Study of Polymers Nonlinear Dynamics

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Abstract: A formalism is presented for the nonlinear dynamics of inextensible stiff polymers within the model of local viscous dissipation. By casting the internal elastic forces in an intrinsic representation, enforcing the constraint of local inextensibility through a Lagrange multiplier function, and utilizing techniques from the differential geometry of curve motion, the dynamics of configurations of arbitrary complexity is reduced to a scalar partial differential equation amenable to analytical and efficient numerical study. As an example, the formalism is applied to the "folding" dynamics of stiff polymers with pairwise self-interactions and intrinsic curvature.

Imaging and manipulation techniques capable of probing the conformation and dynamics of biological macromolecules have revealed a variety of phenomena involving complex molecular configurations. Among these are long DNA molecules undergoing electrophoretic motion in structured environments [1] and collapse from near full extension [2], and actin filaments moved by molecular motors on surfaces [3]. In contrast to studies focusing on the statistical properties of ensembles of molecules, these studies are dynamical investigations of single molecules..

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INTRODUCTION

Central features of these dynamical phenomena are the inextensibility and finite bending elasticity of the polymers. A natural continuum model with these features, the Kratky-Porod or "wormlike" model [4], derives from the elastic theory of thin rods with an energy quadratic in the local curvature. The study of equilibrium aspects of this model is highly developed [5,6], but its dynamical properties in viscously dominated flow are far less well understood. Dynamical formulations that address inexten- sibility date back to the important work on stiff polymers of Harris and Hearst [7], and others [8] who have emphasized the fundamentally nonlocal nature of this constraint. It has been touched upon as well in more recent studies of electrophoresis [9], hairpin defect motion in polymeric liquid crystals [10], supercoiled DNA [11], and motility assays [12], but no general method has been proposed to answer the basic question: What is the motion of a nonstretching flexible polymer in a viscous medium?

Here we develop a unifying formalism for the dynamics of flexible but inextensible polymers within the simplest hydrodynamic model in which the polymer is subject to local viscous forces. The methods are completely general, capable of incorporating both local and nonlocal energetic contributions including elasticity with intrinsic curvature, pair interactions among polymer segments, and external forces. They are also completely intrinsic, making no reference to any idealized reference shape. This is particularly important since from the foundations of elasticity theory [5] we know that the mathematical problem of the equilibrium configurations of such an object is intrinsically nonlinear, and we must expect the same for the dynamics [10]. These nonlinearities arise from the fact that the arc- length parametrization s of a space curve is not independent of its position vector r(s), and while unimportant for weakly curved configurations these nonlinearities are essential for the many complex experimentally observed conformations. Utilizing geometrical methods we reduce the intrinsic nonlinear shape evolution to an extremely compact form as a pair of coupled partial differential equations (PDE's) of a type familiar in the field of pattern formation [13], and for which there are highly developed computational methods.

The complex dynamical processes that may be described by these methods are illustrated with the model problem of a competition between bending elasticity and a pair potential having a short-range repulsion (preventing self- crossing) and an attractive minimum. These elastic and potential forces are mutually frustrating; in order for segments widely separated along the curve to be in the attractive minimum there must be energetically costly bends in the chain. This deterministic "folding" problem is one of the simplest in which to address such issues as the uniqueness of ground states and the pathways to them [14]. In this regard, we expect these methods to be useful in theoretical studies of gene regulation and topoisomerase activity.

The equations of motion derive from an action principle

used often in polymer physics [15] and recently for interfaces and membranes [16]. The polymer is parametrized by $\alpha \in [0, 1]$, with generalized coordinates $\mathbf{r}(\alpha)$ and velocities $\mathbf{r}_t(\alpha)$. If $\mathcal{L}$ is the Lagrangian and R is the Rayleigh dissipation function, the equations of motion are

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \mathbf{r}_t(\alpha)} - \frac{\partial \mathcal{L}}{\partial \mathbf{r}(\alpha)} = -\frac{\partial \mathcal{R}}{\partial \mathbf{r}_t(\alpha)}. \qquad (1)$$

