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General liquid-crystal theory for anisotropically shaped molecules: Symmetry, orientational order parameters, and system free energy

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A general theory of liquid crystals is presented, starting from the group-theory symmetry analysis of the constituting molecules. A particular attention is paid to the type of elastic free-energies and their relationships with the molecular symmetries. The orientational order-parameter tensors are identified for each molecular symmetry, in a consideration of consistently keeping the leading, characteristic elastic free energies in a model. The order parameters are expressed in terms of symmetric traceless tensors, some of high orders, for all major molecular symmetries, including seven groups of axial symmetries and seven groups of polyhedral symmetries. For spatially inhomogeneous liquid crystals, the couplings of these tensors in the elastic energies are derived by expanding the interaction energies between these molecules. The aim is to provide a general view of the molecular symmetries of individual molecules, orientational order parameters characterizing the orientational distribution functions, and the elastic free energies, all under one single group-theory approach.

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I. INTRODUCTION

To order or not to order, this is an essential question in a complex fluid composed of molecules that have anisotropic shapes and interact with each other by potential energies depending on the orientations of the molecules. Under the appropriate physical condition, a liquid-crystal phase can form, which accompanies global or local orientational correlations and could also display coupled spatial ordering. One of the most common examples is a liquid crystal consisting of rodlike rigid molecules, which displays a nematic state where a global orientational ordering can be identified [1].

At the molecular level, the symmetry of the constituting molecules has a direct impact on the orientational and spatial symmetries of the resulting liquid-crystal phases. The self-assembled structures of these molecules spontaneously exhibit various types of local orientational ordering and spatial modulation, which are sensitive to the unique characteristics of the original molecular architecture. At a macroscopic level, on the other hand, it is sometimes difficult to immediately trace the formed states back to the molecular-level symmetry of an observed liquid-crystal phase. The link between the symmetries at these two levels is dictated by identifying order parameters allowed by the molecular-level symmetries and the invariant transformation of the system's free energy as a function of these order parameters. The Landau–de Gennes (LdG) expansion, for example, is a free-energy expansion on the order parameters; typically, the polynomial expansion is up to terms (usually of degree four) that can be used to completely maintain the stability of the resulting phases.

To most of us, the familiar example is a system composed of rodlike linear molecules [Fig. 1(a)], which has the possibility of displaying a variety of disordered and ordered phases (isotropic, nematic, smectic-A, and smectic-C) depending on the physical conditions. The physical properties of the free energy is often described in terms of a second-order, 3×3 order-parameter tensor, and the basic structure of the LdG expansion is now well-known. Such a free energy is expressed in terms of nonspatial derivative terms (the so-called bulk terms) and quadratic products of spatial derivatives of the order parameter tensor (the so-called elastic terms).

Here, when we say "molecule," we refer to a basic unit in the liquid. It can be a real molecule in the usual sense or it can also be a rigid colloid particle that is described by a unique shape. Beyond rodlike shapes, the architectures of liquid-crystal molecules can be more exotic (see, e.g., Fig. 1). For example, much recent interest has been placed on the bent-core molecules [2,3]; one of the liquid-crystal phases that these molecules show is the twist-bend phase [4–6], a modulated nematic phase where the orientation of the nematic director has a spatial modulation. Other molecules, such as crosslike molecules [7–9], have also come into sight; the main order parameter requires the embedding the fourfold rotational symmetry of a single molecule.

A short-cut to study the orientationally ordered state is the use of a model similar to the original Oseen-Frank theory [1,10]. Typically, the orientational properties are oversimplified by using a main-axis director field only, which

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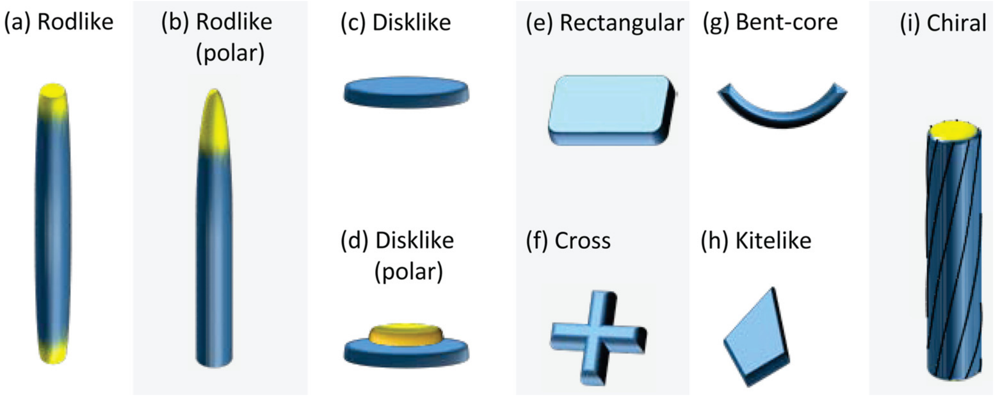


FIG. 1. Common examples of rigid molecules: (a) Rodlike (point group $D_{\infty h}$), (b) Polar rodlike ($C_{\infty v}$), (c) Disklike ($D_{\infty h}$), (d) Polar disklike ($C_{\infty v}$), (e) Rectangular (D_{2h}), (f) Cross (D_{4h}), (g) Bent-core (C_{2v}), (h) Kitelike (C_{2v}), and (i) Chiral (D_n where $n = 10$).

is a unit vector field depending on the spatial location $\boldsymbol{r}$; the free energy is then proposed in terms of spatial derivatives of the vector field, where, at this stage, some of the anticipated orientational-ordering properties are taken into account [11–15]. This has been one of the popular approaches to describe mechanical distortions (bending, splay, twist, etc.) of the director field in response to the external force. Recent progress has been made in proposing extended Oseen-Frank models to study particular phases of systems composed of nontraditionally shaped molecules [16–18]. For example, Ref. [19] is an attempt to propose extensions of the Oseen–Frank theory systematically. However, it is widely appreciated that the Oseen-Frank-type models suffer from a number of difficulties: Its lack of transparency to the symmetry of the constituting molecules, its incapability in describing orientational properties beyond the single main axis (e.g., biaxiality), and its singularity catastrophe at the orientational defect points. These can all be overcome by a LdG model. The concept of the director field is not used in LdG originally and, instead, is produced as a result of the model.

The LdG theory for a system composed of rodlike molecules (straight-line shaped) calls for the identification of a second-order, 3 × 3 tensor order parameter, in which elements are functions of $\boldsymbol{r}$. As it turns out, to build a LdG-type theory for systems beyond rodlike molecules is not simple. The consideration is already nontrivial for spatially homogeneous phases (i.e., the so-called bulk phases). For some systems, high-order and even more-than-one order parameter tensors are required in order to form a complete description. For example, to describe molecules with a twofold symmetry, two second-order tensors were suggested [20–24]; to describe the tetrahedral phase, a third-order order parameter tensor was introduced [25–30]; to describe the cubic phase, a fourth-order tensor was introduced [31]; to describe the phases formed by bent-core molecules [32], four order parameter tensors, one first-order, two second-order, and one-third order, were proposed [33]; to explore additional phases of molecules of twofold, threefold, and tetrahedral symmetries, effects of the third-order tensors were examined [34,35]. In order to describe experimentally observed structures in nonrodlike systems, extensions to include the spatial distortion and modulation of the liquid-crystal structures were also proposed [26,36,37].

Hence, we face two fundamental problems: One is to find suitable order parameters used in a free-energy model for molecules having a certain symmetry and the other is to find the useful terms in a generalized free-energy expansion on these order parameters. A correctly built free-energy model forms the basic step towards understanding of the stability of resulting phases, which can have coupled orientational ordering and spatial modulations. Here we take a top-down approach, going through all major classes of molecular symmetries according to their group-theory classification. Our aim is to provide a complete guide to the types of symmetric traceless order parameters for all major classes of molecules and their elastic free-energy terms.

An individual molecule has built-in symmetries. With the appropriate definition of the symmetric axes, its symmetries can be classified according to symmetry operations in the $O(3)$ point group [38]. Molecules with different architectures may have the same symmetry. Illustrated in Fig. 1 are a few typical liquid-crystal molecules that have been studied in recent years by experiments, computer simulations, and free-energy models. Rodlike and disklike molecules both have axisymmetry and head-to-tail reflection symmetry; they are common examples in traditional liquid-crystal theories [1]. Rodlike and disklike molecules that do not have the head-to-tail reflection symmetry are sometimes referred to as polar molecules, although electric or magnetic dipoles are not necessarily involved. Square-shaped (a special case of cuboid-shaped) [20] and cross-shaped molecules [7,8] are planar molecules that allow fourfold rotation about the plane-normal; the plane itself is a mirror plane. Rectangular platelets naturally have embedded biaxiality at the molecular level [39]. Bent-core [2,3] and kite-shaped [9] molecules are also planar molecules containing an in-plane reflection mirror, now with a twofold rotation axis in the plane. The molecular symmetry are generated not only by its intrinsic chemical bonds but also other types of physical quantities, such as electric or magnetic moments.

The identification of a high-order symmetric traceless tensor as an order parameter for a molecule is not a trivial task. It starts with the formation of the moment tensors, consisting of characteristic tensor products of the main orientational vectors of molecules. Then, to form a symmetric and traceless tensor, one seeks the linear combination of the moment

TABLE I. Summary of the main results. The first column categorizes molecules into classes according the $SO(3)$ group symmetry. The identified order parameters are listed in the second column, where the discussion of the properties of the symmetric traceless tensors can be found in Sec. III A, and the mathematical definition of these tensors can be found in Appendix B. The molecular groups, categorized by further improper rotational operations in the $O(3)$ group (listed in the third column), can share the same orientational order parameter tensors within a class. The basic forms of the bulk free energy for each group as a function of the order parameters are listed in the fourth column. Depending on the symmetries of the systems, the elastic energies are listed in the fifth (I, linear spatial derivatives of the order parameters) and sixth columns (II, quadratic spatial derivatives of the order parameters). The numbers in these three columns refer to the equations in Sec. IV.

Molecular class	Orientational order parameters	Molecular group	Bulk-energy terms	Elastic energy (I)	Elastic energy (II)
C_∞	$\mathsf{Q}^{[0]}, \mathsf{Q}^{[1]}, \mathsf{Q}^{[2]}$	C_∞ Sec. IV C 1	(27)	(28)	(29)
		$C_{\infty h}$ Sec. IV C 2	(27)	0	(29)
		$C_{\infty v}$ Sec. IV C 3	(30)	(31)	(32)
D_∞	$\mathsf{Q}^{[0]}, \mathsf{Q}^{[2]}$	D_∞ Sec. IV D 1	(33)	(34)	(35)
		$D_{\infty h}$ Sec. IV D 2	(33)	0	(35)
C_n	$\mathsf{Q}^{[0]}, \mathsf{Q}^{[1]}, \ldots, \mathsf{Q}^{[n]}$, $\mathsf{M}_1^{[n]}, \mathsf{M}_2^{[n]}$	C_n Sec. IV E 1	(36)	(37)	(38)
		C_{nv} Sec. IV E 2	(39)	(40)	(41)
		C_{nh}, n even Sec. IV E 3	(36)	0	(38)
		C_{nh}, n odd Sec. IV E 4	(42)	(43)	(44)
		S_{2n}, n even Sec. IV E 4	(42)	(43)	(44)
		S_{2n}, n odd Sec. IV E 3	(36)	0	(38)
D_n	n even: $\mathsf{Q}^{[0]}, \mathsf{Q}^{[2]}, \ldots,$ $\mathsf{Q}^{[n]}, \mathsf{M}_1^{[n]}$; n odd: $\mathsf{Q}^{[0]}, \mathsf{Q}^{[2]}, \ldots,$ $\mathsf{Q}^{[n-1]}, \mathsf{M}_1^{[n]}$	D_n, n odd Sec. IV F 1	(45)	(46)	(47)
		D_n, n even Sec. IV F 1	(48)	(49)	(50)
		D_{nh}, n odd Sec. IV F 2	(51)	(52)	(53)
		D_{nh}, n even Sec. IV F 3	(48)	0	(50)
		D_{nd}, n odd Sec. IV F 4	(45)	0	(47)
		D_{nd}, n even Sec. IV F 5	(54)	(55)	(56)
T	$\mathsf{Q}^{[0]}, \mathsf{T}, \mathsf{O}$	T Sec. IV G 1	(57)	(58)	(59)
		T_d Sec. IV G 2	(60)	(61)	(62)
		T_h Sec. IV G 3	(57)	0	(59)
O	$\mathsf{Q}^{[0]}, \mathsf{O}$	O Sec. IV H 1	(63)	(64)	(65)
		O_h Sec. IV H 2	(63)	0	(65)
I	$\mathsf{Q}^{[0]}, \mathsf{H}$	I Sec. IV I 1	(66)	(67)	(68)
		I_h Sec. IV I 2	(66)	0	(68)

tensors. A number of existing literatures discuss various approaches for tensor algebra [40–43]. The exact tensor algebra needed for the current problem is documented in Ref. [44], in which the explicit expression of linearly independent, nonvanishing symmetric traceless tensors allowed by each molecular symmetry is examined. These tensors are expressed in terms of, e.g., the Legendre polynomials and the Chebyshev polynomials.

This paper contains the following main sections.

(1) The $O(3)$ symmetry operations contain two basic types: proper rotations (direct rotations of the axes) and improper rotations (mirror and inverse symmetry operations). Among these, the proper rotations form the $SO(3)$ group, which by itself represents the physical rotation of a molecule-mounted frame. With these $SO(3)$ rotations, the molecule-mounted frame is rotated to new positions but the molecule configurations are identical to the old one. Molecules that have common $SO(3)$ rotations are identified as a class (described in the first column of Table I). The additional mirror and inverse symmetry operations, allowed by the $O(3)$ group, are further used to identify molecules into groups (the third column of Table I). The symmetry properties of molecules are discussed in Sec. II.

(2) The values of the probability distribution function of all rotated orientations of a particular class of molecules are identical due to the symmetry. This has a direct consequence on the moment tensors of the distribution function itself. Some moment tensors (symmetrized and made traceless) hence vanish. At the molecular level, the orientational properties are completely described by the $SO(3)$ operations of a class, which enable us to identify the type of orientational moment tensors of each class. This is discussed in Sec. III.

(3) The symmetry properties of the moment tensors are different among different classes of molecules. The question, then, becomes how many nonvanishing ones should be kept to characterize a specific class. A simple answer would be: One keeps the leading nonvanishing symmetric traceless tensors and neglects all higher order ones. However, this is not complete. The improper rotations have an important consequence on the free-energy expansion, which render some elastic-energy terms to zero. Here the principle of selecting the orientational order parameters is: Keeping as many order parameters as possible but keeping the number of order parameters at minimum, to differentiate the various molecular groups, at the free-energy level. Such a top-down approach oversees the symmetry properties from the group-theory perspective, covering all molecular types in general. Section IV discusses these procedures, and the third column of Table I lists the minimal number of orientational order parameters required under such a principle.

(4) What are the profound consequences of the group-theory exercise carried out in this study? Using a top-down approach, we can examine the possible liquid-crystal states and their relationship to the free-energy terms determined in Sec. IV. From a theoretical analysis, in Sec. V we demonstrate a number of examples where the experimentally observed structures of different groups of molecules, some of which are illustrated in Fig. 1, can be accounted for within the scope of the group theory.

The current study involves a number of concepts in mathematics and the processes of reaching the conclusions are cumbersome. The intermediate mathematical derivations are minimized in the current paper; interested readers can refer to Refs. [44,45] for the original derivations. The main results of the current work are summarized in Table I. This table can be compared with previous results where the order parameters can be over-simplified, and the couplings of different order parameters are hence incomplete (see Sec. III J for discussion). Readers who are not interested in the detailed discussion can directly refer to this table, which could be used in number of ways.

