A Note on the Kinematics of Rigid Molecules in Linear Flow Fields and Kinetic Theory for Biaxial Liquid Crystal Polymers

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Abstract

We present a systematic derivation of the extended Jefferys' orbit for rigid ellipsoidal and V-shaped polymer molecules in linear incompressible viscous flows using a Lagrange multiplier's method based on a constraining force argument [5]. It reproduces the well-known Jefferys' orbit for rotating ellipsoids [12]. The method is simple and applicable to any rigid body immersed in a linear flow field so long as a discrete set of representative points on the rigid body can be identified that possess the same rotational degrees of freedom as the rigid body itself. The kinematics of a single V-shaped rigid polymer driven by a linear flow field are discussed, where steady states exist along with time-periodic states in limited varieties. Finally, we show how the kinematics of the rigid V-shaped polymer can be used in the derivation a kinetic theory for the solution of rigid biaxial liquid crystal polymers.

Keywords: Kinematics, kinetic theory, linear flows, ellipsoids, biaxial liquid crystal polymers, V-shaped polymer.

1 Introduction

The configurational space kinetic theory for rigid polymers or solid suspensions in another fluid is built upon two basic ingredients, the interaction potential to each point in the configurational phase space and the kinematics of the point under imposed flow fields, where each pint in the configurational space represents the full configuration of a polymer or the suspension particle [1, 5]. When the host fluid is viscous and incompressible, the kinematics of the phase point in the configurational space is often derived with respect to an imposed linear flow field which is an exact solution of the Stokes equation. Jefferys studied the kinematics of an ellipsoid immersed in a viscous fluid (Stokes fluid) and derived the well-known Jefferys' orbit for the rotating ellipsoid about its own center of mass [12]. This was later used in many theory development and applications [2, 13, 11, 16]. Eshelby [9] and recently Wetzel and Tucker [17] examined the kinematics of an ellipsoidal inclusion in elastic and viscous media. They derived the explicit formula for the kinematics of the three major axes of an ellipsoidal inclusion using the Eshelby tensor. More recently, a number of theories for polymer blends have been developed based on deformable ellipsoidal droplets, whose constitutive equation also relies on the kinematics of the deformable ellipsoids in imposed linear flow fields [7, 6].

With the surging interest in modeling dynamics of suspensions and/or rigid polymer molecules of biaxial symmetry using kinetic theories, there is the need to provide an on-the-fly method to derive the kinematics of the representative axes of a rotating rigid molecule or particle in imposed

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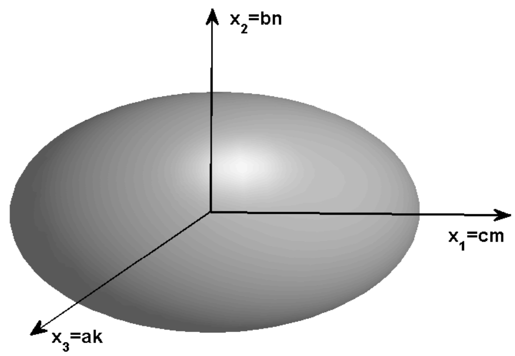

Figure 1: The portrait of an ellipsoid with semiaxes (c, a, b).

linear flows while conveniently neglecting the hydrodynamic interaction. The Lagrange multiplier method discussed in the book by Doi and Edwards outlines an efficient way for devising such a method [5, 8, 10]. The idea is to identify a set of representative points on the rigid body so that the kinematics of the positional vectors of the representative points can fully describe the kinematics of the rigid body while the rigid constraints are taken into account.

In the following, we will detail the approach using two examples: we present the method by deriving the kinematics of a rigid ellipsoid and a biaxial V-shaped rigid liquid crystal polymer, respectively. We will then discuss the kinematics of a V-shaped rigid molecule in plane shear and elongational flows. Finally, we develop a kinetic theory for solutions of V-shaped liquid crystal polymers using the derived kinematics for V-shaped rigid polymers.

2 Revisit of the kinematics of an ellipsoid in linear flow fields

We consider the rotational motion of an ellipsoidal suspension in linear incompressible viscous flows about its center of mass. The ellipsoid is described by three major axes $(\mathbf{m}, \mathbf{n}, \mathbf{k})$ and three corresponding semi-axes (c, b, a) with respect to its center of mass. Since the rotation is about the center of mass, we set up the Cartesian coordinate with its origin coincident with the center of mass in the derivation. We identify three representative points on the ellipsoid, shown in Figure 1,

$$\mathbf{x}_1 = c\mathbf{m}, \quad \mathbf{x}_2 = b\mathbf{n}, \quad \mathbf{x}_3 = a\mathbf{k}. \tag{1}$$

We assign an equal amount of mass to each point. By ignoring the hydrodynamic interaction, the rotation of the ellipsoid can be fully described by the rotation of the three points subject to the six rigid body constraints:

$$\begin{aligned} &C_1 = \|\mathbf{x}_1\|^2 - c^2, C_2 = \|\mathbf{x}_2\|^2 - b^2, C_3 = \|\mathbf{x}_3\|^2 - a^2, \\ &C_4 = \mathbf{x}_1 \cdot \mathbf{x}_2 = 0, C_5 = \mathbf{x}_1 \cdot \mathbf{x}_3, C_6 = \mathbf{x}_2 \cdot \mathbf{x}_3. \end{aligned} \tag{2}$$