R measures the rate of energy dissipation by the viscous forces, and is quadratic in the velocities. Assuming local, isotropic drag with friction coefficient ζ,

$$\mathcal{R} = \frac{\zeta}{2}\int_0^1 d\alpha\, \sqrt{g}\,|\mathbf{r}_t|^2, \qquad (2)$$

where $g = \mathbf{r}_\alpha \cdot \mathbf{r}_\alpha$ is the metric. Since the motions of interest occur at extremely small Reynolds numbers, we neglect inertial terms, the dynamics becomes first order in time derivatives, and the Lagrangian is simply the negative of the general potential energy functional $\mathcal{E}[\mathbf{r}]$. Rewriting (1) in terms of functional derivatives,

$$\zeta \mathbf{r}_t = -\frac{1}{\sqrt{g}}\frac{\delta \mathcal{E}}{\delta \mathbf{r}} \equiv U\hat{\mathbf{n}} + V\hat{\mathbf{b}} + W\hat{\mathbf{t}}, \qquad (3)$$

where $\hat{\mathbf{n}}$, $\hat{\mathbf{b}}$ and $\hat{\mathbf{t}}$ are the unit normal, bi-normal, and tangent vectors and U, V, and W are the associated forces. Equation (3) is like the Rouse model [17], but allows for an arbitrary energy functional $\mathcal{E}$ rather than the simple collection of Hookean springs originally considered in that context. Generalizations of (3) to stochastic dynamics will be described elsewhere.

The no-stretching or local arc length conservation condition (also clearly enforcing fixed total length) is imposed with a Lagrange multiplier function $\Lambda(\alpha)$,

$$\mathcal{E} = \mathcal{E}_0 - \int_0^1 d\alpha\, \sqrt{g}\,\Lambda(\alpha). \qquad (4)$$

Consider first the geometrically simplest case of a polymer confined to the plane, and let U_0 and Wo be those forces derived via Eq. (3) from the intrinsic energy functional $\mathcal{E}_0$ alone. Functional differentiation of (4) yields total normal and tangential forces

$$U = U_0 + \Lambda\kappa \quad \text{and} \quad W = W_0 - \partial_s\Lambda. \qquad (5)$$

The curvature k(s) isdetermined by the Frenet-Serret equations $\hat{\mathbf{t}}_s = -\kappa\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}_s = \kappa\hat{\mathbf{t}}$. In Eq. (4) we see that —A plays the role of a locally varying line tension [9], and thus its contributions to (5) can be interpreted as a Young-Laplace force in the normal direction and a Marangoni force in the tangential direction.

Local inextensibility requires a time-independent metric. This implies $\hat{\mathbf{t}} \cdot \partial_s \mathbf{r}_t = 0$, which from (3) leads to

$$\partial_s W = -\kappa U, \qquad (6)$$

known also in the context of integrable nonstretching curve dynamics [18,19]. Using Eqs. (5) and (6), we find that A obeys an elliptic ordinary differential equation at each instant of time [20]:

$$(\partial_{ss} - \kappa^2)\Lambda(s) = \kappa U_0 + \partial_s W_0. \qquad (7)$$

Equations (3)-(7) constitute a complete dynamical description ofthe polymer shape evolution once an energy functional $\mathcal{E}_0$ is given.

As a sample problem, consider a polymer with bending elasticity and a monomer pair interaction. The elastic contribution to the energy $\mathcal{E}_0$ is

$$\mathcal{E}_e = \frac{1}{2}A\oint ds\,(\kappa - \kappa_0)^2, \qquad (8)$$

in which we have included an intrinsic curvature $k_0(s)$, and where A is an elastic constant. Eq. (8) leads to nonlinear forces

$$U_e = A(\kappa_{ss} + \tfrac{1}{2}\kappa^3 - \partial_{ss}\kappa_0 - \tfrac{1}{2}\kappa\kappa_0^2),$$
$$W_e = A(\kappa_0 - \kappa)\partial_s\kappa_0. \qquad (9)$$

Note that for closed polymers an s-independent k_0 does not enter the dynamics since both of its contributions to the energy (8) are constant if the polymer length and topology are fixed.

If the polymerexperiences an external potential $\mathcal{V}$ or a pair interaction Φ (e.g., from electrostatic, dispersion, or steric forces), it has energy functionals

$$\mathcal{E}_\mathcal{V} = \oint ds\, \mathcal{V}\mathbf{r}((s)), \qquad \mathcal{E}_\Phi = \frac{1}{2}\oint ds \oint ds'\, \Phi(R), \qquad (10)$$

where $R = |\mathbf{r}(s) - \mathbf{r}(s')|$. These produce purely normal forces

$$U_{\mathcal{V}} = -(\kappa + \hat{\mathbf{n}} \cdot \nabla_{\mathbf{r}(s)})\mathcal{V}$$

$$U_{\Phi} = -(\kappa + \hat{\mathbf{n}} \cdot \nabla_{\mathbf{r}(s)}) \oint ds' \, \Phi(R) \,. \qquad (11)$$

