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Steric effects in dispersion forces interactions

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Classically, there have been two different ways to obtain mean-field theories for liquid crystals. One is based on short-range repulsive steric forces and the other on long-range attractive dispersion forces. In the former approach, it is the anisotropic shape of the molecules that leads to the anisotropic interaction, and in the latter it is the anisotropy of the molecular polarizability. In real molecules both causes of anisotropy can be expected to contribute to the effective interaction, and so it is desirable to assess the combined effect of anisotropic long-range attraction and short-range repulsion. Here we present an avenue to this end. We start from dispersion forces interactions and combine them with hard-core repulsions in a formal theory, whose crucial element is the steric tensor, a fourth-rank tensor depending on the anisotropy of the interacting molecules. This tensor can be determined analytically for a special class of molecular shapes.

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I. INTRODUCTION

Molecular interactions are thought to determine the ability of ordered phases to emerge in certain anisotropic fluids. Perhaps the most telling illustration of this paradigm is the isotropic-to-nematic transition in liquid crystals.

A picture often drawn describes liquid crystal molecules as rods or ribbons subject to interactions that tend to make them align alike. Whenever such a tendency prevails over disorganizing causes, an ordered phase is established from the isotropic, disordered phase. This ordering phase transition, which is usually first order, induces a local common molecular orientation.

A satisfactory microscopic theory for liquid crystals must be based on the interactions exchanged by the constituting molecules. Different special models for molecular interactions have been proposed in the last decades. This is not the most appropriate place to review all these models and the still unceasing debate around them; for a broader account, the interested reader is referred, for example, to the review article in [1].

In a mean-field approach, a single molecule is envisaged as immersed in a field produced by the averaged action of all other molecules that surround it. The key ingredient to a mean-field theory is the *pair potential*—that is, the interaction energy of two molecules. For molecules described as rigid particles, the pair potential in general depends on the vector joining the centers of mass of the interacting molecules and on the relative molecular orientation. For flexible molecules, the pair potential is a more complicated function that also depends on the molecular conformations. Our development is confined to molecules treated as rigid. For them, the mean-field theory predicts in general force and torque distributions.

The existing pair potential models for liquid crystals can be divided into three broad categories: short range and repulsive, long range and attractive, and van der Waals type. Correspondingly, these models attribute the collective aligning attitude of molecules to three different mechanisms: to the mutual hindrance of molecules that reflects the anisotropy of their shape, to the dispersion interaction that reflects the anisotropy induced by their oscillating charges [2,3], and to the coexistence of the former effects in a pair potential that combines both short- and long-range forces.

The Onsager hard-core interaction for long rodlike molecules [4] is the most noticeable example in the first category. It is an athermal model, where the ordering transition is driven by increasing density, instead of decreasing temperature. In a way, this model properly describes lyotropic liquid crystals, as the pair potential mimics the pure steric repulsion of molecules. Nonetheless, it can legitimately be presented on the same footing as the models in the other two categories introduced above, as a limiting case of extremely short-range interactions. Though conceptually appealing, the Onsager model fails to represent the isotropic-to-nematic transition faithfully.

Far more successful in this regard is the Maier-Saupe model [5], the simplest and most celebrated example of long-range dispersion models. Crucial to the justification of the mean-field theory associated with this model potential is the assumption that the molecules are isotropically distributed around every probe molecule. As remarked in [6], a relatively small deviation from spherical symmetry already causes the ordering phase transition to disappear.

Such a state of affairs is generally ascribed to the complete neglect of short-range interactions in the purely dispersive Maier-Saupe theory. A remedy to this was provided by the theory of Gelbart and Baron [7,8], where an anisotropic, short-range, repulsive interaction is incorporated in the model alongside a long-range, attractive interaction, which need not be anisotropic. This theory is often referred to as the generalized van der Waals theory; it is computationally demanding and has been explicitly worked out only for special repulsive potentials. It has, however, clearly shown that the anisotropy in the mean-field potential is mostly due to the interplay between the repulsive potential and the isotropic part of the attractive potential [9–11].

Many other models and generalized theories have been proposed. We refer the interested reader to specialized reviews [1,12,13], which also illustrate the intellectual wealth stimulated by the desire to understand the nematic ordering transition.

Often a unifying view is gained by a wise blend of symmetry and averaging. If every molecule is isotropically surrounded by all others, by averaging the interaction energy of a given molecule upon all others with one and the same orientation relative to the selected molecule, one can define an *effective* pair potential, which for rigid molecules depends only on their relative orientation. Formalizing rigorously this averaging is indeed less trivial than it may appear: the major difficulty resides in handling the divergence of the pair potential when the distance between the interacting molecules approaches zero. Such a divergence embodies the ultimate, short-range repulsion between molecules: even in the simplest realization of this repulsion—that is, in the hard-core interaction—the average over the intermolecular distance contributes *per se* to the dependence of the effective pair potential on the relative molecular orientation. This is precisely the avenue taken in this paper. We combine the long-range induced dipole-dipole interactions with a short-range, hard-core interaction, and we compute the effective pair potential, whose anisotropy stems now from both long- and short-range components of the pair potential.

An alternative approach was proposed by Luckhurst and Zannoni [14]. They reconciled the antagonism between short-range, repulsive interactions and long-range, attractive interactions by assuming that the former are responsible for the local organization of molecules in clusters, which in turn are subject to the latter. This syncretic view holds that the molecular clusters bound by short-range interactions are not destroyed at the transition where their long-range organization changes and thus survive in both the isotropic and nematic phases. According to this view, not molecules, but stable clusters would be subject to the effective pair potential. In either interpretation, our formal development remains unaffected.

The paper is organized as follows. In Sec. II, we write in a compact form the dispersion forces interaction. In Sec. III, we describe the excluded region Ω^*, the region in space that a molecule cannot access in the presence of another molecule. A steric tensor is defined in terms of Ω^*, which embodies the anisotropy of the steric interactions. Section IV shows how to construct the excluded region from the molecular shape. For a special class of shapes, this construction is carried out explicitly and the steric tensor is computed analytically in Sec. V. In Sec. VI, the steric effect is determined for two classical dispersive interactions, for uniaxial and biaxial molecules, respectively. Finally, in Sec. VII we summarize our main conclusions. The paper is closed by three appendixes with the mathematical details of our development.

II. DISPERSION FORCES

Deriving the dispersion energy for the long-range induced dipole-dipole interaction of two molecules from the quantum-mechanical perturbation theory requires resorting to a number of approximations if one wishes an explicitly computable formula. In the account given by Stone [15] (see, in particular, Sec. 4.3.2), one approximation plays a dominant role: this is the Unsöld approximation [16], also called the *average-energy* approximation, as employed by London [17]. In the approach of Buckingham [18], this approximation amounts to assuming that all states in the molecules that contribute to their dispersion interaction have excitation energies close to one and the same average, which we correspondingly denote by U_1 and U_2 for each molecule.