We now calculate the velocity at the three discrete points $\mathbf{x}_i, i = 1, 2, 3$, respectively, subject to the constraints (2). The velocity at $\mathbf{x}_i$ is affected by two factors. One is the affine motion of the point, free of the constraints, due to the imposed linear flow $\mathbf{K} \cdot \mathbf{x}_i$, where $\mathbf{K} = \nabla \mathbf{v}$ is the velocity gradient tensor of the linear flow field $\mathbf{v}$, a constant trace-free matrix; and the other is the constraining force exerted by the constraints (2), given by

$$\sum_{p=1}^{6} \lambda_p \frac{\partial C_p}{\partial \mathbf{x}_i}, \tag{3}$$

where $\lambda_p, p = 1, \cdots, 6$ are Lagrange multipliers to be determined later and $C_p, p = 1, \cdots, 6$ are the constraints given in (2). We denote $\mathbf{H}_{ij}$ the mobility matrix for free point $\mathbf{x}_i$ moving in the linear flow driven by an external force $\mathbf{F}_j$ at $\mathbf{x}_j$. The combination of the velocities due to the affine motion and the constraining force due to the rigid constraints yields the total velocity at $\mathbf{x}_i$

$$\dot{\mathbf{x}}_i = \mathbf{K} \cdot \mathbf{x}_i - \sum_{j=1}^{3} \mathbf{H}_{ij} \cdot \sum_{p} \lambda_p \frac{\partial C_p}{\partial \mathbf{x}_j}. \tag{4}$$

Since the representative points are constrained by (2), we differentiate the constraints to obtain

$$\sum_{i=1}^{3} \frac{\partial C_p}{\partial \mathbf{x}_i} \cdot \dot{\mathbf{x}}_i = 0, p = 1, \cdots, 6. \tag{5}$$

Solving these equations, we obtain the Lagrange multiplier λ_p:

$$\lambda_p = (\mathbf{h}^{-1})_{pq} \sum_{i=1}^{6} \frac{\partial C_q}{\partial \mathbf{x}_i} \cdot \mathbf{K} \cdot \mathbf{x}_i, p = 1, \cdots, 6, \tag{6}$$

where

$$\mathbf{h} = (\sum_{ij=1}^{3} \frac{\partial C_p}{\partial \mathbf{x}_i} \cdot \mathbf{H}_{ij} \cdot \frac{\partial C_q}{\partial \mathbf{x}_j}). \tag{7}$$

As the viscous fluids considered here are isotropic, we assume $\mathbf{H}_{ij} = \frac{1}{\zeta}\mathbf{I}\delta_{ij}$, where ζ is the friction coefficient and $\mathbf{I}$ is the identity matrix.

We denote $r_a = \frac{a}{c}$, $r_b = \frac{b}{c}$ as the two aspect ratios of the ellipsoid. Substituting (1) into (4), we arrive at the generalized Jeffrey's orbit for ellipsoids [12]

$$\begin{aligned}
\dot{\mathbf{m}} &= \mathbf{K} \cdot \mathbf{m} - \mathbf{mmm} : \mathbf{K} - \tfrac{r_b^2}{1+r_b^2}\mathbf{n}(\mathbf{n} \cdot \mathbf{K} \cdot \mathbf{m} + \mathbf{m} \cdot \mathbf{K} \cdot \mathbf{n}) - \tfrac{r_a^2}{1+r_a^2}\mathbf{k}(\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{m} + \mathbf{m} \cdot \mathbf{K} \cdot \mathbf{k}),\\
\dot{\mathbf{n}} &= \mathbf{K} \cdot \mathbf{n} - \mathbf{nnn} : \mathbf{K} - \tfrac{1}{1+r_b^2}\mathbf{m}(\mathbf{n} \cdot \mathbf{K} \cdot \mathbf{m} + \mathbf{m} \cdot \mathbf{K} \cdot \mathbf{n}) - \tfrac{r_a^2}{r_a^2+r_b^2}\mathbf{k}(\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{n} + \mathbf{n} \cdot \mathbf{K} \cdot \mathbf{k}),\\
\dot{\mathbf{k}} &= \mathbf{K} \cdot \mathbf{k} - \mathbf{kkk} : \mathbf{K} - \tfrac{1}{1+r_a^2}\mathbf{m}(\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{m} + \mathbf{m} \cdot \mathbf{K} \cdot \mathbf{k}) - \tfrac{r_b^2}{r_a^2+r_b^2}\mathbf{n}(\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{n} + \mathbf{n} \cdot \mathbf{K} \cdot \mathbf{k}).
\end{aligned} \tag{8}$$

The angular velocity of the rotational motion can be identified as

$$\begin{aligned}
\omega = {} & [\tfrac{r_b^2}{r_a^2+r_b^2}\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{n} - \tfrac{r_a^2}{r_a^2+r_b^2}\mathbf{n} \cdot \mathbf{K} \cdot \mathbf{k}]\mathbf{m} + [\tfrac{r_a^2}{1+r_a^2}\mathbf{m} \cdot \mathbf{K} \cdot \mathbf{k} - \\
& \tfrac{1}{1+r_a^2}\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{m}]\mathbf{n} + [\tfrac{1}{1+r_b^2}\mathbf{n} \cdot \mathbf{K} \cdot \mathbf{m} - \tfrac{r_b^2}{1+r_b^2}\mathbf{m} \cdot \mathbf{K} \cdot \mathbf{n}]\mathbf{k}.
\end{aligned} \tag{9}$$

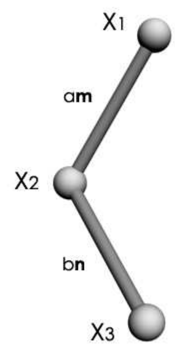

Figure 2: V-shaped rigid body or molecule.

