that the atomic vapors remained close to thermal equilibrium at all times.

In conclusion, we have created long-lived (80 ± 5 s), low-temperature (450 ± 80 pK), and low-density (5 × 10^{10} atoms/cm^{3}) partially condensated atomic vapors using a weakly confining [\Omega = 2 \pi \times (1.12 \pm 0.08) \text{ Hz}] gravito-magnetic trap. These samples are characterized by a thermal velocity \sim 1 \text{ mm/s}, a speed of sound \sim 100 \mu \text{m/s}, and a healing length limited by the \sim 20-\mu \text{m} harmonic oscillator length of the trapping potential. Low-temperature and low-density ensembles are important for spectroscopy, metrology, and atom optics. In addition, they are predicted to experience quantum reflection from material surfaces (26–28).

References and Notes
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Observe the Polymer
Conformation Hysteresis in
Extensional Flow

Charles M. Schroeder,1 Hazen P. Babcock,2,* Eric S. G. Shaqfeh,1,3 Steven Chu2†

Highly extensible Escherichia coli DNA molecules in planar extensional flow were visualized in dilute solution by fluorescence microscopy. For a narrow range of flow strengths, the molecules were found in either a coiled or highly extended conformation, depending on the deformation history of the polymer. This conformation hysteresis persists for many polymer relaxation times and is due to conformation-dependent hydrodynamic forces. Polymer conformational free-energy landscapes were calculated from computer simulations and show two free-energy minima for flow strengths near the coil-stretch transition. Hysteresis cycles may directly influence bulk-solution stresses and the development of stress-strain relations for dilute polymer flows.

The behavior of long-chain, flexible polymer molecules in extension-dominated flows has been the subject of research discussion for more than 30 years (1). Flows of dilute poly-

†Department of Chemical Engineering, *Departments of Physics and Applied Physics, ‡Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA.
‡Present address: Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA.
*To whom correspondence should be addressed. E-mail: schu@stanford.edu
component tend not to perturb polymer conformational changes far from the equilibrium coiled state. However, flows with a dominant extensional component may substantially orient and stretch polymers (2). From a practical standpoint, extensional flows are realized in many polymer-processing applications, including coating, injection molding, and fiber drawing.

A planar (two-dimensional) extensional flow is described by a line of pure fluid extension and an orthogonal line of pure fluid compression. Components of the fluid velocity \((v_x, v_y)\) in the directions of the extensional and compressional axes vary linearly with position such that \(v_x = \epsilon \dot{x}\) and \(v_y = -\epsilon \dot{y}\), where \(\epsilon\) is the strain rate. Planar extensional flow exhibits no rotational components and therefore has the ability to drastically stretch flexible polymer chains even at low flow strengths.

An abrupt coil-stretch transition for polymers in extensional flows is predicted to occur at dimensionless flow strengths \(De = 0.5\) (3), where the Deborah number, \(De = \tau / \epsilon\), is the ratio of two intrinsic time scales: the longest polymer relaxation time \(\tau\) and the characteristic fluid stretching time \(\epsilon^{-1}\). The width of the coil-stretch transition is expected to scale inversely with the contour length of the polymer, so in the limit of very long polymers, the transition is very sharp (4). Experiments based on optical techniques, including birefringence (5, 6) and light scattering (7, 8), have previously been used to infer polymer stretch and orientation. These traditional experiments revealed useful information regarding polymer conformational transitions, but the average behavior of a large ensemble of polymer molecules revealed a broad transition from a coiled to extended state. With the advent of single-molecule observations, even monodisperse samples revealed a large variance in the time it took the molecules to reach their equilibrium extension (9, 10). When the extension of only those molecules that reached their equilibrium length is plotted as a function of \(De\), the transition from coiled to stretched state occurred near \(De = 0.5\) and became more than an order of magnitude sharper than previous observations.

In 1974, de Gennes predicted the existence of a hysteresis cycle in steady-state polymer extension near the critical transition in extensional flows (4). He argued that the hydrodynamic force exerted by the fluid on the polymer would increase as a polymer molecule stretched from its equilibrium coiled state. In the coiled state, interior monomer units are hydrodynamically shielded from the full velocity field as a result of nearby portions of the same polymer chain. However, as the molecule stretches, the fluid is able to exert a stronger frictional grip. Using simple polymer kinetic theory, de Gennes到达了S-shaped equation for the steady-state polymer extension versus \(De\) (Fig. 1) and argued that in a narrow range of flow strengths near the coil-stretch transition, three molecular configurations were possible: a highly stretched “S” state, a compacted coiled “C” state, and a physically unstable “P” configuration.