Letting $\mathbf{A}_1$ and $\mathbf{A}_2$ be the symmetric tensors representing the polarizabilities of the interacting molecules, we give the approximate dispersion energy the compact form

$$U_{\text{disp}} = -\frac{C}{r^6}(\mathbf{U}^* \boxtimes \mathbf{U}^*)[\mathbf{A}_1] \cdot \mathbf{A}_2, \tag{1}$$

where

$$C = \frac{9U_1U_2}{4(U_1+U_2)(4\pi\varepsilon_0)^2},$$

with ε_0 the dielectric constant in vacuum. In Eq. (1), r is the distance between the charge centers p_1 and p_2 of the two molecles, $r := |p_2 - p_1|$, and the uniaxial, second-rank tensor $\mathbf{U}^*$ is built from the unit vector $\boldsymbol{e}^* := \frac{1}{r}(p_2 - p_1)$ directed from p_1 to p_2 according to

$$\mathbf{U}^* := \boldsymbol{e}^* \otimes \boldsymbol{e}^* - \frac{1}{3}\mathbf{I}.$$

We use a dot $\cdot$ to denote the inner product between two second-rank tensors, $\mathbf{A} \cdot \mathbf{B} := \mathrm{tr}(\mathbf{A}\mathbf{B}^{\mathsf{T}})$, where T denotes transposition. Moreover, the fourth-rank tensor $\mathbf{A} \boxtimes \mathbf{B}$ is defined by its action on an arbitrary second-rank tensor $\mathbf{C}$: it delivers the second-rank tensor defined by [19,20]

$$(\mathbf{A} \boxtimes \mathbf{B})[\mathbf{C}] := \mathbf{A}\mathbf{C}\mathbf{B}^{\mathsf{T}} \quad \text{for all } \mathbf{C}. \tag{2}$$

Equation (1) is valid under the assumption that certain oscillators in one molecule, all with frequencies very close to one another, are coupled with similar oscillators in the other molecule. When the oscillators that contribute to the interaction have quite different frequencies, the total dispersion energy U_{disp} acquires several terms, all in the form (1):

$$U_{\text{disp}} = -\frac{1}{r^6}\sum_{h,k} C_{hk}(\mathbf{U}^* \boxtimes \mathbf{U}^*)[\mathbf{A}_{1h}] \cdot \mathbf{A}_{2k}, \tag{3}$$

where $\mathbf{A}_{1h}$ and $\mathbf{A}_{2k}$ are the polarizability tensors corresponding, in each molecule, to the coupled oscillators and

$$C_{hk} = \frac{9U_{1h}U_{2k}}{4(U_{1h}+U_{2k})(4\pi\varepsilon_0)^2},$$

where U_{1h} and U_{2h} are the energies of the coupled states.

In the following, we shall build upon Eq. (1) our explicit representation of the steric effects in dispersion forces interactions, assuming, for simplicity, that in each molecule essentially a single oscillator is involved in the interaction. The general case would then follow by superimposing all individual dispersion interactions including their steric corrections.

III. EXCLUDED REGION

U_{disp} is a potential of *soft forces*. For neutral, nonpolar molecules, it is the first term in a multipolar expansion, valid only if p_1 and p_2 are sufficiently far apart. These long-range forces are complemented by short-range, *hard forces*, which represent the steric hindrance to molecular interactions. While dispersion forces are attractive, as are most long-range forces, hard, steric forces are repulsive. We imagine a simple picture to describe these latter: we think of each charge center p_i $(i=1,2)$ as surrounded by a three-dimensional region Ω_i that represents the range of the repulsive, hard forces. These essentially make Ω_1 and Ω_2 impenetrable to one another, while they are dormant whenever Ω_1 and Ω_2 are not in contact. Each Ω_i, which we call the van der Waals region for the corresponding molecule, reflects the molecular shape, though it need not coincide with it.

Molecular interactions are ultimately responsible for the mesogenic behavior of some molecules which, unlike others, tend to form ordered phases. Often, a theoretical understanding of these ordering transitions has been achieved within the mean-field approximation. Perhaps the most successful application of such an approximation in this area is the Maier-Saupe theory for uniaxial nematic liquid crystals [5]. Replacing the space-dependent dispersion energy (1) with a space-independent one [6] is crucial to the success of this theory. This is achieved by assuming that molecules sharing one and the same relative orientation are isotropically distributed in space around any given probe molecule and by computing an effective interaction energy between the probe and all other molecules.

The interaction energy (1) depends via $\boldsymbol{e}^*$ on the relative position of the two molecules and via $\mathbf{A}_1$ and $\mathbf{A}_2$ on their relative orientation. The relative hindrance of the van der Waals regions introduces in the effective intermolecular forces a dependence upon the relative molecular orientation subtler than the one explicitly appearing in (1). We now make this idea more precise. As shown in Fig. 1, for given Ω_1 and Ω_2, there is a region Ω^* in space, depending on Ω_1 and Ω_2, inaccessible to the charge center p_2, if Ω_1 and Ω_2 are mutually impenetrable.

We call Ω^* the *excluded region*. As suggested by Fig. 1, the boundary $\partial\Omega^*$ of the excluded region is the union of all possible trajectories described by p_2 while $\partial\Omega_2$ glides without rolling over $\partial\Omega_1$. Similarly, the region inaccessible to p_1 by the impenetrability of Ω_2 is enveloped by all possible trajectories described by p_1 while $\partial\Omega_1$ glides without rolling over $\partial\Omega_2$. Since in both cases the relative motion between Ω_1 and Ω_2, regarded as rigid bodies, is purely translational, the excluded regions obtained in these two ways simply differ by a translation.

The *effective pair potential* U_{eff} is defined as the collective energy that a probe molecule exchanges with all other molecules that have the same orientation relative to it. The probe and all these molecules share the same excluded region, at whatever distance they are. Under the assumption that the distribution of these molecules is isotropic in space around the probe molecule, it follows from (1) that U_{eff} is given by

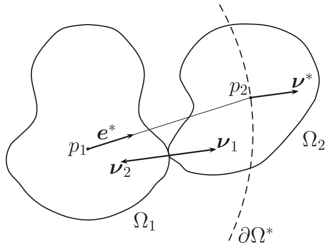

FIG. 1. The van der Waals regions Ω_1 and Ω_2 surrounding the charge centers p_1 and p_2 of the interacting molecules. The unit vector $\boldsymbol{e}^*$ is directed from p_1 to p_2; $\boldsymbol{\nu}_1$ and $\boldsymbol{\nu}_2$ are the unit outer normals to $\partial\Omega_1$ and $\partial\Omega_2$, respectively. The boundary $\partial\Omega^*$ of the excluded region Ω^* is enveloped by p_2 while $\partial\Omega_2$ glides without rolling over $\partial\Omega_1$. The unit vector $\boldsymbol{\nu}^*$ is the outer normal to $\partial\Omega^*$. The region enveloped by all possible trajectories described by p_1 while $\partial\Omega_1$ glides without rolling over $\partial\Omega_2$ would only differ by a translation from Ω^*.

$$U_{\mathrm{eff}} = -C\left(\int_{\mathcal{E}\setminus\Omega^*}\frac{1}{r^6}\mathbf{U}^*\boxtimes\mathbf{U}^*\,dV\right)[\mathbf{A}_1]\cdot\mathbf{A}_2, \tag{4}$$

where the integral extends over the three-dimensional space $\mathcal{E}$ outside the excluded region Ω^*. Though Ω^* can be defined for two arbitrary regions Ω_1 and Ω_2, as in Fig. 1, from now on, we will assume that the two interacting molecules are identical so that Ω_1 and Ω_2 differ only by a rigid rotation $\mathbf{R}$, as do correspondingly $\mathbf{A}_1$ and $\mathbf{A}_2$. We simplify the notation by letting $\Omega_1=\Omega$, $\Omega_2=\Omega'$, $\mathbf{A}_1=\mathbf{A}$, and $\mathbf{A}_2=\mathbf{A}'=\mathbf{R}\mathbf{A}\mathbf{R}^{\mathsf{T}}$. Thus, U_{eff} ultimately depends on $\mathbf{R}$: explicitly through $\mathbf{A}'$, and implicitly through Ω^*. Unveiling this latter dependence will make the steric effect on dispersion forces manifest.