If the starting point of a theoretical study is a particular molecular potential energy, one can follow the recipe given in Sec. IV and produce the coefficients of the bulk and elastic terms listed in the table. Following that there are at least two approaches that can be taken. The first is to completely expand the entropy term as well, to the typical forth-order, as the polynomials of the identified order parameters, to form a LdG-type free energy. The second is to keep the entropy term in a closed form but the interaction energy expanded; to this end, replacing it with a closed expression such as the the Bingham closure [32,46–48] is a useful approach. These approximated models can then be used for analyzing the properties of the ordered phases.

Beyond facilitating the free-energy expansion, the identification of the order parameters for each type of molecules can already aid other theoretical studies. For example, the molecular dynamics or Monte Carlo computer simulations are particle-based and produce an overall mesoscopic structure on the entire system. Our identified orientational order parameters in Table I can be used as the guide to identify the signature of a particular state in a computer simulation study, to relate the molecular based configurations themselves to an ordered state. Another level of theoretical approach would be the direct study of the density distribution functions, such as those based on a molecular theory (Onsager theory and other density functional theories); the results of these are expressed by the multidimensional variables, for which the identified order parameters hold the key to extracting the basic symmetry properties of the produced states [49–57].

It is possible that Table I can be used in inverse design of a particular liquid-crystal state. One takes the free-energy expressions in the last two columns of the table and identifies the desired liquid-crystal state through an analysis of the coupling terms. Then one can trace back to the first and third columns and design the molecules which have the required symmetries.

Given the vast body of the literature on the topic, what are the new materials in the current paper? First, we highlight the group symmetry taken in identifying the order parameter tensors. A broad issue is that what takes to form an order parameter. As carefully addressed in Sec. III A, our central view is that an order parameter tensor is defined through the (proper) rotational symmetries of a molecule-mounted frame, i.e., dictated by the $SO(3)$ group. These are real-space rotational operations that characterize the symmetry of a molecule and disallow the mutual switching between a right-hand frame to and from a left-hand frame. The consideration of other (improper) symmetries is then taken in forming the free-energy expansion, due to the symmetry properties of the interaction energy, which is invariant under operations of $O(3)$, explained in Sec. IV. Note that $SO(3)$ is a subgroup of $O(3)$. This can be contrasted with most previous theoretical studies in which $O(3)$ is taken to form the order parameters, either in a general study [25,58–62] or for specific systems [33]. More discussions can be found in Secs. III J and V D.

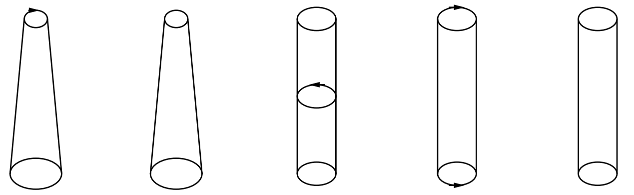
Then we highlight another main result of the current study, i.e., the identification of the elastic energy terms for all molecular groups. These terms form the basic backbone of a theoretical study on spatially inhomogeneous bulk states, shape distortion, confinement, and defect evolution of liquid crystals. It is at this level, $O(3)$ group symmetries are utilized (see Sec. IV). Although the elastic energies of a limited number of molecular groups have been proposed previously [26,32,36,37], as far as we know, the current work represents the first time where the elastic energies are examined systematically for all molecular symmetries.

II. MOLECULAR SYMMETRY

At the molecular level, the molecular symmetry is inherited from how a molecule is built from atoms, where the position of chemical bonds and the difference in chemical composition are the determinant factors. Here we construct our theory for molecules which can be approximated as a rigid body. We do not consider, for example, flexible polymers which contain other internal degrees of freedom. Regardless of the detailed molecular structures, we assume that the orientational and symmetry of a molecule can be represented by a rigid orthonormal coordinate frame (i.e., a body-fixed frame) "permanently" mounted on it, where the axes are denoted by three unit vectors $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ and the origin could be, but not necessarily is, the center of mass of the molecule. The molecular symmetry can then be identified within such a body-fixed coordinate frame, measured by three-dimensional orthogonal transformations, including proper and improper rotations that leave the state of a molecule unchanged. In the language of group theory, each symmetry operation is described by a subgroup of the general orthogonal group $O(3)$, as presented below. Throughout the paper, we adopt the Schönflies notation that can be found in, e.g., Refs. [38,63].

A. Axisymmetric molecules, class C_∞

Three $O(3)$ subgroups fall into this class, all containing a central rotational axis (here for demonstration purposes, assumed to be $\boldsymbol{m}_1$), about which the rotation of an arbitrary angle can take place. The common ground of the symmetry groups C_∞, $C_{\infty v}$, and $C_{\infty h}$ is that they all contain a $SO(3)$ axisymmetry that allows for rotation about $\boldsymbol{m}_1$. In addition,



(a) C_∞ (b) $C_{\infty v}$ (c) $C_{\infty h}$ (d) D_∞ (e) $D_{\infty h}$

FIG. 2. The five basic groups of axisymmetric molecules. The shapes and arrows are representative objects that indicate the basic symmetries listed in the text.

they have the following properties according to their $O(3)$ group:

(1) C_∞: No further symmetry transformations is allowed.

(2) $C_{\infty v}$: A *vertical* mirror plane divides the molecule into two parts that are mirror images of each other.

(3) $C_{\infty h}$: A *horizontal* mirror plane perpendicular to $\boldsymbol{m}_1$ divides the molecule into upper and lower halves that are mirror images to each other.

Figures 2(a)–2(c) illustrate the basic symmetry structures of these molecules.

B. Axisymmetric molecules, class D_∞

The $O(3)$ subgroups D_∞ and $D_{\infty h}$ both contain the $SO(3)$ axisymmetry that allows for rotation of an arbitrary angle about $\boldsymbol{m}_1$ and a twofold rotation symmetry about an axis perpendicular to $\boldsymbol{m}_1$. In addition, they have the following properties according to the $O(3)$ group:

(1) D_∞: No further symmetry transformation is allowed.

(2) $D_{\infty h}$: An additional *horizontal* mirror plane perpendicular to $\boldsymbol{m}_1$ divides the molecules into upper and lower halves that are mirror images to each other.

Figures 2(d) and 2(e) illustrate the basic symmetry structures of these molecules.

C. Finite axial-symmetric molecules, class C_n

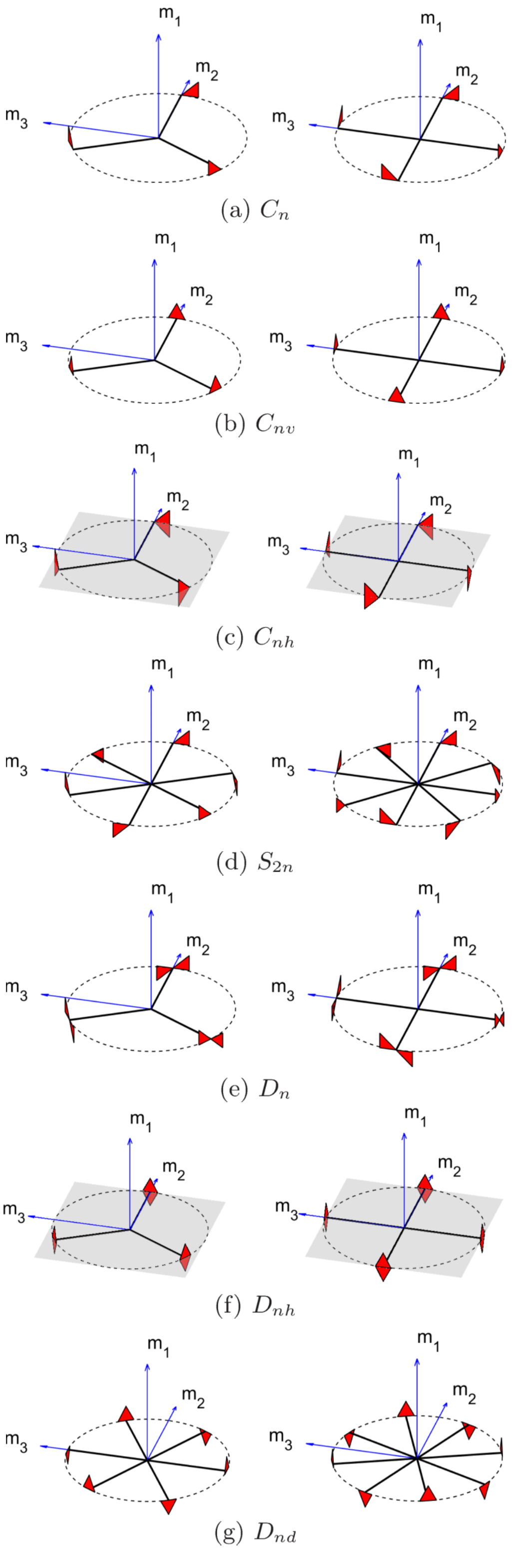
Common to these molecules is the existence of a main rotational axis, assumed to be $\boldsymbol{m}_1$ here, as illustrated in Fig. 3. An n-fold rotational symmetry implies that a rotation about $\boldsymbol{m}_1$ of an angle $2\pi/n$ brings the molecule to the same configuration after the rotation. In addition, C_n, C_{nv}, C_{nh}, and S_{2n} are further distinguished by other improper rotational properties in $O(3)$.

(1) C_n: No other symmetry in the molecule.

(2) C_{nv}: A *vertical* mirror plane containing both $\boldsymbol{m}_1$ and $\boldsymbol{m}_2$ axes divides the molecule to two halves located in the positive and negative $\boldsymbol{m}_3$ domains [Fig. 3(b)]; these halves are mirror images to each other.

(3) C_{nh}: A *horizontal* mirror plane containing both $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$ axes divides the two halves located in positive and negative $\boldsymbol{m}_1$ domains [Fig. 3(c)]; these halves are mirror images to each other.

(4) S_{2n}: The additional symmetry is represented by rotating the molecule with an angle π/n about $\boldsymbol{m}_1$ followed by the mirror plane reflection of the molecule against the plane containing both $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$ axes [Fig. 3(d)].



(a) C_n

(b) C_{nv}

(c) C_{nh}

(d) S_{2n}

(e) D_n

(f) D_{nh}

(g) D_{nd}

FIG. 3. The basic symmetries of the seven groups of molecules with an n-fold rotational symmetry about the principal $\boldsymbol{m}_1$ axis. For illustration purpose, $n = 3$ (left panel) and 4 (right panel) are used, represented by the symmetry formed by the dark arms. These arms have distinct decorations at the end, which further characterize other symmetry properties. The horizontal planes in plots (c) and (f) are shaded to indicate the mirror reflection symmetry against the $\boldsymbol{m}_2$-$\boldsymbol{m}_3$ plane.

D. Finite axial-symmetric molecules, class D_n

Two main rotational axes exist in these molecules. One is the n-fold rotational symmetry about $\boldsymbol{m}_1$ with an angle $2\pi/n$; the other is the twofold rotation about the $\boldsymbol{m}_2$ axis which brings the molecule to the original structure [dihedral symmetry, Figs. 3(e)–3(g)]. The two $O(3)$ subgroups further distinguish D_{nh} and D_{nd} by an improper rotation (here a mirror symmetry).

(1) D_n: No other symmetry in the molecule.

(2) D_{nh}: This class contains all symmetry operations allowed by D_n. In addition, a horizontal mirror plane that contains both $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$ axes yields the same configuration through the mirror reflection [Fig. 3(f)].

(3) D_{nd}: The main rotational symmetry is the rotation of an angle π/n about $\boldsymbol{m}_1$ followed by the mirror plane reflection of the molecule against the plane containing both $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$ axes (same as in S_{2n}). An additional rotation symmetry exists: about a dihedral axis [$\boldsymbol{m}_2$ in Fig. 3(g)], a π rotation brings the molecule to the same state. The combination of the symmetry in S_{2n} and the dihedral rotation effectively defines another mirror-plane operation, where the mirror contains $\boldsymbol{m}_1$ and one of the dark arms in the illustration.

E. Molecules of tetrahedral symmetries, Class T

These are molecules where more-than-one rotational axes can be identified with multiple-fold ($n \geqslant 3$) rotational symmetries. The molecular shapes are generally less anisotropic and more symmetric. Because of this reason, their tendency of forming a liquid-crystal phase is less explored in the literature. However, theoretically, a liquid composed of molecules of any anisotropic shape can form a macroscopically observable, ordered structures. The main symmetry properties are summarized in Fig. 4.

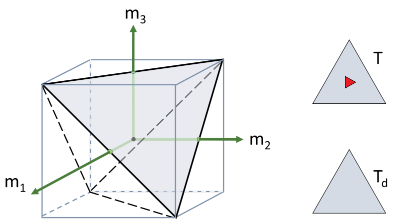
The characteristic rotational symmetries of class T are associated with a regular tetrahedron, shown in Fig. 4(a). These include three proper twofold rotations about $\boldsymbol{m}_1$, $\boldsymbol{m}_2$, and $\boldsymbol{m}_3$, and four proper threefold rotations about four center-to-corner axes, in $SO(3)$. These four axes can be defined through

$$\begin{aligned}
\boldsymbol{n}_1^T &= (\boldsymbol{m}_1 + \boldsymbol{m}_2 + \boldsymbol{m}_3)/\sqrt{3},\\
\boldsymbol{n}_2^T &= (\boldsymbol{m}_1 - \boldsymbol{m}_2 - \boldsymbol{m}_3)/\sqrt{3},\\
\boldsymbol{n}_3^T &= (-\boldsymbol{m}_1 + \boldsymbol{m}_2 - \boldsymbol{m}_3)/\sqrt{3},\\
\boldsymbol{n}_4^T &= (-\boldsymbol{m}_1 - \boldsymbol{m}_2 + \boldsymbol{m}_3)/\sqrt{3},
\end{aligned} \tag{1}$$

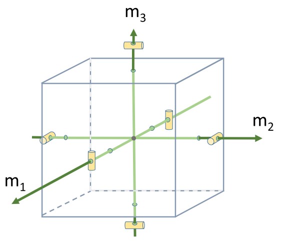
where the superscript T indicates tetrahedral symmetry. For example, the consecutive rotations about one of the threefold axes transforms $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ to $(\boldsymbol{m}_2, \boldsymbol{m}_3, \boldsymbol{m}_1)$, and then $(\boldsymbol{m}_3, \boldsymbol{m}_1, \boldsymbol{m}_2)$. In class T, the three groups T, T_d and T_h are further distinguished by improper rotational properties of $O(3)$.

(1) T: No further symmetry is allowed. Red triangles have been placed at the center of four tetrahedral surfaces, shown in Fig. 4(a), to differentiate T from T_d.

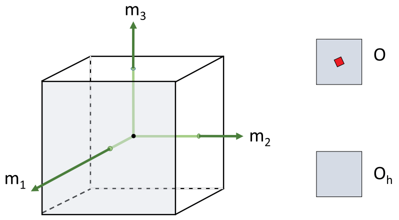
(2) T_d: The symmetry of T_d is exactly the symmetry of a regular tetrahedron. In addition to those rotational symmetries in T, the T_d group also has mirror-reflection symmetries, where the mirrors are those planes that contains two of the threefold axes $\boldsymbol{n}_i^T$ given in (1).



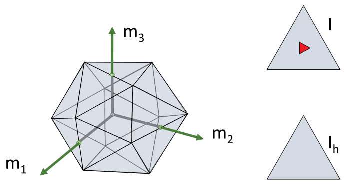
(a) T and T_d.



(b) T_h.



(c) O and O_h.



(d) I and I_h.

FIG. 4. Polyhedral groups that have the symmetry of regular tetrahedron (a, b), cube (c), and regular icosahedron (d). Some of the regularly shaped surfaces have been decorated by red shapes to show the lack of the inversion or mirror symmetries; upon these symmetry operations, the red shapes do not recover its original orientations.

(3) T_h: Here, in addition to all rotational symmetries in T, three mirror planes, each containing two of the $\boldsymbol{m}_i$ axes, exist. To illustrate this particular type of symmetries, we have decorated the $\boldsymbol{m}_i$ axes in Fig. 4(b) by small rod segments.