The behavior of long-chain polymers near this phase transition has been a highly debated topic for several decades. Although the notion of conformational hysteresis was supported by Hinch and Tanner around the same time as de Gennes’ proposal (11–16), in 1985, Fan et al. (17) argued that de Gennes’ S-shaped extension curve was nonphysical and could only arise as the result of mathematical approximations. Wiest et al. (18) broadened the argument against hysteresis with computer simulations of polymers and found no evidence of hysteresis, concluding that de Gennes’ S-shaped curves were indeed nonphysical.

The existence of polymer conformational hysteresis in the coil-stretch transition has important implications with regard to our understanding of phase transitions. The static and dynamic properties of polymers have striking similarities with critical phenomena in many-body systems (19).

For linear polymers with molecular weights \(M\), the configuration hysteresis is possible in a range of \(De\) values (20). Figure 2A shows the pressure–molar volume relation for a substance with the three curves corresponding to different temperatures such that \(T_1 < T_2 < T_3\). Below a critical temperature \(T_c\), a cubic equation of state (such as van der Waals) gives isotherms (such as \(T_3\)) wherein liquid and vapor phases can coexist as an inhomogeneous mixture of two states with well-defined molar volumes. Saturated vapors can be subcooled into metastable states in the absence of liquid nucleation sites; similarly, saturated liquids may be superheated into the two-phase region specified by the dotted line. In both cases, the system is kinetically trapped in a local minimum of free energy. The presence of hysteresis is a signature of a first-order phase transition with an associated latent heat.

By analogy, polymers above a critical length \(M_c\) can exist in two stable states of...
extension corresponding to coiled and extended configurations (Fig. 2B). Because we are considering a single molecule, the simultaneous coexistence of two different conformations is not meaningful. However, a polymer in an initially extended (coiled) state can remain kinetically trapped in the extended (coiled) configuration. If hysteresis is found to exist, the coil-stretch transition must be a first-order transition.

If the hydrodynamic drag forces on a stretched polymer were orders of magnitude greater than the drag on a coil, one could argue on intuitive grounds that hysteresis would be likely. The hydrodynamic drag resistivity \( \zeta^{\text{stretch}} \) for a coiled polymer is expected to scale as the radius of gyration \( R_g \), so that \( \zeta^{\text{coil}} \sim N \), where \( N \) is the number of statistical Kuhn segments and \( v = 0.5 \) or 0.6, depending on solvent conditions. In contrast, the drag resistivity of a long, slender body (21) in viscous flow \( \zeta^{\text{stretch}} \) is

\[
\zeta^{\text{stretch}} \sim N/\ln(L/b)
\]

where \( b \) is the hydrodynamic radius of a monomer unit (22). In the limit of very long polymers, \( \zeta^{\text{stretch}}/\zeta^{\text{coil}} \) weakly diverges and hysteresis becomes plausible. The crucial question is how much greater must \( \zeta^{\text{stretch}} \) be compared with \( \zeta^{\text{coil}} \) for hysteresis to occur. For \( \lambda \)-DNA (\( \sim 150 \) Kuhn segments), \( R_g = 0.73 \) \( \mu \)m (23) and the fluorescently stained contour length is 21.1 \( \mu \)m (24), such that \( \zeta^{\text{stretch}}/\zeta^{\text{coil}} \) is \( \sim 1.7 \). For DNA of \( \sim 2250 \) Kuhn segments, we estimate that \( \zeta^{\text{stretch}}/\zeta^{\text{coil}} \) is only \( \sim 3.3 \). DNA is unusual when compared with synthetic polymers, because the ratio \( L/b \) is unusually large and the logarithm term in the denominator cannot be ignored.

We report here the direct observation of vastly separated coiled and stretched polymer configurations at identical flow strengths (25). We examined genomic-length DNA polymer chains with contour lengths \( L \) from 1.3 to 1.7 mm stained with a fluorescent dye (26). We were able to trap and image individual molecules in extensional flows for many hours with a flow cell (fig. S1), so that sizable strain (\( \varepsilon = \varepsilon_{\text{flow}} \)) can accumulate. The molecular trap is based on a flow cell where the position of the stagnation point is adjustable. If the molecule begins to drift toward one of the two exit ports, the flow impendence in the exit ports is adjusted so that the position of the stagnation point would reverse the direction of the drifting molecule (26). Our device is analogous to one used by Bentley and Leal to control the position of a fluid drop in a four-roll mill device (27). The long observation times of each DNA molecule required special measures (26) that provided long-term stability of the polymer physical properties, including contour length and relaxation time (28).

