

Poisson bracket formulation of nematic polymer dynamics

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We formulate the dynamical theory of nematic polymers, starting from a microscopic Poisson bracket approach. We find that the Poisson bracket between the nematic director and momentum depends on the (Maier-Saupe) order parameter of the nematic phase. We use this to derive reactive couplings of the nematic director to the strain rates. Additionally, we find that local dynamics breaks down as the polymers begin to overlap. We offer a physical picture for both results.

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I. INTRODUCTION AND SUMMARY

The dynamics of linelike objects, from biomolecules to flux lines in superconductors, has become increasingly important to understand. The processing and manufacture of petroleum products, food products, and petroleum-food products requires the control of polymer flow. The remarkable properties of superconductors can be exploited only if flux-flow dynamics is controlled. While the equilibrium statistical mechanics of linelike objects such as directed polymers, flux lines, and dipole chains in ferro- and electrorheological fluids has been formulated from the microscopic physics [1,2], a similar theory has not been developed for the dynamics. While polymer entanglement dramatically affects the dynamics by introducing cosmologically long-time scales, the statics is not affected. Indeed, it is the dynamics of entanglement that aids in pinning of high-temperature superconductors, in the strength of glue and in other remarkable rheological properties. Previously, dynamics have been formulated on a hydrodynamic basis, which ignores the connectivity of the lines [3]. Other approaches include effective theories that use single-polymer response functions and neglect polymer-polymer interactions [4]. Here, we study the dynamics of polymers which, due to steric or other interactions, are already aligned into a nematic state. By considering a system that is orientationally ordered in equilibrium, the effect of flow on alignment can be separated from the effect of alignment on flow.

In this work we formulate the fluctuating hydrodynamics of polymer nematics based on a microscopic, Poisson bracket approach [5]. In this way, we will account for polymer degrees of freedom as well as long-lived hydrodynamic variables. Our principle result is a fundamental derivation of the elusive reactive coupling λ (Ref. [6]) between the director field \mathbf{n} and the velocity field \mathbf{v}

$$\frac{\partial n_\mu}{\partial t} = [\delta_{\mu\nu} - n_\mu n_\nu] \left\{ \frac{1+\lambda}{2} n_\gamma \partial_\gamma v_\nu - \frac{1-\lambda}{2} n_\gamma \partial_\nu v_\gamma \right\}. \quad (1.1)$$

Unlike most parameters in hydrodynamics λ is neither set by

Kubo formulas nor the fluctuation-dissipation theorem. We will show that to the order we work, our result agrees with the analysis of Archer and Larson [7], which is based upon a phenomenological, Landau-theory dynamics [8]. Thus our result both verifies the validity of both a microscopic and a phenomenological approach.

As is typical of the former approach, we develop our theory in steps. First, we identify the hydrodynamic variables. In a polymer nematic system we have four fields of interest: the areal polymer density $\rho(\mathbf{x})$, the momentum density $\mathbf{g}(\mathbf{x})$, the fluctuation of the nematic director $\delta\tilde{\mathbf{n}}(\mathbf{x}) = \mathbf{n}(\mathbf{x}) - \mathbf{n}_0$, and the density of polymer ‘‘heads’’ and ‘‘tails,’’ $\rho_{HT}(\mathbf{x})$. We then write these fields in terms of the positions and momenta of the individual monomers. We consider, as an example, the areal density field $\rho(\mathbf{x})$. Since the polymers are directed, we may write the location of the α th polymer in terms of an affine parameter τ_α , which marks the monomers:

$$\mathbf{R}_\alpha(\tau_\alpha) = [r_\alpha^x(z) + \tau_\alpha h_\alpha^x, r_\alpha^y(z) + \tau_\alpha h_\alpha^y, \tau_\alpha + s_\alpha], \quad (1.2)$$

where $\vec{r}_\alpha(z)$ is the (two-dimensional) displacement of the monomer at height $z = \tau_\alpha + s_\alpha$ away from the ground state, straight-line configuration with the two-dimensional tangent \vec{h}_α and the polymers start at a height $z = s_\alpha$. The expression for the areal density is

$$\rho(\mathbf{x}) = \sum_\alpha \delta^2[\vec{r}_\alpha(z) + (z - s_\alpha)\vec{h}_\alpha - \mathbf{x}_\perp] \Theta[z - s_\alpha] \Theta[e_\alpha - z], \quad (1.3)$$

where e_α is the height of the polymer end. This expression requires further explanation and, at the same time, shows the inherent complexity of this problem. The areal density is a sum of delta functions in the plane at the positions of the polymers. Moreover, since these polymers have heads and tails the product of Heaviside step functions $\Theta(\cdot)$ counts the polymer only if we consider heights between the start and end of the polymer at $z = s_\alpha$ and $z = e_\alpha$, respectively. We will investigate similar expressions for the remaining fields in the next section.

