

THE TRANSMISSION OF SYMMETRY IN LIQUID CRYSTALS*

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Abstract. In liquid crystals, the existing experiments and simulations suggest that for various types of molecules, no homogeneous phase is found breaking the molecular symmetry. It has been proved for rod-like molecules. We conjecture that it holds for two types of two-fold symmetries, and prove it for some molecules with these symmetries.

Key words. Liquid crystals, homogeneous phases, molecular symmetry, phase symmetry.

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1. Introduction The application of liquid crystals benefits from their subtlety in anisotropy, which originates from the anisotropy at the molecular level. Let us consider a rod-like molecule. Except for its location \boldsymbol{x} , we need to express its orientation by a unit vector \boldsymbol{m} . The distribution f thus depends on both \boldsymbol{x} and \boldsymbol{m} , and the anisotropy may originate from either of them. The phases in which f is independent of \boldsymbol{x} are referred to as homogeneous phases. These phases show anisotropy while keeping mobility in all directions. A typical example is the uniaxial nematic phase, where there exists a unit vector \boldsymbol{n} such that $f = f((\boldsymbol{m} \cdot \boldsymbol{n})^2)$.

Symmetry is always a central topic where anisotropy appears. In liquid crystals, we need to discuss the symmetry at both macroscopic level and microscopic level: the phase symmetry and the molecular symmetry. The physical properties are mainly connected to the phase symmetry. Aiming at designing materials of physical properties more delicate, people have been striving for phases of other symmetries. This can be done by exerting external forces or confinements, but it brings limitation to application. With the hope of obtaining different phase symmetries spontaneously, people choose to alter the molecular symmetry. Among these molecules bent-core molecules have attracted considerable interests, whose rigid part possesses a bending (see the molecule in the right of Fig. 1.1). Numerous unconventional liquid crystalline phases have been found for these molecules.

Despite the rich phase behaviors obtained, by far no homogeneous phases have been found breaking the molecular symmetry. The uniaxial nematic phase, the only homogeneous phase rod-like molecules exhibit, is axisymmetric, identical to the symmetry of a rod. It is also the case for cuboids and bent-core molecules, of which the homogeneous phases observed are restricted to the uniaxial and the biaxial nematic phases [13, 1, 2, 7]. It is common that a homogeneous phase has better symmetry than the molecular symmetry. For instance, the non-axisymmetric molecules we mentioned above are all able to form the uniaxial nematic phase. If for a molecule, all the homogeneous phases it exhibits keep at least the molecular symmetry, we refer to it as that the molecular symmetry is transmitted to the phases. We would like to ask a question: will the molecular symmetry always be transmitted to the phases?

The theoretical study of liquid crystals begins from Onsager [18]. He proposed a

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free energy functional for rods,

$$F[f] = \int d\mathbf{m} f(\mathbf{m}) \log f(\mathbf{m}) + \frac{c}{2} \int d\mathbf{m} d\mathbf{m}' f(\mathbf{m}) G(\mathbf{m}, \mathbf{m}') f(\mathbf{m}'), \quad (1.1)$$

where $c > 0$ is an intensity parameter, and f shall meet the normalization condition,

$$\int d\mathbf{m} f(\mathbf{m}) = 1. \quad (1.2)$$

The energy functional considers homogeneous phases only, as it does not include \mathbf{x} . Each phase corresponds to a local minimum.

The energy functional is characterized by the kernel function G that reflects the pairwise molecular interaction. Onsager considered the hard repulsive interaction and calculated the leading term of the excluded volume of two rods

$$cG = 2cl^2 D |\mathbf{m} \times \mathbf{m}'| \quad (1.3)$$

as the kernel function, where l is the length and D is the thickness. Later Maier and Saupe [14] proposed a quadratic approximate kernel function,

$$cG = c_2 (\mathbf{m} \cdot \mathbf{m}')^2. \quad (1.4)$$

Both kernel are applied in the discussion of the isotropic – uniaxial nematic phase transitions of rods. Because the polynomial form brings conveniences, the Maier-Saupe kernel has received much more attention, and is adopted widely in dynamic models [4, 8, 6].