The hysteresis experiment was conducted by first trapping a polymer molecule and measuring its relaxation time with video microscopy. The molecule was then kept in zero-flow conditions for several relaxation times \( \tau_{\text{relax}} \) to ensure a random initial configuration. The polymer was then exposed to extensional flow at a particular \( De \) for several strain units. Next, we extended the same polymer at \( De \approx 5 \) and slowly decreased the pump speed to introduce the molecule to the same \( De \) value. After monitoring the extension for at least 10 units of Hencky strain (\( \sim 30 \) relaxation times), we repeated the process for a flow with a slightly different \( De \) number. DNA molecules \( \sim 575 \mu \)m long were examined first (Fig. 3A). Conformation hysteresis was not observed at any \( De \) for this set of molecules. Trajectories for initially extended polymers with \( L \sim 575 \mu \)m were sluggish to recoil, and we conjecture that the effective energy potential may be flattening at this \( De \), potentially signaling an approach to separated, bistable states.

Figure 3. B to D, shows the transient extension for DNA molecules with \( L \sim 1300 \mu \)m when \( De = 0.30, 0.45 \), and 0.57. For low \( De \) values of \( \sim 0.30 \) (Fig. 3B), the hydrodynamic force exerted on the polymer is not sufficient to maintain an extended configuration. However, at \( De = 0.45 \), initially extended polymer molecules evolve to extensions of \( \sim 670 \mu \)m and remain extended above 13 units of strain (Fig. 3C and fig. S3). The same molecule prepared in an initially coiled state remains at extensions near 41 \mu m over the course of 12 strain units, during which time fluid ele-.
ments have separated by a relative distance of $e^{1/2}$, where $e$ is the natural experimental function. These states remained distinct and were separated by an extension of $\sim 630 \mu m$, which is $\sim 1/2$ $L$ for more than 30 relaxation times. At this $De$, our data indicate that two local energy minima exist for the polymer chain extension, and the energy barrier height is several $kT$, where $kT$ is thermal energy, such that a random Brownian fluctuation does not cause either state to become unpopulated over the course of $e = 12$ ($t_{obs} \sim 1$ hour).

Finally, we probed the transient dynamics of long-chain polymer molecules for $De$ greater than the critical value. For $De = 0.57$ (Fig. 3D), the molecule initially prepared in the coiled state eventually unraveled to a steady extension of $\sim 580 \mu m$.

We measured the extension of several polymer molecules with $L \sim 1.3$ mm at different $De$ values near the critical region. The steady-state extension at different $De$ values is shown in Fig. 3E, where each data point represents the time-averaged steady extension achieved by the polymer over the course of at least 8 to 10 strain units. The appearance of single values of extension for a given $De$ number is a consequence of the initially coiled and stretched conformations achieving the same steady extension. A clear hysteresis region is revealed in which the polymer extension is a strong function of deformation history. Although the hysteresis region occurs over a narrow range of $De$ values, the states are separated by several hundred micrometers of extension and persist for $e \geq 10$, corresponding to hours of observation. Unexpectedly, only a modest change in the drag ratio is needed to produce hysteresis: We estimate that $\xi_{\text{stretch}}/\xi_{\text{cool}} \approx 5$ for 1.3-mm-long polymers. The effect of physical confinement of the DNA in the flow channel on the drag ratio is small (supporting online material text and fig. S2).

Computer simulations of polymer molecules modeled as a series of beads connected by springs were conducted with Brownian dynamics techniques (29, 30). Hydrodynamic interaction effects were incorporated by using a point-force (Rotne-Prager-Yamakawa) interaction between beads along the polymer chain (31). In this model, the disturbance velocity experienced by one bead as a result of a neighboring bead decays to zero as the distance between them grows large. Simulations of polymer chains with $L \approx 1.3$ mm, corresponding to $\approx 9280$ statistical Kuhn segments, were carried out in the same manner as the experiment. Single molecules were initialized in both a randomly coiled and a stretched state at equivalent values of $De$. Conformation hysteresis is apparent (Fig. 4A). The hysteresis is due solely to intramolecular hydrodynamic interactions, because we have not included effects due to physical boundaries confining the polymers.

Polymer chain resistivity, $\xi_{\text{chain}}$, as a function of polymer stretch ($R$), was also extracted from the simulations by coarse graining the internal modes of the multibead spring chain into a simple dumbbell. We calculated the conformational free energy as a function of extension for these large polymers using the $\xi_{\text{chain}}(R)$ functionality. For small $De$ below the coil-stretch transition, only one minimum in the free-energy landscape exists, corresponding to the coiled state. As $De$ increases above values of 0.5, a single minimum exists at large extension, indicating the highly elongated polymer state. The conformational free energy is plotted in Fig. 4B for a narrow range of $De$ near the coil-stretch transition. In this range of $De$, two shallow minima exist in the free energy landscape, giving rise to metastable polymer configurations at a single $De$, and hence conformation hysteresis. If the extrema in the polymer energy landscape are plotted as a function of $De$, an S-shape curve very similar to de Gennes’ original plot of steady-state extension versus flow strength is recovered. The middle branch in the “S” represents the physically unstable configuration and “is the analog of the maximum point in a static potential barrier” (4).