We note here that although expressions such as Eq. (1.2) are awkward, similar expressions could not easily be formed

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in isotropic polymer systems. The essential feature of polymer nematics is that chain contour length corresponds to the common z axis along which all the polymers are more or less aligned. This allows us to formulate our theory in space, so as to incorporate hydrodynamics, while at the same time including the microscopic polymer degrees of freedom. These degrees of freedom are accounted for via the Poisson brackets of the $\vec{r}_\alpha(z)$ with the conjugate momentum $\vec{p}_\alpha(z)$. From these, we can generate the Poisson brackets of the hydrodynamic fields: if we can get a closed set of brackets then we can construct a consistent hydrodynamic theory. However, we see that the areal density (1.3) not only depends on $\vec{r}_\alpha(z)$ but also on the location of the polymer heads and tails as well as the average polymer tangent \vec{h}_α . The head and tail locations are accounted for via the field $\rho_{HT}(\mathbf{x})$ described above. What do we do with the average polymer tangent \vec{h}_α ? Though the nematic phase has two Nambu-Goldstone modes associated with spontaneously broken rotational invariance, there is, in addition, a massive mode, the Maier-Saupe order parameter S , which measures the degree of nematic ordering. The \vec{h}_α are associated with this mode. The order parameter can change locally via changes in the local polymer alignment. Presumably, if the polymers are entangled, the time scale for these rearrangements corresponds to some sort of reptation time required for the release of topological constraints. On the other hand, if the polymers are short (unentangled) then there is a separation of time scales, which allows us to approximately decouple the local Maier-Saupe mode. In both these limits, we can decouple these tilt modes from the monomer modes. This will allow us to preaverage the tilt modes to arrive at effective Poisson brackets for the remaining fields.

The next step in our formulation of dynamics requires a coarse-grained free energy in terms of our macroscopic variables. In Sec. III, we will propose a free energy consistent with the symmetries of the system, which also includes the equilibrium physics of the polymer ends. From this, we will derive dynamical equations for the hydrodynamic variables.

II. DEFINITION OF HYDRODYNAMIC VARIABLES

We start by formulating the theory in terms of microscopic, directed trajectories of the individual polymers, $\{\vec{r}_\alpha(z)\}$, where α labels the polymer and $\vec{r}(z)$ is the displacement of the polymer from its equilibrium position. Recall that the nematic state is characterized by the Maier-Saupe order parameter,

$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}, \quad (2.1)$$

where $\langle \cdot \rangle$ denotes a thermal, ensemble average, and θ is the angle between the nematic director and the ordering axis (taken throughout to be \hat{z}). When $S \neq 1$, the directors do not all line up along \hat{z} . Since the nematic order parameter is set by the details of the isotropic-nematic transition, it is a massive, nonhydrodynamic mode. In order to take into account the ground-state value of S we will assume that the equilibrium polymer trajectory is $\mathbf{R}_\alpha(z) = [(z - s_\alpha)h_\alpha^x, (z - s_\alpha)h_\alpha^y, z]$ and that $\langle \vec{r}_\alpha(z) \rangle = 0$. Thus, the microscopic di-

rector is $d\vec{r}/dz + \vec{h}$. Finally, the μ component of the momentum of polymer α at z is $p_\alpha^\mu(z)$.

Unlike previous formulations [9], we do not consider the traceless symmetric tensor Q_{ij} typically used for nematics. Rather, deep in the nematic state, we are only concentrating on the two Goldstone modes of the broken rotational symmetry. As we shall see, this leads to a closed set of Poisson brackets to lowest order in derivatives and the director fluctuation $\delta\vec{n}$. We will incorporate the ‘‘up-down’’ symmetry of nematics via the symmetry of the free energy, just as is done in the usual equilibrium description of nematics in terms of the unit-vector director field $\hat{\mathbf{n}}$.

A. Canonical variables and separation of time scales

While our description of the chain locations is adequate in terms of $\vec{r}_\alpha(z)$ and \vec{h}_α , we should take care in finding correct canonical variables from which to construct macroscopic Poisson brackets. We imagine starting with a Hamiltonian that is a function the actual polymer location $\mathbf{R}_\alpha(\tau_\alpha)$, as in Eq. (1.2), and the conjugate momentum $\mathbf{p}_\alpha(\tau_\alpha)$. The equations of motion in the x - y plane are

$$\dot{p}_\alpha^i(\tau_\alpha) = -\frac{\delta H}{\delta R_\alpha^i(\tau_\alpha)} \quad \dot{R}^i(\tau_\alpha) = \frac{\delta H}{\delta p_\alpha^i(\tau_\alpha)}. \quad (2.2)$$

