# Characteristic Periodic Motion of Polymers in Shear Flow

Charles M. Schroeder,[1,*,†] Rodrigo E. Teixeira,[1,*] Eric S. G. Shaqfeh,[2,‡] and Steven Chu[3,§]
[1]*Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA*
[2]*Departments of Chemical and Mechanical Engineering, Stanford University, Stanford, California 94305, USA*
[3]*Departments of Physics and Applied Physics, Stanford University, Stanford, California 94305, USA*

(Received 18 December 2004; published 1 July 2005)

The motion of both free and tethered polymer molecules as well as rigid Brownian rods in unbound shear flow is found to be characterized by a clear periodicity or tumbling frequency. Periodicity is shown using a combination of single molecule DNA experiments and computer simulations. In all cases, we develop scaling laws for this behavior and demonstrate that the frequency of characteristic periodic motion scales sublinearly with flow rate.

DOI: 10.1103/PhysRevLett.95.018301    PACS numbers: 83.80.−k, 82.35.−x

Polymer molecules may stretch and orient when subjected to hydrodynamic forces in fluid flow. The conformational response of a polymer molecule is highly dependent on flow type [1,2]. Simple shear flow consists of equal amounts of extension and rotation [3], yielding a planar flow in which the fluid velocity in the flow direction ($v_x$) is a linear function of distance ($y$) from the flow axis along the shear gradient axis, such that $v_x = \dot{\gamma} y$, where $\dot{\gamma}$ is the (constant) shear rate. The unique combination of equal degrees of fluid line stretching/compression and fluid rotation gives rise to intriguing polymer dynamics.

Traditional experimental techniques such as light scattering [4,5] have been used to infer the orientation of polymers in shear flow and the associated distortions of polymer coils from equilibrium. Fluorescence microscopy allows for direct observation of single DNA molecules and has revealed that individual polymers never reach a steady state extension in shear flow [6]. Polymers continually undergo end-over-end tumbling motion as reflected in large fluctuations in chain extension [6,7].

Recently, a novel shear flow device has been used for single molecule experiments of DNA in the flow-gradient plane of simple shear flow [7,8]. This device allows for direct observation of the tumbling dynamics of polymers in flow [7,9]. Here, we show for the first time unambiguous evidence of periodicity in tumbling supported by polymer microstructural experimental data obtained using the flow-gradient device, complemented by results from Brownian dynamics (BD) simulations of DNA. A sequence of images illustrating the time progression of polymer motion for 80 $\mu$m DNA [10] in the flow-gradient plane of shear flow is shown in Fig. 1(a) at $\mathrm{Wi} = 109$, where the Weissenberg number ($\mathrm{Wi} = \dot{\gamma}\tau$) is a dimensionless shear rate defined as the ratio of the longest polymer relaxation time $\tau$ to the characteristic fluid time scale $\dot{\gamma}^{-1}$. Viewing the motion of fluorescent DNA in the flow-gradient plane of shear flow allows for measurement of polymer extension $x$, gradient-direction polymer thickness $\delta_2$ (a microscopic quantity directly related to bulk shear viscosity [7,9,12]), and polymer orientation angle $\theta$ in shear flow. In this context, $\theta$ is measured such that polymer alignment in the flow direction is defined as $\theta = 0$ [13].

Sample time traces of simultaneous experimental measurements of polymer extension, $\delta_2$, and $\theta$ are shown in Fig. 1(b). Transient fractional polymer extension $x/L$, where $L$ is the polymer contour length, exhibits large fluctuations. At $\mathrm{Wi} = 12$, $x/L$ ranges between small values ($\leq 0.1L$) and $\approx \frac{1}{2}L$. Although a single polymer's extension may be wildly fluctuating, the same polymer chain may simultaneously be aligned near the flow axis such that $0 < \theta < \epsilon$, where $\epsilon$ is small. A thermal fluctuation may cause $\theta$ to become negative, often signifying the onset of a polymer tumbling event.