F. Molecules of cubic symmetries, Class O

The basic symmetry of this class of molecules follow the $SO(3)$ rotational symmetry operations of a cube, shown in

Fig. 4(c). The frame $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ in a cube is defined by the three center to face center directions. Each of the $\boldsymbol{m}_i$ axes is a fourfold rotational axis. In addition, the cube also allows threefold rotations about the axes defined in (1). Additional improper rotation symmetry of the $O(3)$ group further distinguishes O and O_h.

(1) O: No further symmetry is allowed. The decoration on the six surfaces of the cube illustrates this fact [see Fig. 4(c)].

(2) O_h: The group O_h exactly contains the symmetry operations of a cube, including the inversion symmetry. Effectively, the combination of the inversion and rotational symmetries can create a mirror symmetry—in this case, three mirror planes, each containing two of $\boldsymbol{m}_i$, and six mirror planes, each containing two of $\boldsymbol{n}_i^T$. Thus, the group O_h include the symmetry operations of both T_d and T_h groups.

G. Molecules of icosahedral symmetries, Class *I*

Molecules belonging to this class have the same $SO(3)$ rotational symmetries of a regular icosahedron, as illustrated in Fig. 4(d). From the icosahedron center to vertices are six rotational axes, about which fivefold rotations can take place. From the icosahedron center to the face centers are 10 rotational axes, about which threefold rotation can take place. Finally, about the three $\boldsymbol{m}_i$ axes and the icosahedron center to edge centers, 15 twofold rotational symmetries exist. The $O(3)$ improper rotation symmetries further distinguish I and I_h.

(1) I: No further symmetry is allowed. To illustrate this fact, the faces of the 20 regular triangles that make up the icosahedron are decorated with red triangles in Fig. 4(d).

(2) I_h: The symmetries in group I_h is exactly those of a regular icosahedron. An inversion symmetry about the icosahedron center is allowed. Combining with the twofold rotational axes, it effectively produces other mirror symmetries.

H. Discussion

In the above, we group molecules according to their $O(3)$ point-group symmetries. Note that the molecules here can be real molecules, large colloid particles, or even Janus nanoparticles synthesized to have anisotropic physicochemical properties. As such, our classification has a larger scope than the molecular symmetries typically described in a standard molecular-symmetry reference for small molecules.

The axisymmetric groups in Sec. II A are related to the groups described in Sec. II C by taking $n \to \infty$. The basic rotational angle for symmetry operation is now infinitesimally small. One can see the relationship,

$$\begin{aligned} &C_n \to C_\infty, \quad D_n \to D_\infty, \quad C_{nv} \to C_{\infty v},\\ &C_{nh},\, S_{2n} \to C_{\infty h}, \quad D_{nh},\, D_{nd} \to D_{\infty h}. \end{aligned} \tag{2}$$

In practice, a C_∞ molecule could be an approximation for a C_n molecule with a rather large n. As we discuss below, the order parameter tensor for C_∞ molecules has a lower tensor order than that of C_n and is easier to handle. Hence, there is a physical reason to keep the C_∞, $C_{\infty h}$, and D_∞ classes in our general theory, whereas they are usually ignored in molecular symmetry classification of small molecules where n rarely becomes large.

III. ORIENTATIONAL ORDER PARAMETERS

A. Symmetric traceless tensor moment

The last section describes the molecular symmetry in a body-fixed coordinate frame $\boldsymbol{m}_1$, $\boldsymbol{m}_2$, and $\boldsymbol{m}_3$ mounted on a molecule. Their orientation in reference to a right-handed laboratory frame can be defined by, e.g., the three Euler angles, α, β, and γ [64,65]. As the result, $\boldsymbol{m}_1$, $\boldsymbol{m}_2$, and $\boldsymbol{m}_3$ are expressed by column vectors in terms of these angles (see the explicit expressions in Appendix A). Below we denote the three axes by a matrix $\mathsf{u} = (\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$, and a solid angle element by $d\Omega = \sin\beta d\beta d\alpha d\gamma$.

In the most general case, the statistical physics of a liquid crystal that has spatial and orientational orderings is described by a distribution function $f(\boldsymbol{r}, \mathsf{u})$, which is a function of six variables: Three for $\boldsymbol{r}$ and three for u. It is assumed here that the distribution function is normalized by

$$\int d\boldsymbol{r} \int d\Omega f(\boldsymbol{r}, \mathsf{u}) = V, \tag{3}$$

where V is the volume occupied by the fluid. The isotropic phase, for example, has a uniform distribution in the orientational space hence the normalized distribution function $f_{\text{iso}} = 1/8\pi^2$.

In a liquid-crystal state, the most important characteristics of the distribution function $f(\boldsymbol{r}, \mathsf{u})$ are usually assessed by the tensor moments of this function,

$$\langle \boldsymbol{m}_{i_1} \otimes \cdots \otimes \boldsymbol{m}_{i_k} \rangle = \int \boldsymbol{m}_{i_1} \otimes \cdots \otimes \boldsymbol{m}_{i_k} f(\boldsymbol{r}, \mathsf{u})\, d\Omega, \tag{4}$$

where the integration covers the entire domain of the Euler angles, and $i_j = 1, 2, 3$ for $j = 1, 2, \ldots, k$. The symbol $\langle \cdots \rangle$ represents an average taken by using $f(\boldsymbol{r}, \mathsf{u})$ as the weight and $\otimes$ the tensor product between two vectors. On the right-hand side, the integrand $\boldsymbol{m}_{i_1} \otimes \cdots \otimes \boldsymbol{m}_{i_k}$ contains k factors of vectors, hence it is a kth-order tensor (it is also called kth rank, but we avoid that because of another meaning associated with the rank of a tensor). As a result, the moment on the left is a function of $\boldsymbol{r}$ for a spatially inhomogeneous system and is $\boldsymbol{r}$-independent otherwise.

However, these tensor moments themselves are not the best choice to describe the orientational ordering; in their original form, they are not all linearly independent. To construct a tensor orientational order parameter, one takes a linear combination of the tensor moments of the same order, with the basic requirement that the tensor order parameter must be symmetric and traceless. This way, the independent components of the tensor can then be easily accounted for, and the leading nonvanishing tensor order parameters can be identified.

For simplicity, here we use a monomial notation to represent symmetric tensors, where a product having no $\otimes$ implies that it is already symmetrized. For example, the symmetric tensors of first, second, and third orders are

$$\begin{aligned} \boldsymbol{m}_1 &= \boldsymbol{m}_1,\\ \boldsymbol{m}_1\boldsymbol{m}_2 &= \tfrac{1}{2}(\boldsymbol{m}_1 \otimes \boldsymbol{m}_2 + \boldsymbol{m}_2 \otimes \boldsymbol{m}_1), \end{aligned}$$

$$
\begin{aligned}
\boldsymbol{m}_1^2 &= \boldsymbol{m}_1 \otimes \boldsymbol{m}_1,\\
\boldsymbol{m}_1\boldsymbol{m}_2\boldsymbol{m}_3 &= \tfrac{1}{6}(\boldsymbol{m}_1 \otimes \boldsymbol{m}_2 \otimes \boldsymbol{m}_3 + \boldsymbol{m}_2 \otimes \boldsymbol{m}_3 \otimes \boldsymbol{m}_1\\
&\quad + \boldsymbol{m}_3 \otimes \boldsymbol{m}_1 \otimes \boldsymbol{m}_2 + \boldsymbol{m}_1 \otimes \boldsymbol{m}_3 \otimes \boldsymbol{m}_2\\
&\quad + \boldsymbol{m}_2 \otimes \boldsymbol{m}_1 \otimes \boldsymbol{m}_3 + \boldsymbol{m}_3 \otimes \boldsymbol{m}_2 \otimes \boldsymbol{m}_1),\\
\boldsymbol{m}_1\boldsymbol{m}_2^2 &= \tfrac{1}{3}(\boldsymbol{m}_1 \otimes \boldsymbol{m}_2 \otimes \boldsymbol{m}_2 + \boldsymbol{m}_2 \otimes \boldsymbol{m}_1 \otimes \boldsymbol{m}_2\\
&\quad + \boldsymbol{m}_2 \otimes \boldsymbol{m}_2 \otimes \boldsymbol{m}_1),
\end{aligned}
$$

where the permutation of the subscripts on the right-hand ensures that the tensor is symmetric. The overall numerical factors used here are consistent with the later definition of Q and M tensors, which can be associated with the Legendre and Chebyshev polynomials.

The second-order identity tensor is a special case,

$$\mathsf{id} = \boldsymbol{m}_1^2 + \boldsymbol{m}_2^2 + \boldsymbol{m}_3^2. \tag{5}$$

It has the simple matrix-element form: all diagonal elements have a value 1 and off diagonal 0. Here the identity tensor is used to generate a symmetric and *traceless* tensor by mixing it with a symmetric tensor, as discussed in Appendix B 2.

B. Construction of orientational order parameters

The symmetric traceless tensors defined above can be used to represent and distinguish different classes of molecules. This is due to a basic symmetry property: Within the ($\boldsymbol{m}_1$, $\boldsymbol{m}_2$, $\boldsymbol{m}_3$) frame, a molecule recovers its original state under a proper rotation operation. Hence, all rotated configurations should be equally probable. The profound consequence is that some low-order symmetric traceless tensors of a particular molecular class vanish. Keeping the leading nonvanishing symmetric traceless tensors, one then identifies the orientational order parameters, in a tensor form, of this class of molecules.

In a mathematical-physics language, the orientation of a molecule is represented by the body-fixed frame $\mathsf{u} = (\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$, in reference to the laboratory frame. Within $SO(3)$, a proper rotation of the molecule in reference to the body-fixed frame can be represented by a rotation matrix g, in which the Euler angles (now defined from the u-frame) have specific values permitted by the allowed symmetry operation. Such a rotation produces a new orientation of the body-fixed frame, in reference to the laboratory frame, represented now by ug (a matrix-matrix product; see Appendix A). Because the states of the molecule in body-fixed frames u and ug are identical, viewed from the laboratory frame, one has

$$f(\boldsymbol{r}, \mathsf{ug}) = f(\boldsymbol{r}, \mathsf{u}). \tag{6}$$

Plugging Eq. (6) into Eq.(4) allows for identification of the symmetry properties of the tensor moments:

$$\langle \boldsymbol{m}_{i_1} \otimes \cdots \otimes \boldsymbol{m}_{i_k} \rangle = \langle \boldsymbol{m}'_{i_1} \otimes \cdots \otimes \boldsymbol{m}'_{i_k} \rangle, \tag{7}$$

where $\mathsf{ug} = (\boldsymbol{m}'_1, \boldsymbol{m}'_2, \boldsymbol{m}'_3)$. These properties can then be carried over to the definition of the corresponding symmetric traceless tensors, which allows for the identification of vanishing ones due to the $SO(3)$ symmetry.

In either real or computer-simulated systems, the body-fixed frame on a molecule can translate and rotate [according to $SO(3)$] in the physical space. Although, from the mathematics of the symmetry analysis, a molecule could be characterized by additional improper rotations in $O(3)$, the actual mirror and inversion transformations of the body-fixed frame can never take place physically. Hence, the transformation matrix g in (6) can only be those of the $SO(3)$ group.

All subgroups of molecules in a class share exactly the same proper rotational symmetries. Then, a common, nonvanishing, symmetric-traceless-tensor set is available for identification of the orientational order parameters of all subgroups in a class. The improper rotational symmetries (mirror planes and center-inversion) divide a class further into subgroup of molecules, but are unused in establishing the symmetry property of the distribution density, Eq. (6). The free energy, on the other hand, is invariant under both proper and improper symmetry transformations. The number of leading order parameter tensors selected here, sometimes beyond one, enables distinguishing of the subgroups at the free-energy level, which is a concept more thoroughly addressed in Sec. IV.

While the principal procedure is clear, the actual derivation for each class of molecules is tedious and cumbersome. We refer to Ref. [44] for mathematical details and omit the intermediate steps. Next we list the main results from such a group-theory exercise.

C. Axisymmetric molecules, class C_∞

Because of the axisymmetry, the Euler angle γ is irrelevant and we can show that the orientational properties are governed by the main axis $\boldsymbol{m}_1$. The zeroth-, first-, and second-order symmetric traceless tensors generated by $\boldsymbol{m}_1$ are

$$\mathsf{Q}^{[0]} = \langle 1 \rangle, \tag{8a}$$

$$\mathsf{Q}^{[1]} = \langle \boldsymbol{m}_1 \rangle, \tag{8b}$$

$$\mathsf{Q}^{[2]} = \left\langle \boldsymbol{m}_1^2 - \tfrac{1}{3}\mathsf{id} \right\rangle. \tag{8c}$$

The superscript with square brackets indicates the order of the tensor. The density variation is described by the zeroth-order tensor. Both $\mathsf{Q}^{[1]}$ and $\mathsf{Q}^{[2]}$ are kept here as the orientational order parameters, as they have different elastic-energy properties to be discussed below. The coefficients of the $\mathsf{Q}^{[n]}$ tensor can be generally related to those of the Legendre polynomial of degree n (see Appendix B).

D. Axisymmetric molecules, class D_∞

Again, the Euler angle γ disappears from the angular matrix u. The additional dihedral rotation in D_∞ makes $\mathsf{Q}^{[1]}$ vanish. Hence together with the density variation described by $\mathsf{Q}^{[0]}$, $\mathsf{Q}^{[2]}$ is the orientational order parameter tensor for class D_∞. Rodlike and disklike molecules belong to the D_∞ class and the use of $\mathsf{Q}^{[2]}$ is common in the literature.

E. Finite axial-symmetric molecules, class C_n

One of the most important symmetry properties of class C_n (also D_n below) is the n-fold rotational symmetry about the $\boldsymbol{m}_1$ axis, where γ is the Euler rotation angle that has a basic unit value $\gamma = 2\pi/n$. A single rotation of this angle changes the directions of $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$ to $\boldsymbol{m}'_2$ and $\boldsymbol{m}'_3$ within the body-fixed frame. As explained in Appendix A, such a rotation operation can be represented by the matrix $\mathsf{g} = (\boldsymbol{m}_1, \boldsymbol{m}'_2, \boldsymbol{m}'_3)$. To complete all rotational positions about the $\boldsymbol{m}_1$ axis, n consecutive rotations with the basic unit angle $\gamma = 2\pi/n$, must be taken, which requires the use of n powers of the g matrix. Hence, we know that a tensor formed by the product of g factors of $\boldsymbol{m}_1$, $\boldsymbol{m}'_2$, and $\boldsymbol{m}'_3$ is required to describe the rotational symmetry in class-C_n (also D_n below). In the Euler-angle representation, after all n factors are considered, a typical matrix element contains terms such as $\cos^n\gamma$ and $\sin^n\gamma$.