With this,

$$\dot{\mathbf{m}} = \omega \times \mathbf{m}, \quad \dot{\mathbf{n}} = \omega \times \mathbf{n}, \quad \dot{\mathbf{k}} = \omega \times \mathbf{k}. \tag{10}$$

In the case of a spheroid, where $r_a = r_b = r$, we use the fact that $\mathbf{nn} + \mathbf{kk} = \mathbf{I} - \mathbf{mm}$. Then, eq. (8.1) reduces to

$$\begin{aligned} \dot{\mathbf{m}} &= \mathbf{K} \cdot \mathbf{m} - \mathbf{mmm} : \mathbf{K} - \tfrac{r^2}{1+r^2}\mathbf{n}(\mathbf{n} \cdot \mathbf{K} \cdot \mathbf{m} + \mathbf{m} \cdot \mathbf{K} \cdot \mathbf{n}) - \tfrac{r^2}{1+r^2}\mathbf{k}(\mathbf{k} \cdot \mathbf{K} \cdot \mathbf{m} + \mathbf{m} \cdot \mathbf{K} \cdot \mathbf{k}) \\ &= \mathbf{K} \cdot \mathbf{m} - \mathbf{mmm} : \mathbf{K} - \tfrac{2r^2}{1+r^2}(\mathbf{D} \cdot \mathbf{m} - \mathbf{mmm} : \mathbf{K}) \\ &= \mathbf{W} \cdot \mathbf{m} + a[\mathbf{D} \cdot \mathbf{m} - \mathbf{mmm} : \mathbf{D}], \end{aligned} \tag{11}$$

where $\mathbf{W} = \frac{\mathbf{K}-\mathbf{K}^T}{2}$ and $\mathbf{D} = \frac{\mathbf{K}+\mathbf{K}^T}{2}$ are the vorticity and rate of strain tensor, respectively, $a = \frac{1-r^2}{1+r^2}$ is a geometric parameter. This is the well-known Jefferys' orbit describing the kinematics of the axis of symmetry of a spheroid [12, 16].

This method can be extended in principle to any rigid bodies so long as (i). the hydrodynamic interaction is negligible, (ii). we can identify a set of representative points on the body that share the same rotational degree of freedom as the rigid body itself when constrained by the rigid body, and (iii). mass is evenly distributed on the rigid body. We next derive the Jefferys' orbit for a V-shaped (bent-core, banana-like, or boomerang) polymer molecule.

3 Kinematics of V-shaped polymer molecules in linear flow fields

We coarse-grain the bent-core, banana or boomerang polymer molecule by a rigid V-shaped rigid body consisting of three beads and two rigid connectors shown in Figure 1. We denote the orientation of the two rigid connectors by $a\mathbf{m}$ and $b\mathbf{n}$, where $\|\mathbf{m}\| = \|\mathbf{n}\| = 1$. We let $\mathbf{x}_i, i = 1, 2, 3$ be the positional vectors of the bead locations which form the skeleton of the V-shaped molecule along with the connectors.

The two connecting vectors are defined by

$$a\mathbf{m} = \mathbf{x}_1 - \mathbf{x}_2, b\mathbf{n} = \mathbf{x}_3 - \mathbf{x}_2. \tag{12}$$

We assume that the two beads at $\mathbf{x}_{1,3}$ have the identical mass while the third one at $\mathbf{x}_2$ may have different mass. We also set the origin of the coordinate system at the center of the mass, which requires

$$\mathbf{x}_1 + c\mathbf{x}_2 + \mathbf{x}_3 = \mathbf{0}, \tag{13}$$

where c is the ratio of the mass of the bead at $\mathbf{x}_2$ to that at $\mathbf{x}_{1,3}$. If all three beads share the same amount of mass, $c = 1$. We next use the Lagrange multiplier's method to derive the time evolution equation of the positional vectors relative to the center of mass under an imposed linear flow field $\mathbf{v} = \mathbf{K}\cdot\mathbf{x}$, where $\mathbf{x}$ is the positional vector with the origin set at the center of mass of the V-shaped rigid body.

The V-shaped rigid body is subject to the following constraints:

$$\|\mathbf{x}_1 - \mathbf{x}_2\| = a, \|\mathbf{x}_3 - \mathbf{x}_2\| = b, \mathbf{x}_1 + c\mathbf{x}_2 + \mathbf{x}_3 = \mathbf{0}, \|\mathbf{x}_3 - \mathbf{x}_1\| = a^2 + b^2 - 2ab\cos\theta, \tag{14}$$

where $\cos\theta = \mathbf{m}\cdot\mathbf{n}$ and θ is the angle between $\mathbf{m}$ and $\mathbf{n}$. These can be rewritten into totally 6 independent scalar constraints given by

$$\begin{aligned}
&C_1 : \mathbf{e}_1 \cdot (\mathbf{x}_1 + c\mathbf{x}_2 + \mathbf{x}_3) = 0,\\
&C_2 : \mathbf{e}_2 \cdot (\mathbf{x}_1 + c\mathbf{x}_2 + \mathbf{x}_3) = 0,\\
&C_3 : \mathbf{e}_3 \cdot (\mathbf{x}_1 + c\mathbf{x}_2 + \mathbf{x}_3) = 0,\\
&C_4 : \|\mathbf{x}_1 - \mathbf{x}_2\|^2 - a^2 = 0,\\
&C_5 : \|\mathbf{x}_3 - \mathbf{x}_2\|^2 - b^2 = 0,\\
&C_6 : \|\mathbf{x}_1 - \mathbf{x}_3\|^2 - [a^2 + b^2 - 2ab\cos\theta] = 0.
\end{aligned} \tag{15}$$

We adopt a mobility matrix $\mathbf{H}_{ij}$ with friction coefficient ζ_i, given by

$$\mathbf{H}_{ij} = \frac{1}{\zeta_i}\mathbf{I}\delta_{ij}, \tag{16}$$

where $\zeta_1 = \zeta_3$. We set $\zeta = \zeta_2/\zeta_1$ and without loss of generality $\zeta_1 = \zeta_3 = 1$ in the following

