

ANALYSIS OF DYNAMIC ACTIONS OF PARTIAL ELASTIC SINGLE POLYMER CHAIN

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ABSTRACT

The ability to determine polymer elasticity and force-extension relations from polymer dynamics in flow has been challenging, mainly due to difficulties in relating equilibrium properties such as free energy to far-from-equilibrium processes. In this work, we determine polymer elasticity from the dynamic properties of polymer chains in fluid flow using recent advances in statistical mechanics. In this way, we obtain the force-extension relation for DNA from single molecule measurements of polymer dynamics in flow without the need for optical tweezers or bead tethers. We further employ simulations to demonstrate the practicality and applicability of this approach to the dynamics of complex fluids. We investigate the effects of flow type on this analysis method, and we develop scaling laws to relate the work relation to bulk polymer viscometric functions. Taken together, our results show that nonequilibrium work relations can play a key role in the analysis of soft material dynamics.

I INTRODUCTION

In recent years, polymeric materials have been studied using single molecule techniques such as atomic force microscopy, optical traps, magnetic tweezers, and fluorescence microscopy.[1,2] Single molecule force spectroscopy allows for direct determination of the elastic force-extension relationships for single proteins or polymers by applying external forces to surface-tethered macromolecules. In addition, these methods can be used to study the molecular response and corresponding forces during the relaxation of stretched polymers to a coiled state. However, these high-precision approaches require active probes, complex instrumentation, and generally involve measurements that are performed in the absence of fluid flow.

Alternatively, polymer chains can be stretched and oriented far from equilibrium using hydrodynamic flow, and well-defined fluid flows are easily generated in microfluidic devices. Single polymer experiments have been complemented with computer simulations to provide a particularly powerful approach to study polymer rheology. In this way, equilibrium force-extension relations for single polymer chains are generally taken to be ingredients (or given functions) for stochastic simulation methods for polymers such as Brownian dynamics (BD). In an alternative

approach, Monte Carlo simulations based on the GENERIC formalism have been used to determine the non-equilibrium free energy and elasticity for polymer chains in flow. Nevertheless, development of new methods to determine equilibrium materials properties such as polymer elasticity from non-equilibrium flow dynamics, and in particular, methods that can be interfaced with single molecule experiments and BD simulations, is critically required.

II METHODS

2.1 Free energy landscape and elasticity

The first experimental demonstration of the JE considered a system defined as an RNA molecule maintained at a defined extension by a conservative force field. In that study, the system was transitioned between states of varying molecular extension by “pulling” on the ends of the RNA using optical tweezers in the absence of flow. In our work, the system is defined as a single polymer molecule driven by flow, and the terminal states of the system are defined by the end-to-end molecular extension of the polymer, regardless of flow. In this way, the system is transitioned between initial and final states of predefined molecular extension by imposing a fluid flow that induces conformational changes in the polymer molecule. Once the molecule reaches a predefined final extension, the work calculation along the dynamic trajectory is halted. Conceptually, halting the work calculation can be envisioned as analogous to “switching off” the imposed flow and maintaining the molecule at the final extension by a conservative field. This step allows for the equilibration of the system to the new steady state. However, this step is not necessary for a dynamic trajectory, because equilibration at the final steady-state does not contribute to the work calculation and therefore does not affect the work relation.

In order to calculate free energy landscapes, polymer molecules are transitioned through a series of states defined by molecular extension λ_i , where the subscript $i = [1, 2]$ represents the initial and final states, respectively, by increasing the flow strength through a series of steps. Once a polymer reaches the desired final state (final molecular extension λ_2), then the work calculation is terminated. Here, a dynamic trajectory is considered as the stretching trajectory up to the first time a molecule reaches a target final extension. For λ -DNA in tethered uniform flow, the flow strength is stepped through $Pe = 20$, whereas in planar extensional flow, the flow strength is stepped up to $Pe = 16.2$. Flow strengths were determined in order to ensure that polymer chains are stretched above 70% of the contour length. At each step, we determine the work distribution and the corresponding ΔF from the work relation. In this way, the free energy and therefore the stored elastic energy of a polymer can be determined over a range of energies up to 3 orders of magnitude. Chain elasticity is determined by differentiating the free energy with respect to chain extension.



