Symmetries of the Doi kinetic theory for nematic polymers of arbitrary aspect ratio: At rest and in linear flows

M. Gregory Forest and Ruhai Zhou
Department of Mathematics, University of North Carolina, Chapel Hill, North Carolina 27599

Qi Wang
Department of Mathematics, Florida State University, Tallahassee, Florida 32306

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The Doi theory has successfully modeled the monodomain shear flow problem for rigid, rodlike nematic polymers. Numerical simulations of the Smoluchowski equation for the orientational probability distribution function (PDF) predict monodomain attractors in regions of nematic concentration N and shear rate $\dot{\gamma}$. Theoretical work has focused on approximate constructions of PDF solutions in linear flow regimes. Here we develop a collection of simple observations, expressed by symmetries of the Smoluchowski equation, which imply global properties that all PDF solutions must obey. The well-known orientational degeneracy of quiescent nematics is a continuous O(3) symmetry. In simple shear, a discrete reflection symmetry survives that is evident in recent numerical simulations and implies bistability of out-of-plane attractors; and rodlike and discotic nematic liquids of reciprocal aspect ratio respond identically up to a fixed rotation of the PDF. Finally, we show the orientational effects due to varying molecular aspect ratio in any linear flow are equivalent to varying the straining component of the flow field.

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I. INTRODUCTION

Numerical simulations, largely based on spherical harmonic expansion [1–10], have been instrumental in establishing agreement between experimental phenomena of nematic polymers and the Doi kinetic theory [11–18] for flowing polymeric liquid crystals. Most notably, monodomain attracting states and their transitions versus shear rate have been correlated with rheological features of sign changes in normal stress differences and structural changes in apparent viscosity and shear stress. These correlations with experiment rely first and foremost on accurate simulation of the Smoluchowski equation for the molecular orientational probability distribution function, and then on the identification of those solutions with monodomain steady or transient states. For example, the logrolling and kayaking solutions, whose major director, respectively, aligns with or oscillates around the vorticity axis in simple shear, were first exhibited with kinetic theory simulations in the early 1990s [2,4]. Attracting out-of-plane states that either align or oscillate *strictly between* the vorticity axis and shearing plane have only recently been discovered [7,8].

The final step in relating theory to experiment, once the phase diagram of attracting states is established, is to evaluate constitutive laws for rheological properties along each stable solution branch. *The brunt of the difficulty therefore lies in the accurate computation* of the full flow-phase diagram of all individual monodomain attractors, their classification as steady or unsteady, stable or unstable, the multiplicity (continuous or discrete) of solution branches, and their transitions (i.e., bifurcations) that may occur by varying shear rate, or strength of the nematic potential (usually modeled as a concentration parameter), or other recent model parameters included in the extended Doi kinetic theory such as molecular aspect ratio (cf. Ref. [19]).

Renewed interest in monodomain dynamics of rigid macromolecular fluids is compelled by recent detailed kinetic theory simulations of Faraoni *et al.* [7] and Grosso *et al.* [8]. These studies reveal striking *kinetic theory phenomena*, as well as clarify previously reported results, in the monodomain response of rigid thin rods to simple shear: (1) A discrete number of stable and unstable solution branches for each fixed shear rate; (2) various bifurcations among these branches, including a period-doubling route to chaotic dynamics in a window of intermediate shear rates for a narrow range of nematic concentration; and (3) a reflection symmetry of out-of-plane states (both steady and periodic) which leads, among other properties, to parameter regimes of bistable orientational response.

From the theory of dynamical systems, one knows that *global features*, i.e., properties of the entire phase space of solutions, are often associated with symmetries. In Ref. [20] the authors developed a collection of symmetries shared by several mesoscopic tensor models, i.e., properties those were apparently robust to closure approximation. These observations are generalized now to the kinetic theory.

II. THE EXTENDED DOI KINETIC THEORY

We first recall the kinetic theory for homogeneous nematic liquids relevant for our purposes [19]. Let $f(\mathbf{m},t)$ be the probability distribution function (PDF) corresponding to the probability that the axis of revolution of the molecule is parallel to direction $\mathbf{m}$ ($\|\mathbf{m}\|=1$) at time t, where the lcp molecule is modeled as an axisymmetric ellipsoid of aspect ratio r (length of the molecule symmetry axis divided by the ra-

dius of the transverse circular cross section). The fluid velocity is denoted by **v**. The Smoluchowski (kinetic) equation for $f(\mathbf{m},t)$ is given by (e.g., [12,21,19])

$$\frac{\partial f}{\partial t}=D_r(a)\boldsymbol{\mathcal{R}}\cdot\left[\left(\boldsymbol{\mathcal{R}}f+\frac{1}{kT}f\boldsymbol{\mathcal{R}}V_{\mathrm{MS}}\right)\right]-\boldsymbol{\mathcal{R}}\cdot[\mathbf{m}\times\dot{\mathbf{m}}f], \tag{1}$$

where $\partial/\partial\mathbf{x}=\boldsymbol{\nabla}$ and $\boldsymbol{\mathcal{R}}=\mathbf{m}\times\partial/\partial\mathbf{m}$ are the spatial and the rotational gradient operator, respectively,

$$\dot{\mathbf{m}}=\boldsymbol{\Omega}\cdot\mathbf{m}+a[\mathbf{D}\cdot\mathbf{m}-\mathbf{D}:\mathbf{mmm}] \tag{2}$$

is the Jeffery orbit of axisymmetric ellipsoidal molecules [22], **D** and $\boldsymbol{\Omega}$ are the rate of strain and vorticity tensors, respectively, defined by

$$\mathbf{D}=\tfrac{1}{2}(\boldsymbol{\nabla}\mathbf{v}+\boldsymbol{\nabla}\mathbf{v}^T),\quad \boldsymbol{\Omega}=\tfrac{1}{2}(\boldsymbol{\nabla}\mathbf{v}-\boldsymbol{\nabla}\mathbf{v}^T), \tag{3}$$

$-1\leqslant a\leqslant 1$ is the molecular shape parameter related to the aspect ratio r by

$$a=\frac{r^2-1}{r^2+1}. \tag{4}$$

The coefficient D_r is an averaged rotary diffusivity, taken to be constant to make contact with [7,8]; an orientation-dependent rotary diffusivity will not change the symmetry properties developed below, but will affect the phase diagram in the simple flows discussed herein; k is the Boltzmann constant, T is the absolute temperature, and V_{MS} is the Maier-Saupe intermolecular potential with strength proportional to the *dimensionless polymer concentration N*,

$$V_{\mathrm{MS}}=-\frac{3NkT}{2}\langle\mathbf{mm}\rangle:\mathbf{mm}. \tag{5}$$

Here

$$\langle(\cdot)\rangle=\int_{\|\mathbf{m}\|=1}(\cdot)f(\mathbf{m},t)d\mathbf{m}. \tag{6}$$

The average, or mesoscopic, molecular orientation is traditionally defined in terms of the second moment of f, **M**, or its traceless equivalent **Q**, the *mesoscopic orientation tensor*,

$$\mathbf{M}=\langle\mathbf{mm}\rangle,\quad \mathbf{Q}=\mathbf{M}-\frac{\mathbf{I}}{3}. \tag{7}$$

These equations, coupled with momentum, mass, and energy balance equations, constitute the extended Doi theory for finite-aspect-ratio nematic fluids. For *isothermal, linear flow fields*, these conservation laws are satisfied identically, and the full system ''simplifies'' to the homogeneous kinetic equation (1).