We now calculate the velocity at the three discrete points $\mathbf{x}_i, i = 1, 2, 3$, respectively, subject to the constraints in (15). The steps are identical to the ones alluded to in the previous section. For V-shaped molecules, however, the matrix

$$\mathbf{h} = \begin{pmatrix} P_{3\times3} & \mathbf{u} \\ \mathbf{u}^T & h_{3\times3} \end{pmatrix}, \tag{17}$$

where

$$\begin{aligned}
&P_{3\times3} = \begin{pmatrix} 2+\frac{c^2}{\zeta} & 0 & 0 \\ 0 & 2+\frac{c^2}{\zeta} & 0 \\ 0 & 0 & 2+\frac{c^2}{\zeta} \end{pmatrix}, \mathbf{u} = (1-c/\zeta)\begin{pmatrix} 2a\mathbf{e}_1\cdot\mathbf{m} & 2b\mathbf{e}_1\cdot\mathbf{n} & 0 \\ 2a\mathbf{e}_2\cdot\mathbf{m} & 2b\mathbf{e}_2\cdot\mathbf{n} & 0 \\ 2a\mathbf{e}_3\cdot\mathbf{m} & 2b\mathbf{e}_3\cdot\mathbf{n} & 0 \end{pmatrix},\\
&h_{3\times3} = a^2\begin{pmatrix} 4(1+1/\zeta) & 4/\zeta r\cos\theta & 4-4r\cos\theta \\ 4/\zeta r\cos\theta & 4r^2(1+1/\zeta) & 4r^2-4r\cos\theta \\ 4-4r\cos\theta & 4r^2-4r\cos\theta & 8(1+r^2-2r\cos\theta) \end{pmatrix},
\end{aligned} \tag{18}$$

$r = b/a$ and $\mathbf{e}_i, i = 1, 2, 3$ are the three base vectors in the fixed Cartesian Coordinate. Three of the Lagrange multipliers can be solved explicitly:

$$\begin{aligned}
\lambda_4 = &-\frac{1}{4d}[(-\cos\theta c^2 - 2\cos\theta c - 6 - 2c^2 - \zeta - \cos\theta\zeta - 2\cos\theta - 6c)(2\zeta + c^2)\mathbf{m}\cdot\mathbf{K}\cdot\mathbf{m} \\
&- (-2\cos\theta + \cos\theta\zeta - 2\cos\theta c + \zeta + c^2 + 2 + 2c)(2\zeta + c^2)(\mathbf{n}\cdot\mathbf{K}\cdot\mathbf{m} + \mathbf{m}\cdot\mathbf{K}\cdot\mathbf{n}) \\
&+ (2c - \cos\theta\zeta + 6\cos\theta + \cos\theta c^2 + 6\cos\theta c + 2 - \zeta)(2\zeta + c^2)\mathbf{n}\cdot\mathbf{K}\cdot\mathbf{n}], \\
\lambda_5 = &\frac{1}{4d}[(-\cos\theta c^2 - 6\cos\theta c - 2 - 6\cos\theta + \zeta + \cos\theta\zeta - 2c)(2\zeta + c^2)\mathbf{m}\cdot\mathbf{K}\cdot\mathbf{m} \\
&+ (-2\cos\theta + \cos\theta\zeta - 2\cos\theta c + \zeta + c^2 + 2 + 2c)(2\zeta + c^2)(\mathbf{n}\cdot\mathbf{K}\cdot\mathbf{m} + \mathbf{m}\cdot\mathbf{K}\cdot\mathbf{n}) \\
&+ (2\cos\theta + 6c + 2c^2 + 2\cos\theta c + \cos\theta c^2 + \cos\theta\zeta + 6 + \zeta)(2\zeta + c^2)\mathbf{n}\cdot\mathbf{K}\cdot\mathbf{n}], \\
\lambda_6 = &-\frac{1}{4(\cos\theta - 1)(\cos\theta + 1)(c+2)^2} \\
&[(2c + \cos\theta c^2 + 2 + 2\cos\theta + \cos\theta\zeta + 2\cos\theta c - \zeta)\mathbf{m}\cdot\mathbf{K}\cdot\mathbf{m} \\
&+ (-2 - c^2 - 2c - 2\cos\theta c - 2\cos\theta - \zeta + \cos\theta\zeta)(\mathbf{n}\cdot\mathbf{K}\cdot\mathbf{m} + \mathbf{m}\cdot\mathbf{K}\cdot\mathbf{n}) \\
&+ (2c + \cos\theta c^2 + 2 + 2\cos\theta + \cos\theta\zeta + 2\cos\theta c - \zeta)\mathbf{n}\cdot\mathbf{K}\cdot\mathbf{n}],
\end{aligned} \tag{19}$$

where $d = (c+2)^2(\cos\theta + 1)(-2\cos\theta + \cos\theta\zeta - 2\cos\theta c + \zeta + c^2 + 2 + 2c)$. The other three $\lambda_{1,2,3}$ are given by the solutions of the linear system:

$$\lambda_1\mathbf{e}_1 + \lambda_2\mathbf{e}_2 + \lambda_3\mathbf{e}_3 = -\frac{2(1 - c\zeta)}{2 + c^2\zeta}(\lambda_4 a\mathbf{m} + \lambda_5 a\mathbf{n}). \tag{20}$$

The kinematic equations for the positional vectors are given by:

$$\dot{\mathbf{x}}_1 = K\cdot\mathbf{x}_1 - [\lambda_1\mathbf{e}_1 + \lambda_2\mathbf{e}_2 + \lambda_3\mathbf{e}_3 + \lambda_4(2a\mathbf{m}) + \lambda_6 2(a\mathbf{m} - b\mathbf{n})] \tag{21}$$

$$\dot{\mathbf{x}}_2 = K\cdot\mathbf{x}_2 - 1/\zeta[(\lambda_1\mathbf{e}_1 + \lambda_2\mathbf{e}_2 + \lambda_3\mathbf{e}_3)c + \lambda_4(-2a\mathbf{m}) + \lambda_5(-2b\mathbf{n})] \tag{22}$$

$$\dot{\mathbf{x}}_3 = K\cdot\mathbf{x}_3 - [\lambda_1\mathbf{e}_1 + \lambda_2\mathbf{e}_2 + \lambda_3\mathbf{e}_3 + \lambda_5(2b\mathbf{n}) + \lambda_6(-2(a\mathbf{m} - b\mathbf{n}))]. \tag{23}$$

