_0 \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \, \delta(c(\tau) - c(\tau')) , \qquad (4)$$

where v_0 is the bare excluded-volume parameter, N_0 is the bare number of monomers, and the integrals include a short-distance cutoff $|\tau - \tau'| > \xi_0$, where ξ_0 is the monomer size, which eliminates the self-interaction of the monomers.

In order to examine the modification of the excluded-volume exponents in the presence of SF, we have to construct an iterative scheme which will tell us how the excluded-volume coupling constant (i.e., the effective binary interaction coefficient) is affected by the process of renormalization which consists of coarse graining and subsequent rescaling of the chain contour.[1] The coarse graining corresponds to regrouping g "bare" monomers into one "dressed" monomer and gives rise to renormalization of the binary interaction coefficient. Invoking the analogy with the case of critical binary fluid mixtures,[12] we assume that the one-loop correction to the dimensionless coupling constant $u_0 = v_0 L^{\epsilon/2}$, where L is a phenomenological length scale, is given by the equation[13]

$$u_1 = u_0 - D(\gamma,0)u_0^2 , \qquad (5)$$

where

$$D(\gamma,0) = \frac{4}{(2\pi)^d} \int d^d k \int_1^g d\tau \int_1^g d\tau' \hat{G}_0(\tau,k)\hat{G}_0(\tau',k) ,$$
$$1 \ll g \ll N_0 . \qquad (6)$$

Here

$$\hat{G}_0(\tau,k) = \exp[-\tfrac{1}{2} k \cdot Q(\tau,0) \cdot k] \qquad (7)$$

is the Fourier transform of the distribution function $G_0(\tau,R)$ for the end-to-end vector R of a chain of contour length τ, and

$$Q(\tau,0) = \langle [c(\tau) - c(0)][c(\tau) - c(0)] \rangle , \qquad (8)$$

where $\langle \cdots \rangle$ denotes an average over the Gaussian random noise θ, and the index 0 in the argument of D implies that c is to be calculated neglecting the excluded-volume contributions. Up to this point the analysis is then quite general and relies only on the assumption that $\hat{G}_0$ is a stationary Gaussian distribution function. Notice that since Eq. (2) is linear (for $v_0 = 0$), this assumption holds even in the presence of arbitrarily large SF.

In equilibrium, $\gamma = 0$, $v_0 = 0$, one readily obtains $Q_{\text{eq}}(\tau,0) = (\tau/d)\mathbf{1}$ and, since to order ϵ^2, the integral in Eq. (6) has to be performed in $d = 4$ dimensions, integration gives $D(0,0) = \pi^{-2}\ln g$ which diverges logarithmically as $g \to \infty$. Substituting into Eq. (5) and carrying out the rescaling transformation[13] $u_0 \to u_l$, $u_l \to g^{-\epsilon/2} \times u_{l+1}$ yields the recursion equation

$$u_{l+1} = u_l + \beta(u_l)\ln g , \quad \beta(u_l) = u_l \left(\frac{\epsilon}{2} - \frac{u_l}{\pi^2} \right) . \qquad (9)$$

The trivial ($u^* = 0$) fixed point of the RG transformation $u_{l+1} \to u_l$ leads to the classical exponent, $v = 0.5$; the nontrivial fixed point, $u^* = \epsilon\pi^2/2$, gives the excluded-volume exponent, $v = 0.5(1 + \epsilon/8)$.

In the presence of SF, solving Eq. (2) to all orders in γ

(for $v_0 = 0$), substituting the solution into Eq. (8), and performing the averaging with respect to the random noise yields the steady-state moment[14]

$$\langle Q_{ss}(t,0) \rangle = \tau \left[1 + \frac{\zeta_0 \tau^2}{12}(\Gamma + \Gamma^T) + \frac{\zeta_0^2 \tau^4}{60} \Gamma \cdot \Gamma^T \right]. \tag{10}$$

Performing the momentum integrations in Eq. (6), one obtains

$$D(\gamma, 0) \propto \int_1^g d\tau \int_1^g d\tau' \frac{1}{(\tau + \tau')^2} \frac{1}{\{1 + \zeta_0^2 \gamma^2 [7(\tau^3 + \tau'^3)^2 + 12\tau\tau'(\tau + \tau')^2(\tau - \tau')^2]/720(\tau + \tau')^2\}^{1/2}}. \tag{11}$$

In the strong shear limit, $\gamma T_R \equiv \gamma \zeta_0 N_0^2 / \pi^2 \gg 1$, the sequence of l RG transformations with $l > l_c \equiv \ln(\gamma \zeta_0 / \pi^2)/2 \ln g$ leads to the strong-shear fixed point for which $\gamma \zeta_0 g^{2l}/\pi^2 \gg 1$, where γ in Eq. (11) is rescaled to $\gamma g^{2(l-1)}$; thus, 1 can be neglected with respect to the term proportional to γ^2 in the denominator in Eq. (11) and the resulting integral converges in the limit $g \to \infty$. The disappearance of the logarithmic divergence with g indicates that the excluded volume becomes irrelevant in the strong shear limit and that one recovers the classical exponent, $v = 0.5$, irrespective of solvent quality.