When Ω^* is a ball of radius R, the integral in Eq. (4) can be evaluated directly and one finds

$$\begin{aligned} U_{\mathrm{eff}} &= -C\left(\int_R^\infty \frac{1}{r^4}\int_{\mathbb{S}^2}\mathbf{U}^*\boxtimes\mathbf{U}^*\,da\right)[\mathbf{A}]\cdot\mathbf{A}' \\ &= -\frac{4\pi C}{3R^3}\langle\mathbf{U}^*\boxtimes\mathbf{U}^*\rangle_{\mathbb{S}^2}[\mathbf{A}]\cdot\mathbf{A}', \end{aligned}$$

where a is the area measure over the unit sphere $\mathbb{S}^2$ and $\langle\cdots\rangle_{\mathbb{S}^2}$ denotes the average over it. By symmetry, $\langle\mathbf{U}^*\boxtimes\mathbf{U}^*\rangle_{\mathbb{S}^2}$ is a linear combination of isotropic fourth-rank tensors; see (A4) in Appendix A. An explicit computation shows that

$$\langle\mathbf{U}^*\boxtimes\mathbf{U}^*\rangle_{\mathbb{S}^2}[\mathbf{A}]\cdot\mathbf{A}' = \frac{1}{45}(\mathbf{A}\cdot\mathbf{A}' + 3\,\mathrm{tr}\mathbf{A}\,\mathrm{tr}\mathbf{A}'), \tag{5}$$

and so, up to a constant that is independent of the relative orientation of the molecules,

$$U_{\text{eff}} = -\frac{4\pi C}{135R^3}\mathbf{A}\cdot\mathbf{A}'. \tag{6}$$

This formula can be further simplified by introducing the traceless parts $\mathbf{A}_0$ and $\mathbf{A}_0'$ of $\mathbf{A}$ and $\mathbf{A}'$, respectively, according to

$$\mathbf{A} = \mathbf{A}_0 + \frac{1}{3}(\text{tr}\,\mathbf{A})\mathbf{I}, \quad \mathbf{A}' = \mathbf{A}_0' + \frac{1}{3}(\text{tr}\,\mathbf{A})\mathbf{I}. \tag{7}$$

By (7),

$$\mathbf{A}\cdot\mathbf{A}' = \mathbf{A}_0\cdot\mathbf{A}_0' + \frac{1}{3}(\text{tr}\,\mathbf{A})^2,$$

and in (6) we can replace $\mathbf{A}$ and $\mathbf{A}'$ by $\mathbf{A}_0$ and $\mathbf{A}_0'$, only altering U_{eff} by an inessential constant. If the polarizability $\mathbf{A}$ is uniaxial about a molecular axis $\boldsymbol{m}_3$,

$$\mathbf{A} = \alpha_{\parallel}\boldsymbol{m}_3\otimes\boldsymbol{m}_3 + \alpha_{\perp}(\mathbf{I} - \boldsymbol{m}_3\otimes\boldsymbol{m}_3),$$

$$\mathbf{A}_0 = (\alpha_{\parallel} - \alpha_{\perp})\left(\boldsymbol{m}_3\otimes\boldsymbol{m}_3 - \frac{1}{3}\mathbf{I}\right), \tag{8}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ denote the polarizabilities along the symmetry axis and perpendicular to it, then (6) yields the classical Maier-Saupe interaction, with $U_{\text{eff}} = -U_0 P_2(\boldsymbol{m}_3\cdot\boldsymbol{m}_3')$, where U_0 is a positive constant, $\boldsymbol{m}_3' = \mathbf{R}\boldsymbol{m}_3$, and $P_2(x) := \frac{1}{2}(3x^2 - 1)$ is the second Legendre polynomial. As we shall see below in Sec. VI, a deviation from the spherical shape of the van der Waals region Ω will entail a steric correction to the Maier-Saupe theory.

We now consider the more general case of a *star-shaped* excluded region Ω^*, which can be represented as

$$\Omega^* = \{p \in \mathcal{E} \mid p - p_1 = r\boldsymbol{e}^*,\ 0 \le r < u^*(\boldsymbol{e}^*)\}, \tag{9}$$

where the radial extension u^* is a function of the unit vector $\boldsymbol{e}^*$. In this case, the radial integration in (4) can still be done explicitly and one finds

$$U_{\text{eff}} = -\frac{4\pi C}{3}\left\langle \frac{1}{u^{*3}}\mathbf{U}^*\boxtimes\mathbf{U}^* \right\rangle_{\mathbb{S}^2}[\mathbf{A}]\cdot\mathbf{A}' = -\frac{4\pi C}{3}\mathbb{I}_{\Omega^*}[\mathbf{A}]\cdot\mathbf{A}', \tag{10}$$

where we have introduced the fourth-rank tensor

$$\mathbb{I}_{\Omega^*} := \left\langle \frac{1}{u^{*3}}\mathbf{U}^*\boxtimes\mathbf{U}^* \right\rangle_{\mathbb{S}^2}. \tag{11}$$

We call $\mathbb{I}_{\Omega^*}$ the *steric tensor* because it depends only on the shape of the excluded region and can in principle be computed once $u^*(\boldsymbol{e}^*)$ is known. The steric tensor also plays a role in expressing the effective pair potential U_{eff} in (3), valid when multiple molecular oscillators participate in the interaction. It readily follows from the reasoning that led us to (10) that

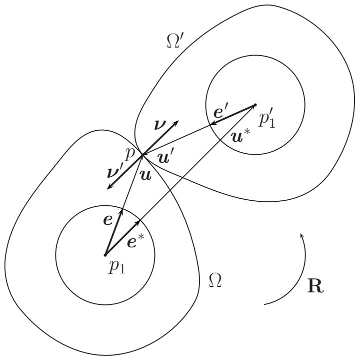

FIG. 2. The regions Ω and Ω', the latter being Ω rotated through $\mathbf{R}$. Ω and Ω' are star shaped with respect to p_1 and p_1', respectively. The unit spheres of which their boundaries are images are also depicted. Ω and Ω' are in contact at the point $p \in \partial\Omega \cap \partial\Omega'$, where $\boldsymbol{\nu}$ and $\boldsymbol{\nu}'$ denote the corresponding outer unit normals. The vectors $\boldsymbol{u}$, $\boldsymbol{u}'$, and $\boldsymbol{u}^*$ are defined as $\boldsymbol{u} := p - p_1$, $\boldsymbol{u}' := p - p_1'$, and $\boldsymbol{u}^* := p_1' - p_1$.

$$U_{\text{eff}} = -\frac{4\pi}{3}\sum_{h,k=1}^{N} C_{hk}\mathbb{I}_{\Omega^*}[\mathbf{A}_h]\cdot\mathbf{A}_k', \tag{12}$$

where N is the number of oscillators in each molecule and $\mathbf{A}_h$ and $\mathbf{A}_k'$ are the corresponding polarizability tensors.

Before we tackle in Sec. V the problem of computing $\mathbb{I}_{\Omega^*}$ for a specific class of molecular shapes, we first address the problem of how to determine u^* for a given molecular shape.