We next limit to the special case: $r = \frac{b}{a} = 1$ and define

$$\mathbf{r}_1 = \mathbf{x}_2 - \frac{\mathbf{x}_1 + \mathbf{x}_3}{2}, \mathbf{r}_2 = \frac{\mathbf{x}_1 - \mathbf{x}_3}{2}. \tag{24}$$

We normalize the two vectors $\mathbf{r}_1, \mathbf{r}_2$ to unit vectors $\mathbf{n}_1, \mathbf{n}_2$, respectively,

$$\|\mathbf{n}_i\| = 1, i = 1, 2. \tag{25}$$

We call $\mathbf{n}_1$ the arrow and $\mathbf{n}_2$ the bow vector, respectively. The kinematic equations for the unit vectors are given by

$$\begin{aligned}
\dot{\mathbf{n}}_1 &= \mathbf{K}\cdot\mathbf{n}_1 + \xi_1\mathbf{n}_1 + \xi_2\mathbf{n}_2\tan\theta/2, \\
\dot{\mathbf{n}}_2 &= \mathbf{K}\cdot\mathbf{n}_2 + \xi_3\mathbf{n}_1\cot\theta/2 + \xi_4\mathbf{n}_2,
\end{aligned} \tag{26}$$

where

$$\begin{aligned}
\xi_1 &= -\mathbf{K} : \mathbf{n}_1\mathbf{n}_1 \\
\xi_2 &= \frac{\sin\theta(c^2 + 4c + 4)}{2(2\cos\theta c + 2\cos\theta - \cos\theta\zeta - c^2 - 2c - 2 - \zeta)}\mathbf{K} : (\mathbf{n}_1\mathbf{n}_2 + \mathbf{n}_2\mathbf{n}_1) \\
\xi_3 &= \frac{\sin\theta(2\zeta + c^2)}{2(2\cos\theta c + 2\cos\theta - \cos\theta\zeta - c^2 - 2c - 2 - \zeta)}\mathbf{K} : (\mathbf{n}_1\mathbf{n}_2 + \mathbf{n}_2\mathbf{n}_1) \\
\xi_4 &= -\mathbf{K} : \mathbf{n}_2\mathbf{n}_2
\end{aligned} \tag{27}$$

Simplifying, we arrive at

$$\begin{aligned}
\dot{\mathbf{n}}_1 &= \mathbf{K}\cdot\mathbf{n}_1 - \mathbf{K}:\mathbf{n}_1\mathbf{n}_1\mathbf{n}_1 + \tfrac{(1-\cos\theta)(c^2+4c+4)}{2(2\cos\theta c+2\cos\theta-\cos\theta\zeta-c^2-2c-2-\zeta)}\mathbf{K}:(\mathbf{n}_1\mathbf{n}_2+\mathbf{n}_2\mathbf{n}_1)\mathbf{n}_2 \\
&= \mathbf{K}\cdot\mathbf{n}_1 - \mathbf{K}:\mathbf{n}_1\mathbf{n}_1\mathbf{n}_1 + s\mathbf{n}_2, \\
\dot{\mathbf{n}}_2 &= \mathbf{K}\cdot\mathbf{n}_2 - \mathbf{K}:\mathbf{n}_2\mathbf{n}_2\mathbf{n}_2 + \tfrac{(1+\cos\theta)(2\zeta+c^2)}{2(2\cos\theta c+2\cos\theta-\cos\theta\zeta-c^2-2c-2-\zeta)}\mathbf{K}:(\mathbf{n}_1\mathbf{n}_2+\mathbf{n}_2\mathbf{n}_1)\mathbf{n}_1 \\
&= \mathbf{K}\cdot\mathbf{n}_2 - \mathbf{K}:\mathbf{n}_2\mathbf{n}_2\mathbf{n}_2 - (k_0+s)\mathbf{n}_1,
\end{aligned} \tag{28}$$

where

$$s = \tfrac{(1-\cos\theta)(c^2+4c+4)}{2(2\cos\theta c+2\cos\theta-\cos\theta\zeta-c^2-2c-2-\zeta)}\mathbf{K}:(\mathbf{n}_1\mathbf{n}_2+\mathbf{n}_2\mathbf{n}_1),\ k_0 = \mathbf{K}:(\mathbf{n}_1\mathbf{n}_2+\mathbf{n}_2\mathbf{n}_1). \tag{29}$$

It follows from (28) that the angular velocity of the rotating rigid body is given by

$$\omega = \tfrac{1}{2}[\textstyle\sum_{i=1}^{3}\mathbf{n}_i\times\mathbf{K}\cdot\mathbf{n}_i + (k_0+2s)\mathbf{n}_3 + \mathbf{n}_3\times((\mathbf{K}\cdot\mathbf{n}_1)\times\mathbf{n}_2 + \mathbf{n}_1\times(\mathbf{K}\cdot\mathbf{n}_2) - \mathbf{K}\cdot\mathbf{n}_3)] \tag{30}$$

We remark that when the mass of the three beads are identical ($c = 1$) and the friction coefficients are identical ($\zeta = 1$), the angular velocity reduces to

$$\omega == (\mathbf{K}:\mathbf{n}_2\mathbf{n}_3)\mathbf{n}_1 - (\mathbf{K}:\mathbf{n}_1\mathbf{n}_3)\mathbf{n}_2 + \frac{1}{1+2\sin^2\frac{\theta}{2}}[\cos^2\frac{\theta}{2}\mathbf{K}:\mathbf{n}_1\mathbf{n}_2 - 3\sin^2\frac{\theta}{2}\mathbf{K}:\mathbf{n}_2\mathbf{n}_1]\mathbf{n}_3. \tag{31}$$

With this, the kinematic equations can be rewritten into

$$\dot{\mathbf{n}}_i = \omega\times\mathbf{n}_i, i = 1,2,3, \tag{32}$$

where $\mathbf{n}_3 = \mathbf{n}_1\times\mathbf{n}_2$.