Axisymmetry is an important concept for rods. A rod is invariant when rotating it about its axis. This is why we can use the vector \mathbf{m} to represent its orientation. On the other hand, a phase is axisymmetric if f is, which is expressed as $f = f(\mathbf{m} \cdot \mathbf{n})$. For the Maier-Saupe kernel, the axisymmetry of f has been proved [11, 5, 28]:

The critical points of (1.1) with the Maier-Saupe kernel (1.4) shall satisfy $f = f((\mathbf{m} \cdot \mathbf{n})^2)$, where \mathbf{n} is a unit vector.

Armed with this result, it is not difficult to find all the solutions. It also provides a solid foundation for the well-known Oseen-Frank theory [19] and Ericksen-Leslie theory [9], which are built based on the axisymmetric assumption much earlier.

Although an elegant result has been acquired for rods, things become much more complicated for generic rigid molecules. When dealing with these molecules, we need a right-handed body-fixed orthonormal frame $(\mathbf{m}_1(P), \mathbf{m}_2(P), \mathbf{m}_3(P))$ to represent the orientation of a molecule. The variable $P \in SO(3)$ determines the orientation of the frame. The matrix representation of P can be written as

$$P = \begin{pmatrix} m_{11} & m_{21} & m_{31} \\ m_{12} & m_{22} & m_{32} \\ m_{13} & m_{23} & m_{33} \end{pmatrix}, \quad (1.5)$$

where $m_{ij}(P) = \mathbf{m}_i \cdot \mathbf{e}_j$ denotes the j th component of \mathbf{m}_i in the space-fixed right-handed orthonormal frame $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$. They can be expressed with three Euler angles

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

by

$$P(\alpha, \beta, \gamma) = \begin{pmatrix} \cos \alpha & -\sin \alpha \cos \gamma & \sin \alpha \sin \gamma \\ \sin \alpha \cos \beta & \cos \alpha \cos \beta \cos \gamma - \sin \beta \sin \gamma & -\cos \alpha \cos \beta \sin \gamma - \sin \beta \cos \gamma \\ \sin \alpha \sin \beta & \cos \alpha \sin \beta \cos \gamma + \cos \beta \sin \gamma & -\cos \alpha \sin \beta \sin \gamma + \cos \beta \cos \gamma \end{pmatrix}. \quad (1.6)$$

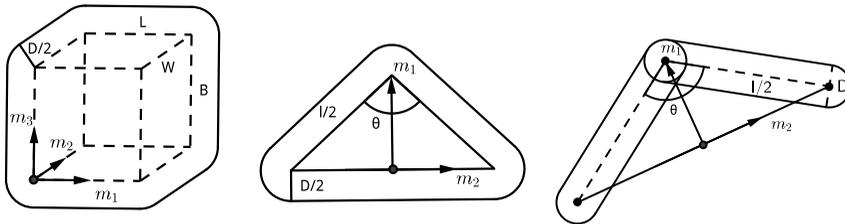


FIG. 1.1. Rigid molecules of two-fold symmetry. From left to right: spherocuboid; isosceles spherotriangle; bent-core molecule.

In this case, the uniform probability measure on $SO(3)$ is given by

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

Sometimes we also use P to represent the body-fixed frame.

The energy functional is now written as

$$F[f] = \int d\nu f(P) \log f(P) + \frac{c}{2} \int d\nu(P) d\nu(P') f(P) G(P, P') f(P'), \quad (1.7)$$

with the normalization condition

$$\int d\nu f(P) = 1. \quad (1.8)$$

The kernel function G depends only on the relative orientation $\bar{P} = P^{-1}P'$, whose elements are denoted by

$$p_{ij} = \mathbf{m}_i \cdot \mathbf{m}'_j.$$

In this paper, we consider molecules with two-fold symmetries. Some molecules of these symmetries are drawn in Fig. 1.1. Each of them is generated by inflating all the points in a set A to a sphere of the same diameter D . For a bent-core molecule, A is a broken line with two equal segments. And for the other two molecules, we add the prefix 'sphero' to the shape of A : for an isosceles spherotriangle, A is an isosceles triangle (including the interior and the boundary); for a spherocuboid, A is a cuboid. These molecules are regarded fully rigid. The body-fixed orthonormal frame for each molecule is posed as drawn in Fig. 1.1. Bent-core molecules and isosceles spherotriangles possess two-fold rotational symmetry about \mathbf{m}_1 and a mirror plane vertical to \mathbf{m}_3 . Spherocuboids possess two-fold rotational symmetries about \mathbf{m}_i , and mirror planes vertical to \mathbf{m}_i .

