

Dynamics of a Tethered Polymer in Shear Flow

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The dynamics of a single polymer tethered to a solid surface in a shear flow was observed using fluorescently labeled DNA chains. Dramatic shear enhanced temporal fluctuations in the chain extension were observed. The rate of these fluctuations initially decreased for increasing shear rate $\dot{\gamma}$ and increased above a critical $\dot{\gamma}$. Simulations revealed that these anomalous dynamics arise from a continual recirculating motion of the chain or *cyclic dynamics*. These dynamics arise from a coupling of the chain velocity in the flow direction to thermally driven fluctuations of the chain in the shear gradient direction.

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Observations of individual DNA chains by fluorescence videomicroscopy have recently provided unique and valuable insights into polymer dynamics. For free chains in elongational flow, this technique revealed complex stretching dynamics which are strongly dependent upon the initial conformation [1,2]. The behavior of free molecules in shear flow was also studied by this technique, experimentally demonstrating the existence of a previously anticipated tumbling motion [3–5]. Observation of individual DNA chains in the course of electrophoresis has played a key role in our understanding of this technique of central importance for biology [6]. The observation of individual DNA molecules has provided polymer physics with a new paradigm, demonstrating that individual chains in an ensemble can behave very differently from each other and from the simplified mental representation of an average random coil developed and extensively used in the previous decades. Tethered polymers are of central importance in a variety of applications such as colloidal stabilization, biocompatibility, lubrication, chromatography, and capillary electrophoresis [7]. In most cases these applications involve shearing of the tethered polymers. Despite this ubiquitous use, the nonequilibrium dynamics of sheared tethered polymers is poorly understood. Most theories [8] so far have relied on a string of blobs representation, which inherently assumes a quasiequilibrium force balance on the chain. Simulations and numerical calculations [9] have focused mostly on average chain properties, neglecting dynamics. These previous studies have engrained a rather static average chain picture for a tethered polymer in shear flow.

Here we apply for the first time videomicroscopic observation of individual DNA chains to the investigation of tethered polymers subject to a shear flow. We show that shearing a tethered chain gives rise to large temporal fluctuations in the chain extension. Simulations reveal that these fluctuations are due to a continual recirculating motion of the chain. These anomalous *cyclic dynamics* shed new light on this difficult and practically important problem.

DNA molecules with a contour length of $18\ \mu\text{m}$ [10] were attached by one end to the bottom of a rectangular microchannel, submitted to shear flow and visualized in real

time using standard fluorescence microscopy techniques (Fig. 1). Images were transferred to a computer and the length of the molecules was determined [11]. The dimensionless flow strength is characterized by the Weissenberg number, $Wi = \dot{\gamma}\tau$, where τ is the longest relaxation time of the polymer and $\dot{\gamma}$ is the shear rate. We determine τ by fitting to a single exponential the decay of the autocorrelation function $\langle x(t)x(t+T) \rangle$ at equilibrium ($Wi = 0$) (x is the chain extension, t is time, and T is the delay time) [12], yielding $\tau = 0.40 \pm 0.04\ \text{s}$ [13].