4 Kinematics of a V-shaped rigid polymer molecule in shear and elongational flows

The rotational motion of an ellipsoid has been studied in [12]. Here, we focus on the driven dynamics of a single V-shaped polymer molecule in two special cases of linear flows: plane shear and elongation, respectively.

4.1 Kinematics in plane shear flows

We examine the kinematics of the V-shaped rigid body under the imposed shear flow

$$\mathbf{v} = (\mu y, 0, 0). \tag{33}$$

In the case of ellipsoid, it was shown that the Jefferys' orbit of a sheared ellipsoid is a time-periodic orbit in [12]. For the V-shaped rigid body suspended in the viscous fluid under simple shear, however, the kinematics are more diversified. In addition to the periodic orbits, there could be steady states. This is witnessed by the fact that

$$\omega = \mathbf{0} \tag{34}$$

has some constant solutions. In fact, if we set

$$\mathbf{n}_1 = \begin{pmatrix} \cos\alpha\sin\beta \\ \sin\alpha\sin\beta \\ \cos\beta \end{pmatrix} \mathbf{n}_2 = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma \\ \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma \\ -\sin\beta\cos\gamma \end{pmatrix}, \tag{35}$$

we find the following family of steady states:

- $\mathbf{n_1} = (\sin\beta, \mathbf{0}, \cos\beta), \mathbf{n_2} = (\pm\cos\beta, \mathbf{0}, \mp\sin\beta), \mathbf{n_1} = (-\sin\beta, \mathbf{0}, \cos\beta), \mathbf{n_2} = (\mp\cos\beta, \mathbf{0}, \mp\sin\beta)$, $0 \le \beta \le \pi$.

In this steady states, the V-shaped rigid body lay on the (x,z) plane with the bow vector in an arbitrary orientation.

The eigenvalues of the coefficient matrix of the linearized system for all steady states are 0, and their corresponding eigenvectors are $\mathbf{v} = (x_1, x_2, x_3)$, where $\frac{x_1}{x_3} = -\frac{3(\cos\theta-1)}{2\cos\beta(2\cos\theta-1)}$, x_2 is arbitrary. Thus, the steady states are neutrally stable.

Besides, the neutrally stable steady states, there are other sustainable time-dependent solutions. The time evolution of the pair of vectors $\mathbf{n}_{1,2}$ are governed by the generalized Jeffery's orbit. If $\mathbf{n}_1$ and $\mathbf{n}_2$ are on the shearing plane, the (x,y) plane, the angular velocity is fixed in the vorticity direction:

$$\omega = \frac{1}{2}(k_0 + 2s + \mathbf{K} : \mathbf{n_2}\mathbf{n_1} - \mathbf{K} : \mathbf{n_1}\mathbf{n_2})\mathbf{n_3}. \tag{36}$$

We parametrize the unit vectors by an angle ϕ:

$$\mathbf{n}_1 = (\cos\phi, \sin\phi, 0), \mathbf{n}_2 = (-\sin\phi, \cos\phi, 0), \mathbf{n_3} = (\mathbf{0}, \mathbf{0}, \mathbf{1}). \tag{37}$$

The angular velocity is given by

$$\omega = -\frac{1}{2}\mu(1 + \cos 2\phi\frac{2\cos\theta - 1}{\cos\theta - 2})\mathbf{n}_3. \tag{38}$$

Clearly, there is no steady state solutions when $\theta \neq 0, \pi$, indicating the existence of the tumbling solution for the V-shaped rigid body. The angular velocity equation yields

$$\dot{\phi} = -\frac{1}{2}\mu(1 + \cos 2\phi\frac{2\cos\theta - 1}{\cos\theta - 2}). \tag{39}$$

The solution of ϕ is given by

$$\int_{\phi_0}^{\phi} \frac{d\phi'}{2 - \cos\theta - \cos 2\phi'(2\cos\theta - 1)} = \frac{\mu t}{2(\cos\theta - 2)} \tag{40}$$

where $\phi(0) = \phi_0$. The period of the rotation can be calculated as

$$T = |\frac{2(\cos\theta - 2)}{\mu}\int_0^{2\pi} \frac{d\phi}{2 - \cos\theta - \cos 2\phi(2\cos\theta - 1)}| = \frac{4\pi}{\mu}\frac{2 - \cos\theta}{\sqrt{3}\sin\theta}. \tag{41}$$

It follows from this formula that

- the period decreases as μ increases, indicating the speed-up effect by shear;
- when θ increases in $(0, \frac{\pi}{2})$, the period decreases; whereas the period increases as θ increases in $(\frac{\pi}{2}, \pi)$.

So the period is the smallest when the V-shaped forms an angle of degree $\pi/2$ and largest as it folds or stretches into a rod. In summary, the steady states are in the (x, z) plane while the time periodic solution can exist in the (x,y) plane.

4.2 Elongational flows

We next consider the imposed elongational flow field with elongational rate ν

$$\mathbf{v} = (-\frac{\nu}{2}x, -\frac{\nu}{2}y, \nu z). \tag{42}$$

Since the elongational flow is symmetric about the z-axis, the orientation of $\mathbf{n}_2$ is arbitrary. There is no time-periodic solutions in elongational flows since it is a much strong flow than the simple shear. The steady states are given by three families of solutions in terms of the Euler angle below.