III. A COLLECTION OF OBSERVATIONS

A. Orientational degeneracy in hydrodynamic equilibrium

Without flow, the kinetic equation (1) reduces to

$$\frac{\partial f}{\partial t}=D_r(a)\boldsymbol{\mathcal{R}}\cdot\left[\left(\boldsymbol{\mathcal{R}}f+\frac{1}{kT}f\boldsymbol{\mathcal{R}}V_{\mathrm{MS}}\right)\right]. \tag{8}$$

Let $\mathbf{U}\in\mathrm{O}(3)$ denotes any orthogonal transformation acting on the configuration space (the sphere S^2) of **m** (see Ref. [23]). We now state the basic fact that is inherent in the seminal works of Onsager [24], Landau [25], de Gennes and Prost [26], Hess [27], and Doi [11].

Orientational degeneracy of quiescent nematic liquids. Every anisotropic solution of Eq. (8) generates a continuous family of solutions parametrized by the group O(3) of orthogonal transformations. That is, every anisotropic solution $f(\mathbf{m},t)$ of Eq. (8), for arbitrary initial data $f(\mathbf{m},t=0)\neq 1/4\pi$, generates an entire O(3) group of solutions, $f(\mathbf{U}\cdot\mathbf{m},t)$, where $\mathbf{U}\in\mathrm{O}(3)$. The isotropic equilibrium $f\equiv 1/4\pi$ is isolated, i.e., a fixed point of the symmetry.

We give a proof to illustrate the generality of potentials for which it holds. First, rewrite Eq. (8) into the form

$$\begin{aligned}\frac{\partial f}{\partial t}&=D_r(a)\boldsymbol{\mathcal{R}}\cdot\left(\boldsymbol{\mathcal{R}}f+\frac{1}{kT}f\boldsymbol{\mathcal{R}}V_{\mathrm{MS}}\right)\\&=D_r(a)\frac{\partial}{\partial\mathbf{m}}\cdot\left[\frac{\partial}{\partial\mathbf{m}}f+\frac{1}{kT}f\frac{\partial}{\partial\mathbf{m}}V_{\mathrm{MS}}\right].\end{aligned} \tag{9}$$

Consider a general class of intermolecular potentials V,

$$V(\mathbf{m},f(\cdot,t))=\int_{\|\mathbf{m}'\|=1}h(\mathbf{m},\mathbf{m}')f(\mathbf{m}',t)d\mathbf{m}', \tag{10}$$

where $h(\mathbf{m},\mathbf{m}')$ is a geometric expression for the excluded volume that must (on physical grounds) satisfy a basic duality relation,

$$h(\mathbf{m},\mathbf{U}^T\cdot\mathbf{m}')=h(\mathbf{U}\cdot\mathbf{m},\mathbf{m}'). \tag{11}$$

This class of potentials, and the symmetry property, includes Maier-Saupe and Onsager potentials as special cases,

$$\begin{aligned}h_{\mathrm{MS}}&=-\tfrac{3}{2}NkT(\mathbf{m}\cdot\mathbf{m}')^2,\\h_O&=\beta NkT\|\mathbf{m}\times\mathbf{m}'\|,\end{aligned} \tag{12}$$

where N is a strength parameter associated with a dimensionless molecular concentration, and β is a parameter proportional to the volume of the molecule. The symmetry (11) states that the excluded-volume potential cannot give the difference if one rotates **m** relative to **m**′ or vice versa. This property applies to any aspect-ratio molecular fluid for which a distinguished molecule axis is specified.

For any orthogonal transformation **U**, an explicit calculation shows that

$$\frac{\partial}{\partial\mathbf{m}}f(\mathbf{U}\cdot\mathbf{m},t)=\mathbf{U}^T\cdot\frac{\partial}{\partial\mathbf{n}}f(\mathbf{n},t), \tag{13}$$

where

$$\mathbf{n}=\mathbf{U}\cdot\mathbf{m}. \tag{14}$$

It then follows that

$$\frac{\partial}{\partial\mathbf{m}}\cdot\frac{\partial}{\partial\mathbf{m}}f(\mathbf{U}\cdot\mathbf{m},t)=\frac{\partial}{\partial\mathbf{n}}\cdot\frac{\partial}{\partial\mathbf{n}}f(\mathbf{n},t). \tag{15}$$

With $f_U(\mathbf{m},t)=f(\mathbf{U}\cdot\mathbf{m},t)$, the intermolecular potential has the property

$$\begin{aligned}V(\mathbf{m},f_U(\cdot,t))&=\int_{\|\mathbf{m}'\|=1}h(\mathbf{m},\mathbf{m}')f(\mathbf{U}\cdot\mathbf{m}',t)d\mathbf{m}'\\&=\int_{\|\mathbf{n}'\|=1}h(\mathbf{m},\mathbf{U}^T\cdot\mathbf{n}')f(\mathbf{n}',t)d\mathbf{n}'\\&=\int_{\|\mathbf{n}'\|=1}h(\mathbf{U}\cdot\mathbf{m},\mathbf{n}')f(\mathbf{n}',t)d\mathbf{n}'\\&=V(\mathbf{n},f(\cdot,t)).\end{aligned} \tag{16}$$

It follows that

$$\begin{aligned}&\frac{\partial}{\partial\mathbf{m}}\cdot\frac{\partial}{\partial\mathbf{m}}V(\mathbf{m},f_U(\cdot,t))=\frac{\partial}{\partial\mathbf{n}}\cdot\frac{\partial}{\partial\mathbf{n}}V(\mathbf{n},f(\cdot,t)),\\&\frac{\partial}{\partial\mathbf{m}}f(\mathbf{U}\cdot\mathbf{m}',t)\cdot\frac{\partial}{\partial\mathbf{m}}V(\mathbf{U}\cdot\mathbf{m},f_U(\cdot,t))\\&\quad=\frac{\partial}{\partial\mathbf{n}}f(\mathbf{n},t)\cdot\frac{\partial}{\partial\mathbf{n}}V(\mathbf{n},f(\cdot,t)).\end{aligned} \tag{17}$$