The invariance of the dynamics under redefinitions of the zero of $\mathcal{V}$ and Φ is easily verified by noting from (11) that if, for instance, $\mathcal{V} \longrightarrow \mathcal{V} + c$ the bare normal force transforms as $U_0 \longrightarrow U_0 - c\kappa$. Equation (7) shows that this corresponds to the shift $\Lambda \longrightarrow \Lambda + c$, so the total force $U_0 + \Lambda\kappa$ is unchanged.

In the absence of potentials $\mathcal{V}$ and F,and with $k_0 \equiv 0$, the normal velocity is $U = A[\kappa_{ss} + (1/2)\kappa^3] + \Lambda\kappa$.

For constant A this gives the "curve-straightening equation" [21], and U = 0 defines Euler elastica in the plane [5]. It resembles "geometric" models of interface motion [22] used for dendrite growth, which invoke expansions of U in powers of the curvature and its derivatives, but it arises here from a variational formulation not envisioned in those nonequilibrium processes.

The intrinsic dynamical evolution is completed by following the time dependence of the tangent angle $\theta(s)$ or curvature k(s) = θ_s according to the PDE's [22], $\zeta\theta_t = -\partial_s U + \theta_s W$ and $\zeta\kappa_t = -(\partial_{ss} + \kappa^2)U + k_s W$. Apart from the clear simplification of considering scalar rather than vector PDE's, these intrinsic dynamics allow for a natural treatment of the inherent numerical stiffness associated with elastic forces. Note that the θ and k evolutions both have the form $\zeta u_t = -Au_{ssss} + \ldots$, where the ellipsis stands for nonlinear terms and terms of lower order in s derivatives. The fourth-order derivative severely limits the acceptable time steps in standard finite-difference schemes, but by its linearity may be treated exactly in pseudospectral methods utilizing integrating factors [23].

The treatment of space curves involves both the curvature $\kappa \geq 0$ and the torsion τ, obeying the Frenet-Serret equations $\hat{\mathbf{t}}_s = \kappa\hat{\mathbf{n}}$, $\hat{\mathbf{n}}_s = -\kappa\hat{\mathbf{t}} + \tau\hat{\mathbf{b}}$, and $\hat{\mathbf{b}}_s = -\tau\hat{\mathbf{n}}$. The curve dynamics may be studied directly at the level of the evolution equations for k and τ,

$$\zeta\kappa_t = \mathcal{O}U - \mathcal{P}V + \kappa_s W,$$
$$\zeta\tau_t = \partial_s[\kappa^{-1}(\mathcal{O}V + \mathcal{P}U)] + 2\kappa\tau U - \kappa_s V + \tau_s W. \qquad (12)$$

where $\mathcal{O} = \partial_{ss} + \kappa^2 - \tau^2$ and $\mathcal{P} = 2\tau\partial_s + \tau_s$. These are unnecessarily complicated. Indeed, the forces that arise from the simplest elastic energy $[\mathcal{E}_e = (A/2)\oint ds\, \kappa^2]$,

$$U_e = -A(\kappa_{ss} + \tfrac{1}{2}\kappa^3 - \kappa\tau^2),$$
$$V_e = -A(2\kappa_s\tau + \kappa\tau_s), \qquad (13)$$

and $W_e = 0$, conspire with (12) to present a formidable computational problem. Moreover, the torsion dynamics is problematical at inflection points, where k = 0.

The curve dynamics can be drastically simplified by utilizing Hasimoto's transformation [24] relating vortex filament motion to the nonlinear Schrodinger equation. Define the complex curvature

$$\psi(s,t) = \kappa(s,t)e^{i\phi}, \qquad \phi(s,t) = \int^s ds' \, \tau(s',t), \quad (14)$$

and the complex velocity Γ perpendicular to the curve,

$$\Gamma = (U + iV)e^{i\phi}. \qquad (15)$$

Then for general U, V, and W, ψ obeys [19]

$$\zeta\psi_t = (\partial_{ss} + |\psi|^2)\Gamma + \psi \,\mathrm{Im} \int^s ds' \, \psi_s \Gamma^* + \psi_s W. \qquad (16)$$