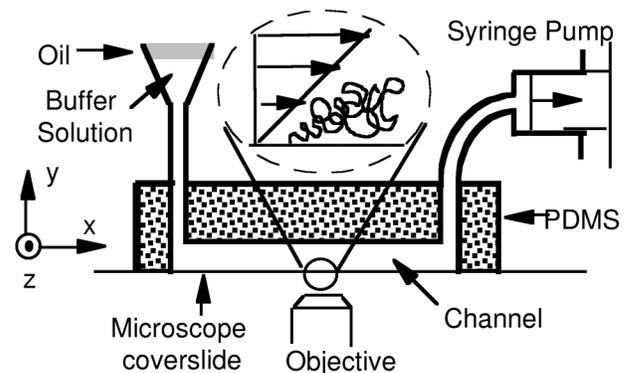


FIG. 1. Schematic of the experimental apparatus. A polydimethylsiloxane flow cell with channels of $500\ \mu\text{m}$ in width, $135\ \mu\text{m}$ in height, and $4\ \text{cm}$ in length was prepared on a coverslip coated with streptavidin [R. Merkel *et al.*, *Nature (London)* **397**, 50 (1999)] and placed in a Zeiss Axiovert 135 TV inverted microscope equipped with a $\times 100$ 1.4 numerical aperture oil immersion objective. A solution of λ -Phage DNA molecules (Pharmacia Biotech Products), biotinylated at one end and fluorescently labeled with YOYO-1 (Molecular Probes), was incubated in the cell until the desired surface density was achieved. A Poiseuille flow profile was created using a microsyringe pump (kd Scientific). The height of the channel ensured a nearly uniform shear flow within the distance of one radius of gyration from the tethering surface. Stained DNA were excited with the 488 line of an argon-ion laser (Coherent) and visualized using a cooled intensified CCD camera (LHESA, Les Ulis, F). The experiments were performed at $24 \pm 3\ ^\circ\text{C}$ in 0.5X TBE buffer (45 mM boric acid, 45 mM Tris[hydroxymethyl]aminomethane, 1.25 mM Ethylenediaminetetraacetic acid). 4% β -mercaptoethanol, $50\ \mu\text{g/ml}$ glucose oxidase, $10\ \mu\text{g/ml}$ catalase, and $2\ \text{mg/ml}$ glucose were added to the solution to minimize photobleaching.

A time series of the configurations of a single molecule is shown in Fig. 2 at four different flow strengths. At small and large Wi conformation fluctuations are modest, but at intermediate Wi the molecule undergoes large shape fluctuations. The stability of the flow was verified at all Wi using $1\ \mu\text{m}$ latex beads (Molecular Probes). Furthermore, we have observed the dynamics of several molecules in the same field of view and found no correlation in their conformations. Thus these shear induced fluctuations are the *intrinsic* response of a tethered polymer to a shear flow.

A quantitative measure of the deformation and shape fluctuations of the chains was performed. The mean extension increases rapidly as a function of Wi for $Wi > 1$ until $Wi \approx 20$ (Fig. 3a). At this point the chain is approximately 60% extended, and it continues to grow very slowly (reaching only 75% its contour length at $Wi = 80$ and 83% at $Wi = 380$). This behavior is in qualitative agreement with the stem-and-flower model [8], though experiments show a slower approach to full extension than predicted in the theory. The extension of a tethered polymer in shear lies between the shear and extensional deformation for free (untethered) polymers (Fig. 3a). Upon shearing the standard deviation of the chain extension about the mean value (Fig. 3b) progressively increases up to a maximum value more than twice the value found at equilibrium when at $Wi = 5.1$. When increasing the flow strength beyond $Wi = 5.1$, these fluctuations decrease, but remain larger than equilibrium values. The rate of the fluctuations in chain extension was analyzed by calculating the autocorrelation function $\langle x(t)x(t+T) \rangle$. We found two distinct regimes. Up to $Wi = 0.88$ the correlations decay *slower* than at equilibrium (Fig. 4a). Increasing the flow strength beyond $Wi = 0.88$ results in a reversal of the trend, with the rate of the fluctuations *increasing* (Fig. 4b). This reversal occurs at $Wi = O(1)$. At a scaling level, this corresponds to the regime where the chain begins to be significantly stretched.

To gain further insight into these nontrivial dynamics we performed Brownian dynamics simulations of a

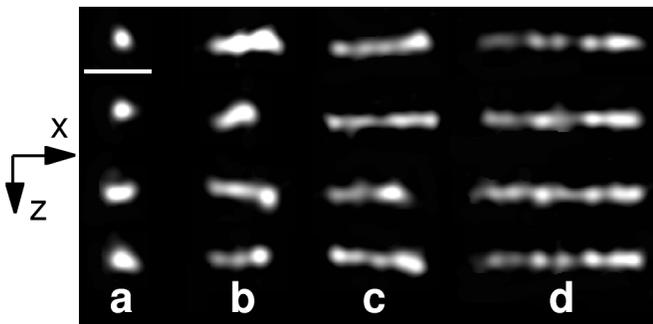


FIG. 2. Time series (top to bottom) of the configurations of single DNA molecules at varying flow strengths. The horizontal scale bar in (a) is $5\ \mu\text{m}$. In each series the images are separated by an interval of τ : (a) equilibrium ($Wi = 0$); (b) $Wi = 5.1$; (c) $Wi = 14.5$; (d) $Wi = 110$.