Combining Eqs. (15), (16), and (17), we have

$$\begin{aligned}\frac{\partial}{\partial t}f_U(\mathbf{m},t)&=D_r(a)\boldsymbol{\mathcal{R}}\cdot\left[\boldsymbol{\mathcal{R}}f_U+\frac{1}{kT}f_U\boldsymbol{\mathcal{R}}V(\mathbf{m},f_U(\cdot,t))\right]\\&=D_r(a)\frac{\partial}{\partial\mathbf{m}}\cdot\left[\frac{\partial}{\partial\mathbf{m}}f_U+\frac{1}{kT}f_U\frac{\partial}{\partial\mathbf{m}}V(\mathbf{m},f_U(\cdot,t))\right],\end{aligned} \tag{18}$$

or equivalently,

$$\begin{aligned}\frac{\partial}{\partial t}f(\mathbf{n},t)&=D_r(a)\frac{\partial}{\partial\mathbf{n}}\cdot\left[\frac{\partial}{\partial\mathbf{n}}f+\frac{1}{kT}f\frac{\partial}{\partial\mathbf{n}}V(\mathbf{n},f(\cdot,t))\right]\\&=D_r(a)\boldsymbol{\mathcal{R}}_\mathbf{n}\cdot\left[\boldsymbol{\mathcal{R}}_\mathbf{n}f+\frac{1}{kT}f\boldsymbol{\mathcal{R}}_\mathbf{n}V(\mathbf{n},f(\cdot,t))\right],\end{aligned} \tag{19}$$

where $\boldsymbol{\mathcal{R}}_\mathbf{n}=\mathbf{n}\times\partial/\partial\mathbf{n}$. Thus, if $f(\mathbf{m},t)$ satisfies Eq. (8), so does $f_U(\mathbf{m},t)$.

The set of equilibrium solutions of Eq. (8) versus nematic concentration N comprises the isotropic-to-nematic phase transition diagram; refer to Refs. [7,28,8]. The two anisotropic solution branches, $f^+(\mathbf{m})$, $f^-(\mathbf{m})$, which exist for sufficiently large N, each correspond to a continuous O(3) group of equilibria, $f^+(\mathbf{U}\cdot\mathbf{m})$, $f^-(\mathbf{U}\cdot\mathbf{m})$, for $\mathbf{U}\in\mathrm{O}(3)$. This rotational symmetry is the fundamental mechanism that Onsager [24], Landau [25] and de Gennes and Prost [26] use to deduce that the *I-N* transition has to be of first order [26].

We emphasize these symmetries give *a priori* control of the ''most probable directions'' of orientation of the quiescent nematic equilibria, f^+ (stable), f^- (unstable). The peak direction of $f^{+,-}$ coincides with the ''major director'' defined in terms of the second-moment **Q**-tensor projection of f. That is, if two PDF $f_{1,2}$ are related by the symmetry $f_1(\mathbf{m})=f_2(\mathbf{U}\cdot\mathbf{m})$, then their second-moment projections $\mathbf{Q}_{1,2}$ automatically satisfy $\mathbf{Q}_1=\mathbf{U}^T\cdot\mathbf{Q}_2\cdot\mathbf{U}$, which reproduces the mesoscopic form of the symmetry [20]. In numerical simulations at nematic concentrations past the *I-N* transition, a random initial distribution $f(\mathbf{m},t=0)$ will converge numerically to one element of the O(3) degenerate solution f^+, from which one can deduce the Euler angles of the ''major director.'' But the inverse problem, where one prescribes the Euler angles of the asymptotic equilibrium distribution, i.e., where one prescribes the specific element $\mathbf{U}\in\mathrm{O}(3)$, is only solved with symmetries.

The construction proceeds as follows. We first borrow a result from the following section, Eq. (32), which characterizes ''in-plane orientation'' at the kinetic equation level of the PDF f, and which preserves the ''in-plane'' definition based on the **Q**-tensor projection of f. This symmetry allows us to initialize random *in-plane, biaxial initial distributions* $f_{\mathrm{ip}}(\mathbf{m},0)$; by the group symmetry, every such orbit is guaranteed to remain in-plane, and therefore all such anisotropic initial data are in the stable manifold of an in-plane nematic equilibrium $f^+_{\mathrm{ip}}(\mathbf{m})$. (Prior to flow, there are infinitely many invariant planes, but we select the *x-y* plane to be consistent with subsequent developments in planar shear, where this is the unique invariant plane.) We first choose biaxial initial data for Fig. 1 whose major director aligns with the z axis, and therefore the distribution converges to the unique uniaxial in-plane distribution peaked along the z axis. We emphasize the PDF must remain peaked along the z axis for all time, *by the symmetry*. Figure 1 plots the projection of this orbit onto the order parameters of the **Q** tensor (equivalently **M**); the directors are not shown, since they are passive during the evolution. Next we rotate the initial data out-of-plane, $f_{\mathrm{op}}(\mathbf{m},0)=f_{\mathrm{ip}}(\mathbf{U}\cdot\mathbf{m},0)$ with the specific choice

$$\mathbf{U}=\begin{pmatrix}\frac{\sqrt{3}}{3}&\frac{\sqrt{3}}{3}&\frac{\sqrt{3}}{3}\\0&\frac{\sqrt{2}}{2}&-\frac{\sqrt{2}}{2}\\-\frac{2\sqrt{6}}{6}&\frac{\sqrt{6}}{6}&\frac{\sqrt{6}}{6}\end{pmatrix}. \tag{20}$$

The numerical integration of this data, by the symmetry, has to agree at all times with the **U** transformation of the in-plane PDF solution. Therefore, the orbit is guaranteed *a priori* to converge to the distribution $f^+(\mathbf{U}\mathbf{m})$. This is confirmed numerically, and offers a good benchmark on the code and visualization routines. Since f_{op} and f_{ip} have **Q** tensor projections related by $\mathbf{Q}_{\mathrm{op}}(t)=\mathbf{U}^T\cdot\mathbf{Q}_{\mathrm{ip}}(t)\cdot\mathbf{U}$ for all time, we are