If \vec{h}_α is constant then these equations of motion are precisely

$$\begin{aligned} \dot{p}_\alpha^i(z) &= \{p_\alpha^i(z), H\} \\ \dot{r}_\alpha^i(z) &= \{r_\alpha^i(z), H\} \end{aligned} \quad (2.3)$$

with

$$\{r_\alpha^i(z), r_\beta^j(z')\} = \{p_\alpha^i(z), p_\beta^j(z')\} = 0, \quad (2.4)$$

and

$$\{r_\alpha^i(z), p_\beta^j(z')\} = \delta_{\alpha\beta} \delta^{ij} \delta(z - z'), \quad (2.5)$$

where i and j run over the x - y plane. We have made the identification $\mathbf{p}_\alpha(z) = \mathbf{p}_\alpha(\tau_\alpha)$ with $z = \tau_\alpha + s_\alpha$. We must also calculate the Poisson bracket of $p_\alpha^z(z)$ with the spatial coordinate. Motion along the z axis should be accounted for in motion of the polymer ends. Indeed, motion of the monomers up or down depends only on the motion of the starting point s_α . Thus,

$$\{r_\alpha^i(z), p_\beta^z(z')\} = 0 \quad (2.6)$$

but

$$\{z_\alpha, p_\beta^z(z')\} = \delta_{\alpha\beta} \delta(z_\alpha - z'), \quad (2.7)$$

where we use the symbol z_α to remind the reader that the commutator does not vanish only for momenta and positions on the same polymer. In other words, z_α takes the place of the z component of $\vec{r}_i(z)$ and $z_\alpha = s_\alpha + \tau_\alpha$. We remind the reader that the fact that the affine parameter τ can be mapped one-to-one with the coordinate height z is precisely the sim-

plification, which we are exploiting. Of course, when we consider hydrodynamic variables, z_α will just become the height coordinate z .

We must now justify our neglect of the dynamics of \vec{h}_α . As we discussed in the Introduction, we can do this in two limits. One limit is when the chains are long and highly entangled. In this case we expect that rearrangements of the nematic texture require topological constraint release or, in other words, reptation. We are concentrating here on dynamics on time scales shorter than the reptation time. We could extend this work by including some sort of reptation-based dynamics for the tilt fields \vec{h}_α , thus incorporating both hydrodynamics and topological constraints in the same theory.

There is another limit of interest. If the polymers are short, we expect that the modes associated with the Maier-Saupe order parameter will be the slowest to relax to an equilibrium distribution. In this case, we expect that on the intermediate time scales we are focusing on, the distribution of \vec{h}_α will also be static, but consistent with the background nematic order. In this case, the tilt modes can be averaged over, thus explicitly removing the dependence of the fields on them. We contrast this average to a thermodynamic average: in this case, the average is over an ensemble of different frozen-in textures while in thermodynamics we take the time average of a single molecule. In both these cases we get the same mean-square average of the tilt field, though the correlations will differ.

Thus, in both the very long polymer and short polymer case we can preaverage the tilt degrees of freedom.

B. Macroscopic fields

We must first define the coarse-grained, macroscopic fields, namely the mass density, the director and the momentum density. The mass density is given by

$$\rho(\mathbf{x}) = \sum_{\alpha} \delta^2[\vec{r}_\alpha(z) + (z - s_\alpha)\vec{h}_\alpha - \mathbf{x}_\perp] \Theta[z - s_\alpha] \Theta[e_\alpha - z]. \quad (2.8a)$$

As described in the Introduction, the terms in the sum come from the following considerations: (1) The Dirac delta function ‘‘counts’’ the areal mass (note that it is a two-dimensional delta function, defined in the xy plane). (2) The pair of Heaviside step functions ($\Theta[\cdot]$) control the polymer lengths. The α th polymer begins at $z = s_\alpha$ and ends at $z = e_\alpha$.

The remaining macroscopic fields are defined via

$$\begin{aligned} [\rho \delta n^i](\mathbf{x}) &= \sum_{\alpha} \left[\frac{dr_{\alpha}^i(z)}{dz} + h_{\alpha}^i \right] \delta^2[\vec{r}_\alpha(z) + (z - s_\alpha)\vec{h}_\alpha - \vec{x}_\perp] \\ &\quad \times \frac{\Theta[z - s_\alpha] \Theta[e_\alpha - z]}{\sqrt{1 + \vec{h}_\alpha^2}} \end{aligned} \quad (2.8b)$$

$$\begin{aligned} g^\mu(\mathbf{x}) &= \sum_{\alpha} p_{\alpha}^{\mu}(z) \delta^2[\vec{r}_\alpha(z) + \vec{h}_\alpha(z - s_\alpha) - \vec{x}_\perp] \\ &\quad \times \Theta[z - s_\alpha] \Theta[e_\alpha - z]. \end{aligned} \quad (2.8c)$$

Note that an additional factor of $(1 + \vec{h}_\alpha^2)^{-1/2}$ arises in the definition of $\delta \vec{n}(\mathbf{x})$ since the normalized unit (average) tangent vector is

$$\mathbf{T}_\alpha = \frac{[h_{\alpha}^x, h_{\alpha}^y, 1]}{\sqrt{1 + \vec{h}_\alpha^2}}. \quad (2.9)$$

Note that the naive definitions of the macroscopic fields, e.g.,

$$\rho(\mathbf{x}) = \sum_{\alpha} \delta^2[\vec{r}_\alpha - \vec{x}_\perp] \Theta[z - s_\alpha] \Theta[e_\alpha - z], \quad (2.10)$$

applies only when $\vec{h}_\alpha \equiv \vec{0}$, or, in other words, when the nematic ground state has Maier-Saupe order parameter, $S = 1$.