bead-spring chain model with wormlike chain elasticity [14]. The lines in Figs. 3 and 4 display the results of these simulations. Strong qualitative and quantitative agreement between the simulations and experiments is found for all flow geometries. The simulations provide extra information, with regard to experiments, by allowing us to follow the chain in the x - y plane. The dynamics of the simulated polymers display a continuous recirculating motion or *cyclic dynamics*. An example of temporal fluctuations and an associated series of sample chain configurations are presented in Fig. 5. Typically, a chain starting in a configuration near the interface (c1) will experience a substantial fluctuation perpendicular to the surface driving it into a stronger flow (c2). The chain then stretches quickly to an extended state (c3) which will slowly rotate towards the interface. This drives the free end of the chain into a region of slower flow (c4) leading to a retraction (c5), until the chain experiences another substantial fluctuation perpendicular that reinitializes the cycle. The power spectrum of the simulated chain extensions shows no distinct peak which suggests a broad distribution of cycling times.

Extending a tethered chain in an homogeneous plug flow (where there is no velocity gradient) leads to more simple dynamics. Stretching the molecule stiffens the restoring

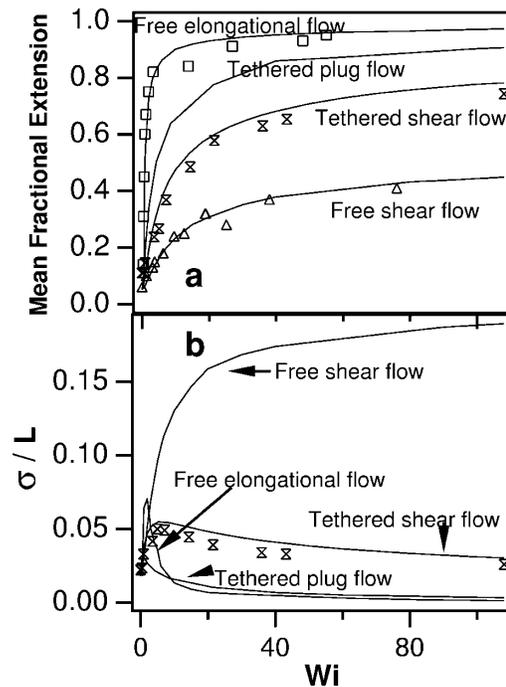


FIG. 3. (a) Mean fractional extension (visual length divided by contour length) versus Wi . The lines are from simulations and the symbols are experimental data. Experimental averages at each Wi were taken over at least five molecules with time averages of 40 s for each molecule. The data for free elongational and free shear flow are from Smith *et al.* [3]. (b) Standard deviation σ of the temporal chain extension divided by chain contour length L versus Wi . The lines are the results of simulations and the symbols are experimental data.

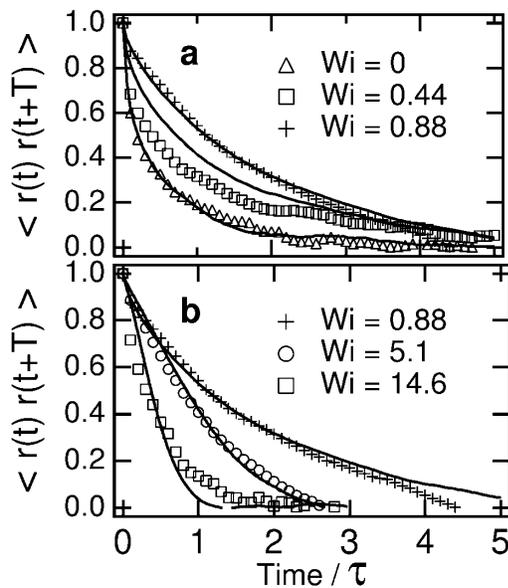


FIG. 4. Time correlation functions of the chain extension. The lines are the results from simulations and the symbols are experimental data. (a) Time correlation functions at $Wi \leq 0.88$. (b) Time correlation functions at $Wi \geq 0.88$.

