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Onsager-theory-based dynamic model for nematic phases of bent-core molecules and star molecules

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ABSTRACT

We construct the molecular model and the tensor model for the dynamics of the nematic phases of bent-core molecules and star molecules in incompressible fluid. We start from the molecular interaction and the molecule–fluid friction, and write down a general formulation based on the molecular shape and the free energy. Then we incorporate an Onsager-theory-based static tensor model to obtain the dynamic molecular model fully determined by the molecular architecture. The tensor model is obtained by adopting the quasi-equilibrium approximation that maintains energy dissipation. For bent-core molecules and star molecules that have the same molecular symmetry, the form of the model is identical. The molecular architecture is differentiated by the coefficients that are derived as functions of molecular parameters. Numerical simulation is carried out for the shear flow problem using both the molecular and the tensor models, focusing on the effect of altering molecular architecture. When the equilibrium phase is biaxial, novel flow modes are found, and the flow mode sequences show delicate dependence on the molecular architecture. The tensor model proves to exhibit all the flow modes found in the molecular model.

1. Introduction

The liquid crystalline flows are studied extensively in the last few decades. The majority of works focus on rod-like molecules that can exhibit uniaxial nematic phase in equilibrium. The earliest and simplest approach is the macroscopic Ericksen–Leslie theory [23], in which the orientation is described by a unit vector. However, this approach is insufficient to investigate singular phenomena, such as defects. For the microscopic approach, Doi [10] established the kinetic equation of the density function (the Smoluchowski equation), which we call the molecular model. Doi theory has been applied to study the spatially homogeneous shear flow problem for rod-like molecules [12,13,21,22]. It has also been extended to inhomogeneous flows [14,27,40,46,47]. Despite its great success, the simulation is time-consuming, making its application to inhomogeneous flows rather restricted. To reduce the dimension of variables, many works aim to construct models in which the orientation is described by tensors. Apart from some phenomenological tensor models [4,29], most tensor models are obtained by closure approximation of Doi theory [2,3,8,11,16,18–20,39,45]. With various closure approximations for different types of flows, the tensor models have proved to be able to capture the phenomena in the molecular model, although no one closure approximation can recover all the phenomena.

When the molecule is not axisymmetric, the phase behavior can become very complicated. As a representative, bent-core molecules have attracted much attention. Even when restrained to nematics phases, they have proved to show the biaxial nematic phase [1,26] and the modulated twist-bend phase [6,9,28]. The nematic phase behavior of bent-core molecules has also been discussed theoretically [5,15,31,32,37]. The most eminent difference between bent-core molecules and rod-like molecules is that numerous experiments have shown that the phase behavior is sensitively dependent on specific molecular architecture [36], which is far from well-understood. The dynamics of bent-core molecules is thus expected to be fascinating. In particular, it is extremely desirable to understand the connection between the molecular architecture and the macroscopic flow pattern.

In [17], a three-level schema is proposed for the modeling of rod-like liquid crystals, applicable for both static and dynamic theory. Starting from the molecular model, one can derive the tensor model, then the vector model (Oseen–Frank and Ericksen–Leslie theory), with all the coefficients determined by molecular parameters and the energy dissipation retained. We have applied the approach to the static theory of rigid molecules with achiral twofold symmetry, two of which are bent-core molecules and star molecules (see Fig. 1). For molecular

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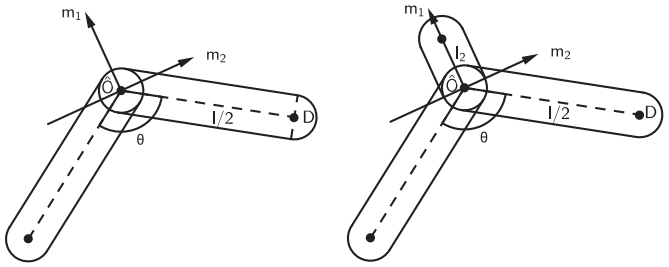

Fig. 1. Bent-core molecule and star molecule.

interaction, we consider the Onsager theory, i.e. adopt the hardcore interaction that is determined by the molecular architecture. We have studied the order parameters and homogeneous phases [43], where we have shown that three tensors, one first-order (vector) and two second-order symmetric, shall be chosen. The elastic energy is derived in [42] to investigate modulated nematic phases. It also enables us to examine how the elastic constants are affected by molecular architecture [44]. The key point is that the order parameters and the form of the free energy are determined by molecular symmetry. In other words, for bent-core and star molecules, or other molecules with the same symmetry such as T-shaped, W-shaped, equilateral-triangular-shaped, and circular-arc-shaped, the order parameters and the form of free energy are identical. The molecular architecture, which is a crucial factor as the experiments indicate, is distinguished by the coefficients that are derived as functions of molecular parameters.