III. PREAVERAGING THE NEMATIC TEXTURE

As we discussed in the Introduction, the Poisson brackets of the hydrodynamic fields cannot close since they all depend on the average polymer tilt \vec{h}_α . As discussed in the preceding, we would like to preaverage over these degrees of freedom to arrive at Poisson brackets for the hydrodynamic fields. This procedure can be justified in two limiting cases.

Consider the dynamics of a single polymer of length L . This can be decomposed into normal modes a la Rouse or Zimm [8]. In either case the n th mode has wave number $q_n = 2\pi n/L$ with a relaxation frequency $\omega_n \propto n^2/L^2$. For very short polymers the separation in time scales between the lowest mode $n = 1$ and the other modes is large. In this limit, we can decouple the longest mode—the tilt mode—characterized by \vec{h} . We could thus average the tilts over the collection of polymers. The mean square of the tilt fields is simply related to the Maier-Saupe order parameter S . We make the distinction between the time average of a single polymer’s tilt field which gives equilibrium statistics and the quenched average over the frozen polymer tilts.

As we imagine lengthening the polymers, the splitting in time scales becomes less pronounced and their spectrum becomes continuous. However, when the polymer is sufficiently long, a new dynamics dominates the longest wave-number modes: reptation dynamics. In this regime, the tilt modes can only relax via activated reptation [10], which is an especially apt description of the likely rearrangements in polymer nematics. Thus, when the polymer is long enough to be entangled we also have a large separation of time scales. As a result, in this limit, we may also treat the polymer tilt field as essentially frozen.

We have now two distinct averages: the first is an average over a massive degree of freedom that sets the value of S . In the present formulation, this average is over \vec{h}_α . The second average is the thermal average over fluctuations about the ground state, i.e. averages over $\vec{r}_\alpha(z)$. We will treat these two averages separately, which amounts to treating the average over \vec{h}_α as a quenched average. To connect with the Maier-Saupe order parameter, we have

$$S = \frac{3}{2} \left(\frac{1}{1 + \overline{h_\alpha^2}} \right) - \frac{1}{2}, \quad (3.1)$$

since $\cos \theta$ in Eq. (2.1) is just the z component of the average tangent vector and where we have denoted the quenched average of X by \bar{X} . Expanding for small $|\vec{h}_\alpha|$, we have $\frac{2}{3}(1 - S) \approx \overline{h_\alpha^2}$. We will then take averages over \vec{h}_α weighted by

$$P(\vec{h}_\alpha) = \frac{1}{2\pi\Delta} e^{-|\vec{h}_\alpha|^2/2\Delta}, \quad (3.2)$$

where $\Delta = \frac{1}{3}(1 - S)$ so that Eq. (3.1) is satisfied.

In order to find the average macroscopic field variables, we must regularize the Dirac delta functions appearing in Eq. (28). To do this we represent them as Gaussians with the widths taken to be the excluded area of each polymer in a fixed z plane. We define

$$\delta^2(\vec{r}; a) = \frac{1}{2\pi a} e^{-|\vec{r}|^2/2a}. \quad (3.3)$$

Then, when we average over \vec{h}_α weighting by Eq. (3.2) we find

$$\overline{\delta^2[\vec{r}_\alpha(z) + (z - s_\alpha)\vec{h}_\alpha - \mathbf{x}_\perp; a]} = \delta^2[\vec{r}_\alpha(z) - \mathbf{x}_\perp; a + \Delta(z - s_\alpha)^2]. \quad (3.4)$$

We can thus calculate the tilt-averaged fields. Since we have only included terms for the tangent vector in Eq. (2.8b) to leading order in \vec{h}_α , we calculate average field values to order Δ

$$\bar{\rho}(\mathbf{x}) = \sum_\alpha \delta^2[\vec{r}_\alpha(z) - \mathbf{x}_\perp; a + \Delta(z - s_\alpha)^2] \Xi_\alpha(z) \quad (3.5a)$$

$$\begin{aligned} [\bar{\rho} \bar{\delta} n^i](\mathbf{x}) &= \sum_\alpha (1 - \Delta) \frac{dr_\alpha^i(z)}{dz} \delta^2[\vec{r}_\alpha(z) - \vec{x}_\perp; a \\ &+ \Delta(z - s_\alpha)^2] \Xi_\alpha(z) - \sum_\alpha (z - s_\alpha) \Delta \partial_i \\ &\times \delta^2[\vec{r}_\alpha(z) - \vec{x}_\perp; a + \Delta(z - s_\alpha)^2] \Xi_\alpha(z) \end{aligned} \quad (3.5b)$$

$$\bar{g}^\mu(\mathbf{x}) = \sum_\alpha p_\alpha^\mu(z) \delta^2[\vec{r}_\alpha(z) - \vec{x}_\perp; a + \Delta(z - s_\alpha)^2] \Xi_\alpha(z), \quad (3.5c)$$

where $\Xi_\alpha(z) \equiv \Theta[z - s_\alpha] \Theta[e_\alpha - z]$.