As it turns out, two kinds of nth-order symmetric traceless tensors, $\mathsf{M}_1^{[n]}$ and $\mathsf{M}_2^{[n]}$, are needed to represent the orientations of $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$, where the subscript labels the kind. Loosely speaking, this is caused by the need of including two orthogonal directions, $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$. For class C_n, it can be shown that the leading nonvanishing symmetric traceless tensors, $\mathsf{M}_1^{[n]}$ and $\mathsf{M}_2^{[n]}$, are nth-order. Hence, both the first- and second-kind $\mathsf{M}_1^{[n]}$ and $\mathsf{M}_2^{[n]}$ are selected as the orientational order parameters of class C_n. Here we list a few examples. The low-order first-kind order parameters are

$$\mathsf{M}_1^{[2]} = \big\langle 2\boldsymbol{m}_2^2 - \big(\mathsf{id} - \boldsymbol{m}_1^2\big)\big\rangle = \big\langle \boldsymbol{m}_2^2 - \boldsymbol{m}_3^2\big\rangle, \tag{9a}$$

$$\mathsf{M}_1^{[3]} = \big\langle 4\boldsymbol{m}_2^3 - 3\big(\mathsf{id} - \boldsymbol{m}_1^2\big)\boldsymbol{m}_2\big\rangle, \tag{9b}$$

$$\mathsf{M}_1^{[4]} = \big\langle 8\boldsymbol{m}_2^4 - 8\big(\mathsf{id} - \boldsymbol{m}_1^2\big)\boldsymbol{m}_2^2 + \big(\mathsf{id} - \boldsymbol{m}_1^2\big)^2\big\rangle, \tag{9c}$$

and the second-kind are

$$\mathsf{M}_2^{[2]} = \langle 2\boldsymbol{m}_2\boldsymbol{m}_3\rangle, \tag{10a}$$

$$\mathsf{M}_2^{[3]} = \big\langle 4\boldsymbol{m}_2^2\boldsymbol{m}_3 - \big(\mathsf{id} - \boldsymbol{m}_1^2\big)\boldsymbol{m}_3\big\rangle, \tag{10b}$$

$$\mathsf{M}_2^{[4]} = \big\langle 8\boldsymbol{m}_2^3\boldsymbol{m}_3 - 4\big(\mathsf{id} - \boldsymbol{m}_1^2\big)\boldsymbol{m}_2\boldsymbol{m}_3\big\rangle. \tag{10c}$$

Appendix A explains how they are constructed with the aid of the first- and second-kind Chebyshev polynomials.

All Q tensors survive the symmetry operations of class C_n. Here there is a dilemma of what need to be selected as the orientational order parameters. For a complete description of the orientational ordering, one needs to keep at least the leading order $\mathsf{M}_1^{[n]}$ and $\mathsf{M}_2^{[n]}$. Then, the matching order in Q is also n and one keeps all $\mathsf{Q}^{[k]}$ tensors, $k = 0, 1, 2, 3, \ldots, n$, up to that order. The last one, $\mathsf{Q}^{[n]}$, for example, is needed to couple the order parameters $\mathsf{M}_1^{[n]}$ or $\mathsf{M}_2^{[n]}$, in the free-energy expansion [see next section].

An important example is the C_2 class of a relatively small $n = 2$. Here $\mathsf{Q}^{[1]}$, $\mathsf{Q}^{[2]}$, $\mathsf{M}_1^{[2]}$, and $\mathsf{M}_2^{[2]}$ are all needed for a complete treatment of the systems consisting of kite or bent-core molecules. See Sec. V D.

F. Finite axial-symmetric molecules, class D_n

The main difference between the D_n and C_n classes is the existence of a twofold symmetry about an axis perpendicular to $\boldsymbol{m}_1$. It eliminates all M_2 tensors and all $\mathsf{Q}^{[\mathrm{odd}]}$ tensors. This greatly reduces the number of order parameters needed for a complete description of the ordered systems, in comparison with those belonging to the counterpart C_n class.

A special example is $n = 4$. Both square and cross molecules belong to this molecular group. From the above assessment, in addition to the density variation $\mathsf{Q}^{[0]}$, three orientational order parameters are required, $\mathsf{Q}^{[2]}$, $\mathsf{Q}^{[4]}$, and $\mathsf{M}_1^{[4]}$. Here,

$$\mathsf{Q}^{[4]} = \big\langle \boldsymbol{m}_1^4 - \tfrac{6}{7}\boldsymbol{m}_1^2\mathsf{id} + \tfrac{3}{35}\mathsf{id}^2\big\rangle,$$

as discussed in Appendix B.

G. Tetrahedral class T

The class T is associated with the symmetry of a tetrahedron. The existence of the twofold rotational axes, as discussed in Sec. II E, can transform the molecule in such a way that two of the $\boldsymbol{m}_i$ axes are rotated to their opposite directions; for example, a molecular frame $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ can be rotated into $(\boldsymbol{m}_1, -\boldsymbol{m}_2, -\boldsymbol{m}_3)$ and recovers its symmetry. This requires that in a moment expansion (4), the powers of $\boldsymbol{m}_1, \boldsymbol{m}_2$, and $\boldsymbol{m}_3$ are simultaneously all even, or simultaneously all odd.

Another type of the essential T symmetry operations is the rotation of the frame $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ into $(\boldsymbol{m}_2, \boldsymbol{m}_3, \boldsymbol{m}_1)$, and then $(\boldsymbol{m}_3, \boldsymbol{m}_1, \boldsymbol{m}_2)$. This implies that the moment tensors should be invariant under such rotations.

Combining the consideration of these two requirements, in addition to the density variation $\mathsf{Q}^{[0]}$, the leading nonvanishing symmetric traceless tensors are

$$\mathsf{T} = \langle \boldsymbol{m}_1\boldsymbol{m}_2\boldsymbol{m}_3\rangle \tag{11}$$

and

$$\mathsf{O} = \big\langle \boldsymbol{m}_1^2\boldsymbol{m}_2^2 + \boldsymbol{m}_2^2\boldsymbol{m}_3^2 + \boldsymbol{m}_3^2\boldsymbol{m}_1^2 - \tfrac{1}{5}\mathsf{id}^2\big\rangle. \tag{12}$$

Both are selected as the orientational order parameters for class T. The need of including both T and O can be further seen in the free-energy expansion.

The definition of T in (11) was also suggested in Ref. [29]. The tensor T can be re-cast into another version,

$$\mathsf{T} = \frac{\sqrt{3}}{8}\sum_{j=1}^{4}\big(\boldsymbol{n}_j^T\big)^3, \tag{13}$$

where the unit vectors $\boldsymbol{n}^T$ are defined in (1). This is an equivalent expression, which was used in Ref. [26]. The tensor O has two identical forms,

$$\mathsf{O} = -\tfrac{1}{2}\big\langle \boldsymbol{m}_1^4 + \boldsymbol{m}_2^4 + \boldsymbol{m}_3^4 - \tfrac{3}{5}\mathsf{id}^2\big\rangle, \tag{14}$$

as suggested in Ref. [25], and

$$\mathsf{O} = -\tfrac{7}{8}\mathsf{Q}^{[4]} - \tfrac{1}{8}\mathsf{M}_1^{[4]}. \tag{15}$$

H. Octahedral class O

All $SO(3)$ rotational symmetries of class T are preserved in class O. Following the last subsection, both tensors T and O are available. A typical fourfold rotational symmetry about one of the three $\boldsymbol{m}_i$ axes in class O (which does not appear in class T) transforms, e.g., $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ into $(\boldsymbol{m}_1, \boldsymbol{m}_3, -\boldsymbol{m}_2)$. As the result, tensor T vanishes. Therefore, the only orientational order parameter of class O is O, in addition to the density variation $\mathsf{Q}^{[0]}$.

I. Icosahedral class I

The characteristic symmetry in class I is the fivefold rotations about a center-vortex axis. This indicates that the orientational order parameter must be, at least, a fifth-order tensor. Although class I allows for symmetry operations of class T, both forth-order tensor T and tensor O cannot survive this requirement. Taking all symmetries into consideration, the leading nonvanishing moment of an orientational distribution function of class I is a sixth-order tensor,

$$\begin{aligned}\mathsf{H} = \langle [&11\boldsymbol{m}_1^2\boldsymbol{m}_2^2\boldsymbol{m}_3^2 \\ &- \sqrt{5}(\boldsymbol{m}_1^2 - \boldsymbol{m}_2^2)(\boldsymbol{m}_2^2 - \boldsymbol{m}_3^2)(\boldsymbol{m}_3^2 - \boldsymbol{m}_1^2)]_0\rangle.\end{aligned} \tag{16}$$

Note that the polynomial inside the average $\langle\cdots\rangle$ must be further expressed in a symmetric and traceless form (the subscript 0; see Appendix B 2).

The symmetries of class I are associated with those of an icosahedron, which has twenty faces and thirty edges [see Fig. 4(d)]. Out of the 30 edges, one can select two pairs that are parallel to each other, and identify a vector $\boldsymbol{n}^I$ connecting the midpoints of the two edges. The tensor H can be identically rewritten in terms of the 15 vectors defined this way, $\boldsymbol{n}_i^I$,

$$\mathsf{H} = \frac{32}{15}\sum_{i=1}^{15}\left\langle\left(\boldsymbol{n}_i^I\right)^6 - \frac{1}{7}\mathsf{id}^3\right\rangle. \tag{17}$$

A similar definition can be found in Ref. [25].

J. Discussion

1. Can we make a simpler approach?

How many orientational order parameter tensors should be used for each class of molecules? One might say that the high-order orientational order parameter tensors selected in the above subsections are overstated (too many tensors). On top of the density variation represented by $\mathsf{Q}^{[0]}$, perhaps taking the single leading tensor of the lowest order would be adequate. This is indeed the view taken by the author of Ref. [25], according to which the above classification was simplified into six categories below.

(1) *Classes C_∞ and C_n*. The orientational order parameter tensor of the lowest order is the first-order $\mathsf{Q}^{[1]}$.

(2) *Classes D_∞ and D_n where $n \geqslant 3$*. The orientational order parameter tensor of the lowest order is the second-order $\mathsf{Q}^{[2]}$.

(3) *Class D_2*. The orientational order parameter tensors of the lowest order are $\mathsf{Q}^{[2]}$ and $\mathsf{M}_1^{[2]}$.

(4) *Class T*. The lowest-order orientational order parameter is the third-order T.

(5) *Class O*. The lowest-order orientational order parameter is the fourth-order O.

(6) *Class I*. The lowest-order orientational order parameter is the sixth-order H.

Depending on the level of the physics under examination, such simplification could be incomplete. The most obvious example is group $C_{\infty v}$ [see Figs. 1(a) and 1(b)]. When the dipolar interactions between rodlike molecules dominate, there is no doubt that $\mathsf{Q}^{[1]}$ is the most important order parameter. On the other hand, there are many recently studied systems of weak dipolar rodlike systems, where the use of $\mathsf{Q}^{[1]}$ is not adequate and $\mathsf{Q}^{[2]}$ must be supplemented [66]. As matter of fact, when the crossover between dipolar rodlike molecules and headless rodlike molecules is examined, both $\mathsf{Q}^{[1]}$ and $\mathsf{Q}^{[2]}$ are at the equal footing and need to be simultaneously examined.

Taking another example, consider rodlike molecules with a square cross section. To seek the nematic ordering along the rod axis, the above simplification of using $\mathsf{Q}^{[2]}$ captures most physics. However, dropping $\mathsf{M}_1^{[4]}$ misses possible fourfold columnar structures, that can form in perpendicular to the main nematic direction. In another closely related example, both flat crosslike and squarelike molecules belong to the D_4 group [see Fig. 1(f)]. The simplified version treats them at the same level as disklike molecules (D_∞ group), where only $\mathsf{Q}^{[2]}$ is used [see Fig. 1(c)]. As $\mathsf{Q}^{[2]}$ only describes the orientational ordering along the disk axis, possible orientational ordering in the plane perpendicular to the disk axis of crosslike and squarelike molecules is entirely missed. This is a problem, particularly, for the study of crosslike and squarelike molecules embedded on a two-dimensional surface, where the additional $\mathsf{M}_1^{[4]}$ can be used to describe the tetrafold ordering of molecules [7,8].

What about studying the same nematic phase where $\mathsf{Q}^{[2]}$ is indeed the dominating orientational features? Rodlike molecules of a circular cross section (D_∞ group) and similar rodlike molecules of a square cross section (D_4 group) can form a similar long-axis nematic state. However, in two topic areas, using $\mathsf{Q}^{[2]}$ alone is not adequate for these rodlike molecules in a nematic state. One is the bending of the nematic texture; the two types of molecules have isotropic (circular base) and anisotropic (square base) elastic responses. The other is the study of liquid-crystal defects induced by geometric frustration; while the D_∞ rodlike molecules have been commonly studied, the defects of the D_4 rodlike molecules have not been adequately explored in the literature.

2. What are the differences from using $O(3)$?

For some molecular groups, the order parameters identified through $O(3)$ and $SO(3)$ symmetries are the same. This includes the D_{2h} group, previously examined by Straley [20], Mulder [21], Bisi *et al.* [22], and the D_{4h} group, previously examined by Blaak and Mulder [7] and Blaak *et al.* [8].

Many theoretical studies used $O(3)$ to identify the order parameters for achiral molecules [25,58–62]. Consequently some order parameters identified in Table I, which are based on $SO(3)$, would be eliminated. Apart from the philosophical difference, what are the practical differences in using the identified order parameters according to these two approaches?

The essential difference between using $O(3)$ and $SO(3)$ for order parameters is reflected by an illuminating example. Nissinen *et al.* [59,60] as well as Turzi and Bisi [61,62] separately introduced general methods to identify the order parameters, according to $O(3)$ classification. Their second-order tensors for C_{2v}, D_2 and D_{2h} are equivalent to our $\mathsf{Q}^{[2]}$ and $\mathsf{M}_1^{[2]}$; at this level, the three structures have the same second-order order parameters as noted by the authors. This is not the case here when we use $SO(3)$. According to our Table I, C_{2v} is distinguished from D_2 and D_{2h} by a nonvanishing $\mathsf{M}_2^{[2]}$. The D_2 and D_{2h} molecules have the same $\mathsf{M}_2^{[2]} = 0$, but are distinguished at the level of the elastic free energies (see the next section). According to our theory, the three can be separately distinguished by using second-order tensors.

For C_{2v}, Lubensky and Radzihovsky [33] used the equivalents of $\mathsf{Q}^{[2]}$ and $\mathsf{M}_1^{[2]}$ in their study of bent-core molecules, when $O(3)$ is also applied to order parameters. Realizing that these two order parameters are inadequate, they introduced a third-order order parameter, in order to describe the possible existence of the "tetrahedron" state. In contrast, according to our theory based $SO(3)$, we have an additional second-order $\mathsf{M}_2^{[2]}$ parameter, which can be used for describing such a state already. See more discussion in Sec. V D.

Amending third-order tensors to a physical problem for which the second-order tensors are inadequate is a common approach. For example, Lubensky and Radzihovsky [33] introduced a third-order, symmetric traceless tensor for C_{2v}. Nissinen *et al.* [59] also suggested to use third-order tensors, in a nonsymmetric form, for S_4 and D_{2d} molecules, While for other molecular groups, e.g., those with threefold symmetries, we also introduce third-order, symmetric traceless order-parameter tensors, for molecules with twofold symmetries, our identification of second-order order parameters is sufficient.

This section explains the necessity of including the complete set of orientational order parameter tensors [established based on $SO(3)$] in a theoretical treatment to model the orientational features of the different molecular classes. The next section explores the symmetry invariance of the free energy [following $O(3)$], in particular, of the elastic terms. As a side note, the use of *symmetric* order parameter tensors facilitates the writing of their first spatial derivatives in three forms: Gradient, diveregene, and curl. In contrast, *nonsymmetric* order parameter tensors have no such simple expressions.

IV. FREE ENERGY AND ITS GRADIENT EXPANSION

A. Molecular model

Though much of the discussion in this section can be carried out without the reference to a molecular model, we introduce some concepts by referencing to a free-energy model that uses a density distribution function $\rho(\boldsymbol{x}, \mathsf{u})$ in its formalism, where both position and orientation of a molecule are concerned. A molecular fluid composed molecules of a single symmetry group is assumed here. Up to the second-virial term, from the general Mayer expansion, we arrive at a free energy that contains the contributions from the entropy and pairwise interaction,

$$\frac{F}{k_BT} = \int d\Omega\, d\boldsymbol{x}\rho(\boldsymbol{x}, \mathsf{u}) \ln \rho(\boldsymbol{x}, \mathsf{u}) + \frac{1}{2}\int d\Omega\, d\boldsymbol{x}\, d\Omega'\, d\boldsymbol{x}'\rho(\boldsymbol{x}, \mathsf{u})G(\boldsymbol{r}, \mathsf{u}, \mathsf{u}')\rho(\boldsymbol{x}', \mathsf{u}'), \tag{18}$$

where $\boldsymbol{r} = \boldsymbol{x}' - \boldsymbol{x}$ is the relative position vector of two considered molecules. The Mayer function $-G(\boldsymbol{r}, \mathsf{u}, \mathsf{u}')$ is expressed by

$$-G(\boldsymbol{r}, \mathsf{u}, \mathsf{u}') = \exp[-v(\boldsymbol{r}, \mathsf{u}, \mathsf{u}')/k_BT] - 1, \tag{19}$$

where $v(\boldsymbol{r}, \mathsf{u}, \mathsf{u}')$ is the pairwise interaction potential energy, where both the distance between and the relative orientations of the molecules are incorporated. The free energy in Eq. (18) is a generalized expression from the Mayer expansion consisting of a fluid that has no orientational dependencies [67]. The kernel function $G(\boldsymbol{r}, \mathsf{u}, \mathsf{u}')$ carries the information on the interaction between molecules, which is the driving mechanism for the formation of liquid-crystal states. The interaction energy between the molecules usually contains attraction and repulsion components. The following general discussion makes no assumption on the nature of the interaction potential energy itself.

