

## Dynamics and configurational fluctuations of single DNA molecules in linear mixed flows

Joe S. Hur,<sup>1</sup> Eric S. G. Shaqfeh,<sup>2</sup> Hazen P. Babcock,<sup>3</sup> and Steven Chu<sup>3</sup>

<sup>1</sup>Department of Chemical Engineering, Stanford University, Stanford, California 94305

<sup>2</sup>Department of Chemical and Mechanical Engineering, Stanford University, Stanford, California 94305

<sup>3</sup>Department of Physics and Applied Physics, Stanford University, Stanford, California 94305

(Received 20 August 2001; published 26 July 2002)

We examine the dynamics of DNA molecules in mixed flows where the ratio of vorticity to strain rate may be slightly above or below unity via Brownian dynamics simulation. We find that the chain dynamics in these flows are dramatically different than those found for simple shear flow. When the strain rate exceeds vorticity, the dynamics are found to be driven by the extra amount of straining. For vorticity-dominated flows, a periodicity in chain extension is observed with considerable chain deformation.

DOI: 10.1103/PhysRevE.66.011915

PACS number(s): 87.14.Gg, 47.50.+d, 87.15.-v

Over the past few decades many fascinating non-Newtonian properties of polymer solutions in flow have been extensively investigated both experimentally and theoretically [1–3]. Much effort has been made to understand the dynamics of polymers in rather simple and ideal flow fields due to the complexity that arises from the coupling of the flow and the polymer dynamics [4–10]. Two of the most often and widely examined ‘ideal’ flow types are purely extensional flow and simple shear flow. Simple shear flow is a limiting case of planar flows where the magnitude of the vorticity exactly equals that of the strain rate. Due to vorticity, a polymer molecule cannot maintain a stable steady configuration even at high flow strength and undergoes tumbling dynamics in shear flow [11–14]. Purely extensional flow, on the other hand, is vorticity free and thus is effective in creating large chain deformation. While there exists a large volume of work investigating the dynamics in these flows, relatively little is known about the dynamics in flows that deviate from these two limiting flows, such as linear mixed flows [9]. Moreover, in real industrial applications and processes, mixed flows, as a local approximation to a more complex flow field, are omnipresent and thus a clear understanding of the polymer dynamics in more general flows is needed. Our goal of this work is to examine the dynamics of single polymer molecules in flows that deviate slightly from simple shear flow and to use the findings to broaden our understanding of the response of polymers in linear mixed flows. Note that de Gennes [15], among others, has designated simple shear flow as a critical flow for polymer configuration dynamics—representing the limiting amount of vorticity necessary to forestall a “coil-to-stretch” transition—and thus examining dynamics near this critical point is also interesting from a fundamental point of view.

In this work, we have used  $\lambda$ -DNA molecules as our model polymer whose dynamics in the aforementioned limiting flow types, i.e., purely extensional and shear flow have recently been thoroughly investigated [11,13,16,17]. Throughout this paper, we will make a direct and detailed comparison to the previous findings as well as to recent complementary experiments.

In our Brownian dynamics simulation we solve the stochastic differential equation in Eq. (1) for individual chain trajectories using two different molecular models. The most

fine-grained nonlinear model that we use is the Kramers’ bead-rod chain where each rod corresponds to one Kuhn length of a  $\lambda$ -DNA molecule. A 150 bead Kramers’ chain matching the same number of Kuhn lengths of a  $\lambda$ -DNA molecule has previously been shown to capture the experimental observations of  $\lambda$ -DNA molecules in shear flow [13]. A more coarse-grained nonlinear model is the wormlike bead-spring model where a number of Kuhn lengths are replaced by a spring for simplicity and individual springs satisfy the wormlike chain law [18]. Three classical linear models that we use for theoretical analysis in elliptic flows are the single-mode Hookean dumb-bell model, the multi-mode Rouse model and the multi-mode Zimm model. The former two models are freely draining whereas the latter includes preaveraged hydrodynamic interactions [19,20],

$$dr_i^\nu = \left[ \frac{\partial u_i^\infty}{\partial x_j} r_j^\nu + \frac{1}{\zeta} F_i^{\nu,c} \right] dt + \sqrt{\frac{2k_B T}{\zeta}} dW_i^\nu. \quad (1)$$