The breakdown of local dynamics

Typically, Poisson brackets for dynamical variables are of the form

$$\{\rho(x), \bar{g}^i(x')\} = -\vec{\nabla}_x[\rho(x) \delta^3(x - x')]. \quad (3.6)$$

The presence of the delta-function in Eq. (3.6) along with a local free energy density leads to local dynamics [11], i.e., every term in the dynamical equations is evaluated at the same point in space and time. Such a result must, of course, be taken with a grain of salt. The delta function is an idealization to a system composed of pointlike constituents. In reality, these delta functions should be replaced with a smeared-out distribution. Usually, this presents no problem—calculations may be done with the smeared-out distribution and the limit may be taken at the end. However, this is not the case in this situation.

From Eq. (3.4), it is easy to see that we may only replace the disorder smeared delta functions with the original distributions (of width a) when $a \gg \Delta(z - s_\alpha)^2$. In other words, it is only when the original width is wider than the disorder-averaged width that the distributions are delta-function like. Since the presence of the term $\Theta[z - s_\alpha] \Theta[e_\alpha - z]$ in the expressions for the hydrodynamic variables limits the maximum value of z , we have $\Delta(z - s_\alpha)^2 < \Delta(e_\alpha - s_\alpha)^2 = \Delta \ell^2$, where ℓ is the typical polymer length. Thus, we see that the original distributions are recovered everywhere whenever $\ell \sqrt{\overline{h^2}} \equiv \ell \sqrt{\Delta} \ll a$. This is easy to interpret; when the average wandering of the polymer away from its starting point, $\ell \sqrt{\Delta}$ is smaller than the interpolymer spacing, we may continue to treat the polymers and their interactions as local. Once the polymers have tipped out of their cages the dynamics will become, necessarily, nonlocal. A force at \mathbf{x} leads to a reaction at \mathbf{x}' if a *single* polymer can go from \mathbf{x} to \mathbf{x}' . Presumably, the typical polymer length ℓ should be replaced by ℓ_p , the polymer persistence length, when $\ell > \ell_p$ and the locality condition becomes $\Delta \ell_p^2 \ll a^2$.

In this delocalized regime the formalism will break down. In particular, the Poisson brackets of the coarse-grained fields, calculated in terms of Eqs. (2.6) and (2.7) will be straightforward but complicated, and will necessarily lead to non-local dynamics, *even if the free-energy density arises from local interactions*. In the Conclusion, we will discuss possible alternatives to a nonlocal formalism based on different sets of variables.

IV. FLUCTUATING HYDRODYNAMICS

We can, however, consider the case of $\Delta \ll 1$. This could arise in the description of flux lines in superconductors or polymer nematics in applied fields where the ground-state polymer configurations are almost always parallel to \hat{z} . In any of these limits, it is appropriate to replace the spread out delta functions $\delta^2[\cdot; a + \Delta(z - s)^2]$ with pointlike delta functions. In this case, we can calculate the Poisson brackets of the average fields in terms of the canonical, microscopic brackets. We find the following, nonzero brackets, to lowest order in derivatives [of both $\vec{r}_\alpha(z)$ and delta functions] and δn :

$$\begin{aligned} \{\bar{\rho}(\mathbf{x}), \bar{g}^\mu(\mathbf{x}')\} &= -[\delta_\nu^\mu - \delta_z^\mu \delta_\nu^z] \partial_x^\nu [\rho(\mathbf{x}) \delta^3(\vec{x} - \vec{x}')] \\ &+ (1 + \Delta) \delta_z^\mu \{\rho_{HT}(\mathbf{x}) \delta^3(\vec{x} - \vec{x}') \\ &- \partial_i [\rho \delta n^i(\mathbf{x}) \delta^3(\vec{x} - \vec{x}')]\} \end{aligned} \quad (4.1a)$$

$$\begin{aligned} \{\bar{\delta}n^i(\mathbf{x}), \bar{g}^\mu(\mathbf{x}')\} = & -[\delta_\nu^\mu - \delta_z^\mu \delta_\nu^z] \delta^3(\vec{x} - \vec{x}') \partial_x^\nu \delta n^i(\mathbf{x}) \\ & + [(1 - \Delta) \delta^{i\mu} \delta_x^\mu - \Delta \delta^{\mu z} \delta_x^z] \delta^3(\vec{x} - \vec{x}') \end{aligned} \quad (4.1b)$$

$$\begin{aligned} \{\bar{g}^\mu(\mathbf{x}), \bar{g}^\nu(\mathbf{x}')\} = & -\partial_x^\nu [g^\mu(\mathbf{x}) \delta^3(\vec{x} - \vec{x}')] \\ & + \partial_x^\mu [g^\nu(\mathbf{x}') \delta^3(\vec{x} - \vec{x}')]. \end{aligned} \quad (4.1c)$$