The molecular symmetry determines the form of G if we require G to be a quadratic polynomial of p_{ij} [27]. With the body-fixed frame chosen as in Fig. 1.1, the kernel is written as

$$cG(\bar{P}) = c_1 p_{11} + c_2 p_{11}^2 + c_3 p_{22}^2 + c_4 (p_{12}^2 + p_{21}^2), \quad (1.9)$$

where c_1 shall be zero if the molecule is nonpolar (such as spherocuboids). The kernel function without the term $c_1 p_{11}$ is introduced by Starley [25] in a form linearly equivalent. It later received extensive numerical study by Virga et al [24, 16, 12, 15, 3], and is also adopted in some dynamic models [22, 23, 10, 21].

The phase symmetry, i.e. the symmetry of a local minimum f , is about the space-fixed frame (\mathbf{e}_i). That the molecular symmetry is transmitted to f is stated as follows.

- For each local minimum f of the kernel (1.9), we can choose a frame (\mathbf{e}_i) such that f has two-fold symmetry about \mathbf{e}_1 and a mirror plane vertical to \mathbf{e}_3 ,
- For nonpolar molecules (namely $c_1=0$), we can choose a frame (\mathbf{e}_i) such that f has two-fold symmetries about \mathbf{e}_i and mirror planes vertical to \mathbf{e}_i ,

We claim the above statement as a conjecture, which is supported by our earlier simulation in [27].

In the current paper, we will prove the following result.

THEOREM 1.1. *For each local minimum f of the kernel (1.9) with $c_1 \geq -1$, we can choose a frame (\mathbf{e}_i) such that f has two-fold symmetries about \mathbf{e}_i and mirror planes vertical to \mathbf{e}_i , if either of the following condition holds:*

- The quadratic form $c_2x^2 + 2c_4xy + c_3y^2$ is not negative definite;*
- It is negative definite, but*

$$\frac{c_4^2}{c_3} - c_2 \leq 2.$$

We have pointed out in our previous work [27] that c_i can, in general, be derived from molecular interaction. If the conditions about coefficients are satisfied for some molecules, we can prove the transmission of symmetry for them. For the molecules in Fig. 1.1, we will show that the condition in the theorem is appropriate for the coefficients derived from excluded-volume interaction. Therefore, we are able to prove that for these molecules with excluded-volume interaction, the symmetry of nematic phases always maintains the molecular symmetry.

The rest of the paper is organized as follows. In Sec. 2, we derive the equivalent conditions for the transmission of symmetry. With these conditions, the problem is reduced to analysis on some tensors. In Sec. 3, we give the proof and application of the theorem. A concluding remark is given in Sec. 4.

2. The equivalent condition Before continuing our discussion on the phase symmetry, we write down the critical points of the energy functional. Generally, the Euler-Lagrange equation of (1.7) yields

$$f(P) = \frac{1}{Z} \exp(-W(P)), \quad (2.1)$$

where

$$W(P) = c \int d\nu(P') G(\bar{P}) f(P'), \quad (2.2)$$

and

$$Z = \int d\nu(P) \exp(-W(P)). \quad (2.3)$$

If the kernel function is a polynomial of p_{ij} , the Euler-Lagrange equation can be reduced to a few equations of tensors. With the kernel (1.9), we can write the energy functional as

$$F = \int d\nu f \log f + c_1 |\mathbf{p}|^2 + c_2 |Q_1|^2 + c_3 |Q_2|^2 + 2c_4 Q_1 : Q_2,$$

where \mathbf{p} , Q_1 and Q_2 are angular moments,

$$\mathbf{p} = \langle \mathbf{m}_1 \rangle, \quad Q_1 = \langle \mathbf{m}_1 \mathbf{m}_1 \rangle, \quad Q_2 = \langle \mathbf{m}_2 \mathbf{m}_2 \rangle,$$

and their components are denoted by p_i and $Q_{\alpha,ij}$ for $i, j=1,2,3$. Here we use the notation $\langle u \rangle = \int d\nu u(P)f(P)$, and dots for tensor contraction. And $W(P)$ can be written as

$$W(P) = c_1 \mathbf{p} \cdot \mathbf{m}_1 + (c_2 Q_1 + c_4 Q_2) : \mathbf{m}_1 \mathbf{m}_1 + (c_3 Q_2 + c_4 Q_1) : \mathbf{m}_2 \mathbf{m}_2. \quad (2.4)$$