In Eq. (1),  $r_i^\nu$  is the position vector of bead  $\nu$ ,  $\zeta$  is the drag coefficient and the Brownian force,  $dW_i^\nu$ , is assumed to be a Wiener process [21] where its amplitude is given by the fluctuation-dissipation theorem [22]. The dimensionless velocity gradient tensor is given by

$$\frac{\partial u_i^\infty}{\partial x_j} = Pe \begin{bmatrix} 0 & 1 & 0 \\ \alpha & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (2)$$

In Eq. (2),  $\alpha$  is the flow type parameter and  $Pe \equiv (\dot{\gamma} l^2)/D$  is a dimensionless strain rate [23]. Note that  $\alpha$  is unity for purely extensional flow, 0 for shear flow and  $-1$  for pure rotational flow. The parameter range of our interest is  $-0.01 \leq \alpha \leq 0.02$  which is slightly above ( $\alpha^+$ ) and below ( $\alpha^-$ ) shear flow. A more appropriate dimensionless flow strength parameter that we use in our analysis is the Weissenberg number defined as  $Wi = Pe \cdot \tau$  where  $\tau$  is the dimensionless longest relaxation time of the molecule [24]. Lastly, the connector force  $F_i^{\nu,c}$  is needed to maintain the inextensibility of the Kramers’ chain, and, in the other appropriate context represents the entropic force of the bead-spring mod-

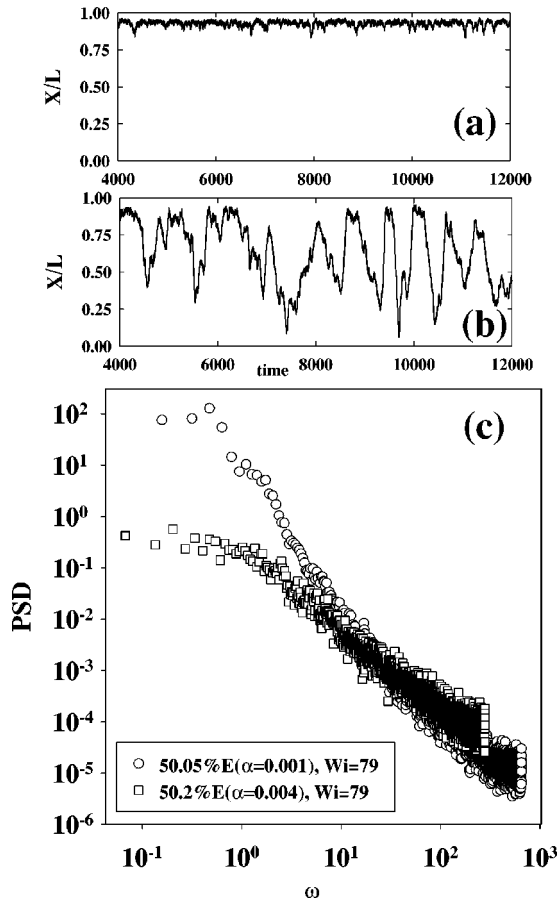


FIG. 1. A plot of sample trajectories of a single Kramers' chain in two different flow types (a)  $\alpha=0.004$  and (b)  $\alpha=0.001$  at  $Wi=79$ . By molecular extension we mean the maximum projected extension in the flow-gradient (1-2) plane and we normalize it by its contour length. (c) The power spectrum (PSD) of the chain extension shown in (a) and (b) versus the dimensionless frequency  $\omega$ .  $\omega$  is the frequency scaled with the longest relaxation time  $\tau$  of the polymer.

els. The details of the simulation technique as well as dimensional scalings are discussed in more detail elsewhere [13,25–27].

In Figs. 1(a) and 1(b), we show the fractional molecular extension of a 150 bead Kramers' chain versus time at steady state for  $Wi=79$  for two different flow types, i.e.,  $\alpha=0.004$  and  $0.001$  (corresponding to 50.2%  $E$  and 50.05%  $E$  respectively). %  $E$  is related to  $\alpha$  as %  $E=50(\alpha+1)$  [28]. One can clearly see the growth of fluctuations in molecular extension as  $\alpha^+$  approaches the shear limit of zero. Note in this context, that concentration fluctuations near phase transitions have been studied in some detail [29,30]. The physics of these similar fluctuations near a coil-to-stretch transition is clear. Brownian fluctuations drive the chain increasingly between the compressional and extensional eigenvectors of the mixed flow. The more frequent collapse of chain extension in flows is due to the fact the chain is more prone to “collapsing” or “flipping” between the two principal axes because the angle between the extension and compression axes gets smaller as  $\alpha^+$  approaches zero [see Fig. (2)].