IV. PERTURBATIVE METHOD

Obtaining the excluded region Ω^* from the van der Waals regions Ω and Ω' is not in general an easy task. A vast literature has been devoted to computing the excluded volume V^* of two hard molecules; as V^* is precisely the volume of Ω^*, we refer the reader to that literature to appreciate the many subtleties involved in the geometric problem of constructing Ω^*. There are essentially two methods used to determine Ω^* and its volume V^*; they are based on *convex-body coordinates* and *Minkowski sums*: illustrations of these methods and appropriate bibliographic sources can be found in [21,22].

Here we further build upon the kinematic construction of Ω^* and develop an analytic method, which we then apply in a perturbative limit. We consider molecules whose shape can be represented like Ω^* in (9),

$$\Omega = \{p \in \mathcal{E} \mid p - p_1 = r\boldsymbol{e},\ 0 \le r < u(\boldsymbol{e})\}, \tag{13}$$

where $\boldsymbol{e}$ is the radial unit vector and u is a scalar mapping on $\mathbb{S}^2$. Like Ω^*, the region Ω is star shaped relative to the charge center p_1. It follows from (13) that $\partial\Omega$ is the image of $\mathbb{S}^2$ under the mapping $\boldsymbol{u}(\boldsymbol{e}) := u(\boldsymbol{e})\boldsymbol{e}$. Figure 2 shows both Ω and the unit sphere $\mathbb{S}^2$ around which $\partial\Omega$ is built.

As shown in Appendix B, the outer normal field $\boldsymbol{\nu}$ to $\partial\Omega$ can be given the concise form

$$\boldsymbol{\nu}(\boldsymbol{e}) = \frac{u\boldsymbol{e} - \boldsymbol{\nabla}_s u}{\sqrt{u^2 + |\boldsymbol{\nabla}_s u|^2}}, \tag{14}$$

where $\boldsymbol{\nabla}_s u$ is the surface gradient of u on $\mathbb{S}^2$.

When Ω is subject to the rotation $\mathbf{R}$, thus becoming Ω', each $\boldsymbol{e}$ on the sphere $\mathbb{S}^2$ around which $\partial\Omega'$ is built can be seen as the image of $\mathbf{R}^{\mathsf{T}}\boldsymbol{e}$ under $\mathbf{R}$, so that Ω' is represented as in (13) with u replaced by

$$u'(\boldsymbol{e}) := u(\mathbf{R}^{\mathsf{T}}\boldsymbol{e}), \quad \forall \quad \boldsymbol{e} \in \mathbb{S}^2. \tag{15}$$

Correspondingly, the outer unit normal $\boldsymbol{\nu}'$ to $\partial\Omega'$ is given by

$$\boldsymbol{\nu}'(\boldsymbol{e}) = \mathbf{R}\boldsymbol{\nu}(\mathbf{R}^{\mathsf{T}}\boldsymbol{e}), \quad \forall \quad \boldsymbol{e} \in \mathbb{S}^2. \tag{16}$$

Figure 2 illustrates the situation we envisage. The shapes Ω and Ω', with their charge centers p_1 and p_1', are in mutual contact at a point p on $\partial\Omega \cap \partial\Omega'$, designated, correspondingly, by $\boldsymbol{e}$ and $\boldsymbol{e}'$ on the unit spheres around which $\partial\Omega$ and $\partial\Omega'$ are built. The vector $\boldsymbol{u}^* := p_1' - p_1$ describes the boundary of $\partial\Omega^*$ of the excluded region, built around the unit sphere centered at p_1; formally, we write

$$\boldsymbol{u}^*(\boldsymbol{e}^*) = u^*(\boldsymbol{e}^*)\boldsymbol{e}^* \quad \text{with} \quad \boldsymbol{e}^* \in \mathbb{S}^2, \tag{17}$$

where u^* is the radial representation of $\partial\Omega^*$ in (9). By construction,

$$u^*(\boldsymbol{e}^*)\boldsymbol{e}^* = u(\boldsymbol{e})\boldsymbol{e} - u'(\boldsymbol{e}')\boldsymbol{e}'$$

and

$$\boldsymbol{\nu}(\boldsymbol{e}) = -\boldsymbol{\nu}'(\boldsymbol{e}').$$

By (15) and (16), these equations may be given a more transparent form

$$u^*\boldsymbol{e}^* = u(\boldsymbol{e})\boldsymbol{e} - u(\mathbf{R}^{\mathsf{T}}\boldsymbol{e}')\boldsymbol{e}', \tag{18a}$$

$$\boldsymbol{\nu}(\mathbf{R}^{\mathsf{T}}\boldsymbol{e}') = -\mathbf{R}^{\mathsf{T}}\boldsymbol{\nu}(\boldsymbol{e}). \tag{18b}$$

In general, the latter equation would determine $\boldsymbol{e}'$ in terms of $\boldsymbol{e}$; then, inserting $\boldsymbol{e}'$ into the former delivers both $\boldsymbol{e}^*$ and u^* as functions of $\boldsymbol{e}$. This task, however, may fail to be accomplished, as Eq. (18b) may fail to be satisfied for all $\boldsymbol{e} \in \mathbb{S}^2$. Moreover, the local contact conditions (18a) and (18b), even if satisfied at a point, may conflict with the mutual impenetrability of Ω and Ω' at some other point. We need to seek global solvability of Eqs. (18a) and (18b); that is, we need to identify, for any given rotation $\mathbf{R}$, the mappings $\boldsymbol{f}' : \boldsymbol{e} \mapsto \boldsymbol{e}'$ and $\boldsymbol{f}^* : \boldsymbol{e} \mapsto \boldsymbol{e}^*$ from a subset $\mathcal{S}_{\mathbf{R}} \subset \mathbb{S}^2$ into and onto $\mathbb{S}^2$, respectively, that turn Eqs. (18a) and (18b) into identities for an appropriate positive u^*. This would, in particular, ensure that the excluded region Ω^* is also star shaped, as desired. Correspondingly, the steric tensor in Eq. (11) could then be converted into an integral over $\mathcal{S}_{\mathbf{R}}$ through the change of variables induced on $\mathbb{S}^2$ by $\boldsymbol{f}^*$. Such an analytic program, however, may easily become prohibitive for sufficiently general shapes Ω. Noticeable examples are convex shapes, for which Eq. (18b) is uniquely solvable, with $\mathcal{S}_{\mathbf{R}} = \mathbb{S}^2$ for all rotations $\mathbf{R}$. Nevertheless, even for this special category of shapes, the functions u^* and $\boldsymbol{f}^*$ may be very complicated, as illuminated in Appendix C for ellipsoids.