The tensors shall satisfy the following equations,

$$\mathbf{p} = \frac{1}{Z} \int d\nu(P') \mathbf{m}'_1 \exp(-W(P')), \quad (2.5)$$

$$Q_1 = \frac{1}{Z} \int d\nu(P') \mathbf{m}'_1 \mathbf{m}'_1 \exp(-W(P')), \quad (2.6)$$

$$Q_2 = \frac{1}{Z} \int d\nu(P') \mathbf{m}'_2 \mathbf{m}'_2 \exp(-W(P')). \quad (2.7)$$

The next lemma gives the equivalent condition on the tensors for the transmission of symmetry.

LEMMA 2.1. *Let f be given by (2.1) and (2.4).*

- a) *f has two-fold symmetry about \mathbf{e}_1 and a mirror plane vertical to \mathbf{e}_3 , if and only if Q_1, Q_2 are diagonal and $p_2 = p_3 = 0$.*
- b) *Assume $c_1 = 0$. f has two-fold symmetries about \mathbf{e}_i and mirror planes vertical to \mathbf{e}_i , if and only if both Q_1 and Q_2 are diagonal.*

Proof. Define

$$R_1 = \text{diag}(1, -1, -1), \quad R_2 = \text{diag}(-1, 1, -1), \quad R_3 = \text{diag}(-1, -1, 1); \quad (2.8)$$

$$J_1 = \text{diag}(-1, 1, 1), \quad J_2 = \text{diag}(1, -1, 1), \quad J_3 = \text{diag}(1, 1, -1). \quad (2.9)$$

That f has two-fold symmetry about \mathbf{e}_i is expressed as $f(R_i P) = f(P)$; and that f has a mirror plane vertical to \mathbf{e}_i is expressed as $f(J_i P J_i) = f(P)$.

- a) Let $f(R_1 P) = f(P)$ and $f(J_3 P J_3) = f(P)$. By (2.1), we have $W(R_1 P) = W(P)$ and $W(J_3 P J_3) = W(P)$. Then by (2.4), it yields

$$T \mathbf{p} = \mathbf{p}, \quad T Q_1 T^T = Q_1, \quad T Q_2 T^T = Q_2, \quad T = R_1, J_3.$$

It requires that $p_2 = p_3 = 0$ and that Q_i are diagonal.

- b) Let $f(R_i P) = f(P)$ and $f(J_i P J_i) = f(P)$, which yields

$$R_i Q_1 R_i^T = Q_1, \quad R_i Q_2 R_i^T = Q_2.$$

It follows that the off-diagonal elements of Q_i equal to zero.

On the other hand, if the tensors meet the above conditions, it is easy to verify that the symmetric requirements are satisfied. \square

Because the space-fixed frame (\mathbf{e}_i) is allowed to be chosen, it is sufficient that there exists a frame such that the tensors satisfy the conditions in the above lemma. In the following lemma, we summarize the existing results in the language of the tensors [27].

LEMMA 2.2. *Let (\mathbf{p}, Q_1, Q_2) be the solution of (2.5)-(2.7).*

- (i) *If $c_1 \geq -1$, then $\mathbf{p} = 0$.*
- (ii) *If there exists a frame (\mathbf{e}_i) in which both Q_1 and Q_2 are diagonalized, then \mathbf{p} is an eigenvector of Q_i .*

Let us compare Lemma 2.2 with Lemma 2.1. To prove the transmission of symmetry, we need to show that there exists a frame (\mathbf{e}_i) in which both Q_1 and Q_2 are diagonalized.

3. Proof and application From the discussion above, we are going to prove Theorem 1.1 by showing that there exists a frame (e_i) in which both Q_1 and Q_2 are diagonalized. In fact, we have proposed in [27] a very special condition of the coefficients such that it holds. But the condition is too strong. In Theorem 1.1, we extend the condition so that it can be applied to some molecules.