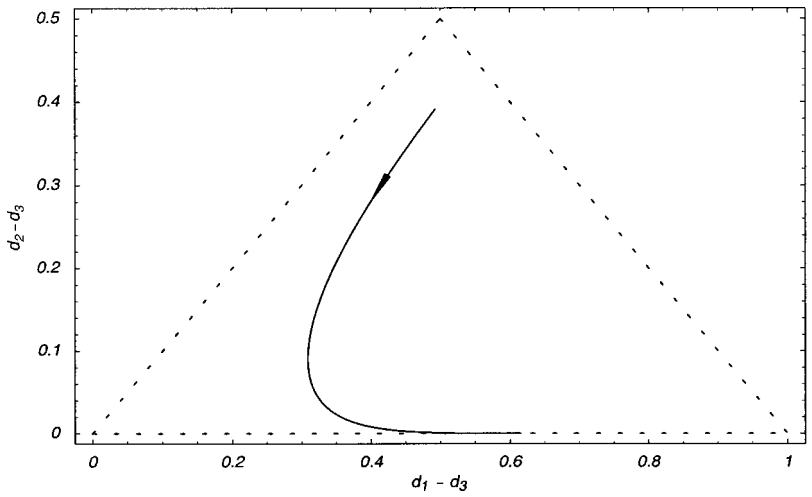

FIG. 1. Orientational symmetry of orbits in the stable manifold of the nematic equilibrium f^+. Fix the strength $N=5$ of the Maier-Saupe potential which is above the *I-N* transition. Two orbits $f_{1,2}(\mathbf{m},t)$ of the Smoluchowski equation without flow (8) are numerically computed; the initial data $f_1(\mathbf{m},0)$ is *in-plane*, defined by Eq. (32) for the *x-y* plane, whereas $f_2(\mathbf{m},0)=f_1(\mathbf{U}\cdot\mathbf{m},0)$ is an *out-of-plane rotation* of f_1 for $\mathbf{U}$ given in Eq. (20). These orbits converge to equilibrium distributions, and orientational symmetry implies $f_2(\mathbf{m},t)=f_1(\mathbf{U}\cdot\mathbf{m},t)$ for all time, which we do not enforce but rather confirm by numerical integration. Each orbit is projected onto the second-moment tensor $\mathbf{M}_{1,2}(t)$, which according to orientational symmetry must be related by a similarity transformation by $\mathbf{U}$, Eq. (20), $\mathbf{M}_2(t)=\mathbf{U}^T\cdot\mathbf{M}_1(t)\cdot\mathbf{U}$. Since eigenvalues are invariant under orthogonal similarity transformations, we can illustrate the symmetry by showing that the eigenvalues of each second-moment are identical during the entire evolution. The eigenvalues are ordered $1\geqslant d_1\geqslant d_2\geqslant d_3\geqslant 0$. Indeed, the curves lie on top of one another, and converge to the *uniaxial* distributions with $d_2=d_3$. Any other $\mathbf{U}\in O(3)$ results in the same curve, illustrating O(3) degeneracy of every orbit of Eq. (8), and likewise the nematic equilibrium f^+.

guaranteed by the O(3) symmetry of Eq. (8) that the eigenvectors are initially transformed by $\mathbf{U}$ and do not vary in time, whereas the eigenvalues (order parameters) of each $\mathbf{Q}$ tensor evolve identically for all time (Fig. 1).

We now recall essential ingredients of Galerkin expansions for the Smoluchowski equation and the projection formula for the second-moment tensor. The spherical harmonic expansion for f [2,4,7,8] is

$$f(\mathbf{m},t)\approx\sum_{l=0}^{L}\sum_{m=-l}^{l}a_{l,m}(t)Y_l^m(\theta,\phi), \tag{21}$$

where Y_l^m are complex spherical harmonic basis functions [29],

$$Y_l^m=P_l^m(\cos\theta)e^{im\phi}, \tag{22}$$

where P_l^m are Legendre polynomials, θ, ϕ are spherical coordinates with θ being the polar angle and ϕ being the latitude angle, and L is the order of truncation in the Galerkin approximation.

In the Appendix, we give an explicit form (48) of the dynamical system for the amplitudes $a_{l,m}(t)$ which results from the above expansion for f in the Smoluchowski equation with and without an imposed linear flow field. These equations are not new; this form is used to prove the flow-nematic kinetic symmetries.

The three amplitudes $a_{2,0}, a_{2,1}, a_{2,2}$ uniquely specify the second-moment tensor $\mathbf{Q}$,

$$Q_{xx}=-\frac{2}{3}\sqrt{\frac{\pi}{5}}a_{2,0}+\sqrt{\frac{8\pi}{15}}\mathrm{Re}(a_{2,2}), \tag{23}$$

$$Q_{yy}=-\frac{2}{3}\sqrt{\frac{\pi}{5}}a_{2,0}-\sqrt{\frac{8\pi}{15}}\mathrm{Re}(a_{2,2}), \tag{24}$$

$$Q_{xy}=-\sqrt{\frac{8\pi}{15}}\mathrm{Im}(a_{2,2}), \tag{25}$$

$$Q_{xx}=-\sqrt{\frac{8\pi}{15}}\mathrm{Re}(a_{2,1}), \tag{26}$$

$$Q_{yz}=\sqrt{\frac{8\pi}{15}}\mathrm{Im}(a_{2,1}), \tag{27}$$

where, $\mathrm{Re}(\cdot)$ and $\mathrm{Im}(\cdot)$ represent the real and the imaginary part, respectively.

The amplitudes $a_{l,m}(t)$ of f are equivalent to the moments of the distribution f; one way to recover a continuous (without flow) or discrete (with flow) symmetry from the moment equations is through a transformation on the space of solutions which maps orbits of the dynamical system $a_{l,m}(t)$ onto new orbits. All discrete flow symmetries are described below in this way.

B. Mirror symmetry of all out-of-plane responses to simple shear

In this section we specialize the linear velocity field in Eq. (1) to simple shear with arbitrary shear rate $\dot{\gamma}$, represented in standard Cartesian coordinates,

$$\mathbf{v}=\dot{\gamma}(y,0,0). \tag{28}$$

In Ref. [20], we prove that the preclosure form of the mesoscopic Doi theory admits a reflection symmetry: any orbit $\mathbf{Q}(t)$ of the mesoscopic theory generates another orbit symmetric about the shearing plane. A constructive algorithm is given: retain the same values of in-plane components, $Q_{xx}, Q_{xy}, Q_{yy}, Q_{zz}$, and reverse the sign of both out-of-plane components, Q_{xz}, Q_{yz}. Any out-of-plane solution will generate a solution that is distinct pointwise in time; if the entire orbit is not symmetric with respect to the vorticity axis, then the solutions are distinct. Logrolling and classical kayaking orbits that rotate around the vorticity axis are mapped to themselves, and therefore are unique. This discrete reflection symmetry is compactly represented in terms of a similarity transformation of the mesoscopic tensor $\mathbf{Q}(t)$, employing the planar reflection transformation $\mathbf{V}_2$,

$$\mathbf{V}_2^T \cdot \mathbf{Q}(t) \cdot \mathbf{V}_2, \tag{29}$$

where the Cartesian representation of reflection through the (x,y) plane is

$$\mathbf{V}_2 = \mathrm{diag}(1,1,-1). \tag{30}$$

These two formulations of shear-induced mirror symmetry are now generalized to the Smoluchowski equation (1) with imposed shear flow (28).