We propose the following general descriptive cycle for the motion of polymers in strong shear flow such that $\mathrm{Wi} > 1$ [Fig. 1(c)] based on flow-gradient plane observations of the dynamical behavior of many DNA molecules. The cycle begins in the upper left portion of Fig. 1(c) where polymer orientation angle is positive ($\theta_1 \gg 0$). At this stage, $\delta_2$ is generally larger than equilibrium values which implies a substantial velocity gradient across the molecules, leading to polymer stretch. After the stretch phase, the orientation angle is small but positive ($\theta_2 > 0$). A polymer may now align in the flow direction such that $\theta_3 \approx 0$, leading to small differences in fluid velocity across the molecule and hence small hydrodynamic forces exerted on the chain. A Brownian fluctuation causes the polymer orientation angle to become negative ($\theta_4 < 0$) and leads to polymer collapse and highly negative values of $\theta$ ($\theta_5 \ll 0$). Finally, the polymer tumbles, $\theta$ changes sign from negative to positive, and the cycle begins anew.

A polymer may choose other dynamical paths than those described above. For example, in the second stage of the cycle when the molecule is stretched [Fig. 1(c)], a polymer may thermally fluctuate to a slightly larger angle, resulting in a restretching event. Conversely, a polymer may slightly recoil to smaller extensions when the orientation angle is small ($\theta_3 \approx 0$). Both of these types of polymer motion were observed in experiment [7]. As shown in the trajectories of $x/L$ and $\theta$ [Fig. 1(b)], polymer extension may

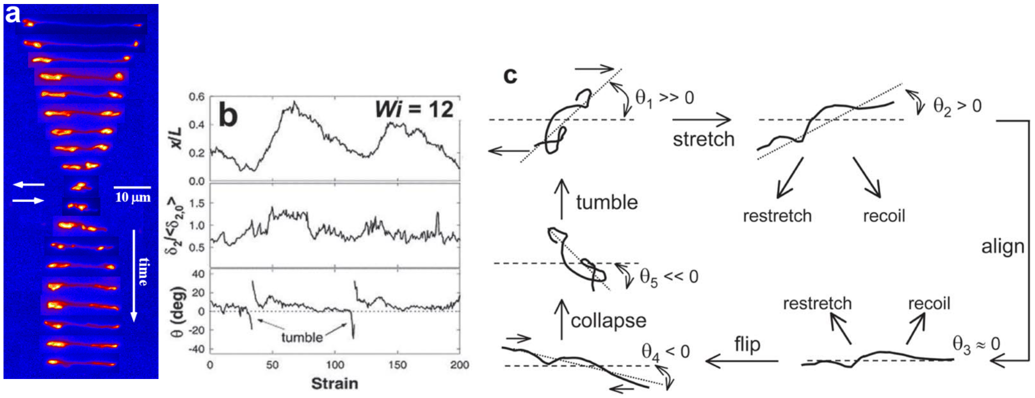

FIG. 1 (color online). Dynamics of DNA in steady, unbound shear flow. (a) Time sequence of images of fluorescent DNA ($L = 80\ \mu$m) at Wi = 109 in shear flow clearly illustrating end-over-end tumbling motion. Time between images is ≈ 10 s. (b) Trajectories of fractional polymer extension $x/L$, gradient-direction polymer thickness $\delta_2$, and polymer orientation angle $\theta$ for lambda DNA at Wi = 12. Accumulated fluid strain ($\gamma$) is defined as observation time $t_{\mathrm{obs}}$ nondimensionalized with shear rate ($\gamma = t_{\mathrm{obs}}\dot{\gamma}$). (c) Descriptive cycle of periodic polymer motion in shear flow.

exhibit large fluctuations between tumbling events, during which time $\theta$ is nearly constant at positive values. Therefore, polymer extension may undergo a variety of stretching and coiling events that may have a broad distribution of time scales. In general, end-over-end polymer tumbling events are not correlated with specific behavior in polymer extension, $x$. However, polymer tumbling motion is directly demonstrated in time traces of $\theta$.

Evidence of periodic polymer motion, if present, should appear in the power spectral density (PSD) [14,15] of time-fluctuating polymer conformational properties. We examined PSDs of polymer extension and orientation angle $\theta$ using results from experiments and computer simulations of polymers using BD techniques [9]. As noted by previous research [1,6], PSDs of polymer extension in steady shear flow exhibit no peaks, suggesting that no deterministic cycle is associated with polymer motion as characterized by molecular extension in the flow direction. However, the lack of apparent periodicity in polymer extension does not preclude a cyclical mechanism of polymer motion based on the interplay between advection of the polymer in the flow direction and diffusion of the polymer chain in the gradient direction.