Proof of Theorem 1.1. We know that $\mathbf{p}=0$ from Lemma 2.2. Therefore

$$W(P) = (c_2Q_1 + c_4Q_2) : \mathbf{m}_1\mathbf{m}_1 + (c_3Q_2 + c_4Q_1) : \mathbf{m}_2\mathbf{m}_2.$$

(a) Write the quadratic form in the standard form,

$$c_2x^2 + c_3y^2 + 2c_4xy = \lambda_1(d_1x + d_2y)^2 + \lambda_2(d_2x - d_1y)^2.$$

We may suppose that $\lambda_2 \geq 0$. Hence

$$\begin{aligned} W(P) &= \lambda_1(d_1Q_1 + d_2Q_2) : (d_1\mathbf{m}_1\mathbf{m}_1 + d_2\mathbf{m}_2\mathbf{m}_2) \\ &\quad + \lambda_2(d_2Q_1 - d_1Q_2) : (d_2\mathbf{m}_1\mathbf{m}_1 - d_1\mathbf{m}_2\mathbf{m}_2). \end{aligned}$$

Denote

$$\tilde{Q}_1 = d_1Q_1 + d_2Q_2, \quad \tilde{Q}_2 = d_2Q_1 - d_1Q_2.$$

and

$$\tilde{q}_1 = d_1\mathbf{m}_1\mathbf{m}_1 + d_2\mathbf{m}_2\mathbf{m}_2, \quad \tilde{q}_2 = d_2\mathbf{m}_1\mathbf{m}_1 - d_1\mathbf{m}_2\mathbf{m}_2.$$

Select a space-fixed frame such that \tilde{Q}_1 is diagonal. We will show that \tilde{Q}_2 is also diagonal in this frame. Let J_1 and J_3 be defined in (2.9). Then

$$m_{i1}(J_1PJ_3) = -m_{i1}(P), m_{i2}(J_1PJ_3) = m_{i2}(P), m_{i3}(J_1PJ_3) = m_{i3}(P), \quad i = 1, 2.$$

Thus

$$\tilde{q}_{2,12}(J_1PJ_3) = -\tilde{q}_{2,12}(P), \quad \tilde{q}_{2,13}(J_1PJ_3) = -\tilde{q}_{2,13}(P), \quad \tilde{q}_{2,23}(J_1PJ_3) = \tilde{q}_{2,23}(P).$$

Let

$$W_1(P) = \lambda_1\tilde{Q}_1 : \tilde{q}_1 + \lambda_2(\tilde{Q}_{2,ii}\tilde{q}_{2,ii} + 2\tilde{Q}_{2,23}\tilde{q}_{2,23}).$$

We have $W_1(J_1PJ_3) = W_1(P)$, and

$$\begin{aligned} W(P) &= W_1(P) + 2\lambda_2(\tilde{Q}_{1,12}\tilde{q}_{2,12}(P) + \tilde{Q}_{1,13}\tilde{q}_{2,13}(P)). \\ W(J_1PJ_3) &= W_1(J_1PJ_3) + 2\lambda_2(\tilde{Q}_{1,12}\tilde{q}_{2,12}(J_1PJ_3) + \tilde{Q}_{1,13}\tilde{q}_{2,13}(J_1PJ_3)) \\ &= W_1(P) - 2\lambda_2(\tilde{Q}_{1,12}\tilde{q}_{2,12}(P) + \tilde{Q}_{1,13}\tilde{q}_{2,13}(P)). \end{aligned}$$

For any function $h(P)$ and $L_1, L_2 \in SO(3)$, it holds $\int d\nu h(P) = \int d\nu h(L_1PL_2)$. Therefore

$$\begin{aligned} &\tilde{Q}_{2,12}^2 + \tilde{Q}_{2,13}^2 \\ &= \frac{2 \int d\nu \exp(-W(P))(\tilde{Q}_{2,12}\tilde{q}_{2,12} + \tilde{Q}_{2,13}\tilde{q}_{2,13})}{2 \int d\nu \exp(-W(P))} \\ &= \frac{\int d\nu [\exp(-W(P)) - \exp(-W(J_1PJ_3))](\tilde{Q}_{2,12}\tilde{q}_{2,12} + \tilde{Q}_{2,13}\tilde{q}_{2,13})}{\int d\nu [(\exp(-W(P)) + \exp(-W(J_1PJ_3)))]} \\ &= \frac{\int d\nu \exp(-W_1(P))(\tilde{Q}_{2,12}\tilde{q}_{2,12} + \tilde{Q}_{2,13}\tilde{q}_{2,13}) \sinh(-2\lambda_2(Q_{1,12}\tilde{q}_{2,12} + Q_{1,13}\tilde{q}_{2,13}))}{\int d\nu \exp(-W_1(P)) \cosh(-2\lambda_2(Q_{1,12}\tilde{q}_{2,12} + Q_{1,13}\tilde{q}_{2,13}))}. \end{aligned}$$