Reflection symmetry in terms of the spherical harmonic expansion of the orientational distribution function f. Every solution $f(\mathbf{m},t)$ of Eq. (1) has spherical harmonic amplitudes $a_{l,m}(t)$, which generate another PDF solution $f^{\mathrm{sym}}(\mathbf{m},t)$ with amplitudes

$$(-1)^m a_{l,m}(t). \tag{31}$$

Moreover, the orientational distributions f and f^{sym} are mirror symmetric with respect to the shearing plane, generalizing the mesoscopic symmetry (29).

In-plane configurations remain in-plane for all time. We define an in-plane subspace of orientational distribution functions by the infinite set of conditions which generalize the $\mathbf{Q}$ tensor in-plane conditions $Q_{xz} = Q_{yz} = 0$,

$$a_{l,m} = 0 \quad \text{for all } m \text{ odd}. \tag{32}$$

The entire in-plane subspace is invariant under the flow of the Smoluchowski equation (1).

All in-plane orbits $f(\mathbf{m},t)$ are mapped to themself by this symmetry. Invariance of this subspace further implies in-plane orientational configurations cannot become out-of-plane, nor can any out-of plane configurations become in-plane, in finite time. Out-of-plane orbits whose major director does not align with the vorticity axis nor rotate about the vorticity axis must remain tilted to one side of the shearing plane. Explicit examples include branches of out-of-plane steady and periodic states identified in Ref. [7], which they explicitly show to occur in mirror-symmetric pairs. This symmetry explains their observations, but also implies *every orbit in the stable and unstable manifolds of every solution, in-plane or out-of-plane, has a mirror-symmetric orbit.* Figure 2 illustrates the reflection symmetry in simple shear. Figure 2(a) illustrates two mirror-symmetric orbits for a fixed shear rate and nematic concentration; the equator in this figure is the shear plane and the north pole is the vorticity axis. The orbit in the northern hemisphere converges to a ''tilted, out-of-plane periodic'' attractor, shown in Fig. 2(b). Each orbit and attractor are mirrored by another numerical solution generated either by reflecting the initial data through the shearing plane and solving for *f*, or applying the symmetry to the entire northern hemisphere orbit. Here, the PDF *f* is projected onto the second-moment tensor, from which the major director is extracted at each time step.

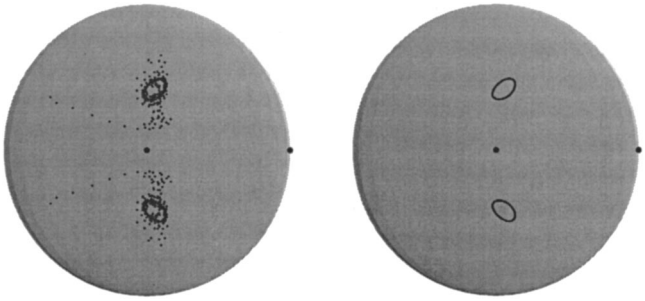

FIG. 2. Reflection-symmetric, out-of-plane, periodic solutions of the shear-driven Smoluchowski equation (1) for infinite-aspect-ratio, rodlike macromolecules ($a=1$), nematic concentration $N=5.5$, and normalized shear rate $\mathrm{Pe}=6$. The primary director of the $\mathbf{Q}$-tensor projection of $f(\mathbf{m},t)$ is shown for each attracting monodomain state, illustrating discrete mirror symmetry with respect to the shearing plane. The equator corresponds to the shear plane; the central dot represents the flow direction (x) and the edge dot represents the flow gradient direction (y). These symmetric attractors, reported in Ref. [7], may be viewed as either ''tilted kayaking orbits'' or ''out-of-plane wagging orbits.'' The right figure shows the attractor. The left figure shows the orbit that converges to this attractor from a pair of arbitrarily chosen out-of-plane initial data, related only by Eq. (31). The data is recorded from every 15th time step.

Other consequences for the dynamics of monodomains follow. For example, if a tumbling or wagging in-plane orbit is the unique attractor, then out-of-plane orbits converge symmetrically from both sides of the shearing plane; a similar phenomenon occurs for convergence to steady in-plane attractors. Likewise, many in-plane solutions are unstable to out-of-plane perturbations; their unstable manifolds are mirror symmetric. We note that the PDF solutions identified with the logrolling steady state (whose major director aligns with the vorticity axis) and the classical Larson-Ottinger kayaking orbit (whose major director rotates around the vorticity axis) are *mapped onto themselves by this symmetry*; therefore such monodomain attractors are isolated and do not occur in pairs.

Another proof of the mirror-reflection symmetry (31) is gained by fixing the coordinate representation of the PDF *f* in the Smoluchowski equation (1); afterwards we apply the reflection transformation, for which the equation remains invariant. We write this result in terms of any finite-aspect-ratio fluid with molecular geometry parameter *a*, a fixed shear flow (28), and a corresponding solution *f* of the kinetic equation (1). We note that

$$\mathbf{V}_2\cdot\mathbf{v}_{\rm shear}=\mathbf{v}_{\rm shear},\quad \mathbf{V}_2\cdot\boldsymbol{\Omega}\cdot\mathbf{V}_2^T=\boldsymbol{\Omega},\quad \mathbf{V}_2\cdot\mathbf{D}\cdot\mathbf{V}_2^T=\mathbf{D}. \tag{33}$$

So, the time evolution of $\mathbf{n}=\mathbf{V}_2\cdot\mathbf{m}$ obeys Eq. (2) and

$$\begin{aligned}\boldsymbol{\mathcal{R}}\cdot(\mathbf{m}\times\dot{\mathbf{m}}f_{\mathbf{V}_2}(\mathbf{m},t))&=\frac{\partial}{\partial\mathbf{m}}\cdot(\dot{\mathbf{m}}f_{\mathbf{V}_2}(\mathbf{m},t))=\frac{\partial}{\partial\mathbf{n}}\cdot(\dot{\mathbf{n}}f(\mathbf{n},t))\\&=\boldsymbol{\mathcal{R}}_{\mathbf{n}}\cdot[\mathbf{n}\times\dot{\mathbf{n}}f(\mathbf{n},t)].\end{aligned} \tag{34}$$

The flow-independent part follows from our proof of the orientational degeneracy in equilibrium. Thus, we have established a transformation between solutions of the two Smoluchowski equations defined by the triples

$$(a,\mathbf{v}_{\rm shear},f),\quad (a,\mathbf{V}_2\cdot\mathbf{v}_{\rm shear},f_{\mathbf{V}_2}). \tag{35}$$

C. Orientational equivalence between rodlike and discotic nematic fluids in simple shear, for finite and infinite aspect ratios