force and leads to a monotonic decrease in the magnitude of the fluctuations and to an increase in their rate ([15] and Fig. 3). The dynamics in shear flow is more complicated due to the presence of a velocity gradient.

Consider now a simplified model involving a Hookean (linear) spring attached at one end to an impenetrable surface and at the other end to a single Brownian bead. The equations of motion in the y and z directions are simply that of a bead in a harmonic well and are not affected by the flow. The velocity of the bead in the x direction has contributions from thermal fluctuations, the spring, and the flow. However, the shear flow is a function of distance from the surface (y) and hence the equation of motion in the x direction is coupled to the dynamics in the y direction. Thermal fluctuations in the x and y directions are of the same magnitude. However, a fluctuation of order δ in y will be convected by the flow and result in an x fluctuation of order δWi . Hence, at large Wi ($Wi > 1$), the fluctuations in the transverse direction y will be the dominant contribution to the temporal fluctuations observed in the x direction. These essential elements in the equations of motion, which give rise to the observed shear enhanced fluctuations, are directly analogous to the phenomenon of shear enhanced dispersion in Brownian suspensions originally discovered by Taylor [16] over 40 years ago. The existence of a recirculating motion is also contained in our simple model. The deterministic trajectory of a bead starting at a position x_0, y_0 will approach the tethering point through a semicircular path. Thermal fluctuations in the y direction reinitiate such cyclic paths. For a Hookean spring, then, one expects that fluctuations will increase with increasing Wi and that the autocorrelation functions

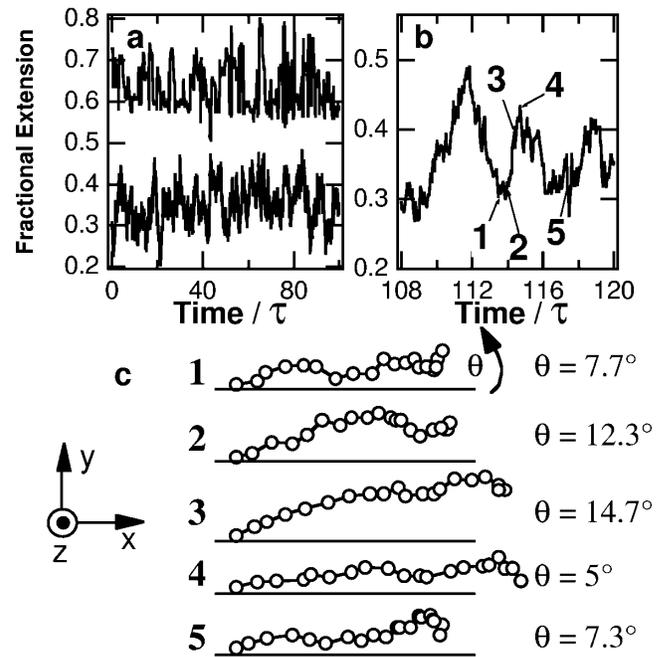


FIG. 5. Results from simulations for $Wi = 5.1$. (a) Temporal chain fluctuations for simulations (bottom data set) and sample experimental data (top data set displaced by 0.4 for clarity). (b) Temporal chain fluctuations (zoom). (c) Cyclic chain dynamics. The five different configurations correspond to the points indicated in (b). The angle θ is the orientation of the vector joining the tethering point to the center of mass of the chain, with regard to the tethering surface.

will eventually collapse onto a single curve lying to the right of the $Wi = 0$ curve. Including nonlinear elasticity would have an opposing effect, decreasing fluctuations at large Wi and leading to faster decays in the autocorrelation functions, in qualitative agreement with our observations.