Polymer rotation in shear flow has been previously studied. Aust *et al.* [16] observed that autocorrelations of $R_g^2$, the mean squared radius of gyration, appeared to be weakly periodic in time for Wi ≈ 1 in polymer simulations. Liu and co-workers [17], using BD simulations of bead-rod polymer chains, noted that the position of individual beads along the flow axis relative to the chain center of mass appeared to oscillate in time.

PSDs of polymer orientation angle $\theta$ are plotted in Fig. 2(a) for single molecule DNA experiments and for results from BD simulations of free draining (FD) polymers and molecules with intramolecular hydrodynamic interactions (HI) and excluded volume (EV) interactions [9] at Wi = 49. PSD results from experiment and simulation show a peak at low frequencies. Power at low frequencies is associated with polymer motion driven by convection occurring on time scales longer than diffusive motion associated with thermal fluctuations.

We investigated the scaling of PSD peak frequencies ($\nu^{\mathrm{peak}}$) as a function of Wi [Fig. 2(b)]. Experiments on 80 $\mu$m DNA showed $\nu^{\mathrm{peak}}\tau \sim \mathrm{Wi}^{0.66}$ for $29 \leq \mathrm{Wi} \leq 584$. As determined from BD simulations of DNA, $\nu^{\mathrm{peak}}\tau \sim \mathrm{Wi}^{0.62}$ for $2 \leq \mathrm{Wi} \leq 10^4$. Frequencies of polymer tumbling events ($\nu^{\mathrm{tumb}}$) observed from single molecule DNA experiments are also shown in Fig. 2(b). Polymer tumbling events were classified by a visual observation of clear, end-over-end polymer motion with a corresponding negative to positive transition in $\theta$. The frequency of angle events in

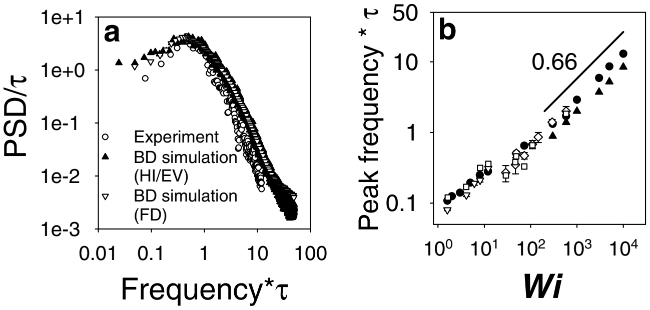

FIG. 2. Periodic dynamical behavior of polymers in steady shear flow. (a) Power spectral density (PSD) of polymer orientation angle for DNA in steady shear flow for experiment and simulation at Wi = 49. PSDs and frequencies are made dimensionless with polymer relaxation times, $\tau$. (b) Scaling of peak frequencies ($\nu^{\mathrm{peak}}$) from PSDs of $\theta$ from experiment (□) and simulation (●). Tumbling frequencies ($\nu^{\mathrm{tumb}}$) from experimental observations of 22 $\mu$m (▽) and 84 $\mu$m (◇) DNA motion agree well with PSD peaks. Also shown is frequency of negative to positive $\theta$ transitions reaching $\theta^{\mathrm{average}}$ as a function of Wi (▲).

which $\theta$ transitions from a negative to a positive value, reaching (at least) the average value of $\theta$ at each Wi, is also shown in Fig. 2(b). Good agreement between dimensionless frequencies in tumbling events from both experiment and simulation is shown, demonstrating that peaks in the PSDs of $\theta$ occur at frequencies corresponding to inherent frequencies in the tumbling cycle of DNA in shear flow.

To understand the origin of the observed scaling frequency $\nu^{\text{peak}}\tau \sim \text{Wi}^{0.62}$ for polymers in shear flow, characteristic time scales for polymer motion [7] are constructed within the context of dynamical polymer behavior illustrated in Fig. 1(c). We ascribe time scales for polymer motion in the stretch, align, flip, and collapse phases of polymer dynamics such that:

$$\nu^{\text{tumb}}\tau \propto \frac{\tau}{t^{\text{stretch}} + t^{\text{align}} + t^{\text{flip}} + t^{\text{collapse}}}. \tag{1}$$