For this reason, we resort to a perturbative approach and apply the method now outlined to a special class of molecular shapes. Specifically, we set

$$u(\boldsymbol{e}) = R[1 + \varepsilon v(\boldsymbol{e})], \tag{19}$$

where $R > 0$ is a given radius, $\varepsilon > 0$ is a small perturbation parameter, and v is a bounded, smooth mapping defined on $\mathbb{S}^2$. Without loss of generality, we may normalize v by requiring that

$$\langle v \rangle_{\mathbb{S}^2} = 0, \tag{20}$$

so that R can be interpreted as the average molecular radius. Equation (19) represents a convex, spheroidal molecule. It readily follows from (19) and (14) that for such a molecule the outer unit normal takes the form

$$\boldsymbol{\nu}(\boldsymbol{e}) = \boldsymbol{e} - \varepsilon \boldsymbol{\nabla}_s v(\boldsymbol{e}) + o(\varepsilon). \tag{21}$$

This mapping is clearly one to one on $\mathbb{S}^2$ whenever the second surface gradient $\nabla_s^2 v$ on $\mathbb{S}^2$ is bounded. Under this assumption, which we make from here on, the shape Ω is convex and so will also be Ω^*. By use of (21) in (18b), we arrive at an implicit function for $\boldsymbol{e}'$,

$$\boldsymbol{e}' = -\boldsymbol{e} + \varepsilon[\boldsymbol{\nabla}_s v(\boldsymbol{e}) + \mathbf{R}\boldsymbol{\nabla}_s v(\mathbf{R}^{\mathsf{T}}\boldsymbol{e}')] + o(\varepsilon),$$

from which, since $\boldsymbol{e}' = -\boldsymbol{e} + O(\varepsilon)$, it follows that

$$\boldsymbol{e}' = -\boldsymbol{e} + \varepsilon[\boldsymbol{\nabla}_s v(\boldsymbol{e}) + \mathbf{R}\boldsymbol{\nabla}_s v(-\mathbf{R}^{\mathsf{T}}\boldsymbol{e})] + o(\varepsilon). \tag{22}$$

By (22), (18a) becomes

$$\begin{aligned} u^*(\boldsymbol{e}^*)\boldsymbol{e}^* = {} & R\{2 + \varepsilon[v(\boldsymbol{e}) + v(\mathbf{R}^{\mathsf{T}}\boldsymbol{e})]\}\boldsymbol{e} \\ & - \varepsilon R[\mathbf{R}\boldsymbol{\nabla}_s v(-\mathbf{R}^{\mathsf{T}}\boldsymbol{e}) + \boldsymbol{\nabla}_s v(\boldsymbol{e})] + o(\varepsilon). \end{aligned} \tag{23}$$

As Ω' is described by u' in (15), Ω^*, which is to be a spheroid like Ω, is described by

$$u^*(\boldsymbol{e}^*) = R^*[1 + \varepsilon v^*(\boldsymbol{e}^*)] + o(\varepsilon), \tag{24}$$

where both R^* and v^* are unknown. Inserting (24) into (23) and observing that both $\boldsymbol{\nabla}_s v(\boldsymbol{e})$ and $\mathbf{R}\boldsymbol{\nabla}_s v(-\mathbf{R}^{\mathsf{T}}\boldsymbol{e})$ are orthogonal to $\boldsymbol{e}$, we obtain

$$R^* = 2R, \quad v^*(\boldsymbol{e}) = \frac{1}{2}[v(\boldsymbol{e}) + v(-\mathbf{R}^{\mathsf{T}}\boldsymbol{e})] \tag{25a}$$

and

$$\boldsymbol{e}^* = \boldsymbol{e} - \frac{1}{2}\varepsilon[\boldsymbol{\nabla}_s v(\boldsymbol{e}) + \mathbf{R}\boldsymbol{\nabla}_s v(-\mathbf{R}^{\mathsf{T}}\boldsymbol{e})] + o(\varepsilon). \tag{25b}$$

Equations (22) and (25b) are the perturbative representations of the functions $\boldsymbol{f}'$ and $\boldsymbol{f}^*$. Thus, for any given R and v representing Ω through (19), Eqs. (25a) and (25b) determine explicitly the corresponding representation of Ω^* through (24). In the following section, this representation will lead us to an explicit formula for the steric tensor $\mathbb{I}_{\Omega^*}$.

V. STERIC EFFECT

One assumption in the original derivation of the Maier-Saupe interaction is that for the averaging process the distribution of the molecules is spherically symmetric. This is a particularly questionable assumption, because the interaction energy decays with the sixth power of the intermolecular distance, and so the most important contributions stem from the nearest molecules. Maier and Saupe suggest [23] that the steric effect can be taken into account by considering small groups of molecules that would then be roughly spherically symmetric. This leads merely to a renormalization of the constants. Here, without abandoning the assumption on spherical spatial symmetry for the distribution of molecular charge centers, we explore directly the effect of nonspherical molecular shapes on the dispersion interactions.

As we have seen in Sec. IV, for spheroidal molecules the excluded region is given by the explicit representation (24) with R^* and v^* as in (25a). Then, for small ε,

$$\frac{1}{{u^*}^3} = \left(\frac{1}{R^*}\right)^3 (1 - 3\varepsilon v^*) + o(\varepsilon),$$

and by (11),

$$\mathbb{I}_{\Omega^*} = \left(\frac{1}{R^*}\right)^3 (\langle \mathbf{U}^* \boxtimes \mathbf{U}^* \rangle_{\boldsymbol{e}^* \in \mathbb{S}^2} - 3\varepsilon \langle v^*(\boldsymbol{e}) \mathbf{U} \boxtimes \mathbf{U} \rangle_{\boldsymbol{e} \in \mathbb{S}^2}) + o(\varepsilon), \tag{26}$$

where

$$\mathbf{U} = \boldsymbol{e} \otimes \boldsymbol{e} - \frac{1}{3}\mathbf{I}.$$

For definiteness, we made explicit the variables in both averages appearing in Eq. (26); in the second, we also take advantage of the fact that, at the lowest order in ε, $\boldsymbol{f}^*$ is the identity on $\mathbb{S}^2$ [see Eq. (25b)]. The first term on the right-hand side of Eq. (26) is the same that was found in Sec. III for a spherical excluded region, and the second term gives the steric correction to the dispersion interaction. To make this more explicit, we consider the multipole expansion of v in terms of Cartesian tensors:

$$v(\boldsymbol{e}) = \boldsymbol{E} \cdot \boldsymbol{e} + \mathbf{E} \cdot \overline{\boldsymbol{e} \otimes \boldsymbol{e}} + \mathbf{E}^{(3)} \cdot \overline{\boldsymbol{e} \otimes \boldsymbol{e} \otimes \boldsymbol{e}} + \mathbf{E}^{(4)} \cdot \overline{\boldsymbol{e} \otimes \boldsymbol{e} \otimes \boldsymbol{e} \otimes \boldsymbol{e}} + \cdots, \tag{27}$$

where $\overline{\cdots}$ denotes the (symmetric) irreducible part of a tensor, $\boldsymbol{E}$ is the *shape dipole*, $\mathbf{E}$ is the *shape quadrupole*, and the $\mathbf{E}^{(i)}$'s are the higher moments. The gauge (20) forbids any constant term in (27). Because $\mathbf{U} \boxtimes \mathbf{U}$ is even in $\boldsymbol{e}$, the odd-rank tensors in the expansion (27) do not contribute to the steric tensor (26). The first relevant term is the shape quadrupole, a symmetric traceless second-rank tensor which can be computed for a given $v(\boldsymbol{e})$ as

$$\mathbf{E} = \frac{15}{2} \langle v \overline{\boldsymbol{e} \otimes \boldsymbol{e}} \rangle_{\mathbb{S}^2} = \frac{15}{2} \left\langle v \left(\boldsymbol{e} \otimes \boldsymbol{e} - \frac{1}{3}\mathbf{I} \right) \right\rangle_{\mathbb{S}^2}. \tag{28}$$