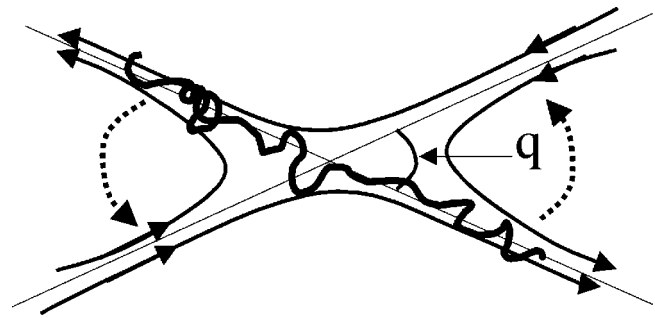


FIG. 2. A schematic of  $\alpha^+$  flows. The polymer chain is aligned along the principal axis and the angle between the extension and compression axes is denoted as  $q$ . As indicated by the dashed arrows, Brownian motion can displace the molecule toward the compressional axis causing the collapse of extension.

The power spectrum (PSD) of the chain extension in Fig. 1(c) shows the growth in power and the development of a midrange frequency “collapsing” or “flipping” regime as  $\alpha^+ \rightarrow 0$ . This regime has already been reported in simple shear flow [31,13]. These large fluctuations have also been witnessed in recent experiments [32]. For the elliptic vorticity-dominated flow ( $\alpha=-0.006$  or 49.7%  $E$ ) as shown in Fig. 4(a), interestingly, a periodicity in molecular extension is observed. By averaging the time trace of one chain over a long period of time we have calculated the steady average molecular extension. As shown in Fig. 3(a), the steady molecular extension of a Kramers' chain undergoes a coil-stretch transition in flows that have positive  $\alpha$  values, or equivalently flows that have more straining than vorticity, however, the transition is not as sharp as the purely extensional flow ( $\alpha=1$ , or 100%  $E$ ) case.

For the elliptic vorticity-dominated flow, the chain has deformed considerably compared to its equilibrium size contrary to previous predictions by deGennes [15]. For the purely rotational flow (0%), as predicted, the chain remains in its unperturbed coiled state. The positive eigenvalues of the velocity tensor [Eq. (2)] correspond to the amount of

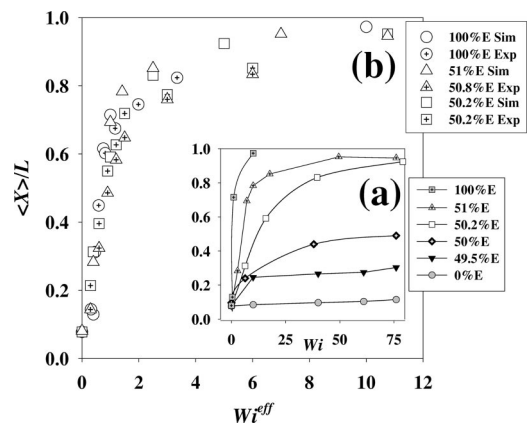


FIG. 3. (a) A plot of the steady average fractional extension of 150 bead Kramers' chains versus  $Wi$  at different %  $E$  values. (b) A plot of the steady average fractional extension of 150 bead Kramers' chains versus  $Wi^{eff}=Wi\sqrt{\alpha}$  at positive  $\alpha^+$  values compared to the experimental data by Babcock *et al.* [32].