Polymer stretching, alignment, and collapse are advection-driven processes, and it has been shown in previous work [7] that $t^{\text{stretch}}$, $t^{\text{align}}$, and $t^{\text{collapse}}$ scale with flow strength as $\frac{\langle x\rangle}{Wi\langle\delta_2\rangle}$. From BD simulations, $\frac{\langle x\rangle}{\langle\delta_2\rangle} \sim \text{Wi}^{0.34}$ giving $t^{\text{stretch}} \propto t^{\text{align}} \propto t^{\text{collapse}} \propto \text{Wi}^{-0.66}$. The flipping stage is a diffusive process such that $t^{\text{flip}} \propto \frac{\langle\delta_2\rangle^2}{D(\delta_2)}$ where $D(\delta_2)$ is the gradient-direction diffusivity of a portion of the polymer chain. Doyle *et al.* [18] found $D(\delta_2) \sim \delta_2^{-2/3}$ from BD simulations of polymers, yielding $t^{\text{flip}} \propto \langle\delta_2\rangle^{8/3} \propto \text{Wi}^{-0.67}$. Although this analysis ignores polymer restretching and recoiling events, good agreement for the scaling of the tumbling frequency with flow strength is demonstrated [19].

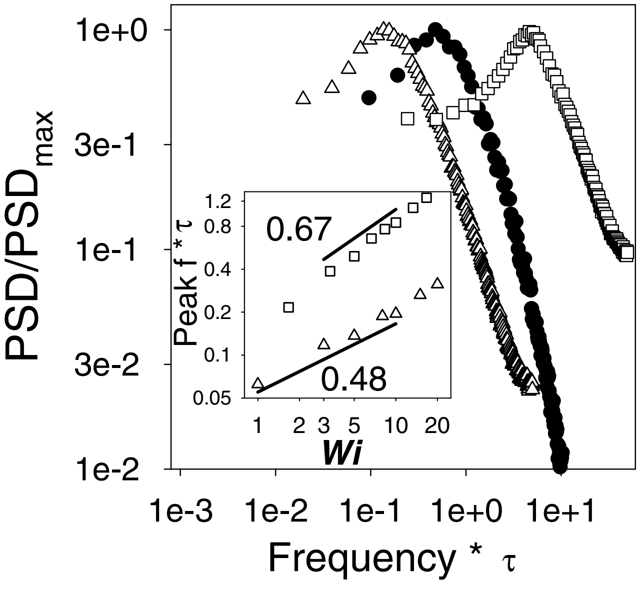

FIG. 3. Power spectral densities of orientation angle $\theta$ for free DNA in unbounded shear (●), tethered DNA in shear flow (△), and infinite aspect ratio Brownian rods (□) in steady shear flow. (Inset) Scaling of peak frequencies from PSDs of $\theta$ for tethered polymers and Brownian rods in shear flow.

We also investigated the dynamical behavior of two additional Brownian systems: tethered polymers in simple shear flow and Brownian rods in unbounded shear flow. The PSDs of orientation angle $\theta$ for these systems and for free DNA in shear flow are plotted in Fig. 3 based on results from BD simulations. Clearly, the PSD of $\theta$ for each Brownian system shows a prominent peak in the low frequency range. The behavior of tethered polymers in shear flow has been investigated in previous studies [20,21]. In these works, PSDs of polymer extension exhibit no peaks, suggesting that cycling times (as reflected in polymer extension) are broadly distributed.

The inset of Fig. 3 shows the scaling of the peak frequency in the PSD of orientation angle $\theta$ for tethered DNA and rigid Brownian rods of infinite aspect ratio in shear flow. In the case of tethered polymers, peaks in the PSD of $\theta$ appear for the approximate range $1 \leq \text{Wi} \leq 10$. The dynamical behavior of tethered polymers in shear flow is qualitatively different than for free polymers in unbounded shear: simply put, a tether point at an interface disallows end-over-end tumbling events. Rather than tumbling, "cyclic dynamics" occurs when the polymer stretches, rotates toward the interface, retracts, and stretches again [20,21]. The time scale associated with the thickening in $\delta_2$ is a diffusive process such that $t^{\text{thick}} \propto \frac{\langle\delta_2\rangle^2}{D(\delta_2)}$. From BD simulations, we found that $\langle\delta_2\rangle \sim \text{Wi}^{-0.16}$, $\langle x\rangle \sim \text{Wi}^{0.64}$, and $\langle x'\rangle \sim \text{Wi}^{0.40}$ over the range $1 \leq \text{Wi} \leq 10$, where a prime denotes fluctuations of a quantity about its mean value. With these quantities, $t^{\text{thick}} \sim \langle\delta_2\rangle^{8/3} \sim \text{Wi}^{-0.43}$. During the stretch step, the distance a chain may extend equals (on average) the size of chain extension fluctuations. Therefore, the time scale for stretch ($t^{\text{stretch}}$) is $t^{\text{stretch}} \propto \frac{\langle x'\rangle}{\text{Wi}\langle\delta_2\rangle}$, giving $t^{\text{stretch}} \sim \text{Wi}^{-0.44}$. For tethered DNA, scaling of peak frequencies from PSDs of $\theta$ follows the power law $(\nu^{\text{peak}}\tau) \sim \text{Wi}^{0.48}$, compared with $(\nu^{\text{cycle}}\tau) \sim \text{Wi}^{0.44}$ from scaling arguments.