From now on, we neglect higher orders and consider

$$v = \mathbf{E} \cdot \overline{\boldsymbol{e} \otimes \boldsymbol{e}} = \boldsymbol{e} \cdot \mathbf{E}\boldsymbol{e}, \tag{29}$$

bearing in mind that tr $\mathbf{E}=0$. By (25a), Eq. (29) leads to

$$v^*(\boldsymbol{e}) = \frac{1}{2} \boldsymbol{e} \cdot (\mathbf{E} + \mathbf{E}')\boldsymbol{e}, \tag{30}$$

where $\mathbf{E}' = \mathbf{R}\mathbf{E}\mathbf{R}^{\mathsf{T}}$. The steric tensor (26) can then be found explictly by noting that [see (A5)]

$$\langle (\mathbf{U} \boxtimes \mathbf{U})_{ijkl} e_m e_n \rangle_{\mathbb{S}^2} S_{mn} A_{kl} A'_{ij} = \frac{2}{315} \mathbf{S} \cdot [3 \operatorname{tr} \mathbf{A}(\mathbf{A} + \mathbf{A}') - 2\mathbf{A}\mathbf{A}'] \tag{31}$$

for symmetric tensors $\mathbf{A}$, $\mathbf{A}'$, and $\mathbf{S}$, with tr $\mathbf{S}=0$ and tr $\mathbf{A}$ $=$tr $\mathbf{A}'$. With this, by (10) and (11), the effective dispersion pair potential becomes

$$U_{\text{eff}} = -\frac{4\pi C}{945{R^*}^3} \{7(\mathbf{A} \cdot \mathbf{A}' + 3(\operatorname{tr} \mathbf{A})^2) - 3\varepsilon(\mathbf{E} + \mathbf{E}') \cdot [3 \operatorname{tr} \mathbf{A}(\mathbf{A} + \mathbf{A}') - 2\mathbf{A}\mathbf{A}']\} + o(\varepsilon). \tag{32}$$

For the further discussion it is convenient to introduce in (32) the tensors $\mathbf{A}_0$ and $\mathbf{A}'_0$ defined in (7); one then obtains

$$U_{\text{eff}} = -\frac{4\pi C}{2835{R^*}^3} \{7[3\mathbf{A}_0 \cdot \mathbf{A}'_0 + 10(\operatorname{tr} \mathbf{A})^2] - 3\varepsilon(\mathbf{E} + \mathbf{E}') \cdot [7 \operatorname{tr} \mathbf{A}(\mathbf{A}_0 + \mathbf{A}'_0) - 6\mathbf{A}_0\mathbf{A}'_0]\}, \tag{33}$$

valid up to first order in ε.

VI. SPECIAL INTERACTIONS

We now consider the special case where the shape quadrupole and polarizability tensor share the same eigenframe, given by three orthonormal molecular vectors $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$. Then both tensors can be represented as linear combinations of the identity $\mathbf{I}$ and the two orthogonal tensors

$$\mathbf{q} := \boldsymbol{m}_3 \otimes \boldsymbol{m}_3 - \frac{1}{3}\mathbf{I}, \quad \mathbf{b} := \boldsymbol{m}_1 \otimes \boldsymbol{m}_1 - \boldsymbol{m}_2 \otimes \boldsymbol{m}_2.$$

We write the quadrupolar shape tensor as

$$\varepsilon\mathbf{E} = \rho\mathbf{q} + \beta\mathbf{b}, \tag{34}$$

where ρ and β are small parameters, and then

$$\varepsilon\mathbf{E}' = \rho\mathbf{q}' + \beta\mathbf{b}' \tag{35}$$

with $\mathbf{q}' = \mathbf{R}\mathbf{q}\mathbf{R}^{\mathsf{T}}$ and $\mathbf{b}' = \mathbf{R}\mathbf{b}\mathbf{R}^{\mathsf{T}}$.

A. Maier-Saupe interaction

For the Maier-Saupe interaction the polarizability tensor $\mathbf{A}$ is uniaxial as in (8). Equivalently, $\mathbf{A}$ and $\mathbf{A}'$ can also be written as

$$\mathbf{A} = \alpha\mathbf{I} + \Delta\alpha\mathbf{q}, \quad \mathbf{A}' = \alpha\mathbf{I} + \Delta\alpha\mathbf{q}', \tag{36}$$

where $\alpha = \frac{1}{3}\mathrm{tr}\mathbf{A} = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$ and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$. With the aid of the identities (A6), U_{eff} in (33) is found to be, up to a constant,

$$U_{\mathrm{eff}} = -\frac{4\pi C(\Delta\alpha)^2}{135R^{*3}}\left\{\left[1 + 2\rho\left(\frac{2}{7} - \frac{3\alpha}{\Delta\alpha}\right)\right]\mathbf{q}\cdot\mathbf{q}' - \beta\left(\frac{2}{7} + \frac{3\alpha}{\Delta\alpha}\right)(\mathbf{q}\cdot\mathbf{b}' + \mathbf{b}\cdot\mathbf{q}')\right\}. \tag{37}$$

This formula embodies the steric correction to the classical Maier-Saupe interaction energy. It suggests a few comments.

First, since both $\alpha_\parallel$ and $\alpha_\perp$ are positive and

$$\frac{2}{7} - \frac{3\alpha}{\Delta\alpha} = -\frac{5\alpha_\parallel + 16\alpha_\perp}{7\Delta\alpha},$$

the sign of the correction to the coefficient of $\mathbf{q}\cdot\mathbf{q}'$ is opposite to the sign of $\rho\,\Delta\alpha$, meaning that the molecular long axis interaction is depressed if the molecular shape quadrupole is resonant, as it were, with the anisotropic polarizability tensor, and it is enhanced otherwise. Thus, for $\beta=0$, a uniaxial shape quadrupole prolate along the symmetry axis $\boldsymbol{m}_3$ would depress the bare Maier-Saupe interaction when $\Delta\alpha > 0$, whereas it would enhance it when $\Delta\alpha < 0$.

Second, for $\beta \neq 0$—that is, for a biaxial shape quadrupole—the dispersion interaction between molecules with uniaxial polarizability tensors becomes effectively biaxial. As shown by Luckhurst and Romano [24] by simulation and lately confirmed within a general mean-field theory [27], a biaxial interaction potential like (37) with $\beta \neq 0$ does not promote condensed biaxial phases. However, at variance with the classical Maier-Saupe potential, the transition temperature for such a potential would depend on the coefficient of the biaxial correction, which here is a function of the molecular shape.

B. Straley interaction

We now consider the more general case of an arbitrary, possibly biaxial polarizability with eigenvalues α_{11}, α_{22}, and α_{33}. This can be written as

$$\mathbf{A} = \alpha\mathbf{I} + \Delta\alpha\mathbf{q} + \frac{1}{2}\Delta\alpha_\perp\mathbf{b}, \tag{38}$$

with the average polarizability $\alpha = \frac{1}{3}\mathrm{tr}\mathbf{A} = \frac{1}{3}(\alpha_{11} + \alpha_{22} + \alpha_{33})$ and the polarizability anisotropies $\Delta\alpha = \alpha_{33} - \frac{1}{2}(\alpha_{11} + \alpha_{22})$ and $\Delta\alpha_\perp = \alpha_{11} - \alpha_{22}$. (When $\alpha_{11} = \alpha_{22}$, this reduces to the Maier-Saupe interaction discussed in the preceding subsection.) The effective pair potential then takes the form

$$U_{\mathrm{eff}} = -\frac{\pi C}{945R^{*3}}\{a\mathbf{q}\cdot\mathbf{q}' + b(\mathbf{q}\cdot\mathbf{b}' + \mathbf{b}\cdot\mathbf{q}') + c\mathbf{b}\cdot\mathbf{b}'\}, \tag{39}$$

with

$$a := \Delta\alpha[28\Delta\alpha + 8\rho(2\Delta\alpha - 21\alpha) - 24\beta\,\Delta\alpha_\perp], \tag{40a}$$

$$b := 14\Delta\alpha\,\Delta\alpha_\perp - 2\beta(4\Delta\alpha^2 + 3\Delta\alpha_\perp^2) - 42\alpha(2\beta\,\Delta\alpha + \rho\,\Delta\alpha_\perp), \tag{40b}$$

$$c := \Delta\alpha_\perp[7\Delta\alpha_\perp - 4\beta(2\Delta\alpha + 21\alpha) - 4\rho\Delta\alpha_\perp]. \tag{40c}$$