We now establish a remarkable equivalence in the shear response of nematic liquids with reciprocal aspect ratios r and $1/r$. This result was previously established in Ref. [20] for tensor models, which we recall. The $\mathbf{Q}_r$ tensor (the subscript labels aspect ratio r) response to simple shear at fixed nematic concentration N for rods ($r>1$) generates the orientational response at the same shear rate and concentration for a discotic liquid of aspect ratio $1/r$. Indeed they are related by the explicit transformation

$$\mathbf{Q}_{r^{-1}}=\mathbf{V}_{\pm}^T\cdot\mathbf{Q}_r\cdot\mathbf{V}_{\pm}, \tag{36}$$

where $\mathbf{V}_{\pm}$ is a pure clockwise $(-)$ counterclockwise $(+)$ rotation by $\pi/2$ rad. in the shearing plane that fixes the vorticity axis,

$$\mathbf{V}_+=\begin{pmatrix}0&1&0\\-1&0&0\\0&0&1\end{pmatrix},\quad \mathbf{V}_-=\mathbf{V}_+^T. \tag{37}$$

All mesoscopic orientational responses of rodlike and discotic liquids in simple shear are related by this 1:1 correspondence. We now extend this result to kinetic theory. Recall the molecular geometry parameter in Eq. (1), $a=(r^2-1)/(r^2+1)$, where r is the molecular aspect ratio. Thus, r and $1/r$ correspond to a and $-a$, which appears parametrically in Eq. (1).

Rod-discotic correspondence in simple shear. Fix any shear rate $\dot\gamma$ and nematic concentration N; rodlike (discotic) liquids are parametrized by positive (negative)-aspect-ratio parameter $|a|$ $(-|a|)$. Each solution $f_{|a|}(\mathbf{m},t)$ of the Smoluchowski equation (1) for arbitrary initial data $f(\mathbf{m},t=0)$ has the spherical harmonic expansion (21) with a unique set of amplitude functions $a^+_{l,m}(t)$. Transform the initial data and corresponding PDF solution as follows:

$$\begin{aligned}a^-_{l,m}(0)&=i^m a^+_{l,m}(0),\quad i=\sqrt{-1},\\ a^-_{l,m}(t)&=i^m a^+_{l,m}(t).\end{aligned} \tag{38}$$

From these data, construct the distribution function $f_{-|a|}(\mathbf{m},t)$ by the spherical harmonic expansion (21). Then, $f_{-|a|}$ is a solution of Eq. (1) for fluids with aspect-ratio parameter $-|a|$ and initial data $f(\mathbf{m},0)$ defined by $a^-_{l,m}(0)$.

To prove that this symmetry maps all solutions of Eq. (1) for aspect ratio r to solutions for aspect ratio $1/r$, it is a routine calculation to verify the following symmetry of the dynamical system for the amplitudes $a_{l,m}$ given in the Appendix. With $i=\sqrt{-1}$,

$$F^j_{l,m}=i^m F^j_{l,m},\quad l=2,4,...,\quad -l\leqslant m\leqslant l \tag{39}$$

for $j=1,2,3$ under the above transformation (38). We remark that the corresponding result for mesoscopic tensor models [20] is far easier to discover and prove, from which this symmetry was found.

If one iterates this transformation, then individual solutions $f(\mathbf{m},t)$ are mapped to themselves if they are in-plane, but to their mirror symmetry through the shear plane if they are out-of-plane.

In Fig. 3 we illustrate this symmetry by plotting all solution branches, stable and unstable, of the Smoluchowski equation (1) for all aspect-ratio parameters $a\in[-1,+1]$, at a particular fixed concentration N and fixed shear rate Pe. We graph the projection of all solutions f onto second-moment $\mathbf{Q}$-tensor components, as noted in the caption. Note that the above symmetry implies $a_{2,0}$, which is proportional to the in-plane component Q_{zz}, is an even function of a; $\mathrm{Re}(a_{2,2})$, which is proportional to the in-plane quantity $Q_{xx}-Q_{yy}$, is an odd function of a; the out-of-plane components $\mathrm{Re}(a_{2,1})$ and $\mathrm{Im}(a_{2,1})$, which are proportional to Q_{xz} and Q_{yz}, respectively, are mapped onto one another by the symmetry, i.e., $Q_{xz}(-a)=Q_{yz}(a)$. These symmetries are evident in Fig. 3. Since periodic solutions are represented by a pointwise statistic (maximum value of the indicated component over one period), the odd symmetry of $\mathrm{Re}(a_{22})$ is not evident for the periodic branches in Fig. 3(b).

There is another formulation of the rod-discotic symmetry. A one-to-one correspondence exists between the orientational distribution functions f for two nematic liquids of aspect-ratio parameters a and $-a$. This transformation can be formulated in the following way. The Smoluchowski equation (1) is uniquely specified by a triple $(a,\mathbf{v},f)$, where a is the molecular geometry parameter, $\mathbf{v}$ is a linear flow, and f is the PDF for fixed N, Pe. Let

$$\mathbf{n}=\mathbf{V}_{\pm}\cdot\mathbf{m}. \tag{40}$$

We note the following properties of the rotational transformations:

$$\mathbf{V}_{\pm}\cdot\boldsymbol{\Omega}\cdot\mathbf{V}_{\pm}^T=\boldsymbol{\Omega},\quad \mathbf{V}_{\pm}\cdot\mathbf{D}\cdot\mathbf{V}_{\pm}^T=-\mathbf{D}. \tag{41}$$

It then follows from Eq. (2) that *for simple shear* (28)

$$\dot{\mathbf{n}}=\boldsymbol{\Omega}\cdot\mathbf{n}-a[\mathbf{D}\cdot\mathbf{n}-\mathbf{D}:\mathbf{nnn}], \tag{42}$$

so the Jeffery molecular orbit equation for $\mathbf{n}$ is recovered if we replace a by $-a$, i.e., the Jeffery orbit is invariant under the transformation $(a,\mathbf{m})\rightarrow(-a,\mathbf{n}=\mathbf{V}_{\pm}\cdot\mathbf{m})$. The result fol-