Now we turn to the dynamics of non-axisymmetric liquid crystals. Macroscopic dynamic models have been proposed for the biaxial nematic phase [7,24,30] as an extension of the Ericksen–Leslie theory. Their applications are even more limited than the Ericksen–Leslie theory, because multiple nematic phases may coexist. Meanwhile, to our knowledge, no tensor model has been proposed. As for the microscopic approaches, the Smoluchowski equation is adopted to investigate the dynamics of ellipsoids [34,35] and bent-core molecules [33]. These works present some inspiring results on the homogeneous shear flow problem, obtaining several flow modes different from rod-like molecules. Despite this, they are far from sufficient for the aim to build connection between molecular architecture and flow pattern. One apparent limitation is that the model in these works includes only the local biaxial interaction. A less noticeable but much more serious drawback is the inconsistency of the coefficients with the molecular architecture. Some coefficients are phenomenological, and some are derived from different molecular architecture. It makes the model unable to definitely claim that certain flow patterns are resulted from a certain molecule, because it is solely the coefficients that differentiate molecular architecture. The results also show inconsistency in symmetry. The appearance of nonzero mixed second moments does not comply the twofold molecular symmetry, which we will discuss in our numerical results. These shortcomings shall be overcome in this paper.

The main goal of this paper is to establish a dynamic model that clearly reflects the effect of molecular architecture on flow patterns. We consider the hardcore molecular interaction and the friction between molecules and the fluid. For the molecule–fluid friction, we write down the general formulation. Then we carefully adopt the same molecular architecture as in the static model, so that we can build the free energy into the dynamic model consistently. In this way, we are able to write down the molecular model, with the energy dissipation law, fully based on molecular architecture and physical parameters. Since it makes no difference in derivation, we write down a generic model that is available for future applications to inhomogeneous flows. Similar to the static model, for bent-core molecules and star molecules, the dynamic model shares the same form because they have the same molecular symmetry. This is also the case if we consider other types of microscopic interactions. The molecular architecture is differentiated by the coefficients that are deduced from molecular parameters.

We then derive the dynamic tensor model that describes the orientation more concisely, which has not been considered in literature and is our second goal. We deduce the equation of the three tensors appearing in the free energy from the Smoluchowski equation. The high-order tensors appearing in the tensor model are expressed by the three tensors using quasi-equilibrium approximation, a generalization of the Bingham closure, which keeps the energy dissipation law. Also, the tensor model inherits the property that the form and coefficients are determined by the molecular symmetry and the molecular parameters, respectively.

For the numerical simulation, we restrain our attention to the shear flow problem. We examine the flow modes for both bent-core molecules and star molecules, illustrating the ability of the model to systematically study the variation of flow modes resulting from adjusting molecular architecture. The results we obtain are consistent with the molecular symmetry. In particular, we choose the parameters in the vicinity of the uniaxial–biaxial phase boundary in quiescent fluid, which is not studied previously. We find that the flow mode sequences do not vary much in uniaxial regions, but exhibit big change in the biaxial region. Moreover, in the biaxial region, we find flow modes that do not resemble any one reported previously. Also, we compare the results obtained from the molecular model and the tensor model. The tensor model is able to exhibit all the flow modes found in the molecular model, although under different parameters. The sequence is mostly identical at low shear rates.

The paper is organized as follows. In Section 2 we derive the molecular model. In Section 3 we derive the tensor model and prove the energy dissipation along with the quasi-equilibrium closure approximation. In Section 4 we use both the molecular model and the tensor model to examine the shear flow problem. Concluding remarks are given in Section 5.

2. Molecular model

2.1. Notations

We view the molecules that form liquid crystalline states as fully rigid. Thus, we may choose a body-fixed orthogonal frame $(\hat{O}; \boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ to describe the position and the orientation of a molecule. In a space-fixed orthogonal coordinate system $(O; \boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)$, they can be expressed in terms of $\boldsymbol{x} = \overrightarrow{O\hat{O}}$ and a three-dimensional proper rotation $P \in SO(3)$. In the language of matrix, P is a 3×3 orthogonal with $\det P = 1$ such that

$$(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3) = (\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)P. \tag{2.1}$$

The elements of $P^T = (m_{ij})$ are the components of $\boldsymbol{m}_i$, denoted by $m_{ij} = \boldsymbol{m}_i \cdot \boldsymbol{e}_j$.

In some cases, we need to specify a point on the molecule, and we use its coordinates $\hat{\boldsymbol{r}}$ in the body-fixed frame $(\hat{O}; \boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$. Every $P \in SO(3)$ can be expressed by Euler angles α, β, γ:

$$P(\alpha, \beta, \gamma) = \begin{pmatrix} \cos\alpha & -\sin\alpha\cos\gamma & \sin\alpha\sin\gamma \\ \sin\alpha\cos\beta & \cos\alpha\cos\beta\cos\gamma & -\cos\alpha\cos\beta\sin\gamma \\ & -\sin\beta\sin\gamma & -\sin\beta\cos\gamma \\ \sin\alpha\sin\beta & \cos\alpha\sin\beta\cos\gamma & -\cos\alpha\sin\beta\sin\gamma \\ & +\cos\beta\sin\gamma & +\cos\beta\cos\gamma \end{pmatrix}, \tag{2.2}$$

with

$$\alpha \in [0, \pi], \quad \beta, \gamma \in [0, 2\pi).$$

The uniform probability measure on SO_3 is given by

$$\mathrm{d}\nu = \frac{1}{8\pi^2}\sin\alpha \mathrm{d}\alpha\mathrm{d}\beta\mathrm{d}\gamma.$$