Since $\lambda_2 \geq 0$, the right side ≤ 0 . Similarly, we can prove that $\tilde{Q}_{2,23} = 0$. Thus \tilde{Q}_2 is diagonal.

(b) From the condition, we can find d_1, d_2 and $0 < \epsilon \leq 2$ such that

$$-c_2 = \epsilon + d_1^2, \quad -c_3 = d_2^2, \quad -c_4 = d_1 d_2.$$

Hence

$$W(P) = -(d_1 Q_1 + d_2 Q_2) : (d_1 \mathbf{m}_1 \mathbf{m}_1 + d_2 \mathbf{m}_2 \mathbf{m}_2) - \epsilon Q_1 : \mathbf{m}_1 \mathbf{m}_1.$$

Similar to the first part of the theorem, we may suppose that $d_1 Q_1 + d_2 Q_2$ is diagonal, and let

$$W_1(P) = -(d_1 Q_1 + d_2 Q_2) : (d_1 \mathbf{m}_1 \mathbf{m}_1 + d_2 \mathbf{m}_2 \mathbf{m}_2) - \epsilon (Q_{1,ii} m_{1i}^2 + 2Q_{1,23} m_{12} m_{13}).$$

It also holds $W_1(J_1 P J_3) = W_1(P)$. Similar to what is done in (a), we obtain

$$\begin{aligned} & Q_{1,12}^2 + Q_{1,13}^2 \\ & \quad \frac{\int d\nu \exp(-W_1(P)) (Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13})}{\sinh(2\epsilon(Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13}))} \\ & = \frac{\int d\nu \exp(-W_1(P)) \cosh(2\epsilon(Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13}))}{\cosh(2\epsilon(Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13}))}. \end{aligned}$$

Since $0 < \epsilon \leq 2$, using $x \tanh(x) < x^2$ ($x \neq 0$), we obtain

$$\begin{aligned} & Q_{1,12}^2 + Q_{1,13}^2 \\ & \quad \frac{\int d\nu \exp(-W_1(P)) 2\epsilon (Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13})^2}{\cosh(2\epsilon(Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13}))} \\ & \leq \frac{\int d\nu \exp(-W_1(P)) \cosh(2\epsilon(Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13}))}{\cosh(2\epsilon(Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13}))}. \end{aligned}$$

But

$$\begin{aligned} (Q_{1,12} m_{11} m_{12} + Q_{1,13} m_{11} m_{13})^2 & \leq m_{11}^2 (Q_{1,12}^2 + Q_{1,13}^2) (m_{12}^2 + m_{13}^2) \\ & = (Q_{1,12}^2 + Q_{1,13}^2) m_{11}^2 (1 - m_{11}^2) \\ & \leq \frac{1}{4} (Q_{1,12}^2 + Q_{1,13}^2). \end{aligned}$$

Therefore we get

$$Q_{1,12}^2 + Q_{1,13}^2 \leq \frac{\epsilon}{2} (Q_{1,12}^2 + Q_{1,13}^2) \leq Q_{1,12}^2 + Q_{1,13}^2,$$

leading to $Q_{1,12} = Q_{1,13} = 0$. Thus Q_1 is diagonal.

□

Now we apply the theorem to the molecules drawn in Fig. 1.1. We will focus on the theoretical aspect. For the classification of homogeneous phases, we refer to our previous work [27]. The coefficients c_i in the kernel function can be written as functions of molecular parameters. This is done by fitting the excluded volume $V(\bar{P})$, one of the interactions most commonly considered, with the quadratic kernel (1.9). The parameters include (see Fig. 1.1): the diameter of sphere D ; for isosceles spherotriangles and bent-core molecules, the length of lateral or arm $l/2$, the top angle θ ; and for spherocuboids, the length of three edges W, B, L .