It is worthwhile to compare tethered and free polymers. A free chain is able to rotate to and past the stagnation streamline, leading to tumbling motion [5]. Experiments [3] and simulations [17] show that in this case length fluctuations monotonically increase with Wi and reach a constant value for large Wi . For a tethered chain, the wall sterically blocks end-over-end tumbling. In addition, the combination of an attachment point and repulsive forces exerted by the wall on the rest of the chain maintains in the chain an asymmetric exposition to the flow which contributes to the extension. These two effects lead, for the tethered sheared chain, to a mean extension larger than the free sheared one, but smaller than those of a tethered chain in plug flow or a free chain in elongational flow. Furthermore, the tethered shear chain fluctuations are smaller than those of the free sheared one, but larger than those of the tethered chain in plug flow or a free chain in elongational flow.

To conclude, our experiments revealed for the first time the strong shear enhanced fluctuations of tethered polymers subjected to a shear flow near a planar surface. These dynamics are well described by stochastic simulations of

a bead-spring chain with wormlike chain elasticity. They can be associated with *cyclic dynamics*, due to a coupling of the flow field gradient with thermally driven fluctuations of the chain in the shear gradient direction.

It would be interesting to examine longer molecules, for which simulations [17] predict the fluctuations should increase in magnitude and persist for a broader range of Wi . Another natural question which arises is the relevance of the present findings for polymer brushes. A recent model [18], based on a stationary distribution of configurations, suggests that a brush submitted to flow could split into two populations, with a few highly extended chains bearing most of the stress. The dynamic couplings uncovered here suggest that strong shear induced *temporal* fluctuations could also affect the collective motion or *breathing modes* [19] in polymer brushes. Interestingly, polymer brushes show anomalous rheology in oscillatory shear flow, which is still not fully understood [20,21]. It would be interesting to investigate if certain frequencies of the shear induced fluctuations observed here could be excited in an oscillatory flow, leading to resonance effects. Also, preliminary experiments [22] show that DNA brushes can be constructed, suggesting that the current study could be extended to brushes.

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- [10] λ -DNA was labeled with YOYO-1 at a dye/base pair ratio of 1:10. When stained at a dye/base pair ratio of 1:4 the contour length increases from the unstained value of 16.3 to 21 μm . We assumed the length of the DNA increases linearly with the concentration of dye to calculate a DNA contour length of 18 μm .
- [11] It was not possible to clearly distinguish the ends of the chains for all Wi and all times. As in previous DNA studies [3], we define the visual length of a chain as the difference in the x coordinates of the beginning and ending fluorescence in an image, after subtracting the background. Data analysis was automatically performed by an algorithm written in NIH Image.
- [12] A semilog plot of the autocorrelation function at $Wi = 0$ displays a linear slope after 0.2 s. This portion of the curve was fitted to a single exponential to attain τ .
- [13] The relaxation time of a free λ -DNA in viscous solvents has been reported by Smith and Chu [2]. Extrapolating from the Smith and Chu data leads to $\tau = 0.074$ s for a free λ -DNA in our solvent and assuming that a chain held at one extremity is equivalent to a chain of double its size leads to a value of $\tau = 0.21$ s. Thus hydrodynamic interactions of the DNA with the wall roughly doubles τ .
- [14] A chain consisting of 20 beads connected by springs with wormlike chain constants [J.F. Marko and E.D. Siggia, *Macromolecules* **28**, 8759 (1995)] was chosen as a good compromise between realism and computer efficiency. The parameters in the model are consistent with those of λ -DNA at the dye concentration used here (18 μm contour length [10] and persistence length of 0.053 μm). The simulations neglect hydrodynamic interactions. Simulations and experiments [R.G. Larson, T.T. Perkins, D.E. Smith, and S. Chu, *Phys. Rev. E* **55**, 1794 (1997)] have shown that the drag coefficient for free λ -DNA changes very little upon deformation and including intrachain hydrodynamic interactions leads to modest corrections.
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