What happens in the presence of hydrodynamic interactions (HI)? In equilibrium, the main effect of HI is to change the Rouse relaxation time T_R into the Zimm relaxation time $T_Z \equiv (6\pi\eta/kT)\xi^z$, where η is the solvent shear viscosity, $\xi \equiv \xi_0 N^v$ is the Flory radius of the polymer, and $z = d$ is the dynamic exponent and where, to facilitate the comparisons with the blob model,[15] we have reintroduced the temperature T. In the case of the excluded-volume effect, the same argument as above leads to a similar conclusion: Excluded volume becomes irrelevant in the strong SF limit, $\gamma T_Z \gg 1$, and one obtains $v = \frac{1}{2}$.

Is the dynamic exponent z modified by strong SF? In order to answer this question we resort to the blob picture according to which the effect of shear is negligible within a blob of linear size $\xi_c = (kT/6\pi\eta\gamma)^{1/z}$, such that the excluded volume is important only within individual blobs.[15] The foregoing RG analysis can be readily reinterpreted in terms of the blob model by saying that the crossover to the new fixed point takes place at $l_c' \equiv \ln(kT/6\pi\eta\gamma\xi_0^z)/zv \ln g$, such that $g^{l_c'}$ is just the number of monomers contained in each blob. In order to understand what happens on larger scales we note that the average length over which the hydrodynamic effect is still important in SF is $\xi_h = (\eta/\rho\gamma)^{1/2}$, where ρ is the solvent density. This length scale determines the transition between the viscous and inertial regimes in the solvent and is large compared to microscopic dimensions. For macroscopically realizable velocity gradients the ratio $\xi_h/\xi_c \propto (\gamma t)^{1/z - 1/2}$, where t is a microscopic time scale, is much greater than unity (for $z > 2$), and we conclude that the hydrodynamic interaction is effective on length scales much larger than the blob size. Moreover, since $\xi_h^2/\xi^2 \propto N^{1/2}/\gamma T_Z \gg 1$ for $\gamma T_Z \gg 1$ (but finite), we expect that, within the range of validity of the elastic model, HI

remains unaffected by the shear over distances comparable to chain dimensions. We conclude that the dynamic exponent is not affected by the shear, i.e., $z = d$ even in the limit of strong SF.

What are the experimentally observable consequences of our analysis? The suppression of the excluded-volume exponents can, in principle, be observed in light scattering and birefringence experiments and in computer simulations of high-molecular-weight polymers in good solvents subjected to strong SF. Another candidate is the intrinsic viscosity which decreases with γ in the strong shear limit (shear thinning[16]). Although one cannot expect our results to be directly applicable to the above problem, it would be interesting to study ratios of the intrinsic viscosities in good and θ solvents as a function of the velocity gradients, since crossover behavior is expected at $\gamma T_Z \gtrsim 1$. Further work along these lines is now in progress.

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[1]P. G. de Gennes, Scaling Concepts in Polymer Physics (Cornell Univ. Press, Cornell, 1979).

[2]A. Chow, A. Keller, A. J. Müller, and J. A. Odell, Macromolecules 21, 250 (1988).

[3]Y. Rabin, J. Polym. Sci. Lett. Ed. 23, 11 (1985).

[4]A. Onuki, J. Phys. Soc. Jpn. 54, 3656 (1985).

[5]Y. Rabin, F. S. Henyey, and R. K. Pathria, Phys. Rev. Lett. 55, 201 (1985).

[6]P. G. de Gennes, J. Chem. Phys. 60, 5030 (1974).

[7]R. B. Bird, H. H. Saab, P. J. Dotson, and X. J. Fan, J. Chem. Phys. 79, 5729 (1983).

[8]S. Puri, B. Schaub, and Y. Oono, Phys. Rev. A 34, 3362

(1986).

[9]K. Yamazaki, and T. Ohta, J. Phys. A **15**, 287 (1982).

[10]Y. Oono, and K. F. Freed, J. Chem. Phys. **75**, 1009 (1981).

[11]Y. Shiwa, Phys. Lett. **103A**, 211 (1984).

[12]A. Onuki and K. Kawasaki, Ann. Phys. (N.Y.) **121**, 456 (1979).

[13]Y. Oono, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1985), Vol. 61.

[14]H. C. Ottinger, J. Chem. Phys. **87**, 3156 (1987).

[15]A. Onuki, J. Phys. Soc. Jpn. **55**, 1041 (1986).

[16]R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (Wiley, New York, 1976), Vol. 1.