Since by (34) ρ and β are small perturbation parameters, it is easily seen that $a > 0$. Thus, by setting

$$U_0 := \frac{\pi C a}{945R^{*3}}, \quad \gamma := \frac{b}{a}, \quad \lambda := \frac{c}{a}, \tag{41}$$

Eq. (39) can be given the following form put forward by Straley [25,26] for general biaxial molecules:

$$U_{\mathrm{eff}} = -U_0\{\mathbf{q}\cdot\mathbf{q}' + \gamma(\mathbf{q}\cdot\mathbf{b}' + \mathbf{b}\cdot\mathbf{q}') + \lambda\mathbf{b}\cdot\mathbf{b}'\}. \tag{42}$$

Before Straley, Freiser [28,29] proposed a model for thermotropic liquid crystals composed of biaxial molecules, which appeared as a natural extension of the Maier-Saupe theory: Freiser posited the effective pair potential

$$U_{\mathrm{eff}} = -U_0^*\mathbf{A}\cdot\mathbf{A}', \tag{43}$$

where U_0^* is a characteristic coupling energy. As shown by (6), for spherical molecules, this formula would result from a dispersion interaction involving a single oscillator in each molecule. Clearly, by (38), (43) is a special case of (42), this latter reducing to the former when $\lambda = \gamma^2$. Similarly, again for spherical molecules, (42) can be interpreted in the language of dispersion forces if we imagine three independent oscillators at right angles in each molecule [30]. It is remarkable that for nonspherical molecules a steric quadrupolar correction to a bare Freiser interaction changes it into a Straley interaction, which dispersion forces could only justify through multiple oscillators.

The connection between the Straley and Freiser interactions is deeper than this illustrates. As shown in [27], the effective pair potential in Eq. (42) can be given the diagonal form

$$U_{\mathrm{eff}} = -U_0(\alpha_1\mathbf{q}_1\cdot\mathbf{q}_1' + \alpha_2\mathbf{q}_2\cdot\mathbf{q}_2'), \tag{44}$$

with

$$\mathbf{q}_{1,2} = \mathbf{q} + \gamma_{1,2}\mathbf{b}.$$

Equation (44) shows the Straley interaction as composed by the superposition of two Freiser interactions; there, the tensors $\mathbf{q}_{1,2}$ have different expressions for different values of γ and λ. Precisely, for $\gamma \neq 0$,

$$\gamma_{1,2} = \frac{3\lambda - 1 \pm \sqrt{(3\lambda - 1)^2 + 12\gamma^2}}{6\gamma}$$

and

$$\alpha_1 = \frac{\gamma_2 - \gamma}{\gamma_2 - \gamma_1}, \quad \alpha_2 = \frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1},$$

while for $\gamma=0$ one simply has $\mathbf{q}_1 = \mathbf{q}$, $\mathbf{q}_2 = \mathbf{b}$, $\alpha_1 = 1$, and $\alpha_2 = \lambda$.

For $\lambda > \gamma^2$, both α_1 and α_2 are positive, and so both interactions in the diagonal decomposition (44) are attractive. The potential U_{eff} is called *fully attractive*. For $\lambda = \gamma^2$, either

α_1 or α_2 vanishes: Equation (44) still reduces to a single attractive term. The potential U_{eff} is called *simply attractive*. For $\lambda < \gamma^2$, either α_1 or α_2 is negative, and Eq. (44) is a superposition of attractive and repulsive interactions. The potential U_{eff} is called *partly repulsive*. The discriminating parabola $\lambda = \gamma^2$ in the (γ, λ) plane has also been referred to as the *dispersion parabola* [27,31].

For the particular realization (39) of the Straley interaction, one readily sees from (40a)–(40c) and (41) that U_{eff} is fully attractive, simply attractive, or partly repulsive depending on whether the discriminant $\Delta := b^2 - ac$ is negative, zero, or positive. When $\rho = \beta = 0$—that is, when the steric effect is neglected—U_{eff} in (39) is simply attractive. In general, it is found that Δ is a perfect square,

$$\Delta = 4[\rho\Delta\alpha_\perp(4\Delta\alpha - 21\alpha) + \beta(42\alpha\Delta\alpha + 4\Delta\alpha^2 - 3\Delta\alpha_\perp^2)]^2 \geq 0. \tag{45}$$

This shows that U_{eff} in (39) can never be represented by a point that lies in the (γ, λ) plane above the dispersion parabola, and so accounting for the steric effect cannot change a bare Freiser interaction into a fully attractive Straley interaction. This outcome supports the intuitive view presented in [27] that partly repulsive interactions reflect somehow steric hindrance. However, Δ can vanish, thus rendering U_{eff} simply attractive, even in the presence of a steric effect. For example, for $\beta \neq 0$, $\Delta = 0$ whenever

$$\frac{\rho}{\beta} = \frac{3\eta^2 - 42\xi - 4\xi^2}{\eta(4\xi - 21)},$$

where

$$\xi := \frac{\Delta\alpha}{\alpha} \quad \text{and} \quad \eta := \frac{\Delta\alpha_\perp}{\alpha}$$

are subject to the bounds $-\frac{3}{2} < \xi < 3$ and $-3 < \eta < 3$. On the other hand, if $\beta = 0$, so that the shape quadrupole is uniaxial, Δ vanishes only if $\Delta\alpha_\perp = 0$—that is, only if the polarizability tensor is also uniaxial. Thus, for spheroidal biaxial molecules, the steric hindrance may either map a bare Freiser interaction into another, represented by a new, effective polarizability tensor and possibly a different coupling energy, or transform it into a partly repulsive Straley interaction.

VII. CONCLUSION

We computed the formal contribution of molecular hindrance to the dispersion forces interactions of two rigid molecules. This steric effect is embodied by the steric tensor $\mathbb{I}_{\Omega^*}$ defined by (11) for a star-shaped excluded region Ω^*, the region that the repulsion between molecular cores makes inaccessible to both. This is an attempt, different from the others we are aware of, to give a rigorous account of the interplay between attractive, long-range forces and repulsive, short-range forces in molecular interactions.

To explore analytically the steric effect in a specific class of molecular shapes, we considered spheroidal molecules and, for simplicity, we restrained up to the quadrupolar term the multipolar expansion of their shape representation. We showed how a biaxial quadrupolar shape can turn the classical Maier-Saupe interaction potential for uniaxial nematic liquid crystals into a biaxial interaction potential in the family envisaged by Straley on the basis of pure symmetry. The specific steric correction to the Maier-Saupe interaction is not capable of promoting biaxial phases, but it affects the transition temperature. In a similar way, we explored the consequences of the steric effect on a bare Freiser interaction, a dispersion interaction between single oscillators in molecules with biaxial polarizability tensors. The steric effect transforms this interaction into a partly repulsive Straley interaction, this corroborating the view that the Straley interactions represented by the potential (42) with $\lambda < \gamma^2$ somehow embody molecular hindrance [27].