For cuboids (the case $D=0$), Starley computed $V(\bar{P})$ at specific \bar{P} and did the interpolation to obtain c_i [25]. They are given by

$$\begin{aligned} c_2 &= c [-B(W^2 + L^2) - W(L^2 + B^2) + 4WBL - (L^2 - BW)(B - W)], \\ c_3 &= c [-B(W^2 + L^2) - W(L^2 + B^2) + 4WBL + (L^2 - BW)(B - W)], \\ c_4 &= c [-B(W^2 + L^2) - W(L^2 + B^2) + L(W^2 + B^2) + 2WBL]. \end{aligned}$$

Compared with interpolation, a more accurate method is to use the L^2 -projection, i.e. to minimize the distance

$$\min \int d\nu(\bar{P}) |V(\bar{P}; \Theta) - G(\bar{P}; c_i)|^2,$$

where Θ is the set of molecular parameters. By solving this problem, we can write c_i as functions of Θ . All the c_i given in the following are obtained from this method.

The coefficients given in [20] for spherocuboids, based on the excluded volume calculated in [17], are

$$\begin{aligned} c_2 &= \frac{15c}{16} \left[-B(W^2 + L^2) - W(L^2 + B^2) + 4WBL - (L^2 - BW)(B - W) - \frac{\pi D}{2}(L - B)^2 \right], \\ c_3 &= \frac{15c}{16} \left[-B(W^2 + L^2) - W(L^2 + B^2) + 4WBL + (L^2 - BW)(B - W) - \frac{\pi D}{2}(L - W)^2 \right], \\ c_4 &= \frac{15c}{16} \left[-B(W^2 + L^2) - W(L^2 + B^2) + L(W^2 + B^2) + 2WBL - \frac{\pi D}{2}(L - W)(L - B) \right]. \end{aligned}$$

When $D=0$, they are proportional to the Starley's. The coefficients for spherotriangles, computed in [27], are

$$\begin{aligned} c_1 &= \frac{3}{8} cl^2 DK(\theta) \geq 0, \\ c_2 &= -\frac{15}{64} cl^3 \sin\theta \cos^2 \frac{\theta}{2} - \frac{15\pi}{128} cl^2 D \cos^4 \frac{\theta}{2}, \\ c_3 &= -\frac{15}{64} cl^3 \sin\theta \sin \frac{\theta}{2} (1 + \sin \frac{\theta}{2}) - \frac{15\pi}{128} cl^2 D \sin^2 \frac{\theta}{2} (1 + \sin \frac{\theta}{2})^2, \\ c_4 &= -\frac{15}{128} cl^3 \sin\theta (1 + \sin \frac{\theta}{2}) - \frac{15\pi}{128} cl^2 D \cos^2 \frac{\theta}{2} \sin \frac{\theta}{2} (1 + \sin \frac{\theta}{2}). \end{aligned}$$

For bent-core molecules, the coefficients can be calculated numerically as is described in [27]. They are proportional to cl^3 and depend on two dimensionless parameters D/l and θ . It needs to be pointed out that $c_1 \geq 0$ for bent-core molecules.