We have been forced to introduce an additional hydrodynamic field, $\rho_{HT}(\mathbf{x})$, the density of polymer heads and tails, defined as

$$\begin{aligned} \rho_{HT}(\mathbf{x}) \equiv & \sum_\alpha (1 - \Delta) \{ \delta^2[\vec{r}_\alpha(s_\alpha) - \vec{x}_\perp] \delta(z - s_\alpha) \\ & - \delta^2[\vec{r}_\alpha(e_\alpha) - \vec{x}_\perp] \delta(e_\alpha - z) \}. \end{aligned} \quad (4.2)$$

Note that the second term in Eq. (4.1a) is exactly equal to $\partial_z \bar{\rho}(\mathbf{x})$. In other words, we have

$$(1 - \Delta) \partial_z \bar{\rho}(\mathbf{x}) + \partial_i [\bar{\rho} \delta \bar{n}_i(\mathbf{x})] = \rho_{HT}(\mathbf{x}). \quad (4.3)$$

This constraint is the familiar constraint of line liquids [12,13], which conserves polymer number but for polymer ends. The prefactor of $(1 - \Delta)$ comes from the average over the z direction. In other words, the rotationally invariant conservation law is $\vec{n}_0 \cdot \nabla \rho + \nabla \cdot \vec{n} = \rho_{HT}$. When averaging over the intrinsic randomness of \vec{n}_0 , we get a factor of $(1 - \Delta)$ in front of $\partial_z \rho$. It is not present in other terms because they are higher order in derivatives and powers of $\delta \vec{n}$.

A. Equations of motion

With these Poisson brackets we can systematically derive the reactive terms of hydrodynamics. The viscosities will appear in accord with the symmetries of the system. Being uniaxial there will be five viscosities [14], characterized by the viscous stress tensor $V_{\alpha\beta} = \eta_{\alpha\beta\gamma\beta} A_{\gamma\beta}$, where

$$\begin{aligned} \eta_{\mu\nu\gamma\beta} = & \eta_1 [n_\mu n_\nu n_\gamma n_\beta] + \eta_2 [\delta_{\mu\gamma}^\perp \delta_{\nu\beta}^\perp + \delta_{\mu\beta}^\perp \delta_{\nu\gamma}^\perp - \delta_{\mu\nu}^\perp \delta_{\gamma\beta}^\perp] \\ & + \eta_4 [\delta_{\mu\nu}^\perp \delta_{\gamma\beta}^\perp] + \eta_3 [n_\mu n_\gamma \delta_{\nu\beta}^\perp + n_\nu n_\gamma \delta_{\mu\beta}^\perp + n_\mu n_\beta \delta_{\nu\gamma}^\perp \\ & + n_\nu n_\gamma \delta_{\mu\beta}^\perp] + \eta_5 [\delta_{\mu\nu}^\perp n_\gamma n_\beta + n_\mu n_\nu \delta_{\gamma\beta}^\perp], \end{aligned} \quad (4.4)$$

where $\delta_{\mu\nu}^\perp = \delta_{\mu\nu} - n_\mu n_\nu$. The form of V is fixed by symmetries: by nematic inversion it must be even in \vec{n} and by the Kubo formulas [5] it must be symmetric under $\mu \leftrightarrow \nu$, $\gamma \leftrightarrow \beta$ and $(\mu\nu) \leftrightarrow (\gamma\beta)$, and $A_{\gamma\beta} = \frac{1}{2} (\partial_\gamma v_\beta + \partial_\beta v_\gamma)$ is the strain rate tensor constructed out of the fluid velocity \vec{v} . Expanding $\vec{n} = \hat{z} + \delta \vec{n}$ we can find the viscosity tensor in the nematic phase.

The free energy from which we will derive the reactive terms is:

$$F' = \int d^3x \left\{ \frac{\vec{g}^2}{2\rho} + F_{\text{equil}} \right\}, \quad (4.5)$$

where the equilibrium free energy is the sum of terms

$$F_{\text{equil}} = F_{\delta \vec{n}} + F_{\text{pol}} \quad (4.6)$$

and

$$F_{\delta \vec{n}} = \int d^3x \left\{ \frac{K_1}{2} (\nabla \cdot \delta \vec{n})^2 + \frac{K_2}{2} (\nabla \times \delta \vec{n})^2 + \frac{K_3}{2} (\partial_z \delta \vec{n})^2 \right\} \quad (4.7)$$

is the usual Frank free energy for a nematic, while

$$F_{\text{pol}} = \int d^3x \left\{ \frac{B}{2} \delta \rho^2 + \frac{G}{2} [\partial_z \delta \rho + \rho_0 \nabla \cdot \delta \vec{n}]^2 \right\} \quad (4.8)$$

is the free energy of the polymer [2]. In Eq. (4.8), B is the two-dimensional bulk modulus, $\rho_0 = \rho - \delta \rho$ is the average, areal polymer density, and G is the fugacity for hairpins and free ends. We have replaced ρ_{HT} with the expression in Eq. (4.3), to lowest order in the field fluctuations $\delta \rho$ and $\delta \vec{n}$ [which is why we drop the factor of $(1 - \Delta)$ in front of $\partial_z \delta \rho$]. The parameter G is given by $G = k_B T \ell / 2 \rho_0$ where ℓ is the typical polymer length [2]. Terms of the form $\delta \rho \nabla \cdot \delta \vec{n}$ are not allowed due to the $\vec{n} \rightarrow -\vec{n}$ symmetry of the nematic phase.