III RESULT AND DISCUSSION

For a general microscopic system, external forces can be applied to perform work and transition the system between states. External forces can follow autonomous or non-autonomous dynamics. In autonomous dynamics, all of the external forces or agents are maintained at fixed values, and the system evolves accordingly. However, in non-autonomous dynamics, at least one of the forces varies systematically in time. Based on these distinctions, an equilibrium state is defined when the applied forces are conservative and autonomous. Therefore, the equilibrium statement of the JE can be applied to systems where the initial and final states are prescribed by autonomous and conservative forces. In this work, the terminal states of our system (defined by a polymer molecule at a fixed molecular extension) satisfy these conditions.

$$e^{-\beta\Delta F} = \langle e^{-\beta W} \rangle.$$

Previous applications of the JE have focused on bead-tethered macromolecular systems. In this case, systems are driven from an initial equilibrium state (State a) to a final equilibrium state (State b) by applying forces that follow non-autonomous dynamics, and work is performed on the system. Upon reaching the final state (State b), no additional work is done on the system. A physical example is an RNA “pulling” experiment performed using optical tweezers, wherein the bead-tethered ends of an RNA hairpin are perturbed by optical forces. Here, the bead is maintained in a potential energy well given by the optical trap.

In this work, we show that the JE can be applied to polymeric systems driven by hydrodynamic flow, provided that the initial and final states of the polymer are defined by molecular extension (see Methods). We note that the initial state must be a well-defined equilibrium state. In particular, we show that transitions between states of defined molecular extension can be analyzed in the context of non-equilibrium work relations. Work is performed on a polymer chain by a hydrodynamic force (via fluid motion), which changes the molecular stretch of a polymer between an initial state (State a, initial molecular extension λ_1) and a final state (State b, final molecular extension λ_2). In one approach, transitions between states of defined molecular extension λ_i are made by increasing flow strength through a series of steps in fluid velocity. Upon reaching the final state, an external conservative field (in the absence of flow) could be used to allow for equilibration, though this approach is not easily available in experiments. In a second approach that is more amenable to experiments, a polymer can be transitioned from an



equilibrated state at λ_1 (zero flow) to a second non-equilibrated state of stretch λ_2 by a large step in flow strength. We demonstrate the validity of both approaches in this article.

3.1 Work relations and system control parameters

Non-equilibrium work relations and fluctuation theorems have previously been considered in the context of dissipative forces. Furthermore, recent experiments have employed high-precision measurements involving optically trapped beads in the presence of flow to demonstrate the validity of these theorems. Here, we apply non-equilibrium work relations to dilute polymeric solutions driven by purely dissipative forces.

For dynamic processes driven by external fluid flows, the JE requires an accurate definition of work done on bodies suspended in a flowing fluid. A large body of previous work in this area has focused on force-extension measurements, where the work done on a molecule is simply defined by the force exerted to stretch the molecule over a well-defined distance. However, polymeric systems driven by hydrodynamic flow require a definition of the work performed on a polymer molecule by a flowing fluid. Recently, a work definition was used to show that a Hookean dumbbell model for polymers in extensional flow satisfies a fluctuation theorem, however, the Hookean model does not accurately capture dynamics in strong flows and it is unclear a priori that this work expression yields the equilibrium Jarzynski work. In this section, we show theoretically that this work definition is the valid expression for applying the equilibrium statement of the JE to polymer molecules driven by flow.

To obtain a work expression for a Langevin description of polymers in flow, we first consider a classical mechanical system consisting of N particles in contact with a heat bath at temperature β^{-1} . The microscopic state of the system is specified by the $3N$ -dimensional position vector \mathbf{r} and the $3N$ -dimensional momentum vector \mathbf{p} of the particles through the Hamiltonian $H(\mathbf{r}, \mathbf{p})$. In order to move to a Langevin description of the system, it is essential to identify a reaction coordinate $x(\mathbf{r})$ through which a potential of mean force $\Phi(x)$ can be expressed as:

$$e^{-\beta\Phi(x)} = \int d\mathbf{r} d\mathbf{p} \delta(x - x'(\mathbf{r})) e^{-\beta H(\mathbf{r}, \mathbf{p})}$$

where $\delta(x)$ is the Dirac-delta distribution. Consider the case where the system is now guided (or perturbed) by an external potential V_α , such as in steered molecular dynamics simulations. Here, α is the control parameter that defines the state of the system. In this case, the potential function of the new system $U(x; \alpha)$ is the sum of the potential of mean force and the external potential, such that $U(x; \alpha) = \Phi(x) + V_\alpha(x)$. When applying the JE to systems controlled by conservative forces, the work definition is given as

$$w = \int_0^\tau dt \dot{\alpha} \frac{\partial U(\mathbf{x}; \alpha)}{\partial \alpha}$$