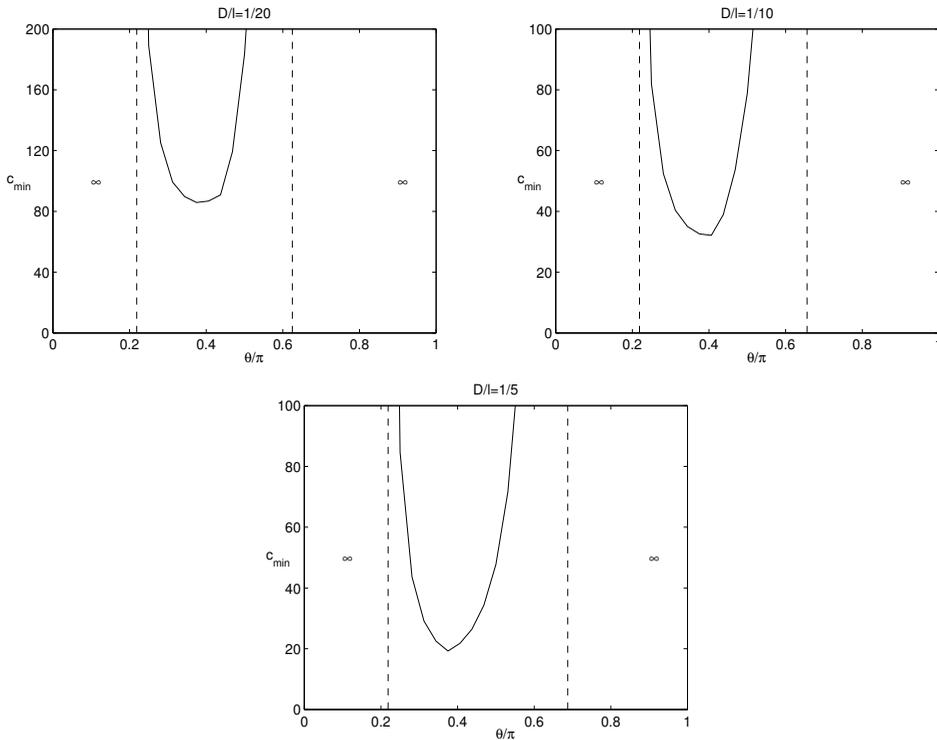
The coefficients derived from spherocuboids and spherotriangles satisfy the first condition. In fact, for spherocuboids, it gives

$$c_4^2 - c_2 c_3 = k(W - B)^2 (B - L)^2 (L - W)^2 \geq 0,$$

where k is a positive number. For spherotriangles, we have

$$c_4^2 - c_2 c_3 = \left(\frac{15cl^3 \sin\theta}{128} \right)^2 (2\sin \frac{\theta}{2} - 1)^2 (\sin \frac{\theta}{2} + 1)^2 \geq 0.$$

Since the product of two eigenvalues equals to $c_2 c_3 - c_4^2 \leq 0$, it follows from the theorem that for both molecules, Q_1 and Q_2 share an eigenframe.

FIG. 3.1. Minimal c that makes $\epsilon > 2$, c_{\min} .

Now we turn to bent-core molecules. Because c_i are proportional to the cl^3 , we set $l=2$ without loss of generality. Then we have

$$\epsilon = -\frac{c_2 c_3 - c_4^2}{c_3} = -c \cdot \frac{c_2^{(0)} c_3^{(0)} - (c_4^{(0)})^2}{c_3^{(0)}},$$

if $c_2 c_3 - c_4^2 > 0$, where $c_i^{(0)}$ stands for the value at $c=1$. Note that the theorem still holds when switching c_2 and c_3 . Therefore the minimal c to make $\epsilon \geq 2$ is

$$c_{\min} = \frac{\max\{-2c_2^{(0)}, -2c_3^{(0)}\}}{c_2^{(0)} c_3^{(0)} - (c_4^{(0)})^2}.$$

We calculate c_{\min} for $D/l=1/20, 1/10, 1/5$, plotted in Fig. 3.1. In the regions outside the dashed line, which are labeled with ∞ , it holds $c_4^2 - c_2 c_3 \geq 0$. In the intermediate region, the value of c_{\min} is large enough to generate modulation, which is discussed in another paper [26].

4. Concluding remarks We have proved that Q_1 and Q_2 share an eigenframe conditionally. Here we would like to provide more computational results suggesting that it holds always for the kernel (1.9). In fact, we do simulation with $c_4=0$ and $c_2+c_3=-20$ ($c_2, c_3 \leq 0$), $c_1 \in [0, 3]$. Even if $c_1=0$, it is far from the condition in the theorem. To evaluate the distance between two eigenframes, we calculate the Frobenius

norm $\|Q_1Q_2 - Q_2Q_1\|_F$, which equals to zero when two eigenframes coincide. It turns out that $\|Q_1Q_2 - Q_2Q_1\|_F \leq 10^{-9}$, indicating that Q_1 and Q_2 shall share an eigenframe.

Summarizing the existing results, we claim a conjecture that the phase symmetry maintains molecular symmetry for the quadratic kernels suitable for two types of two-fold symmetries. We give a proof with a condition that is applicable to spherocuboids, spherotriangles and bent-core molecules with the excluded-volume interaction. A complete proof is yet to be reached and shall be an interesting problem. It is also intriguing to see whether it holds for higher-order kernel and other symmetries.

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