Rigid, non-Brownian rods with finite aspect ratios undergo regular tumbling motion in shear flow described by Jeffery's orbits with a well-defined period $T^{\text{rod}} = \frac{2\pi}{\dot{\gamma}} \times (A + \frac{1}{A})$, where $A$ is the rod aspect ratio [22,23]. The motion of Brownian rods in shear flow is not deterministic and a nonlinear scaling of the frequency of rotational motion with flow rate is observed. Scaling analysis for rigid Brownian rods reveals that the tumbling frequency follows the law $\nu^{\text{rod}} \propto \text{Wi}^{2/3}$, which agrees well with simulation results (Fig. 3, inset).

In this work, we provide experimental and theoretical evidence for the periodic motion of polymer orientation angle $\theta$ for three distinct Brownian systems in simple shear flow. In all cases, the frequency associated with characteristic periodic motion scales sublinearly with flow rate due to the balance between chain advection in the flow direction and polymer diffusion in the gradient direction, which ultimately determines the size of $\delta_2$. Because of the interplay between polymer advection and diffusion, the relative velocity across the molecule does not scale linearly with flow rate for the dominant portion of the cycle.

The observations in this Letter were made possible by observations of single molecules. Whereas ensemble-averaged measurements such as light or neutron scattering would average out the asynchronous tumbling of a large number of particles, observations of single molecules allow for direct characterization of the microstructural conformational flow behavior of polymers.

We thank D. Saintillan for providing Brownian rod simulations and M. Gallo and E. Chan (US Genomics) for generously providing dsDNA samples. This work was supported, in part, by grants from the Materials Research Science and Engineering Center Program of the National Science Foundation (NSF), the Air Force Office of Scientific Research, and the NSF.

---

*These authors contributed equally to this work.

†Present address: Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138.

‡Electronic address: eric@chemeng.stanford.edu

§Present address: Lawrence Berkeley National Laboratory, Berkeley, CA 94720.

[1] H. P. Babcock, R. T. Teixeira, J. S. Hur, E. S. G. Shaqfeh, and S. Chu, Macromolecules **36**, 4544 (2003).

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

[3] G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, Cambridge, England, 2000).

[4] A. Link and J. Springer, Macromolecules **26**, 464 (1993).

[5] E. C. Lee, M. J. Solomon, and S. J. Muller, Macromolecules **30**, 7313 (1997).

[6] D. E. Smith, H. P. Babcock, and S. Chu, Science **283**, 1724 (1999).

[7] R. E. Teixeira, H. P. Babcock, E. S. G. Shaqfeh, and S. Chu, Macromolecules **38**, 581 (2005).

[8] Shear flow is generated between two parallel, optically transparent quartz microscope slides translating in opposite directions [7]. In short, DNA molecules are imaged in the gap between slides, and image distortions are minimized by matching the index of refraction ($n$) of the shearing walls to the solution ($n = 1.458$) by adjusting the sucrose concentration to 67.1%(w/w), yielding a solution viscosity of 300$c$P.

[9] C. M. Schroeder, R. E. Teixeira, E. S. G. Shaqfeh, and S. Chu, Macromolecules **38**, 1967 (2005).