In this section, we establish the procedure of deriving the free-energy model by an expansion in terms of the tensor order parameters introduced in the last section. We first describe the general framework and then arrive at some general principles about the expansion, regardless of particular molecular symmetry. The expansion for each molecular symmetry is then determined. Our goal is to describe the type of terms existing in a free-energy expansion, in particular, of the second term in Eq. (18).

In most molecular systems, the density and orientational distributions are coupled to form a single distribution function, $\rho(\boldsymbol{x}, \mathsf{u})$. The usual assumption in a molecular theory is the normalization condition,

$$\int \rho(\boldsymbol{x}, \mathsf{u})\, d\boldsymbol{x}\, d\Omega = n, \tag{20}$$

where n is the total number of rigid molecules. Then,

$$\rho(\boldsymbol{x}, \mathsf{u}) = \rho_0 f(\boldsymbol{x}, \mathsf{u}), \tag{21}$$

where the normalization condition in (3) is assumed and $\rho_0 = n/V$ is the overall density.

The first term in (18) is usually referred to as the entropy term, containing both orientational and translational entropies. If required, one can expand the entropy term in terms of presumably small order parameter tensors. The leading quadratic terms of the order parameter tensors contain coupled terms, if more-than-one order parameters are required for description of the system. To compare with the entropy term within a LdG theory, the expanded series typically contains (coupled) cubic and quartic terms in the orientational order parameters. The coefficients of the quartic terms are normally positive, to ensure that a particular ordered state are stabilized with a finite bound. Once a set of orientational order parameters are selected, every term in the order-parameter expansion from the entropy has a determined coefficient; that is, no free coefficients are left in the theory.

The second term in (18), $\tilde{F}_2$, is the determinant factor that drives the system into orientational ordered state in the bulk and controls the form of the distortion-energy terms. The main concern here is the group symmetry of the system and effects on the pairwise interaction. The molecular symmetry operations dominate the type of terms that are nonvanishing in an expansion of $\tilde{F}_2$ in terms of the order parameters.

B. Gradient expansion and symmetries

We take the second term in (18), $\tilde{F}_2$, as a typical interaction energy to start a gradient expansion. The conclusions are not limited to the particular form in (18) and can be generalized beyond.

TABLE II. Most general form of the quadratic terms of the interaction-energy expansion, in terms of symmetric traceless tensors $\mathsf{A}^{[n]}$ and $\mathsf{B}^{[n]}$. The terms are grouped by the bulk energy (no derivatives), elastic energy I (first derivatives), and elastic energy II (second derivatives).

Bulk energy	Elastic energy I	Elastic energy II
$\mathsf{A}^{[n]}\cdot\mathsf{B}^{[n]}$	$\mathsf{A}^{[n-1]}\cdot(\nabla\cdot\mathsf{B}^{[n]})$, $\mathsf{A}^{[n]}\cdot\nabla\times\mathsf{B}^{[n]}$	$\nabla\mathsf{A}^{[n]}\cdot\nabla\mathsf{B}^{[n]}$, $(\nabla\cdot\mathsf{A}^{[n]})\cdot(\nabla\cdot\mathsf{B}^{[n]})$, $\nabla\mathsf{A}^{[n-2]}\cdot(\nabla\cdot\mathsf{B}^{[n]})$, $(\nabla\cdot\mathsf{A}^{[n]})\cdot(\nabla\times\mathsf{B}^{[n-1]})$

The kernel term in $\tilde{F}_2$ relates the interaction between molecules at two different spatial points, $\boldsymbol{x}$ and $\boldsymbol{x}'$. Considering a Taylor expansion of $f(\boldsymbol{x}', \mathsf{u}') = f(\boldsymbol{x}+\boldsymbol{r}, \mathsf{u}')$ up to the second order, one has

$$\tilde{F}_2 = \sum_{k=0}^{2}\frac{\rho_0^2}{2k!}\int d\boldsymbol{x}\,d\Omega\,d\Omega' f(\boldsymbol{x},\mathsf{u})K^{[k]}(\mathsf{u},\mathsf{u}')\cdot\nabla^k f(\boldsymbol{x},\mathsf{u}'), \tag{22}$$

where a kth-order symmetric tensor is introduced,

$$K^{[k]}(\mathsf{u},\mathsf{u}') = \int G(\boldsymbol{r},\mathsf{u},\mathsf{u}')\boldsymbol{r}^k\,d\boldsymbol{r}, \tag{23}$$

for $k = 0, 1, 2$. Following the convention used in a LdG theory, higher order terms, $k > 2$, are dropped. When the $(k = 1)$-term vanishes, the procedure is known as the square-gradient expansion.

Two symmetry properties of the kernel function are used here. The interaction between a pair of molecules only depends on their relative positions and orientations. Hence the interaction energy is invariant when the coordinates of the two interacting molecules are exchanged, which implies

$$G(-\boldsymbol{r},\mathsf{u}',\mathsf{u}) = G(\boldsymbol{r},\mathsf{u},\mathsf{u}'). \tag{24}$$

The second property is that no matter how the entire space is rotated, the interaction energy should always have the same value. That is, the kernel function is invariant under any symmetry transformation of the $SO(3)$ space, t, which implies

$$G(\mathsf{t}\boldsymbol{r},\mathsf{t}\mathsf{u},\mathsf{t}\mathsf{u}') = G(\boldsymbol{r},\mathsf{u},\mathsf{u}'). \tag{25}$$

These properties are used in determining the symmetry properties of $K^{[k]}(\mathsf{u},\mathsf{u}')$. The dependence of $K^{[k]}$ on both u and u' are then expanded in tensor powers of these two variables. Then, the u-related power terms, in combination with the $f(\boldsymbol{x},\mathsf{u})$-factor in (22), produce tensor moments, formally expressed in (4). Similarly the u'-related power terms, in combination with the $f(\boldsymbol{x},\mathsf{u}')$-factor in (22), produce tensor moments as well. All the tensor moments are then further expressed in symmetric traceless forms.

Before proceeding further, the following tensor notations are assumed. Let $\mathsf{A}^{[n]}$ be an nth-order symmetric traceless tensor. Three types of derivatives can be written

$$\begin{aligned}\nabla\mathsf{A}^{[n]} &= \partial_i\mathsf{A}^{[n]}_{j_1\dots j_n},\\ \nabla\cdot\mathsf{A}^{[n]} &= \sum_i\partial_i\mathsf{A}^{[n]}_{j_1\dots j_{n-1}i},\\ \nabla\times\mathsf{A}^{[n]} &= \sum_{ij}\epsilon_{ijk}\partial_i\mathsf{A}^{[n]}_{j_1\dots j_{n-1}j},\end{aligned}$$

where ϵ_{ijk} is the Levi-Civita symbol. The inner product between two tensors, $\mathsf{A}^{[n]}$ and $\mathsf{B}^{[n]}$, is a scalar,

$$\mathsf{A}^{[n]}\cdot\mathsf{B}^{[n]} = \sum_{\text{all } i}\mathsf{A}^{[n]}_{i_1\dots i_n}\mathsf{B}^{[n]}_{i_1\dots i_n}. \tag{26}$$

The most general form in a tensor expansion of $\tilde{F}_2$ is shown in Table II. At this stage, no symmetry analysis beyond those shown in (24) and (25) is considered. Next, we incorporate the molecular symmetries discussed in Sec. 1, and specify surviving terms under the symmetry operations.

Recall that the molecular symmetry is characterized by orthogonal transformations that produce the same molecular state. Hence, under these $O(3)$ transformations, the kernel function G has the same values because of the symmetry. There are two types of symmetry operations in $O(3)$. The proper rotational operations are those of $SO(3)$, which are used in defining the order parameter tensors in the last section. This restricts us to consider the selected order parameter tensors (second column of Table I) in the free-energy expansion of order parameter tensors ($\mathsf{A}^{[n]}$ and $\mathsf{B}^{[n]}$ of Table II).

The second type of symmetry operations, the improper rotations (inversion and mirror symmetries), also make the kernel function unchanged. Due to the integration over $\boldsymbol{r}$ in the definition of Eq. (23), an improper rotation that changes the variables in $G(\boldsymbol{r},\mathsf{u},\mathsf{u}')$ can be converted to a proper rotation that changes the variables in $K^{[k]}(\mathsf{u},\mathsf{u}')$ by a simple $\boldsymbol{r}$ inversion. The end result, due to the kth power of $\boldsymbol{r}$, is that $K^{[k]}(\mathsf{u},\mathsf{u}')$ is either odd or even, under these improper rotation considerations. The direct consequence is that not all terms in Table II, with the selected order parameters of certain molecular class, survive for a particular molecular group. For molecular groups within the same molecular class, the different improper rotations in each molecular group lead to different surviving terms. Going through the mathematical analysis of all 24 groups in Table I is obviously tedious [45]. Below we list the main results of this consideration.

The zeroth-order tensor $\mathsf{Q}^{[0]}$ describes the density variation from 1, of a homogeneous liquid. In the rest of this paper, we implicitly assume that all $\mathsf{Q}^{[0]}$ represent the difference $\mathsf{Q}^{[0]} - 1$.

C. Axisymmetries, class C_∞

The order parameters are $\mathsf{Q}^{[0]}, \mathsf{Q}^{[1]}, \mathsf{Q}^{[2]}$.

1. Group C_∞

We can show these terms are nonvanishing.

(1) In the bulk energy,

$$\mathsf{Q}^{[0]}\cdot\mathsf{Q}^{[0]},\ \mathsf{Q}^{[1]}\cdot\mathsf{Q}^{[1]},\ \mathsf{Q}^{[2]}\cdot\mathsf{Q}^{[2]}. \tag{27}$$

(2) In elastic energy I,

$$\begin{gathered}\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[1]}),\ \mathsf{Q}^{[1]}\cdot(\nabla\cdot\mathsf{Q}^{[2]}),\\ \mathsf{Q}^{[1]}\cdot\nabla\times\mathsf{Q}^{[1]},\ \mathsf{Q}^{[2]}\cdot\nabla\times\mathsf{Q}^{[2]}.\end{gathered} \tag{28}$$

(3) In elastic energy II,

$$\begin{aligned}&\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{Q}^{[1]}\cdot\nabla\mathsf{Q}^{[1]},\ (\nabla\cdot\mathsf{Q}^{[1]})\cdot(\nabla\cdot\mathsf{Q}^{[1]}),\\&\nabla\mathsf{Q}^{[2]}\cdot\nabla\mathsf{Q}^{[2]},\ (\nabla\cdot\mathsf{Q}^{[2]})\cdot(\nabla\cdot\mathsf{Q}^{[2]}),\\&\nabla\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[2]}),\ (\nabla\cdot\mathsf{Q}^{[2]})\cdot(\nabla\times\mathsf{Q}^{[1]}).\end{aligned}\tag{29}$$

2. Group $C_{\infty h}$

The bulk energy is given by (27), and the elastic energy II is given by (29). All terms in the elastic energy I vanish.

3. Group $C_{\infty v}$

We can show these terms are available.

(1) In the bulk energy,

$$\mathsf{Q}^{[0]}\cdot\mathsf{Q}^{[0]},\ \mathsf{Q}^{[1]}\cdot\mathsf{Q}^{[1]},\ \mathsf{Q}^{[2]}\cdot\mathsf{Q}^{[2]}.\tag{30}$$

(2) In elastic energy I,

$$\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[1]}),\ \mathsf{Q}^{[1]}\cdot(\nabla\cdot\mathsf{Q}^{[2]}).\tag{31}$$

(3) In elastic energy II,

$$\begin{aligned}&\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{Q}^{[1]}\cdot\nabla\mathsf{Q}^{[1]},\ (\nabla\cdot\mathsf{Q}^{[1]})\cdot(\nabla\cdot\mathsf{Q}^{[1]}),\\&\nabla\mathsf{Q}^{[2]}\cdot\nabla\mathsf{Q}^{[2]},\ (\nabla\cdot\mathsf{Q}^{[2]})\cdot(\nabla\cdot\mathsf{Q}^{[2]}),\ \nabla\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[2]}).\end{aligned}\tag{32}$$

D. Axisymmetries, class D_∞

The order parameters are $\mathsf{Q}^{[0]}$ and $\mathsf{Q}^{[2]}$.

1. Group D_∞

We can show that the following terms are available.

(1) In the bulk energy,

$$\mathsf{Q}^{[0]}\cdot\mathsf{Q}^{[0]},\ \mathsf{Q}^{[2]}\cdot\mathsf{Q}^{[2]}.\tag{33}$$

(2) In elastic energy I,

$$\mathsf{Q}^{[2]}\cdot\nabla\times\mathsf{Q}^{[2]}.\tag{34}$$

(3) In elastic energy II,

$$\begin{aligned}&\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{Q}^{[2]}\cdot\nabla\mathsf{Q}^{[2]},\\&(\nabla\cdot\mathsf{Q}^{[2]})\cdot(\nabla\cdot\mathsf{Q}^{[2]}),\ \nabla\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[2]}).\end{aligned}\tag{35}$$

2. Group $D_{\infty h}$

The bulk energy is given by (33), and the elastic energy II is given by (35). All terms in elastic energy I vanish.

E. Finite axial-symmetries molecules, class C_n

Recall that the order parameters are $\mathsf{Q}^{[k]}$, $(k=0,\dots,n)$, $\mathsf{M}_1^{[n]}$, $\mathsf{M}_2^{[n]}$. In what follows, we shall write down the terms of the order $\leqslant n-1$ first, followed by nth-order terms.