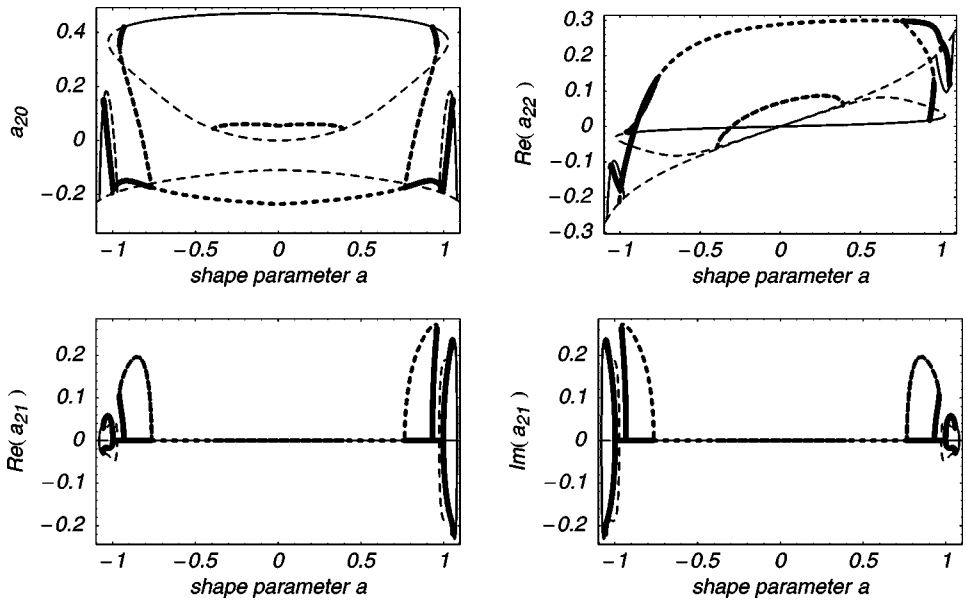

FIG. 3. Illustration of the rod-discotic symmetry of monodomain orientational distributions for nematic liquids in simple shear. All stable and unstable solution branches are depicted for $a \in [-1,1]$, equivalently $r \in [-\infty,+\infty]$, for the Smoluchowski equation (1) with fixed nematic concentration $N=6$, and relatively strong normalized shear rate $\mathrm{Pe}=8.5$. Four spherical harmonic amplitude components are plotted, which correspond to the projection of the orientational distribution f onto the second-moment tensor, as seen from Eq. (27): the in-plane components $a_{2,0}$ (proportional to Q_{zz}) and $\mathrm{Re}(a_{2,2})$ (proportional to $Q_{xx}-Q_{yy}$), and the out-of-plane components $\mathrm{Re}(a_{2,1})$ (proportional to Q_{xz}) and $\mathrm{Im}(a_{2,1})$ (proportional to Q_{yz}). The solid thin line indicates a stable steady solution; the dashed thin line indicates an unstable steady solution branch; the solid thick line indicates stable periodic solutions; the dashed thick line indicates unstable periodic solutions. For periodic solutions, the maximum value of the indicated quantity is given, which breaks the perfect odd symmetry of $\mathrm{Re}(a_{22})$ in the top right graph. The figures illustrate: a_{20} is an even function of a; $\mathrm{Re}(a_{22})$ is an odd function of a; and $\mathrm{Re}(a_{21})$ for a maps onto $\mathrm{Im}(a_{21})$ for $-a$.

lows from Eqs. (15)–(17) and (34). Thus, we establish the one-to-one correspondence between the Smoluchowski equations, and therefore between all solutions,

$$(a,\mathbf{v}_{\mathrm{shear}},f)\rightarrow(-a,\mathbf{V}_{\pm}\cdot\mathbf{v}_{\mathrm{shear}},f_{\mathbf{V}_{\pm}}). \tag{43}$$

As illustrated in Fig. 3, all phase transitions (bifurcations versus N or Pe), all stable and unstable, steady or transient, monodomain states occur simultaneously for rods and discotics of reciprocal aspect ratios. We caution that the constitutive stress equaiton does not preserve this symmetry, since Miesowicz viscosities and elasticity constants vary greatly between rodlike and discotic nematic polymers [19]. Therefore, this one-to-one correspondence is for the orientational, homogeneous response to imposed shear. The rheological response and subsequent structure formation do not share this correspondence.

D. One-to-one correspondence between different aspect-ratio fluids in related linear flows

We again note that the Smoluchowski equation (1) defines a "triple": $(a,\mathbf{v},f(\mathbf{m},t))$. Consider an arbitrary *linear flow* decomposed into symmetric and antisymmetric parts,

$$\mathbf{v}=(\boldsymbol{\Omega}+\mathbf{D})\cdot\mathbf{x}. \tag{44}$$

We observe from Eq. (1) that the rate-of-strain tensor $\mathbf{D}$ and geometry parameter a enter linearly and only through their product. This fact underlies symmetries of the system (1) which we describe in terms of the triple defined above,

$$(a,\mathbf{v},f)\rightarrow(1,(\boldsymbol{\Omega}+a\mathbf{D})\cdot\mathbf{x},f), \tag{45}$$

$$(a,\mathbf{v},f)\rightarrow(-1,(\boldsymbol{\Omega}-a\mathbf{D})\cdot\mathbf{x},f), \tag{46}$$

$$(a_1,\mathbf{v},f)\rightarrow\left(a_2,\left(\boldsymbol{\Omega}+\frac{a_1}{a_2}\mathbf{D}\right)\cdot\mathbf{x},f\right). \tag{47}$$

The first two symmetries imply an *identical monodomain* response f of: any finite aspect-ratio fluid with geometry parameter a in any linear flow field, *and* extremely thin rodlike *or* discotic fluids, respectively, in a linear superposition of the identical linear flow field perturbed by a pure-strain velocity component. This correspondence has experimental implications for monodomain behavior, as indicated in Ref. [20]. For example, the monodomain response to the linear flow of an entire aspect-ratio spectrum of monodisperse nematic liquids can be inferred from flow experiments on a single large-aspect-ratio nematic liquid by controlling the amplitude of the straining component while holding the vorticity component fixed. Alternatively, a finite-aspect-ratio, monodisperse nematic liquid in simple shear can be used to mimic more general linear flows of extremely thin rodlike or discotic fluids. The last symmetry shows that the orientational distributions of any two distinct aspect-ratio liquids

can be placed in one-to-one correspondence by varying the strain component of the velocity while holding the vorticity component fixed.

This symmetry provides physical intuition as to why molecular aspect-ratio variations could lead to significant experimental changes relative to thin rodlike fluids. In Ref. [20] we find dramatic changes in flow phase diagrams when the molecular aspect ratio is reduced to the range of 5:1 to 3:1. Steady-unsteady transitions, new types of monodomains, and even a period-doubling transition to chaotic monodomain dynamics, result solely from aspect-ratio variations. Corresponding sensitivity of kinetic flow phase diagrams to molecular aspect ratio will be discussed elsewhere. We emphasize that these properties are *restricted* to linear flows and homogeneous orientational distributions, and *do not* imply such direct relationships for rheological behavior.