[10] An inverted, home-built microscope equipped for epifluorescence and a Micromax 512BFT CCD camera (Roper Scientific) were used to image both $\lambda$ DNA (48.5 kbp, Gibco BRL, 22 $\mu$m stained contour length) and $\approx 80$ $\mu$m DNA (185 kbp, US Genomics). DNA was stained with YOYO-1 fluorescent dye (Molecular Probes) at a ratio of 1 dye per 4 base pairs. Concentrations of DNA in the observation buffers were extremely dilute ($c \approx 10^{-5}$ $c^*$, where $c^*$ is the polymer overlap concentration) to prevent intermolecular interactions. Solution buffers contained 10 mM tris/tris-HCl ($p$H 8.0), 10 mM NaCl, and 1 mM EDTA. Photobleaching of the dye was substantially slowed by addition of 0.3%(v/v) glucose, glucose oxidase (0.05 $\mu$g/$\mu$L), catalase (0.01 $\mu$g/$\mu$L), and 1%(v/v) $\beta$-mercaptoethanol [11]. Average polymer relaxation times are calculated as previously described [11] and are 28 s and 251 s for 22 and 80 $\mu$m DNA, respectively. Experiments were conducted at 17 °C.

[11] C. M. Schroeder, E. S. G. Shaqfeh, and S. Chu, Macromolecules **37**, 9242 (2004).

[12] R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (Wiley, New York, 1987), 2nd ed., Vol. 2.

[13] The radius of gyration tensor ($G_{ij}$) is experimentally measured for polymers in flow and is defined as [7,9] $G_{ij} = \frac{\Sigma_{p,q} I(p,q) R_i^{p,q} R_j^{p,q}}{\Sigma_{p,q} I(p,q)}$, where subscripts denote tensorial indices, $R_i^{p,q}$ is a two-dimensional vector from the polymer center of mass to the $p$th column and $q$th row image pixel, and $I(p, q)$ gives the polymer image intensity at the $p$th column and $q$th row pixel above the average background image intensity. The polymer orientation angle $\theta$ is then defined as $\tan(2\theta) = \frac{2G_{12}}{G_{11} - G_{22}}$, where orientation angles are taken to be positive when measured from the flow axis toward the gradient axis in shear flow. The gradient-direction polymer thickness is defined as $\delta_2 = \sqrt{G_{22}}$.

[14] W. H. Press *et al.*, *Numerical Recipes in Fortran 77* (Cambridge University Press, Cambridge, England, 1997).

[15] The power spectral density (PSD) [6,9,14] is defined as the Fourier transform of the autocorrelation of a real-valued, fluctuating quantity $x(t)$ given by $C_{x,x}(T) = \langle x(t)x(t+T)\rangle$, where brackets denote a time-averaged quantity, $t$ is time, and $T$ is an offset time. The PSD of a stationary stochastic process is $P(\nu) = \int_{-\infty}^{\infty} C_{x,x}(T) e^{-2i\pi\nu T} dT$, where $P(\nu)$ is the power of a signal at frequency $\nu$ and $i = \sqrt{-1}$.

[16] C. Aust, S. Hess, and M. Kröger, Macromolecules **35**, 8621 (2002).

[17] S. Liu, B. Ashok, and M. Muthukumar, Polymer **45**, 1383 (2004).

[18] P. S. Doyle, E. S. G. Shaqfeh, and A. P. Gast, J. Fluid Mech. **334**, 251 (1997).

[19] Polymer tumbling dynamics in shear flow have also been studied using cross correlations of polymer extension ($x$) and gradient thickness ($\delta_2$) [7,9,24,25]. We observe that PSDs calculated from cross correlations of $x$ and $\delta_2$ also show peaks at specific frequencies which scale sublinearly with flow strength with the same approximate power law as peaks from PSDs of $\theta$ (not shown).

[20] P. S. Doyle, B. Ladoux, and J.-L. Viovy, Phys. Rev. Lett. **84**, 4769 (2000).

[21] B. Ladoux and P. S. Doyle, Europhys. Lett. **52**, 511 (2000).

[22] G. B. Jeffery, Proc. R. Soc. A **102**, 161 (1922).

[23] F. P. Bretherton, J. Fluid Mech. **14**, 284 (1962).

[24] M. Chopra and R. G. Larson, J. Rheol. (N.Y.) **46**, 831 (2002).

[25] N. J. Woo, E. S. G. Shaqfeh, and B. Khomami, J. Rheol. (N.Y.) **48**, 299 (2004).