1. Group C_n

The bulk energy contains

$$\begin{aligned}&\mathsf{Q}^{[k]}\cdot\mathsf{Q}^{[k]},\quad k=0,1,\dots,n-1;\\&\mathsf{A}^{[n]}\cdot\mathsf{B}^{[n]},\quad \mathsf{A}^{[n]},\mathsf{B}^{[n]}\in\{\mathsf{Q}^{[n]},\mathsf{M}_1^{[n]},\mathsf{M}_2^{[n]}\}.\end{aligned}\tag{36}$$

Elastic energy I contains

$$\begin{aligned}&\mathsf{Q}^{[k-1]}\cdot(\nabla\cdot\mathsf{Q}^{[k]}),\ \mathsf{Q}^{[k]}\cdot\nabla\times\mathsf{Q}^{[k]},\quad k=1,2,\dots,n-1;\\&\mathsf{Q}^{[n-1]}\cdot(\nabla\cdot\mathsf{B}^{[n]}),\ \mathsf{B}^{[n]}\in\{\mathsf{Q}^{[n]},\mathsf{M}_1^{[n]},\mathsf{M}_2^{[n]}\},\\&\mathsf{A}^{[n]}\cdot\nabla\times\mathsf{B}^{[n]},\quad \mathsf{A}^{[n]},\mathsf{B}^{[n]}\in\{\mathsf{Q}^{[n]},\mathsf{M}_1^{[n]},\mathsf{M}_2^{[n]}\}.\end{aligned}\tag{37}$$

Elastic energy II contains

$$\begin{aligned}&\nabla\mathsf{Q}^{[k]}\cdot\nabla\mathsf{Q}^{[k]},\ k=0,1,\dots,n-1;\\&(\nabla\cdot\mathsf{Q}^{[k]})\cdot(\nabla\cdot\mathsf{Q}^{[k]}),\ k=1,2,\dots,n-1;\\&(\nabla\cdot\mathsf{Q}^{[k]})\cdot(\nabla\times\mathsf{Q}^{[k-1]}),\ \nabla\mathsf{Q}^{[k-2]}\cdot(\nabla\cdot\mathsf{Q}^{[k]}),\\&\qquad k=2,3,\dots,n-1;\\&\nabla\mathsf{A}^{[n]}\cdot\nabla\mathsf{B}^{[n]},\ (\nabla\cdot\mathsf{A}^{[n]})\cdot(\nabla\cdot\mathsf{B}^{[n]}),\ \nabla\mathsf{Q}^{[n-2]}\cdot(\nabla\cdot\mathsf{B}^{[n]}),\\&(\nabla\cdot\mathsf{A}^{[n]})\cdot(\nabla\times\mathsf{Q}^{[n-1]}),\\&\qquad \mathsf{A}^{[n]},\mathsf{B}^{[n]}\in\{\mathsf{Q}^{[n]},\mathsf{M}_1^{[n]},\mathsf{M}_2^{[n]}\}.\end{aligned}\tag{38}$$

2. Group C_{nv}

The bulk energy contains

$$\begin{aligned}&\mathsf{Q}^{[k]}\cdot\mathsf{Q}^{[k]},\quad k=0,1,\dots,n-1;\\&\mathsf{Q}^{[n]}\cdot\mathsf{Q}^{[n]},\ \mathsf{Q}^{[n]}\cdot\mathsf{M}_1^{[n]},\ \mathsf{M}_1^{[n]}\cdot\mathsf{M}_1^{[n]},\ \mathsf{M}_2^{[n]}\cdot\mathsf{M}_2^{[n]}.\end{aligned}\tag{39}$$

Elastic energy I contains

$$\begin{aligned}&\mathsf{Q}^{[k-1]}\cdot(\nabla\cdot\mathsf{Q}^{[k]}),\quad k=1,2,\dots,n-1;\\&\mathsf{Q}^{[n-1]}\cdot(\nabla\cdot\mathsf{Q}^{[n]}),\ \mathsf{Q}^{[n-1]}\cdot(\nabla\cdot\mathsf{M}_1^{[n]}),\\&\mathsf{Q}^{[n]}\cdot\nabla\times\mathsf{M}_2^{[n]},\ \mathsf{M}_1^{[n]}\cdot\nabla\times\mathsf{M}_2^{[n]}.\end{aligned}\tag{40}$$

Elastic energy II contains

$$\begin{aligned}&\nabla\mathsf{Q}^{[k]}\cdot\nabla\mathsf{Q}^{[k]},\ k=0,1,\dots,n-1;\\&(\nabla\cdot\mathsf{Q}^{[k]})\cdot(\nabla\cdot\mathsf{Q}^{[k]}),\ k=1,2,\dots,n-1;\\&\nabla\mathsf{Q}^{[k-2]}\cdot(\nabla\cdot\mathsf{Q}^{[k]}),\ k=2,3,\dots,n-1;\\&\nabla\mathsf{A}^{[n]}\cdot\nabla\mathsf{B}^{[n]},\ (\nabla\cdot\mathsf{A}^{[n]})\cdot(\nabla\cdot\mathsf{B}^{[n]}),\ \nabla\mathsf{Q}^{[n-2]}\cdot(\nabla\cdot\mathsf{B}^{[n]}),\\&\qquad \mathsf{A}^{[n]},\mathsf{B}^{[n]}\in\{\mathsf{Q}^{[n]},\mathsf{M}_1^{[n]}\},\\&\nabla\mathsf{M}_2^{[n]}\cdot\nabla\mathsf{M}_2^{[n]},\ (\nabla\cdot\mathsf{M}_2^{[n]})\cdot(\nabla\cdot\mathsf{M}_2^{[n]}),\\&(\nabla\cdot\mathsf{M}_2^{[n]})\cdot(\nabla\times\mathsf{Q}^{[n-1]}).\end{aligned}\tag{41}$$

3. Groups C_{nh} (n even) and S_{2n} (n odd)

The bulk energy is given by (36). Elastic energy I vanishes. Elastic energy II is given by (38).

4. Groups S_{2n} (n even) and C_{nh} (n odd)

The bulk energy contains

$$\begin{aligned}&\mathsf{Q}^{[k]}\cdot\mathsf{Q}^{[k]},\quad k=0,1,\dots,n-1;\\&\mathsf{Q}^{[n]}\cdot\mathsf{Q}^{[n]},\ \mathsf{M}_1^{[n]}\cdot\mathsf{M}_1^{[n]},\ \mathsf{M}_1^{[n]}\cdot\mathsf{M}_2^{[n]},\ \mathsf{M}_2^{[n]}\cdot\mathsf{M}_2^{[n]}.\end{aligned}\tag{42}$$

Elastic energy I has

$$\begin{aligned}&\mathsf{Q}^{[n-1]}\cdot(\nabla\cdot\mathsf{M}_1^{[n]}),\ \mathsf{Q}^{[n-1]}\cdot(\nabla\cdot\mathsf{M}_2^{[n]}),\\&\mathsf{Q}^{[n]}\cdot\nabla\times\mathsf{M}_1^{[n]},\ \mathsf{Q}^{[n]}\cdot\nabla\times\mathsf{M}_2^{[n]}.\end{aligned}\tag{43}$$

Elastic energy II has

$$
\begin{aligned}
&\nabla Q^{[k]}\cdot\nabla Q^{[k]},\ k=0,1,\dots,n-1;\\
&(\nabla\cdot Q^{[k]})\cdot(\nabla\cdot Q^{[k]}),\ k=1,2,\dots,n-1;\\
&(\nabla\cdot Q^{[k]})\cdot(\nabla\times Q^{[k-1]}),\ \nabla Q^{[k-2]}\cdot(\nabla\cdot Q^{[k]}),\\
&\qquad k=2,3,\dots,n-1;\\
&\nabla Q^{[n]}\cdot\nabla Q^{[n]},\ (\nabla\cdot Q^{[n]})\cdot(\nabla\cdot Q^{[n]}),\\
&(\nabla\cdot Q^{[n]})\cdot(\nabla\times Q^{[n-1]}),\ \nabla Q^{[n-2]}\cdot(\nabla\cdot Q^{[n]}),\\
&\nabla M_1^{[n]}\cdot\nabla M_1^{[n]},\ \nabla M_1^{[n]}\cdot\nabla M_2^{[n]},\ \nabla M_2^{[n]}\cdot\nabla M_2^{[n]},\\
&\big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\cdot M_1^{[n]}\big),\ \big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\cdot M_2^{[n]}\big),\\
&\big(\nabla\cdot M_2^{[n]}\big)\cdot\big(\nabla\cdot M_2^{[n]}\big).
\end{aligned}\tag{44}
$$

F. Finite axial-symmetric molecules, class D_n

The order parameters are the following:

(1) If n is even: $Q^{[k]},\ (k=0,2,\dots,n),\ M_1^{[n]}$.

(2) If n is odd: $Q^{[k]},\ (k=0,2,\dots,n-1),\ M_1^{[n]}$.

1. Group D_n

Two case are considered here.

(1) When n is odd, the bulk energy has

$$
\begin{aligned}
&Q^{[k]}\cdot Q^{[k]},\quad k=0,2,\dots,n-1;\\
&M_1^{[n]}\cdot M_1^{[n]}.
\end{aligned}\tag{45}
$$

Elastic energy I has

$$
\begin{aligned}
&Q^{[k]}\cdot\nabla\times Q^{[k]}\quad k=2,4,\dots,n-1;\\
&Q^{[n-1]}\cdot\big(\nabla\cdot M_1^{[n]}\big),\ M_1^{[n]}\cdot\nabla\times M_1^{[n]}.
\end{aligned}\tag{46}
$$

Elastic energy II has

$$
\begin{aligned}
&\nabla Q^{[k]}\cdot\nabla Q^{[k]},\ k=0,2,\dots,n-1;\\
&(\nabla\cdot Q^{[k]})\cdot(\nabla\cdot Q^{[k]}),\ \nabla Q^{[k-2]}\cdot(\nabla\cdot Q^{[k]}),\\
&\qquad k=2,4,\dots,n-1;\\
&\nabla M_1^{[n]}\cdot\nabla M_1^{[n]},\ \big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\cdot M_1^{[n]}\big),\\
&\big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\times Q^{[n-1]}\big).
\end{aligned}\tag{47}
$$

(2) When n is even, the bulk energy has

$$
\begin{aligned}
&Q^{[k]}\cdot Q^{[k]},\quad k=0,2,\dots,n-2;\\
&Q^{[n]}\cdot Q^{[n]},\ Q^{[n]}\cdot M_1^{[n]},\ M_1^{[n]}\cdot M_1^{[n]}.
\end{aligned}\tag{48}
$$

Elastic energy I has

$$
\begin{aligned}
&Q^{[k]}\cdot\nabla\times Q^{[k]}\quad k=2,4,\dots,n-2;\\
&Q^{[n]}\cdot\nabla\times Q^{[n]},\ Q^{[n]}\cdot\nabla\times M_1^{[n]},\ M_1^{[n]}\cdot\nabla\times M_1^{[n]}.
\end{aligned}\tag{49}
$$

Elastic energy II has

$$
\begin{aligned}
&\nabla Q^{[k]}\cdot\nabla Q^{[k]},\ k=0,2,\dots,n-2;\\
&(\nabla\cdot Q^{[k]})\cdot(\nabla\cdot Q^{[k]}),\ \nabla Q^{[k-2]}\cdot(\nabla\cdot Q^{[k]}),\\
&\qquad k=2,4,\dots,n-2;\\
&\nabla Q^{[n]}\cdot\nabla Q^{[n]},\ \nabla Q^{[n]}\cdot\nabla M_1^{[n]},\ \nabla M_1^{[n]}\cdot\nabla M_1^{[n]},\\
&\big(\nabla\cdot Q^{[n]}\big)\cdot\big(\nabla\cdot Q^{[n]}\big),\ \big(\nabla\cdot Q^{[n]}\big)\cdot\big(\nabla\cdot M_1^{[n]}\big),\\
&\big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\cdot M_1^{[n]}\big),\\
&(\nabla Q^{[n-2]})\cdot(\nabla\cdot Q^{[n]}),\ (\nabla Q^{[n-2]})\cdot\big(\nabla\cdot M_1^{[n]}\big).
\end{aligned}\tag{50}
$$

2. Group D_{nh} (n odd)

The bulk energy has

$$
\begin{aligned}
&Q^{[k]}\cdot Q^{[k]},\quad k=0,2,\dots,n-1;\\
&M_1^{[n]}\cdot M_1^{[n]}.
\end{aligned}\tag{51}
$$

Elastic energy I has

$$
Q^{[n-1]}\cdot\big(\nabla\cdot M_1^{[n]}\big).\tag{52}
$$

Elastic energy II has

$$
\begin{aligned}
&\nabla Q^{[k]}\cdot\nabla Q^{[k]},\ k=0,2,\dots,n-1;\\
&(\nabla\cdot Q^{[k]})\cdot(\nabla\cdot Q^{[k]}),\ \nabla Q^{[k-2]}\cdot(\nabla\cdot Q^{[k]}),\\
&\qquad k=2,4,\dots,n-1;\\
&\nabla M_1^{[n]}\cdot\nabla M_1^{[n]},\ \big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\cdot M_1^{[n]}\big).
\end{aligned}\tag{53}
$$

3. Group D_{nh} (n even)

The bulk energy is given by (48). Elastic energy I vanishes. Elastic energy II is given by (50).

4. Group D_{nd} (n odd)

The bulk energy is given by (45). Elastic energy I vanishes. Elastic energy II is given by (47).

5. Group D_{nd} (n even)

The bulk energy has

$$
\begin{aligned}
&Q^{[k]}\cdot Q^{[k]},\quad k=0,2,\dots,n-2;\\
&Q^{[n]}\cdot Q^{[n]},\ M_1^{[n]}\cdot M_1^{[n]}.
\end{aligned}\tag{54}
$$

Elastic energy I has

$$
Q^{[n]}\cdot\nabla\times M_1^{[n]}.\tag{55}
$$

Elastic energy II has

$$
\begin{aligned}
&\nabla Q^{[k]}\cdot\nabla Q^{[k]},\ k=0,2,\dots,n-2;\\
&(\nabla\cdot Q^{[k]})\cdot(\nabla\cdot Q^{[k]}),\ \nabla Q^{[k-2]}\cdot(\nabla\cdot Q^{[k]}),\\
&\qquad k=2,4,\dots,n-2;\\
&\nabla Q^{[n]}\cdot\nabla Q^{[n]},\ \big(\nabla\cdot Q^{[n]}\big)\cdot\big(\nabla\cdot Q^{[n]}\big),\\
&\big(\nabla Q^{[n-2]}\big)\cdot\big(\nabla\cdot Q^{[n]}\big),\\
&\nabla M_1^{[n]}\cdot\nabla M_1^{[n]},\ \big(\nabla\cdot M_1^{[n]}\big)\cdot\big(\nabla\cdot M_1^{[n]}\big).
\end{aligned}\tag{56}
$$

G. Tetrahedral class T

We recall the orientational order parameters are T and O.

1. Group T

In the bulk energy, we have

$$
Q^{[0]}\cdot Q^{[0]},\ T\cdot T,\ O\cdot O.\tag{57}
$$

In elastic energy I, we have

$$\mathsf{T}\cdot\nabla\times\mathsf{T},\ \mathsf{T}\cdot(\nabla\cdot\mathsf{O}),\ \mathsf{O}\cdot\nabla\times\mathsf{O}. \tag{58}$$

In elastic energy II, we have

$$\begin{aligned}&\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{T}\cdot\nabla\mathsf{T},\ (\nabla\cdot\mathsf{T})\cdot(\nabla\cdot\mathsf{T}),\\&\nabla\mathsf{O}\cdot\nabla\mathsf{O},\ (\nabla\cdot\mathsf{O})\cdot(\nabla\cdot\mathsf{O}),\ (\nabla\times\mathsf{T})\cdot(\nabla\cdot\mathsf{O}).\end{aligned} \tag{59}$$

2. *Group T_d*

In the bulk energy, we have

$$\mathsf{Q}^{[0]}\cdot\mathsf{Q}^{[0]},\ \mathsf{T}\cdot\mathsf{T},\mathsf{O}\cdot\mathsf{O}. \tag{60}$$

In elastic energy I, we have

$$\mathsf{T}\cdot(\nabla\cdot\mathsf{O}). \tag{61}$$

In elastic energy II, we have

$$\begin{aligned}&\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{T}\cdot\nabla\mathsf{T},\ (\nabla\cdot\mathsf{T})\cdot(\nabla\cdot\mathsf{T}),\\&\nabla\mathsf{O}\cdot\nabla\mathsf{O},\ (\nabla\cdot\mathsf{O})\cdot(\nabla\cdot\mathsf{O}).\end{aligned} \tag{62}$$

The difference between two groups T_d and T_h is the coupling between T and O, which is the reason why we keep these two tensors as order parameters.

3. *Group T_h*

The bulk energy and elastic energy II are given by (57) and (59), respectively. Elastic energy I is zero.

H. Octahedral class *O*

The orientational order parameter is O.

1. *Group O*

In the bulk energy, we have

$$\mathsf{Q}^{[0]}\cdot\mathsf{Q}^{[0]},\ \mathsf{O}\cdot\mathsf{O}. \tag{63}$$

In elastic energy I, we have

$$\mathsf{O}\cdot\nabla\times\mathsf{O}. \tag{64}$$

In elastic energy II, we have

$$\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{O}\cdot\nabla\mathsf{O},\ (\nabla\cdot\mathsf{O})\cdot(\nabla\cdot\mathsf{O}). \tag{65}$$

2. *Group O_h*

The bulk energy and elastic energy II are given by (63) and (65), respectively. Elastic energy I is zero.