We argue that the coiled and stretched polymer configurations in the hysteretic region are kinetically separated. The free-energy barrier separating the two states is typically much larger than $kT$, and random Brownian fluctuations were not strong enough to cause the polymer molecules to make transitions between coiled and extended states during the course of our observation. However, given a much longer observation time, the molecule may spend a fraction of time in both states, depending on the height of the barrier and the relative energy position of the coiled and stretched wells.

In addition to the implications of hysteresis with regard to first-order conformational phase transitions, hysteresis cycles may also have practical implications. For example, the extensional viscosity $n^{ext}$ of a dilute polymer solution may be substantially larger (by a factor of $10^6$ or $10^7$) for a “prestretched” sample that had experienced a step strain in its processing history (12), imparting a larger viscous contribution to the total solution stress resulting from the long, extended portions of the polymer molecules. With hysteresis, the steady-state conformation of a polymer in flow becomes a function of its processing history, and steady-state solutions that neglect transient behavior become ambiguous (12). Our results suggest that hydrodynamic interac-

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**Fig. 4. Computer simulations of polymer molecules using Brownian dynamics techniques. (A) Transient molecular extension compared with Hencky strain for DNA consisting of $\sim 9280$ Kuhn segments with $L \approx 1.3$ mm. Initially stretched molecules (75% of the contour length) evolve to extensions several hundred micrometers greater than initially coiled polymers, as observed in the experiment. (B) Polymer conformational free energy landscape calculated for DNA with $L \approx 1.3$ mm. For a narrow range of $De$ near the coil-stretch transition, two minima in the polymer conformational free energy exist. The double-walled potential shown in the plot gives rise to hysteresis cycles in polymer conformation.
tions should be an important feature of polymer theories attempting to model stresses in extensional flows. We anticipate that the effects of hydrodynamic interactions will be crucial for description of more flexible synthetic polymers such as polystyrene, with a smaller ratio of persistence length to hydrodynamic radius, and hence larger extensibility (L/R) ratios.

Finally, conformational hysteresis may play a role in turbulent-drag reduction, an effect discovered by B. A. Toms a half century ago (32): high molecular weight polymers mixed with fluids at an extremely dilute level (~1 part per million by weight) can reduce the drag resistance in turbulent flow by as much as 80% (33). Two types of explanations of this effect have been proposed. The first conjecture, originally proposed by Lumley (34), argues that the drag reduction occurs at the boundary between the turbulent-core region and the laminar zone near the pipe surface. Polymers that have been extended by (transient) elongational flows can enter the boundary layer and reduce the momentum transfer between the rapidly moving fluid and the laminar layer. Polymers would remain extended for longer periods of time in their stretched state because of conformational-dependent drag. Hysteresis would further magnify this effect. For synthetic polymers that exhibit a large amount of turbulent-drag reduction, t \_stretch/\tau \_0 \_relax is estimated to be ~18. In contrast, Tabor and de Gennes have argued (35) that polymers in turbulent flows experience rapidly varying extensional flows so that the coil-stretch transition disappears entirely. Instead, they propose that energy is transferred in turbulent flows though a cascade of eddies to smaller size scales where it is finally dissipated. Long polymers interrupt this cascade by storing some of this energy in the form of an elastic modulus that is then delivered back to the moving fluid.

**Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization**

Michael S. Strano,1,† Christopher A. Dyke,2† Monica L. Usrey,1 Paul W. Barone,1 Mathew J. Allen,2 Hongwei Shan,2 Carter Kittrell,2 Robert H. Hauge,2 James M. Tour,2,3† Richard E. Smalley2,4,†

Diazonium reagents functionalize single-walled carbon nanotubes suspended in aqueous solution with high selectivity and enable manipulation according to electronic structure. For example, metallic species are shown to react to the near exclusion of semiconducting nanotubes under controlled conditions. Selectivity is dictated by the availability of electrons near the Fermi level to stabilize a charge-transfer transition state preceding bond formation. The chemistry can be reversed by using a thermal treatment that restores the pristine electronic structure of the nanotube.

The main hurdle to the widespread application of single-walled carbon nanotubes is their manipulation according to electronic structure (7). All known preparative methods (2-4) lead to polydisperse materials of semiconducting, semimetallic and metallic electronic types. Recent advances in the solution-phase dispersion (5, 6), along with spectroscopic identification using band-gap fluorescence (7) and Raman spectroscopy (8), have greatly improved the ability to monitor electrically distinct nanotubes as suspended mixtures and have led to definitive assignment of the optical features of semiconducting (7), as well as metallic and semimetallic, species (8).

We now report selective reaction pathways of carbon nanotubes in which covalent chemical functionalization (9) is controlled by differ-