We are now able to derive the equations of motion for \vec{g} , $\delta \vec{n}$, and $\delta \rho$ (where we have dropped the bar over the variables denoting the \vec{h} average). They are (with $\vec{v} = \vec{g}/\rho$)

$$\partial_t \rho = -\partial_i g_i + (1 + \Delta) \rho_{HT} v_z - \partial_i (\delta n_i g_z) \quad (4.9a)$$

$$\partial_t \delta n_i = -\partial_j (v_j \delta n_i) + (1 - \Delta) \partial_z v_i - \Delta \partial_i v_z - \Gamma \frac{\delta F[\delta n_i]}{\delta (\delta n_i)} + \theta_i \quad (4.9b)$$

$$\begin{aligned} \partial_t g_\mu = & -\partial_\nu \left(\frac{g_\mu g_\nu}{\rho} \right) + [\delta_\nu^\mu - \delta_z^\mu \delta_\nu^z] \rho \partial_\nu \left(\frac{\delta F[\rho]}{\delta \rho} \right) \\ & + \partial_\alpha V_{\alpha\mu} + \xi_\mu, \end{aligned} \quad (4.9c)$$

where, in order to approach thermodynamic equilibrium, the noise terms $\xi_i(\vec{x}, t)$ and $\theta_i(\vec{x}, t)$ have the following correlations [15]:

$$\langle \xi_\mu(\vec{x}, t) \xi_\beta(\vec{x}', t') \rangle = 2k_B T \eta_{\mu\nu\gamma\beta} \partial_\nu \partial_\gamma \delta^3(\vec{x} - \vec{x}') \delta(t - t'). \quad (4.10a)$$

$$\langle \theta_\mu(\vec{x}, t) \theta_\nu(\vec{x}', t') \rangle = 2k_B T \Gamma \delta_{\mu\nu}^\perp \delta^3(\vec{x} - \vec{x}') \delta(t - t') \quad (4.10b)$$

$$\langle \xi_\mu(\vec{x}, t) \theta_\nu(\vec{x}', t') \rangle = 0. \quad (4.10c)$$

There are a number of features of these equations worth mention. First, we see that the typical polymer lengths come into the equations through the coupling G , present in the equations for $\partial_t \delta n_i$ and $\partial_t g_\mu$. When G is large, corresponding to long polymers, we may take the density, $\rho_{HT} = 0$. In the short molecule limit, presumably $G \approx 0$. There is a crossover wavevector $k_c = \sqrt{2B\rho_0^3/(k_B T \ell)}$ below which the system behaves as a pure nematic and above which the length of the polymers becomes important. There is a corresponding time scale $\omega_c \propto k_c^2 \sim 1/\ell$, which delineates a similar short-to-long crossover.

In the short-polymer limit, care must be taken due to the nature of the approximation under which the Poisson brackets were derived. In particular, since we treat the polymer tangent field as a vector, we are, in principle, distinguishing \vec{n} and $-\vec{n}$. However, for small fluctuations around equilibrium, long polymer nematics should not sample the entire space of fluctuations: it is very unlikely that an entire polymer will rotate by π around the x or y axis. This simplification is what enabled us to get a closed set of Poisson brackets order by order in a derivative expansion. The effect of hairpins could be put in explicitly through the introduction of a hairpin-density field [2].

B. Reactive couplings in the nematodynamic limit

Finally, we note that Eq. (4.9b) gives an expression for the elusive reactive parameter λ [5] in nematodynamics. By rotational invariance, $\vec{n} \rightarrow -\vec{n}$ and the constraint $\vec{n}^2 = 1$, the reactive part of the equation of motion for \vec{n} has the form

$$\frac{dn_\mu}{dt} = \delta_{\mu\nu}^\perp \left[\frac{1+\lambda}{2} n_\gamma \partial_\gamma v_\nu - \frac{1-\lambda}{2} n_\gamma \partial_\nu v_\gamma \right]. \quad (4.11)$$

We can thus identify

$$\lambda = 1 - 2\Delta = \frac{1+2S}{3}. \quad (4.12)$$

This is in general agreement with the results of Forster [6] who calculated the value of λ within a Poisson bracket formalism for $Q_{\mu\nu}$ the symmetric, traceless order parameter for short molecule nematic liquid crystals [14]. He found that

$$\lambda = \frac{1+2\alpha S}{3}, \quad (4.13)$$

where $\alpha = (I_l + 2I_t)/(I_l - I_t)$ is a parameter depending on the moments of inertia I_l and I_t of the nematogens parallel and perpendicular to the nematic axis, respectively. We thus recover Forster's result when $\alpha = 1$ or, in other words, when the aspect ratio I_l/I_t of the nematogens becomes infinite. Presumably, this is a consequence of taking delta-function densities in the transverse plane.