I. Icosahedral class *I*

The orientational order parameter is H.

1. *Group I*

The bulk energy has two terms

$$\mathsf{Q}^{[0]}\cdot\mathsf{Q}^{[0]},\ \mathsf{H}\cdot\mathsf{H}. \tag{66}$$

The elastic energy I has one term,

$$\mathsf{H}\cdot\nabla\times\mathsf{H}. \tag{67}$$

The elastic energy II has terms,

$$\nabla\mathsf{Q}^{[0]}\cdot\nabla\mathsf{Q}^{[0]},\ \nabla\mathsf{H}\cdot\nabla\mathsf{H},\ (\nabla\cdot\mathsf{H})\cdot(\nabla\cdot\mathsf{H}). \tag{68}$$

2. *Group I_h*

The bulk energy and elastic energy II are given by (66) and (68), respectively. Elastic energy I is zero.

V. EXAMPLES

Generally, the free energy of the system (18) is the sum of the entropy and interaction terms. The interaction term is expanded in the last section, in a quadratic form, as functions of the orientational order parameters discussed in Sec. III. The expansion is obtained from the general consideration of symmetry properties without the reference to the particular molecular geometries. That geometry is completely specified by the interaction energy $v(\boldsymbol{r},\mathsf{u},\mathsf{u}')$ between two molecules, appearing in the Mayer function (19) and directly gives rise to the coefficients of each terms listed in the last section. When the coefficient of a quadratic term listed in the above section becomes negative and overpowers the counterpart of a presumably expandable entropy, an instability arises and the system has a possibility to undergo a phase transition to a state characterized by that quadratic term.

When would this happen? These coefficients depend on two basic parameters in a given system, the overall density ρ_0 and temperature T. The former enters into the current theory through the coefficients of the entropy term (proportional to ρ_0) and interaction term (proportional to ρ_0^2). The latter is the direct result of the pre-factor $1/k_BT$ of v, in the Mayer function. In a more complex density-function theory where the interaction term is replaced by another form, ρ_0 and T may appear in a more complex manner. A liquid, which has an interaction potential that contains the hard-core repulsion only (when two molecules overlap, $v=\infty$ and nonoverlap, $v=0$), is commonly referred to as a lyotropic liquid crystal, and there is no T dependence. Otherwise, if an attraction potential exists, the T dependence can drive a phase transition and the system is referred to as thermotropic. In the following discussion, the coefficients of the expanded terms are generally addressed, without the explicit reference to either lyotropic or thermotropic systems.

Out of all tensors, the scalar $\mathsf{Q}^{[0]}$ is special and it characterizes the density variation. In a spatially homogeneous system, $\mathsf{Q}^{[0]}=1$, all free-energy terms involving $\mathsf{Q}^{[0]}=1$ can be simplified. Indeed, most conventional LdG expansions take $\mathsf{Q}^{[0]}=1$ from the beginning. Such an approximation misses the possible density variation, needed in considering, for example, the smectic states. Here, in order to develop a general free-energy expansion, $\mathsf{Q}^{[0]}$ is retained in the formalism, in three typical forms, $[\mathsf{Q}^{[0]}-1]^2$, $[\nabla\mathsf{Q}^{[0]}]^2$, and coupling of $\nabla\mathsf{Q}^{[0]}$ with other tensors, where $\mathsf{Q}^{[0]}$ is normalized by

$$\frac{1}{V}\int d\boldsymbol{r}\mathsf{Q}^{[0]}=1.$$

Both $[Q^{[0]}-1]^2$ and $[\nabla Q^{[0]}]^2$ terms are not independently discussed below, as the basic assumption is that, without coupling to orientational ordering, the system stays in a spatially homogeneously state. The main effect of these two terms is the penalty to the formation of orientationally ordered states that require the coupling to a nonvanishing $\nabla\mathsf{Q}^{[0]}$. This is

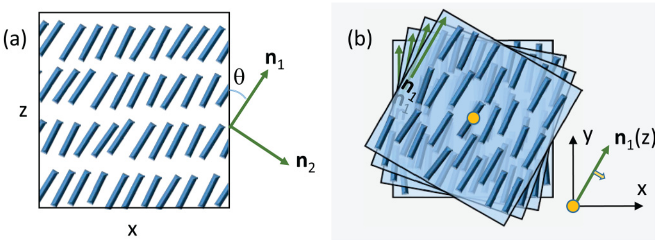


FIG. 5. Illustration of (a) the general case of an ordered smectic state of the $D_{\infty h}$ group, and (b) the cholesteric phase of the D_∞ group. In (a) the main and secondary axes of the orientational ordering are $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$. In (b) The main nematic director, lying on the xy plane, rotates about z, layer by layer.

different from the common practice in a LdG model, where $[\mathsf{Q}^{[0]}]$ is treated as 1 and all $\mathsf{Q}^{[0]}$-related terms are dropped.

A. Example: $D_{\infty h}$ group

This is the familiar example of the liquid-crystal phases formed by rodlike [Fig. 1(a)] and disklike [Fig. 1(c)] molecules. The only relevant orientational order parameter is the 3 × 3 "Q-tensor," $\mathsf{Q}^{[2]}$. In a diagonalized form,

$$\mathsf{Q}^{[2]} = S\big(\boldsymbol{n}_1^2 - \mathrm{id}/3\big) + P\big(\boldsymbol{n}_2^2 - \boldsymbol{n}_3^2\big), \tag{69}$$

where S is the main axis scalar order parameter, P is the scalar biaxial order parameter, and $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are the main and secondary nematic directors. The only bulk term from Table I is $\mathsf{Q}^{[2]} \cdot \mathsf{Q}^{[2]}$. In the diagonalized representation, it becomes

$$\tfrac{2}{3}S^2 + 2P^2.$$

In combination with the entropic term, this forms the basic model for the isotropic-nematic phase transition of $D_{\infty h}$, if the system is spatially homogeneous.

There are four derivative terms from Table (I), $|\nabla\mathsf{Q}^{[2]}|^2$, $|\nabla\cdot\mathsf{Q}^{[2]}|^2$, $|\nabla\mathsf{Q}^{[0]}|^2$ and $\nabla\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[2]})$. In reference to the coordinates used in Fig. 5, the first two are

$$|\nabla\mathsf{Q}^{[2]}|^2 = \tfrac{2}{3}(\partial_z S)^2 + 2(\partial_z P)^2, \tag{70}$$

$$|\nabla\cdot\mathsf{Q}^{[2]}|^2 = \frac{4}{9}\cos^2\theta(\partial_z S)^2 + \sin^2\theta\left[\partial_z\left(P - \frac{1}{3}S\right)\right]^2. \tag{71}$$

A linear combination of these two form the essential model for the formation of the smectic-A and smectic-C states. Depending on the final, relative magnitudes of the coefficients of the $(\partial_z S)^2$ and $(\partial_z P)^2$, a system can undergo various sequences of phase transitions: Nematic-to-smectic-A (where $P = 0$ and $\theta = 0$), nematic-to-smectic-C (where $P \neq 0$ and $\theta \neq 0$), or nematic-to-smectic-A followed by smectic-A-to-smectic-C. The coupling to the density modulation are given by $\nabla\mathsf{Q}^{[0]}\cdot(\nabla\cdot\mathsf{Q}^{[2]})$, and the free energy is penalized by $|\nabla\mathsf{Q}^{[0]}|^2$.

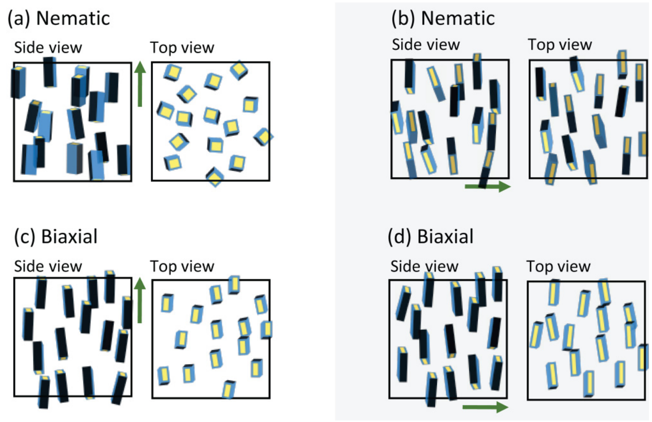


FIG. 6. Illustration of two modes of nematic states of the D_{2h} group. The left column shows the nematic and biaxial states ordered along the mean main axes of long molecules; the right column shows the nematic and biaxial states ordered along the mean normals of platelike molecules. The main nematic directors are specified by the green arrows.

B. Example: D_∞ group

A short, rigid DNA molecule is an example of a chiral molecule. Figure 1(i) illustrates an $n = 10$ chiral molecule, for which, D_∞ becomes a good approximation as $n \gg 1$. The D_∞ group lacks the horizontal mirror symmetry in the $D_{\infty h}$ group, hence allows the existence of elastic energy I in Eq. (34). In addition to the same types of nematic, smectic-A, and smectic-C states that can be stablized in a liquid of $D_{\infty h}$ molecules, this additional term can drive the system into a cholesteric phase.

To illustrate this we take a simplified assumption of a spatially homogeneous S, but a spatially dependent main-axis director vector $\boldsymbol{n}_1(z)$. The coordinate system in Fig. 5(b), where $\boldsymbol{n}_1(z)$ is on the xy plane, allows us to write

$$\mathsf{Q}^{[2]}\cdot\nabla\times\mathsf{Q}^{[2]} = \tfrac{2}{3}S^2\boldsymbol{n}_1\cdot\nabla\times\boldsymbol{n}_1.$$

In a cholesteric state, with the particular choice of the axes in Fig. 5(b), the nematic director $\boldsymbol{n}_1(z)$ rotates about the z axis. The above term drives the system into such a state, when the coefficient is sufficiently negative [68–70].

C. Example: D_{2h} group

The symmetry of this molecular group is typical of a rectangular block, illustrated in Fig. 6. In addition to $\mathsf{Q}^{[2]}$, another order parameter tensor $\mathsf{M}_1^{[2]}$ must be considered (see Table I). Although different definitions have been used for the order parameters in the literature [20,22,24], to model the D_{2h} group of molecules, one can equivalently map these order parameters to our notations. For example, the use of the Wigner D-functions in Refs. [21,24] is identical to the use of Q and M, as discussed in Appendix B 3.

The spatially homogeneous nematic states are taken as an example here. The bulk free energy, as listed in Table I, gives rise to the coupling between the two second-order tensors,

$$a_1\mathsf{Q}^{[2]}\cdot\mathsf{Q}^{[2]} + a_2\mathsf{Q}^{[2]}\cdot\mathsf{M}_1^{[2]} + a_3\mathsf{M}_1^{[2]}\cdot\mathsf{M}_1^{[2]}, \tag{72}$$

where a_1, a_2 and a_3 are coefficients that depend on the molecular shapes. Two independent modes, each consisting of a linear combination of the two order parameters $\mathsf{Q}^{[2]}$ and $\mathsf{M}_1^{[2]}$, can then be established. Each of these two modes corresponds to an ordered nematic state, together with a possible, associated biaxial state. When the remixed coefficient of a mode is sufficiently negative, this mode is then stabilized.

The physical interpretation of these nematic states are illustrated in Fig. 6. The nematic-1 state is formed by almost rodlike, long rectangle molecules and the main nematic director coincides with the direction of the mean long axes of the molecules. Its associated biaxial state has the same main nematic director but a secondary nematic director is developed because of the rectangular shape of the cross section. The nematic-2 state is formed by near-square-like plate molecules. The main nematic axis is parallel to the mean plate normals and there is an isotropic distribution of the orientation of the edges of the plates. Further orientational ordering of the edge directions gives rise to a biaxial state associated with the nematic-2 state [20,22].

D. Example: C_{2v} group

Bent-core or kitelike molecules (Fig. 1) belong to this group. The body-mounted axes are demonstrated in Fig. 7. According to the current theory, in addition to $\mathsf{Q}^{[0]}$, four orientational order parameters, $\mathsf{Q}^{[1]}$, $\mathsf{Q}^{[2]}$, $\mathsf{M}_1^{[2]}$, and $\mathsf{M}_2^{[2]}$, are present, up to second-order tensors.

A number of spatially homogeneous phases (referred to as the bulk phase in most references) are possible based on an analysis of these order parameters. All previous studies include two second-order order parameter tensors, which, as we mentioned in Sec. V C, are equivalent to $\mathsf{Q}^{[2]}$ and $\mathsf{M}_1^{[2]}$ in this paper. The coupling between these two tensors has a typical form in Eq. (72). Following the discussion in Sec. V C, two nematic states and their associated biaxial states are possible. These are plotted in Figs. 7(a)–7(d), which can be compared with their counter parts in Figs. 6(a)–6(d). Hence, at this level, C_{2v} would have the same states as those of D_{2h}, as noted before [59–62].

The addition of the first-order order parameter tensor (a vector) $\mathsf{Q}^{[1]}$ to the above picture produces a richer number of bulk states. Figures 7(e) and 7(f) are illustrations of two polar nematic states where the mean vector $\langle \boldsymbol{m}_1\rangle$ is nonzero, for both near-rodlike (left) and near-plate (right) molecules.

In all previous theoretical studies, the orientational order parameter tensor $\mathsf{M}_2^{[2]}$ was neglected for C_{2v} because of their usage of $O(3)$ group in identification of order parameters. From Table I, $\mathsf{M}_2^{[2]} \cdot \mathsf{M}_2^{[2]}$ exists independent of $\mathsf{Q}^{[2]}$ and $\mathsf{M}_1^{[2]}$. The local distributions of two possible nematic states, in which

$$\mathsf{M}_2^{[2]} = 2\langle \boldsymbol{m}_2\boldsymbol{m}_3\rangle$$

are finite, are shown in Figs. 7(g) and 7(h) for both near-rodlike (left) and near-plate (right) molecules. These states have been observed experimentally [71].

The missing $\mathsf{M}_2^{[2]}$ in an $O(3)$ theory is crucial for description of the phases sketched in Figs. 7(g) and 7(h). To remedy the missing symmetry, realized by Lubensky and Radzihovsky of Ref. [33], a third-order symmetric traceless tensor $\langle \boldsymbol{m}_1\boldsymbol{m}_3^2 - \frac{1}{5}\mathsf{id}\boldsymbol{m}_1\rangle$ was introduced. The states in Figs. 7(g) and 7(h), for example, was argued by Lubensky and Radzihovsky to exist if such a third-order symmetric traceless tensor is introduced, among other effects. In contrast, together with $\mathsf{Q}^{[1]}$, the three second-order tensors in our $SO(3)$ theory for order parameters are adequate for description of all phases in the figure. In addition, spatially modulated states can also be described [32,72].