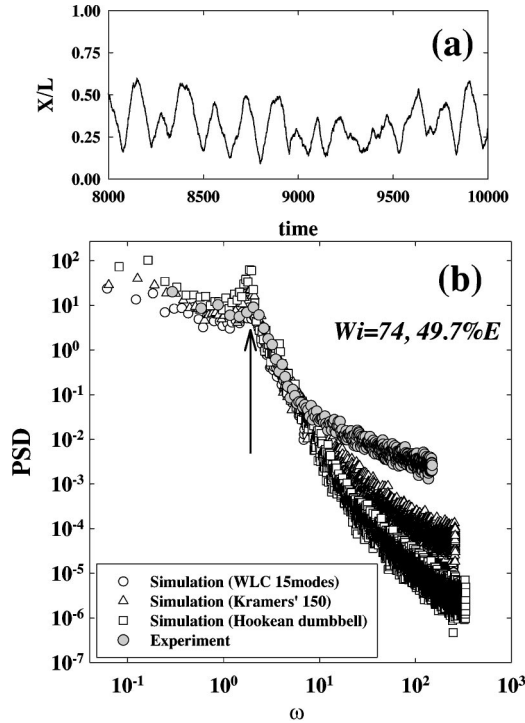


FIG. 4. (a) A plot of sample trajectory of a single Kramers' chain  $\alpha = -0.006$  at  $Wi = 74$  (b) The dimensionless power spectrum (PSD) of the extension fluctuations ( $\alpha = -0.006, 49.7\%E$ ) at  $Wi = 74$  for the Kramers' chain, the wormlike chain and the Hookean dumbbell model plotted against the experimental data by Babcock *et al.* [32]. The frequency is scaled with the longest relaxation time of the polymer in (b) as in Fig. 1(c).

straining or stretch along the principal axes and one can rescale the flow strength parameter  $Wi$ , namely,  $Wi^{eff} = Wi\sqrt{\alpha}$ . In Fig. 3(b) the steady average molecular extension at various  $Wi^{eff}$  is shown with experimental data by Babcock *et al.* [32] and all data overlap onto a universal curve [33]. The fact that the chains undergo a sharp coil-stretch transition based on  $Wi^{eff}$  suggests that the steady dynamics of molecules are driven by the effective straining for flows with positive  $\alpha$  values. To characterize the frequency dependence of the fluctuations of chain extension observed in the elliptic flow [Fig. 4(a),  $\alpha = -0.006(49.7\%E)$ ], we show the PSD for the Kramers' chain, the wormlike chain, the Hookean dumb-bell model and the experimental data by Babcock *et al.* [32] in  $\alpha = -0.006(49.7\%E)$  flow at  $Wi = 74$  in Fig. 4(b). A distinct peak is observed in the PSD at a dimensionless frequency ( $\Omega$ ) of 1.8.

To examine the origin of the peak we have derived the analytic PSD [ $S(\Omega)$ ] of molecular extension in the flow direction in linear mixed flows using the Hookean dumb-bell model, which was shown to capture the underlying physics of the tumbling dynamics of DNA molecules in shear flow [13]. The derivation is valid for  $\alpha \leq 0$  since the linear dumb-bell model is only a valid approximation for small deformation,

$$S(\Omega; R_1) = \langle R_g^2 \rangle \tau^H \frac{16}{3} \left[ \frac{1 + 4\Omega^2 + 4Wi^2}{[1 - 4\Omega^2 - 4Wi^2\alpha]^2 + 16\Omega^2} \right]. \quad (3)$$

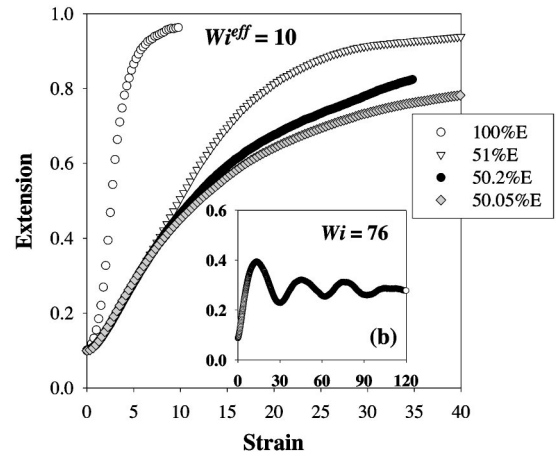


FIG. 5. The ensemble averaged molecular extension of the Kramers' chain in the start up of  $\alpha = 0.02(51\%E)$ ,  $\alpha = 0.004(50.2\%E)$ , and  $\alpha = 0.001(50.05\%E)$  flows versus strain ( $Pe \cdot t$ ) at  $Wi^{eff} = 10$ . (b) The ensemble averaged molecular extension of the Kramers' chain in the start up of elliptic flow [ $\alpha = -0.01(49.5\%E)$ ] versus strain at  $Wi = 76$ .