Three important featuresarise from this formulation. (i) The form of $\Gamma_e = (U_e + iV_e)e^{i\phi}$ is remarkably compact:

$$\Gamma_e = -A(\psi_{ss} + \tfrac{1}{2}|\psi|^2\psi). \qquad (17)$$

(As noted previously [25], nonplanar elastica [26] are defined by the time-independent nonlinear Schrodinger equation $\Gamma_e + \Lambda\psi = 0$.) (ii) The dynamics of inflection points is mathematically well defined, behaving much like phase slips in one-dimensional superconducting wires [27]. (iii) The dynamics $\zeta\psi_t = -A\psi_{ssss} + \cdots$ is again amenable to integrating factor methods. Finally, by defining the complex vector $\boldsymbol{\omega} = (\hat{\mathbf{n}} + i\hat{\mathbf{b}})\exp(i\phi)$, the Frenet-Serret equations become $\boldsymbol{\omega}_s = -\psi\hat{\mathbf{t}}$, $\boldsymbol{\omega}_s^* = -\psi^*\hat{\mathbf{t}}$, $\hat{\mathbf{t}}_s = (\psi^*\boldsymbol{\omega} + \psi\boldsymbol{\omega}^*)/2$, and the curve may be reconstructed from ψ and ψ^* alone.

We turn finally to the folding problem described in the introduction. The issue we address by simulations is how the presence of preferentially curved segments may determine the chosen folded configurations of an elastic polymer. In the context of DNA supercoiling there is experimental [28] and theoretical evidence [29] for the localization of regions of high intrinsic curvature at hairpin loops, an effect that may be relevant to structural regulation.

Figure 1 shows the succession of straightening processes that takes a highly distorted initial configuration to a ground state having three hairpin loops [30]. These shapes have length L = 10 X 2 π, with a Lennard- Jones potential $\Phi(r) = 4\epsilon(r^{-12} - r^{-6})$ of strength $\epsilon/A = 0.05$, and a spontaneous curvature $k_0(s)$ having three plateaus (as shown in the lower panel). The three regions along the chain in which $k_0 > 0.5$ are indicated by heavy lines, and it is apparent that the relaxation process indeed localizes the regions of intrinsic bend at the hairpin loops. The two sequences shown have the same initial condition, but the second has the peaks in $k_0(s)$ shifted along the chain. We see that this same ground state (modulo rotations and reflections) may be obtained even when the peaks in k0 do not correspond to those in the initial condition; these and other results show in at least a limited sense that this ground state is reached independent of initial conditions. As an aside, we note that these structures bear an intriguing resemblance to those of transfer RNA.

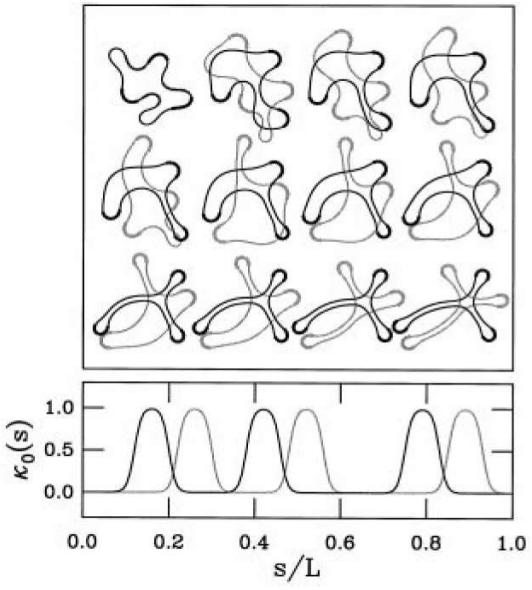

FIG. 1. Folding of a closed elastic polymer in two dimensions. Time evolution proceeds from upper left to lower right. Regions of the polymer for which $k_0(s) > 0.5$ (lower panel) are indicated by heavy lines. Two temporal evolutions are shown (black and gray), corresponding to the same initial condition, but with a displacement of the function $k_0(s)$ along the chain.

We expect that the methods outlined will be useful in the context of the full hydrodynamic problem of stiff polymer dynamics with its associated long-range interactions [17,31], and related studies of the motion of defect lines in liquid crystals [32]. They may also be generalized to include an internal twist degree of freedom relevant to supercoiling, and to allow for local stretching, relevant to recent experiments on DNA "combing" by a moving meniscus [33]. Other applications include the more abstract problem of nonlocal relaxational dynamics of knotted space curves [34].

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