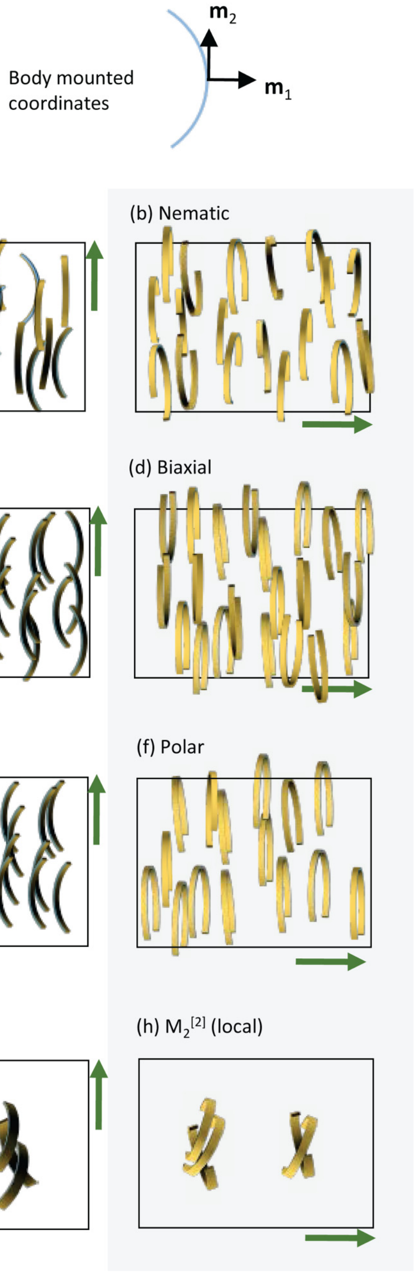


FIG. 7. Illustration of a bend-core molecule with body-mounted coordinates $\boldsymbol{m}_1$, $\boldsymbol{m}_2$, and $\boldsymbol{m}_3$ (pointing to the readers from the plane), as well as (a)–(h) examples of spatially homogenous nematic phases. The left column are molecules ordered with a main nematic axis in the mean $\boldsymbol{m}_2$ directions and the right column in the mean $\boldsymbol{m}_3$ directions. The main nematic directors are specified by the green arrows.

VI. SUMMARY

This paper explores the relationship between the group symmetries of a liquid-crystal molecule (Sec. II), the orientational order parameters that can be used to describe such symmetries when a large number of molecules form a liquid crystal (Sec. III), and the free-energy terms that are used to describe the structures of spatially inhomogeneous and orientationally ordered states (Sec. IV). Although many efforts have been previously made in the literature, the current attempt is to develop a complete theory for all major classes of molecules, where the selections of the order parameters are considered together with the number of essential terms in the free-energy expansion. The main concern here is the symmetries of the system and how the pairwise interaction is expressed by symmetric traceless tensors. The molecular symmetry operations dominate the type of terms that are nonvanishing in an expansion of the interaction energy in terms of the identified order parameters.

The subject matter has been the central focus in the liquid-crystal community. The most common approach is to take a LdG-type model, which contains leading terms in a free-energy expansion on the order parameter tensors. Over many years, a number of general theories have been formulated [7,8,20,22,24]. As far as we know, our study here represents the first systematic examination of the elastic energies in relationship with molecular symmetries. The leading order parameter tensors, as summarized in Table I, are kept at a level where the elastic free-energy terms are consistently presented in a meaningful form. This approach differs from the philosophy taken in Ref. [25], where only one or two leading orientational order-parameter tensors are kept.

The partial inclusion of higher-order tensors as the orientational order parameters were previously explored. For example, in Ref. [7] a theoretical study of the interaction energy, which contains a cross product of the orientational vectors associated with two molecules, is carried out. Such a form is characteristic of the D_{2h} group, and exists in molecules following the D_{4h} or O_h symmetries. Thus in that study, some fourth-order Wigner-D functions (that are equivalent to components of symmetric traceless tensors) was included, in order to account for the symmetries in D_{4h} and O_h. In other studies, third-order tensors are considered in addition to lower-order ones, to described the tetrahedral ordering [27,29]. When the goal is to describe the particular molecular and overall structural symmetries, rigorous analyses on order parameters can also be found in the literature [73–76]. However, not *all* nonvanishing free-energy terms are consistently discussed.

Some recent LdG models were developed by including multiple order parameters, without asking their molecular origins. For example, in Refs. [36,37] the LdG models expanded in terms of vector and second-order orientational parameter tensors are studied; in Ref. [33], the LdG model of first-, second-, and third-order orientational tensor is considered. A general scheme is summarized for description of a number of distinct phases in terms of second-, third-, and fourth-order tensors, in Refs. [30,31]. Their connections to particular molecular symmetries is opaque. This connection is important for identification of all elastic energy terms, which has an important consequence on the resulting structural properties of stabilized phases.

ACKNOWLEDGMENTS

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APPENDIX A: ORTHONORMAL FRAME, EULER ANGLES, AND ROTATION OPERATIONS

The orientation of an orthonormal frame, $\mathsf{u} = (\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$, that is mounted on a molecule, is determined by the coordinates of the three axes in a stationary laboratory frame. The three axes can be defined by the three Euler angles α, β, γ. A standard transformation yields the column vectors

$$\begin{aligned}
\boldsymbol{m}_1 &= (\cos\beta, \sin\beta\cos\alpha, \sin\beta\sin\alpha)^t, && \text{(A1a)}\\
\boldsymbol{m}_2 &= (-\sin\beta\cos\gamma, \cos\beta\cos\alpha\cos\gamma - \sin\alpha\sin\gamma, \\
&\quad \times \cos\beta\sin\alpha\cos\gamma + \cos\alpha\sin\gamma)^t, && \text{(A1b)}\\
\boldsymbol{m}_3 &= (\sin\beta\sin\gamma, -\cos\beta\cos\alpha\sin\gamma - \sin\alpha\cos\gamma, \\
&\quad - \cos\beta\sin\alpha\sin\gamma + \cos\alpha\cos\gamma)^t, && \text{(A1c)}
\end{aligned}$$

where the superscript t denotes the transpose.

Thus, u can be regarded as an Euler rotational matrix, and it defines a rotation operation in reference to a laboratory frame. For example, two consecutive rotation operations, u followed by w, each has their own Euler angles, can be expressed in terms of the matrix product wu. In another example, the components, in the $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ frame, of any vector $\boldsymbol{v}$ can be calculated from the matrix-vector product $\mathsf{u}\boldsymbol{v}$. Yet in one more example, one takes a rotation operation (represented by the rotational matrix g) in the body-fixed frame u, which itself is rotated from the laboratory frame; such an operation can be regarded as a combination of two rotation events, first a rotation represented by g from a laboratory frame (when u still coincides with the laboratory frame), and second a rotation operation to set the u frame in space. The combined operation is then represented by the matrix product ug.

APPENDIX B: SYMMETRIC TRACELESS TENSORS

We summarize the algebraic properties of the symmetric traceless tensors used in this paper. The derivations of these properties are documented in Ref. [44].

1. Symmetric traceless tensors generated by monomials

The basic form (a monomial) of a kth-order symmetric tensor used in this paper is

$$\begin{aligned}
\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}\mathsf{id}^l &= \underbrace{\boldsymbol{m}_1 \otimes \cdots}_{k_1} \otimes \underbrace{\boldsymbol{m}_2 \otimes \cdots}_{k_2} \\
&\quad \times \otimes \underbrace{\boldsymbol{m}_3 \otimes \cdots}_{k_3} \otimes \underbrace{\mathsf{id} \otimes \cdots}_{l},
\end{aligned}$$

where $k = k_1 + k_2 + k_3 + 2l$ and id is the second-order identity tensor $\mathsf{id}_{ij} = \delta_{ij}$, which is defined from $\mathsf{id} = \boldsymbol{m}_1^2 + \boldsymbol{m}_2^2 + \boldsymbol{m}_3^2$. The symmetric form of a tensor made from the product of k vectors $\{\boldsymbol{x}_j\}$ is obtained from

$$\boldsymbol{x}_1\boldsymbol{x}_2\ldots\boldsymbol{x}_k = \frac{1}{k!}\sum_{\sigma}\boldsymbol{x}_{\sigma_1}\otimes\boldsymbol{x}_{\sigma_2}\otimes\cdots\otimes\boldsymbol{x}_{\sigma_k},$$

where $\{\sigma_j\}$ represent all possible permutations of the indices $1, 2, \dots, k$.

One can make the monomial $\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}$ traceless, now carrying a subscript 0, $[\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}]_0$. When $k_3 = 0$ or 1, a traceless tensor is produced from the summation [44]

$$\begin{aligned}\big[\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}\big]_0&\\ =\sum_{2j_1\leqslant k_1, 2j_2\leqslant k_2} a^{k_1,k_2,k_3}_{j_1,j_2}\boldsymbol{m}_1^{k_1-2j_1}\boldsymbol{m}_2^{k_2-2j_2}\boldsymbol{m}_3^{k_3}\mathsf{id}^{j_1+j_2},&\end{aligned}\tag{B1}$$

where the coefficients are given by

$$\begin{aligned}a^{k_1,k_2,k_3}_{j_1,j_2}&=(-1)^{j_1+j_2}\binom{j_1+j_2}{j_1}\\ &\quad\times\frac{k_1!k_2!(2k-1-2j_1-2j_2)!!}{(k_1-2j_1)!(k_2-2j_2)!(2k-1)!!(2j_1+2j_2)!!}.\end{aligned}\tag{B2}$$

When $k_3\geqslant 2$, the symmetric traceless tensors are deduced from

$$\big[\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}\big]_0=\big[\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\big(-\boldsymbol{m}_1^2-\boldsymbol{m}_2^2\big)^j\boldsymbol{m}_3^{k_3-2j}\big]_0,\tag{B3}$$

where j is the integer such that $2j\leqslant k_3\leqslant 2j+1$.

2. Symmetric traceless tensors and the special functions

The nth-order symmetric traceless tensor $\mathsf{Q}^{[n]}$ is generated from $\boldsymbol{m}_1^n$,

$$\begin{aligned}\mathsf{Q}^{[n]}&=\langle[\boldsymbol{m}_1^n]_0\rangle\\ &=\left\langle\sum_{2j\leqslant n}(-1)^j\frac{n!(2n-1-2j)!!}{(n-2j)!(2n-1)!!(2j)!!}\boldsymbol{m}_1^{n-2j}\mathsf{id}^j\right\rangle.\end{aligned}$$

The coefficients in the above are proportional to those of the Legendre polynomials. Define

$$\tilde{L}_n(y,z)=\frac{2^n(n!)^2}{(2n)!}z^{n/2}L_n(y/\sqrt{z}),$$

where $L_n(x)$ is the nth-degree Legendre polynomial. Such a definition makes the coefficient of the y^n term 1. One can then formally write

$$\mathsf{Q}^{[n]}=\langle\tilde{L}_n(\boldsymbol{m}_1,\mathsf{id})\rangle.\tag{B4}$$

The two tensors, $\mathsf{M}_1^{[n]}$ (first kind) and $\mathsf{M}_2^{[n]}$ (second kind), involve powers of $\boldsymbol{m}_1$, $\boldsymbol{m}_2$, $\boldsymbol{m}_3$. Their expressions can be associated with the properties of the nth-degree, first- and second-kind Chebyshev polynomials, $T_n(x)$ and $U_n(x)$. Define

$$\tilde{T}_n(y,z)=z^{n/2}T_n(y/\sqrt{z})$$

and

$$\tilde{U}_n(y,z)=z^{n/2}U_n(y/\sqrt{z}).$$

One can then show

$$\begin{aligned}\mathsf{M}_1^{[n]}&=\big\langle\tilde{T}_n\big(\boldsymbol{m}_2,\mathsf{id}-\boldsymbol{m}_1^2\big)\big\rangle\\ &=\big\langle\big[\tilde{T}_n\big(\boldsymbol{m}_2,-\boldsymbol{m}_1^2\big)\big]_0\big\rangle,\end{aligned}\tag{B5a}$$

$$\begin{aligned}\mathsf{M}_2^{[n]}&=\big\langle\tilde{U}_{n-1}\big(\boldsymbol{m}_2,\mathsf{id}-\boldsymbol{m}_1^2\big)\boldsymbol{m}_3\big\rangle\\ &=\big\langle\big[\tilde{U}_{n-1}\big(\boldsymbol{m}_2,-\boldsymbol{m}_1^2\big)\boldsymbol{m}_3\big]_0\big\rangle.\end{aligned}\tag{B5b}$$

3. Connection to Wigner D-matrix

The main text uses symmetric traceless tensors to characterize the orientational properties of the liquid crystal molecules. In some studies, for example, in Refs. [7,24,27,58,77], instead of tensors, the Wigner D-functions are used as the basic tools to represent the orientational properties. Here the equivalence of these two approaches are discussed.

In the above, the nth-order symmetric traceless tensors are formed in terms of the basic units $[\boldsymbol{m}_1^{k_1}\boldsymbol{m}_2^{k_2}\boldsymbol{m}_3^{k_3}]_0$ where $k_1+k_2+k_3=n$ and $k_3=0$ or 1. The total number of the tensors is $2n+1$. To relate to the Wigner D-functions, consider the Jacobi polynomial of degree n. Define $\tilde{P}_m^{(\tau,\tau)}(y,z)=z^{m/2}P_m^{(\tau,\tau)}(y/\sqrt{z})$, where $P_m^{(\tau,\tau)}(x)$ is the Jacobi polynomial with the index (τ,τ). One can show that the following $2n+1$ tensors are all symmetric and traceless:

$$\begin{aligned}&\mathsf{V}_{k,1}^{[n]}(\mathsf{u})=\tilde{P}_{n-k}^{(k,k)}(\boldsymbol{m}_1,\mathsf{id})\tilde{T}_k\big(\boldsymbol{m}_2,\mathsf{id}-\boldsymbol{m}_1^2\big),\ 0\leqslant k\leqslant n,\\ &\mathsf{V}_{k,2}^{[n]}(\mathsf{u})=\tilde{P}_{n-k}^{(k,k)}(\boldsymbol{m}_1,\mathsf{id})\tilde{U}_{k-1}\big(\boldsymbol{m}_2,\mathsf{id}-\boldsymbol{m}_1^2\big)\boldsymbol{m}_3,\\ &\qquad 1\leqslant k\leqslant n,\end{aligned}\tag{B6}$$

where $\mathsf{u}=(\boldsymbol{m}_1,\boldsymbol{m}_2,\boldsymbol{m}_3)$. A special case is when u coincides with the laboratory frame, for which $\mathsf{u}=\mathsf{id}$.

The Wigner D-functions are widely used when functions of β,α,γ are expanded,

$$\begin{aligned}&D^n_{mm'}(\alpha,\beta,\gamma)\\ &\quad=c^n_{mm'}\exp(-\sqrt{-1}m\alpha)d^n_{mm'}(\beta)\exp(-\sqrt{-1}m'\gamma),\end{aligned}$$

where the functions $d^n_{mm'}(\beta)$ are trigonometric polynomials and coefficients $c^n_{mm'}$ constants (see, for example, Ref. [78]). The Wigner D-functions can be connected to the symmetric traceless tensors,

$$\begin{aligned}D^n_{j,j'}&=\lambda\big\{\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})+\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})\big]\\ &\quad+\sqrt{-1}\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})-\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})\big]\big\},\\ D^n_{-j,-j'}&=\lambda\big\{\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})+\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})\big]\\ &\quad-\sqrt{-1}\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})-\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})\big]\big\},\\ D^n_{-j,j'}&=\lambda\big\{\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})-\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})\big]\\ &\quad+\sqrt{-1}\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})+\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})\big]\big\},\\ D^n_{j,-j'}&=\lambda\big\{\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})-\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})\big]\\ &\quad-\sqrt{-1}\big[\mathsf{V}_{j,1}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',2}^{[n]}(\mathsf{u})+\mathsf{V}_{j,2}^{[n]}(\mathsf{id})\cdot\mathsf{V}_{j',1}^{[n]}(\mathsf{u})\big]\big\}.\end{aligned}$$

Here λ is a normalization constant that depends on $|j|$ and $|j'|$ only and $\mathsf{V}_{0,2}^{[n]}=0$. Hence, the Wigner D-functions are related to the symmetric traceless tensors.

Thus, the mean symmetric traceless tensors, evaluated based on a distribution function $f(\boldsymbol{r}, \mathsf{u})$, are just linear combinations of the coefficients of the Wigner D-functions, when $f(\boldsymbol{r}, \mathsf{u})$ is expanded. One can show, for example, $\mathsf{Q}^{[n]}$, $\mathsf{M}_1^{[n]}$ and $\mathsf{M}_2^{[n]}$ are related to the coefficients of $\mathsf{V}_{0,1}^{[n]}(\mathsf{u})$, $\mathsf{V}_{n,1}^{[n]}(\mathsf{u})$, and $\mathsf{V}_{n,2}^{[n]}(\mathsf{u})$.

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