Systems driven by nonconservative forces (e.g., as encountered in hydrodynamic flows) are typically multidimensional in the reaction coordinate. Therefore, we consider a Langevin description of polymer chain dynamics in flow such that:

$$\zeta \dot{\mathbf{x}} = -\frac{\partial U(\mathbf{x}; \alpha)}{\partial \mathbf{x}} + \mathbf{f} + \xi$$

3.2 Free energy landscapes and chain elasticity

Using nonequilibrium work distributions, we applied the JE to calculate the stored elastic energy for polymer chains as a function of molecular extension, beginning with BD simulations (figure 1). We first determined the free energy landscape for single DNA molecules stretched in an extensional flow (figure 1a) and in tethered uniform flow (figure 1a, inset) using λ -DNA as a model system. In order to map the free energy landscape for λ -DNA from molecular stretching trajectories, we simulated the response of polymer chains to series of step increases in flow strength W_i . During transitions between successive steps of constant molecular extension, we determined the work done by the fluid to stretch a polymer from one extension to another. In this way, we used a method known as stratification, wherein the overall free energy change ΔF_{tot} for a process is determined by summing the free energy changes for a series of sub-processes.

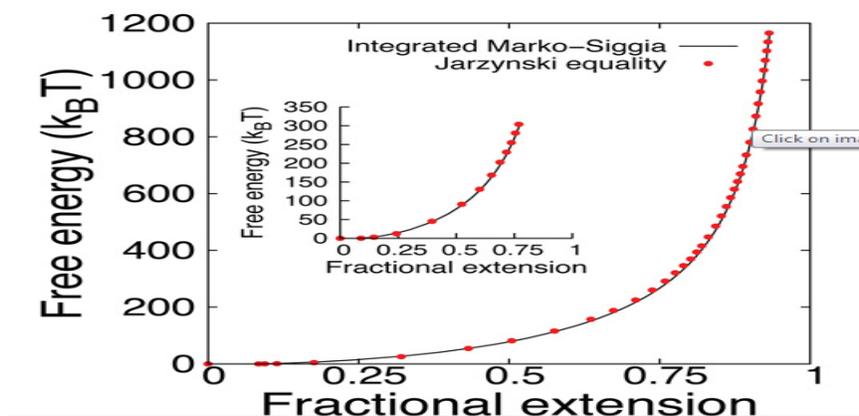


Figure 1a Free energy landscape for λ -DNA ($L \approx 21 \mu\text{m}$)

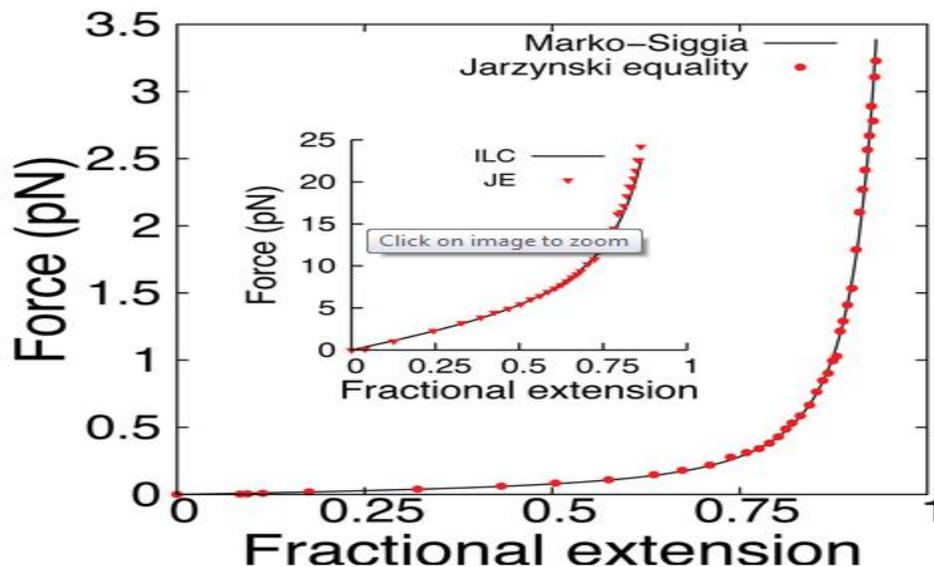


Figure 1 b Polymer elasticity for λ -DNA ($L \approx 21 \mu\text{m}$)

IV CONCLUSION

We determine polymer elasticity from the dynamic properties of polymer chains in fluid flow using recent advances in statistical mechanics. In this way, we obtain the force-extension relation for DNA from single molecule measurements of polymer dynamics in flow without the need for optical tweezers or bead tethers. We further employ simulations to demonstrate the practicality and applicability of this approach to the dynamics of complex fluids.

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