In Eq. (3),  $R_1$  denotes the end-to-end vector in the flow direction,  $R_g$  is the radius of gyration,  $\tau^H$  is the Hookean relaxation time, and  $\Omega$  denotes the frequency made dimensionless with  $\tau^H$ . We have confirmed from simulation data that the dumb-bell model correctly captures the longest mode of the Kramers' chain in elliptic flows. The critical dimensionless frequency at which the chain end-to-end vector in the flow direction oscillates can be calculated from Eq. (3),

$$\Omega^{crit}(R_1) = \frac{[-1 - 4Wi^2 + 4Wi\sqrt{(\alpha - 1)^2Wi^2 - \alpha}]^{1/2}}{4\pi}. \quad (4)$$

We note that Eq. (4) holds only for  $Wi \gg \sqrt{1/2[-(1/2\alpha) - 1]}$  if  $\alpha$  is small. For smaller values of  $Wi$  (i.e., near purely Brownian systems) no peak exists in the PSD. Using the parameter  $\alpha = -0.006$  and  $Wi = 74$  in Fig. 4), we obtain  $\Omega^{crit}(R_1) = 0.909$  which is half of the observed frequency. The factor of two difference is due to the fact that  $R_1$  can take both positive and negative values whereas molecular extension is always positive. We approach the affine limit, i.e.,  $\Omega^{crit}(R_1)$  asymptotes to the orbit frequency of a fluid particle,  $(Wi\sqrt{-\alpha})/2\pi$  as  $Wi \rightarrow \infty$ . We have extended the PSD derivation to the multimode Rouse and the Zimm model and found no quantitative difference in  $\Omega^{crit}$  [34]. Note that resonant oscillations in elliptic vortices have been given as the mechanism for elastic instabilities in previous work [35].

Finally, we have examined the transient dynamics of DNA molecules to test if the dynamics were similar in character in the startup of these flows. In Fig. (5) we show the evolution of molecular extension in flows with positive  $\alpha^+$  at  $Wi^{eff} = 10$  as we suddenly impose the flow. The molecular extension gradually approaches its steady value for all flows but slower growth is observed for smaller  $\alpha^+$ . In comparison to

this finding, an overshoot in molecular extension was observed in the start up of shear flow in both experiment and simulation [12,14]. This result again confirms the fact the dynamics of polymers in positive  $\alpha^+$  flows is primarily driven by the extra amount of straining. For the elliptic flows, we see an oscillation in chain extension which decays exponentially as shown in Fig. 5(b). The frequency of the oscillation is found to scale as  $Wi\sqrt{-\alpha}$  and its amplitude decays as the longest relaxation time ( $\tau$ ).

In this work, we have demonstrated that the dynamics of  $\lambda$ -DNA molecules can change dramatically depending on the ratio of vorticity and straining in linear mixed flows by examining individual polymer molecules in flows that deviate slightly from shear flow using Brownian dynamics simulation.

This work was supported by NSF under CPIMA Cooperative agreement Contract No. DMR-9808677.