- $\beta = 0$ and α and γ are arbitrary, $\mathbf{n}_1 = (0, 0, 1), \mathbf{n}_2 = (\cos\alpha, \sin\alpha, 0)$. The arrow $\mathbf{n}_1$ is fixed in the direction of the flow while the bow is arbitrary in the plane transverse to the flow.
- $\mathbf{n}_1 = (\cos\alpha, \sin\alpha, 0), \mathbf{n}_2 = (0, 0, -1)$. The bow is in the flow direction while the arrow points to the transverse direction to the flow.
- $\mathbf{n}_3 = (0, 0, 1), \mathbf{n}_1 = (\cos\alpha, \sin\alpha, 0), \mathbf{n}_2 = (-\sin\alpha, \cos\alpha, 0)$. The arrow and the bow vector are both in the (x,y) plane transverse to the flow direction.

The linear stability analysis shows that the first and the second family of steady states are stable while the third one is not.

With the Jefferys' orbit available now for the V-shaped rigid body immersed in viscous solvent, we next develop a kinetic theory for solutions of homogeneous biaxial liquid crystal polymers of V-shaped molecules generalizing the work of Doi-Hess [5] and demonstrating how the kinematics of the V-shaped rigid polymer can be used in the derivation.

5 Kinetic theory for V-shaped biaxial liquid crystal polymers (BLCPs)

We denote the angular momentum operator by

$$\mathbf{L} = i\mathbf{x} \times \frac{\partial}{\partial \mathbf{x}}, \tag{43}$$

where $\mathbf{x}$ is the positional vector in Cartesian space $\mathbf{R}^3$. We denote the complex conjugate of $\mathbf{L}$ by $\mathbf{L}^*$, the two base vectors of the polymer molecule by $\mathbf{m} = \mathbf{n}_1, \mathbf{n} = \mathbf{n}_2$, and the third one by $\mathbf{k} = \mathbf{m} \times \mathbf{n}$. We assume the two arm of the V-shaped BLCP molecule have the equal length, i.e., $a = b$. In the rotating molecular frame $\mathbf{m}, \mathbf{n}, \mathbf{k}$, the base vectors are parametrized in the Cartesian coordinate by three Euler angles (α, β, γ):

$$\begin{aligned}
\mathbf{m} &= (\cos\alpha\sin\beta, \sin\alpha sin\beta, \cos\beta)^T,\\
\mathbf{n} &= (\cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma, \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma, -\sin\beta\cos\gamma)^T,\\
\mathbf{k} &= (-\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma, -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma, \sin\beta\sin\gamma)^T.
\end{aligned} \tag{44}$$

Let $f(\mathbf{m}, \mathbf{n}, \mathbf{k}, t)$ be the probability density function for the orientation of V-shaped rigid molecules. We adopt the generalized coordinate method to derive the transport equation for f [5]. The Smoluchowski equation for the time evolution of the pdf f is given by [5, 3, 4, 18]

$$\frac{d}{dt}f = \mathbf{L}^* \cdot (D_r \mathbf{L}\mu f) - \mathbf{L}^* \cdot (\mathbf{g}f), \tag{45}$$

where μ is the normalized chemical potential of the polymer system,

$$\mu = \ln f + \frac{1}{k_B T} V, \tag{46}$$

V is the mean-field potential including the intermolecular potential and the external potential,

In the molecular frame $(\mathbf{m}, \mathbf{n}, \mathbf{k})$.

$$\begin{aligned}
&\mathbf{L} = \mathbf{m}L_m + \mathbf{n}L_n + \mathbf{k}L_k,\\
&L_m = i\tfrac{\partial}{\partial\gamma},\\
&L_n = i(\cos\gamma\cot\beta\tfrac{\partial}{\partial\gamma} + \sin\gamma\tfrac{\partial}{\partial\beta} - \tfrac{\cos\gamma}{\sin\beta}\tfrac{\partial}{\partial\alpha}),\\
&L_k = i(\sin\gamma\cot\beta\tfrac{\partial}{\partial\gamma} + \cos\gamma\tfrac{\partial}{\partial\beta} + \tfrac{\sin\gamma}{\sin\beta}\tfrac{\partial}{\partial\alpha}),\\
&\mathbf{g} = i[\mathbf{mK} : \mathbf{nk} - \mathbf{nK} : \mathbf{mk} +\\
&\tfrac{\mathbf{k}}{1+2\sin^2\frac{\theta}{2}}(\cos^2\tfrac{\theta}{2}\mathbf{K} : \mathbf{mn} - 3\sin^2\tfrac{\theta}{2}\mathbf{K} : \mathbf{nm})],\\
&D_r = diag(\tfrac{D_r^0}{2a^2\sin^2\frac{\theta}{2}}, \tfrac{3D_r^0}{2a^2\cos^2\frac{\theta}{2}}, \tfrac{3D_r^0}{2a^2(3-2\cos^2\frac{\theta}{2})}).
\end{aligned} \tag{47}$$

We note that the angular velocity of the molecule $\omega = -i\mathbf{g}$. The intermolecular potential $V = V(f, \mathbf{m}, \mathbf{n}, t)$ includes the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole interaction among each segment on the V-shaped molecule [14]. D_r^0 is a characteristic rotary diffusivity [15].

The extra elastic stress tensor for the BLCP system is calculated by an extended virtual work principle [5, 16, 15]. Here, we only present the result. Details are referred to [16, 15]. We denote the flow vector $(\mathbf{g})$ by

$$\mathbf{g} = K : \alpha_m \mathbf{m} + K : \alpha_n \mathbf{n} + K : \alpha_k \mathbf{k}. \tag{48}$$