It is interesting to compare this result to the work of Archer and Larson [7]. In the same limit of infinite aspect ratio, they found an expression for λ in terms of the expectations of the second- and fourth-rank order parameters, $\langle P_2 \rangle \equiv S$ and $\langle P_4 \rangle$, where P_2 and P_4 are the second and fourth Legendre polynomials evaluated at $x = \cos \theta$:

$$\lambda = \frac{15\langle P_2 \rangle + 48\langle P_4 \rangle + 42}{105\langle P_2 \rangle}. \quad (4.14)$$

To be consistent, we should expand Eq. (4.14) in powers of $\Delta = (1-S)/3$ to compare with Eq. (4.12) and compare linear terms. First, to linear order in Δ ,

$$\langle \cos^4 \theta \rangle = 1 - 2\langle \tilde{h}_\alpha^2 \rangle \approx (1 - \langle \tilde{h}_\alpha^2 \rangle)^2 \approx \langle \cos^2 \theta \rangle^2 \quad (4.15)$$

and so $\langle P_4 \rangle \approx (35S^2 - 10S - 7)/18$, which gives

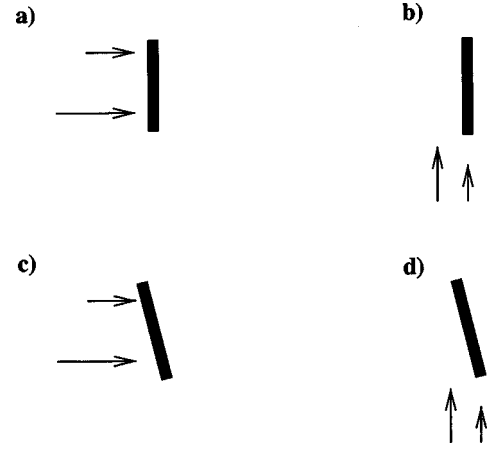


FIG. 1. Velocity fields and nematic directors with various gradients and molecular orientations. (a) and (c) gradient in the z direction of v_\perp . This will rotate the director for all values of S . (b) and (d) gradient in the x direction of v_z . Only in (d) will this rotate the molecule, i.e., when $S < 1$.

$$\lambda = 1 + \frac{2}{3}(S-1) + \frac{2}{9}(S-1)^2 + \dots \quad (4.16)$$

Thus, to leading order in $(S-1) = 3\Delta$ Eq. (4.14) agrees with Eq. (4.12). Thus, within the $S \approx 1$ limit our result should be consistent with the data as in Ref. [7]. We note, moreover, that since the isotropic-to-nematic phase transition is first order, S does not grow continuously from 0. Indeed, in Maier-Saupe theory $S \approx 0.44$ at this transition [14], and thus $\Delta \approx 0.2$. Therefore the deviation between our result and the more exact result (4.14) should be small sufficiently well aligned samples. However, although Eq. (4.12) may be quantitatively reasonable, it misses an essential qualitative feature: it is always less than 1 and thus predicts that nematics will always tumble.

Though the linear result in Δ fails to predict the crossover from flow aligning to tumbling behavior, the virtue of our derivation of λ is that we get a direct interpretation of its origin. In a highly aligned sample with $S = 1$ only gradients of v_\perp along the z direction can lead to rotations of the molecule (see Fig. 1). On the other hand, when $S < 1$, gradients in the x direction of v_z can also rotate the molecules and so the polymer nematics would always be in a tumbling mode. A higher order analysis in powers of Δ would be required to see if a $\lambda > 1$ could come from our direct approach.

V. CONCLUSIONS

In summary, we have derived the Poisson brackets of the relevant degrees of freedom for a polymer nematic. We have shown that these canonical brackets become highly nonlocal when the polymers start to overlap. In the limit where the polymers do not overlap, we have presented a microscopic derivation of the reactive coupling λ , a coupling which is not a long-wavelength limit of a correlation function.

Our analysis requires a ‘‘locality condition’’ in order to be trustworthy. While this may appear restrictive, one might imagine that, at some level of coarse graining the polymers, the no overlap condition might be met. If we were to clump polymer regions correlated in the xy plane together and

coarse grain to the scale of this “entanglement correlation length” ξ_e , our analysis may be applicable. Our analysis is *especially* applicable to flux lines in superconductors. There, $\rho_{HT} \equiv 0$ and there is no problem, even in principle, to considering the flux line tangents as vectors. The flux lines, in addition, have $\Delta = 0$, simplifying the theory further. It is perhaps in this context that one could hope to make the most theoretical progress.

This derivation has shown the inherent, unavoidable non-locality in polymer nematic dynamics. An interesting possibility is to focus on a different set of conserved or almost conserved variables. For instance, it may be possible to reformulate this dynamics in terms of an entanglement density by calculating the Hopf density [16], a scalar that measures the local curvature of the director configuration—for long polymers curvature is a measure of local entanglement. This

density could be used as a starting point for a phenomenological theory of “entanglement dynamics.” Another variable of interest might be the repton density, which measures length per unit length [17]. It may be possible to develop a hydrodynamics for this field as well [18].

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