- 
- [1] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
- [2] R.B. Bird, C.F. Curtiss, R.C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids : Vol. 2 Kinetic Theory* (Wiley, New York, 1987).
- [3] R.G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, Oxford, 1999).
- [4] E.C. Lee, M.J. Solomon, and S.J. Muller, *Macromolecules* **30**, 7313 (1997).
- [5] A. Link and J. Springer, *Macromolecules* **26**, 464 (1993).
- [6] B.H.A.A. vandenBrule, *J. Non-Newtonian Fluid Mech.* **47**, 357 (1993).
- [7] D. Petera and M. Muthukumar, *J. Chem. Phys.* **111**, 7614 (1999).
- [8] C.C. Hua, J.D. Schieber, and D.C. Venerus, *J. Rheol.* **43**, 701 (1999).
- [9] G.G. Fuller, L.G. Leal, *Rheol. Acta* **19**, 580 (1981); R.C.-Y. Ng, L.G. Leal, *J. Rheol.* **37**, 443 (1993); J. Remmelgas and L.G. Leal, *J. Non-Newtonian Fluid Mech.* **89**, 231 (2000).
- [10] J.J. Magda *et al.*, *Macromolecules* **26**, 1696 (1993).
- [11] T.T. Perkins, D.E. Smith, and S. Chu, *Science* **276**, 2016 (1997); D.E. Smith and S. Chu, *ibid.* **281**, 5381 (1998)
- [12] H.P. Babcock *et al.*, *Phys. Rev. Lett.* **85**, 2018 (2000).
- [13] J.S. Hur, E.S.G. Shaqfeh, and R.G. Larson, *J. Rheol.* **44**, 713 (2000)
- [14] J.S. Hur, E.S.G. Shaqfeh, H.P. Babcock, D.E. Smith, and S. Chu, *J. Rheol.* **45**, 421 (2001).
- [15] P.G. deGennes, *J. Chem. Phys.* **60**, 5030 (1974).
- [16] R.G. Larson *et al.*, *J. Rheol.* **43**, 267 (1999); L. Li and R.G. Larson, *Macromolecules* **33**, 1411 (2000); R. G. Larson, *J. Non-Newtonian Fluid Mech.* **94** (2000).
- [17] U.S. Agarwal, *J. Chem. Phys.* **113**, 3397 (2000); J. Remmelgas and L.G. Leal, *J. Non-Newtonian Fluid Mech.* **89**, 231 (2000); A. Dua and B.J. Cherayil, *J. Chem. Phys.* **112**, 8707 (2000); A. Dua and B.J. Cherayil, *ibid.* **113**, 10776 (2000); C. Pierleoni and J.P. Ryckaert, *ibid.* **113**, 5545 (2000); X. Wang and A.P. Chatterjee, *Macromolecules* **34**, 1118 (2001).
- [18] J.F. Marko and E.D. Siggia, *Macromolecules* **28**, 8759 (1995).
- [19] P.E. Rouse, *J. Chem. Phys.* **21**, 1272 (1953).
- [20] B.H. Zimm, *J. Chem. Phys.* **24**, 269 (1956).
- [21] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1985).
- [22] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw Hill, New York, 1965).
- [23]  $Pe$  is defined as  $(\dot{\gamma}l^2)/D$  where  $l$  is the Kuhn length,  $\dot{\gamma}$  is a dimensionless strain/shear rate,  $D$  is the diffusivity and thus  $Pe$  is a ratio of diffusion time scale and characteristic convective time scale.
- [24]  $\tau$  was determined by fitting the remaining 30% of the average molecular extension  $[x(t)]$  of 400–2000 initially stretched chains to a single exponential function ( $\langle x(t)^2 \rangle = A \cdot \exp^{(-t/\tau)} + B$ ). The longest relaxation time calculated in this manner is in quantitative agreement with those calculated from either normal stress or birefringence decay.
- [25] For the Kramers' chain simulation, we use 150 bead chains and for the worm-like and Rouse chain simulation we use 15 spring chains. The chains were equilibrated for 20 times each longest relaxation time ( $\tau^{model}$ ) before they were put in flow. The steady simulations were run upto  $10^9 - 10^{10}$  time steps using a single chain and the transient runs were averaged over 500-800 chains at each time step.
- [26] T.W. Liu, *J. Chem. Phys.* **90**, 5826 (1989).
- [27] P.S. Doyle, E.S.G. Shaqfeh, and A.P. Gast, *J. Fluid Mech.* **334**, 251 (1997).
- [28] 50.05%  $E$  stands for 50.05% straining and 49.95% vorticity. For shear flow, there's equal contribution from straining and vorticity. The angle between the principal axes can be defined as  $q = 2 \tan^{-1}(\sqrt{\alpha})$  for flows that have larger contribution from straining than vorticity and is only  $3.6^\circ$  and  $7.2^\circ$  for the 50.05%  $E$ , 50.2%  $E$  flows respectively.
- [29] G.H. Fredrickson and E. Helfand, *J. Chem. Phys.* **87**, 697 (1987).
- [30] F.S. Bates and G.H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525 (1990).
- [31] D.E. Smith, H.P. Babcock, and S. Chu, *Science* **283**, 1724 (1999).
- [32] H.P. Babcock *et al.* (unpublished).
- [33] A similar overlap of birefringence data of a polymer solution at various  $\alpha^+$  was reported by Fuller *et al.* [9]. We have also calculated the steady birefringence of  $\lambda$ -DNA molecules using Kramers' chains and have found a universal curve for various  $\alpha^+$  over a range of  $Wi^{eff}$  suggesting that birefringence reflects the sharp coil-stretch transition of the molecule.
- [34] J.S. Hur, Ph.D. thesis, Stanford University, 2001.
- [35] H. Haj-hariri and G.M. Homsy, *J. Fluid Mech.* **353**, 357 (1997).