The elastic stress tensor can then be expressed in terms of the angular momentum $(\mathbf{L})$ as follows:

$$\begin{aligned}
\tau_e^{\alpha\beta} &= \nu k_B T \langle \alpha_m^{*\alpha\beta} L_m \mu + \alpha_n^{*\alpha\beta} L_n \mu + \alpha_k^{*\alpha\beta} L_k \mu \rangle\\
&= \nu k_B T[-\langle \mathbf{L}^* \cdot \vec{\alpha}^{\alpha\beta}\rangle + \langle \alpha_m^{*\alpha\beta} L_m \mathcal{U} + \alpha_n^{*\alpha\beta} L_n \mathcal{U} + \alpha_k^{*\alpha\beta} L_k \mathcal{U}\rangle],
\end{aligned} \tag{49}$$

where ν is the number density of the LCP molecule, k_B is the Boltzmann constant, T is the absolute temperature, $\vec{\alpha}^{\alpha\beta} = (\alpha_m^{\alpha\beta}, \alpha_n^{\alpha\beta}, \alpha_k^{\alpha\beta})$ is a third order tensor and $\mathbf{L}^* \cdot \vec{\alpha}^{\alpha\beta} = \sum_{i=1}^3 L_i \alpha_i^{\alpha\beta}$. There is also a elastic external force

$$\mathbf{F}_e = -\nu k_B T \langle \nabla \mu \rangle. \tag{50}$$

The viscous stress for V-shaped BLCPs, τ_v, follows from a model calculation involving energy dissipation (W), given by [5]:

$$W = \mathbf{K} : \tau_v. \tag{51}$$

In this calculation, we model the V-shaped molecule as a geometric object consisting of two joined arms, each of which is made up of a finite number of small beads of spherical shapes [5]. The hydrodynamic interaction due to the presence of multiple beads is neglected. Under the velocity gradient $\mathbf{K} = \nabla \mathbf{v}$, each arm rotates about the center of mass of the V-shaped object with the angular velocity ω. The velocity of the n^{th} bead (in the k^{th} arm, k=1,2) relative to the fluid is:

$$\mathbf{V}_n^k = \omega \times \mathbf{u}^k - \mathbf{K} \cdot \mathbf{u}^k, \tag{52}$$

where $\mathbf{u}^k$ is the distance vector of the n^{th}-bead in the k^{th} rod measured from the center-of-mass of the molecule, which is given by:

$$\mathbf{x}_{C.M} = \frac{a}{2}\cos(\frac{\theta}{2})\mathbf{m}. \tag{53}$$

Hence,

$$\begin{aligned} &\mathbf{u}^{1,2} = (s - \tfrac{a}{2})\cos(\tfrac{\theta}{2})\mathbf{m} + (\pm s)\sin(\tfrac{\theta}{2})\mathbf{n}, \\ &\mathbf{V}_n^1 = r_1[(\mathbf{K} : \mathbf{mk})\mathbf{k} - \mathbf{K}\cdot\mathbf{m}] + r_2[(\mathbf{K} : \mathbf{nk})\mathbf{k} - \mathbf{K}\cdot\mathbf{n}] + \mathbf{K} : \alpha_{3v}(r_1\mathbf{n} - r_2\mathbf{m}), \\ &\mathbf{V}_n^2 = r_1[(\mathbf{K} : \mathbf{mk})\mathbf{k} - \mathbf{K}\cdot\mathbf{m}] + r_3[(\mathbf{K} : \mathbf{nk})\mathbf{k} - \mathbf{K}\cdot\mathbf{n}] + \mathbf{K} : \alpha_{3v}(r_1\mathbf{n} - r_3\mathbf{m}), \end{aligned} \tag{54}$$

where s is the arclength measured from the origin along either arm whose range is $[0, a]$, $\alpha_{3v} = -i\alpha_3$ is a real second order tensor. We denote $r_1 = (s - \frac{a}{2})\cos(\frac{\theta}{2}), r_{2,3} = (\pm s)\sin(\frac{\theta}{2})$. It follows that

$$\mathbf{u}^1 = (r_1, r_2, 0), \mathbf{u}^2 = (r_1, r_3, 0). \tag{55}$$

$(\mathbf{K} : \alpha_k)$ is the k^{th} component of the flow-vector $\mathbf{g}$. We assume that the frictional force acting on each segment is $\mathbf{F}_n^k = \zeta \mathbf{V}_n^k$, where ζ is the friction coefficient. Then, the work done by the frictional force per unit time and unit volume is:

$$W = \nu k_B T \textstyle\sum_{n,k}\langle \mathbf{F}_n^k \cdot \mathbf{V}_n^k\rangle = \nu k_B T\zeta[\int_0^a \langle \mathbf{V}_1 \cdot \mathbf{V}_1\rangle ds + \int_0^b \langle \mathbf{V}_2 \cdot \mathbf{V}_2\rangle ds]. \tag{56}$$

The details of the calculation is given in [15]. Using eq.(51,56), we obtain the viscous stress as follows

$$\begin{aligned} \tau^v = \nu k_B T\zeta \tfrac{a^3}{6}\nabla \mathbf{v} : [&\cos^2(\tfrac{\theta}{2})\langle \mathbf{mmmm}\rangle + 4\sin^2(\tfrac{\theta}{2})\langle \mathbf{nnnn}\rangle + \tfrac{\sin^2(\frac{\theta}{2})\cos^2(\frac{\theta}{2})}{(1+2\sin^2(\frac{\theta}{2}))^2}(4 + 5\sin^2(\tfrac{\theta}{2})) \\ &\langle(\mathbf{mn} + \mathbf{nm})(\mathbf{mn} + \mathbf{nm})\rangle]. \end{aligned} \tag{57}$$

The total stress for the biaxial liquid crystal polymer system is then given by

$$\tau = -p\mathbf{I} + \tau_e + \tau_v. \tag{58}$$

The usual incompressibility condition for incompressible fluids and the momentum balance equation supply the remaining equations for the theory

$$\begin{aligned} &\nabla \cdot \mathbf{v} = 0. \\ &\rho \tfrac{d\mathbf{v}}{dt} = \nabla \cdot \tau + \mathbf{F}_e + \mathbf{F}_o, \end{aligned} \tag{59}$$

where ρ is the density of the biaxial liquid crystal polymer fluid and $\mathbf{F}_o$ is the external force exerted on the fluid per unit volume other than the elastic force.

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