IV. CONCLUSION

Several symmetries of the extended Doi kinetic theory for finite- and infinite-aspect-ratio fluids in shear and related linear flows are now established, extending results from Ref. [20] for mesoscopic, moment-averaged approximations of the kinetic theory. These symmetries have been presented in abstract as well as in constructive form. A continuous O(3) family of orientational probability distributions f for quiescent nematic liquids is characterized for every anisotropic initial orientational distribution. In simple shear, the PDF f for out-of-plane initial data generates an explicit mirror-symmetric solution f^{sym} with respect to the shearing plane. This symmetry explains previously reported bistable, out-of-plane, steady and periodic solutions [7], and further implies a mirror symmetry of all stable and unstable manifolds of in-plane and out-of-plane solution branches. Finally, orientational responses are shown to be in one-to-one correspondence for rodlike and discotic nematic liquids in simple shear, and a similar correspondence is provided between finite- and infinite-aspect-ratio nematic liquids in linear flows related by a straining perturbation. All symmetries are illustrated with exact solutions or bifurcation diagrams, using codes developed in the sequel to this paper [28], where applications of these symmetries are pursued.

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APPENDIX

The dynamical system for the amplitudes $\{a_{l,m}(t)\}$ in the spherical harmonic expansion of f, Eq. (21), results from a routine Galerkin procedure (cf., Refs. [2,4,6]) applied to the Smoluchowski equation (1) and Jeffery orbit dynamics (2). This system of ODEs can be represented in the form

$$\frac{d}{dt}(a_{l,m}) = F^1_{l,m} + F^2_{l,m} + F^3_{l,m},$$

where

$$F^1_{l,m} = -D_r(\mathbf{m},a)l(l+1)a_{l,m},$$

$$F^2_{l,m} = \frac{4\pi}{5}N(-1)^m D_r(\mathbf{m},a) \times \sum_{p=-2}^{2}\sum_{n=l-2}^{l+2} a_{n,m-p}a_{2,p}q(l,m,n,p),$$

$$F^3_{l,m} = i\frac{1}{4}\sqrt{\frac{8\pi}{15}}(-1)^m\mu\Bigg\{\sum_{n=l-2}^{l+2} a_{n,m}q_1(l,m,n) + a\sum_{n=l-2}^{l+2} a_{n,m+2}q_2(l,m,n) + a\sum_{n=l-2}^{l+2} a_{n,m-2}q_3(l,m,n)\Bigg\}.$$

All numbers q appearing above are real constants arising in spherical harmonic expansions,

$$q(l,m,n,p) = -\tfrac{1}{2}[c_{l,m,1}c_{2,p,1}|n,m-p;j,p+1;l,-m-1\rangle + c_{l,m,2}c_{2,p,2}|n,m-p;2,p-1;l,-m+1\rangle] + mp|n,m-p;j,p;l,-m\rangle,$$

$$q_1(l,m,n) = c_{l,m,2}|l,-m+1;n,m;2,-1\rangle - c_{l,m,1}|l,-m-1;n,m;2,1\rangle + 2m[\sqrt{\tfrac{10}{3}}|l,-m;n,m;0,0\rangle - \sqrt{\tfrac{2}{3}}|l,-m;m,k;2,0\rangle],$$

$$q_2(l,m,n) = c_{l,m,1}|l,-m-1;n,m+2;2,-1\rangle + 2m|l,-m;n,m+2;2,-2\rangle,$$

$$q_3(l,m,n) = -c_{l,m,2}|l,-m+1;n,m-2;2,1\rangle + 2m|l,-m;n,m-2;2,2\rangle,$$

where

$$c_{l,m,1} = \sqrt{(l-m)(l+m+1)},$$

$$c_{l,m,2} = \sqrt{(l+m)(l-m+1)},$$

the symbol $|n,k;j,p;l,m\rangle$ denotes the integral of the product of three spherical harmonics,

$$\int_{\|\mathbf{m}\|=1} Y^k_n Y^p_j Y^m_l d\mathbf{m}$$

(e.g., Ref. [29]). By the parity property of the spherical harmonics, any $a_{l,m}$ with odd l is zero, and we only need to retain coefficients $a_{l,m}$ with non-negative m. In simulations that generate figures in the body, we assume constant D_r to make contact with Refs. [7,8]; all symmetry properties are valid for variable or constant rotary diffusivity.

Reflection symmetry in simple shear

The dynamical system (48) provides an alternative form of the discrete reflection symmetry of f in simple shear. To prove that these ODEs are invariant under the transformation

$$a_{l,m} \to -a_{l,m}, \quad l=2,4,...,L_{\max}, \quad m \text{ odd},$$

$$a_{l,m} \to a_{l,m}, \quad l=2,4,...,L_{\max}, \quad m \text{ even},$$

we split the variables $\{a_{l,m}\}$'s into two groups, one having odd second index m, another even second index m. The first group of variables forms a vector $\mathbf{a}_1$, and the second group of variables forms a vector $\mathbf{a}_2$. Then, the dynamical system (48) for the spherical harmonic amplitudes can be represented in the form

$$\frac{d\mathbf{a}_1}{dt} = \mathbf{F}_1(\mathbf{a}_1, \mathbf{a}_2),$$

$$\frac{d\mathbf{a}_2}{dt} = \mathbf{F}_2(\mathbf{a}_1, \mathbf{a}_2).$$

The mirror symmetry follows if we can show that $\mathbf{F}_1$ is an odd function of $\mathbf{a}_1$ and $\mathbf{F}_2$ is an even function of $\mathbf{a}_1$. Since $\mathbf{F}_1$ contains those functions $F^j_{l,m}$ with m odd and $\mathbf{F}_2$ contains those functions $F^j_{l,m}$ with m even, we only need to check that $F^j_{l,m}$ is an odd function of $\mathbf{a}_1$ for odd m and $F^j_{l,m}$ is an even function of $\mathbf{a}_1$ for even m. This is obviously true for the term $F^1_{l,m}$, because of the fact that $D_r(\mathbf{m},a)$ is an even function of any variable $a_{l,m}$. For the second term, $F^2_{l,m}$ contains the product of the form

$$a_{n,m-p}a_{2,p}.$$

For odd m, one and only one of $m-p$ and p is odd. Therefore the product is an odd function of the first group of variables $\mathbf{a}_1$. For even integer m, the integers $m-p$ and p must be both even or both odd. So the product is an even function of the first group of variables $\mathbf{a}_1$. The third term $F^3_{l,m}$ only contains linear terms. If m is odd, then all of $a_{n,m}, a_{n,m+2}, a_{n,m-2}$ have odd second index, so $F^3_{l,m}$ is an odd function of the first group of variables $\mathbf{a}_1$. On the other hand, if m is even, then all of $a_{n,m}, a_{n,m+2}, a_{n,m-2}$ have even second index, so $F^3_{l,m}$ does not have any term relating to the first group of variables $\mathbf{a}_1$. Therefore, this third term is an even function of $\mathbf{a}_1$. These arguments establish the symmetry of solutions about the in-plane subspace formed by the first group of variables $\mathbf{a}_1$, with the second group vanishing.

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