It has been known since the seminal paper of Onsager [4] that the ordering phase transitions of nematogenic molecules can also be explained by a purely athermic theory based on excluded volume interactions. For biaxial molecules in the family of spherocuboids [22], it was shown in [32] that the quadrupolar component of the excluded volume interaction is partly repulsive for all geometric parameters describing the molecular shape. Such a conclusion reached for purely hard-core repulsive interactions somehow parallels the one reached here on the partly repulsive nature of the steric correction to a bare Freiser interaction. As hard-core repulsive interactions result in a quadrupolar attraction, albeit partly repulsive, so does the molecular hindrance in a single oscillator dispersion interaction, at least for spheroidal molecular shapes.

A few questions are raised by these conclusions: first, whether the steric tensor $\mathbb{I}_{\Omega^*}$ can be computed, possibly numerically, for nonspheroidal molecules; second, which is the nature of the steric correction to a general Straley interaction, not necessarily in the spheroidal approximation; and third, whether the pure dispersion model put forward by Bates and Luckhurst for V-shaped molecules [33], which in the way it is formulated could apply as well to X-shaped molecules, can be tailored to V-shaped molecules by accounting for their specific shape in computing the steric correction. We hope that these questions can be answered by future work.

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APPENDIX A: ALGEBRAIC IDENTITIES

The average of a tensor product of n unit vectors $\boldsymbol{e} \otimes \cdots \otimes \boldsymbol{e}$ over $\mathbb{S}^2$ is a totally symmetric isotropic tensor of rank n. In particular, for ranks 2, 4, and 6, one has

$$\langle e_i e_j \rangle_{\mathbb{S}^2} = \frac{1}{3}\delta_{ij}, \tag{A1}$$

$$\langle e_i e_j e_k e_l \rangle_{\mathbb{S}^2} = \frac{1}{15}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \tag{A2}$$

and

$$\langle e_i e_j e_k e_l e_m e_n \rangle_{\mathbb{S}^2} = \frac{1}{105}(\delta_{ij}\delta_{kl}\delta_{mn} + \cdots), \tag{A3}$$

where the ellipsis stands for the 14 further products of three δ's with different combinations of the six indices. The numerical factors of $\frac{1}{(n+1)!!}$ can be found, for example, by taking traces or considering contractions of the tensors with n unit vectors $\boldsymbol{e}_z$.

Using the above identities, one readily finds that for $(\mathbf{U}\boxtimes\mathbf{U})_{ijkl} = e_i e_j e_k e_l - \frac{1}{3}(e_i e_k \delta_{jl} + e_j e_l \delta_{ik}) + \frac{1}{9}\delta_{ik}\delta_{jl}$

$$\langle (\mathbf{U}\boxtimes\mathbf{U})_{ijkl} \rangle_{\mathbb{S}^2} = \frac{1}{15}(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk}) - \frac{2}{45}\delta_{jl}\delta_{ik}. \tag{A4}$$

Similarly,

$$\begin{aligned} &\langle (\mathbf{U}\boxtimes\mathbf{U})_{ijkl} e_m e_n \rangle_{\mathbb{S}^2} \\ &\quad = \langle e_i e_j e_k e_l e_m e_n \rangle_{\mathbb{S}^2} - \frac{1}{135}\delta_{ik}\delta_{jl}\delta_{mn} \\ &\qquad - \frac{1}{45}(\delta_{im}\delta_{jl}\delta_{kn} + \delta_{in}\delta_{jl}\delta_{km} + \delta_{ik}\delta_{jm}\delta_{ln} \\ &\qquad + \delta_{ik}\delta_{jn}\delta_{lm}). \end{aligned} \tag{A5}$$

The tensors $\mathbf{q} := \boldsymbol{m}_3 \otimes \boldsymbol{m}_3 - \frac{1}{3}\mathbf{I}$ and $\mathbf{b} := \boldsymbol{m}_1 \otimes \boldsymbol{m}_1 - \boldsymbol{m}_2 \otimes \boldsymbol{m}_2$ form together with the identity $\mathbf{I}$ a basis for all diagonal tensors in the frame $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$. The following identities hold for products of $\mathbf{q}$ and $\mathbf{b}$:

$$\mathbf{q}^2 = \frac{1}{3}\mathbf{q} + \frac{2}{9}\mathbf{I},$$

$$\mathbf{b}^2 = -\mathbf{q} + \frac{2}{3}\mathbf{I},$$

$$\mathbf{q}\mathbf{b} = \mathbf{b}\mathbf{q} = -\frac{1}{3}\mathbf{b}. \tag{A6}$$

APPENDIX B: NORMAL TO A STAR-SHAPED REGION

In this appendix we represent the outer unit normal field to the boundary of a star-shaped region Ω.

Let $\boldsymbol{u}$ be a smooth mapping from $\mathbb{S}^2$ into the surface $\partial\Omega := \boldsymbol{u}(\mathbb{S}^2)$. Imagine a curve on $\mathbb{S}^2$ parametrized as $t \mapsto \boldsymbol{e}(t) \in \mathbb{S}^2$. Here differentiation with respect to t will be denoted by a superimposed dot. The vector $\dot{\boldsymbol{e}}$ is everywhere tangent to $\mathbb{S}^2$, and t can be rescaled so that $\dot{\boldsymbol{e}}$ has unit length at any selected value $t = \bar{t}$. We can always choose two such curves $\boldsymbol{e}_1(t)$ and $\boldsymbol{e}_2(t)$ so that $\dot{\boldsymbol{e}}_1 \cdot \dot{\boldsymbol{e}}_2 = 0$ and $\dot{\boldsymbol{e}}_1 \times \dot{\boldsymbol{e}}_2 = \boldsymbol{e}$ for $t = \bar{t}$. Correspondingly, the curves $\boldsymbol{u}_i(t) := \boldsymbol{u}(\boldsymbol{e}_i(t))$, for $i = 1, 2$, describe trajectories on $\partial\Omega$. The normal $\boldsymbol{\nu}$ can then be written as

$$\boldsymbol{\nu} = \frac{\dot{\boldsymbol{u}}_1 \times \dot{\boldsymbol{u}}_2}{|\dot{\boldsymbol{u}}_1 \times \dot{\boldsymbol{u}}_2|}. \tag{B1}$$

For $\boldsymbol{u}(\boldsymbol{e}) = u(\boldsymbol{e})\boldsymbol{e}$, with u as in (19),

$$\dot{\boldsymbol{u}}_i = u(\boldsymbol{e})\dot{\boldsymbol{e}}_i + [\nabla_s u(\boldsymbol{e}) \cdot \dot{\boldsymbol{e}}_i]\boldsymbol{e}, \quad \text{for } i = 1, 2, \tag{B2}$$

where $\nabla_s u$ is the surface gradient of u on $\mathbb{S}^2$. It follows from (B2) that

$$\dot{\boldsymbol{u}}_1 \times \dot{\boldsymbol{u}}_2 = u[u\boldsymbol{e} - (\nabla_s u \cdot \dot{\boldsymbol{e}}_1)\dot{\boldsymbol{e}}_1 - (\nabla_s u \cdot \dot{\boldsymbol{e}}_2)\dot{\boldsymbol{e}}_2] = u[u\boldsymbol{e} - \nabla_s u],$$

since $(\dot{\boldsymbol{e}}_1, \dot{\boldsymbol{e}}_2)$ is a local basis on $\mathbb{S}^2$, and $\boldsymbol{e}$ and $\nabla_s u$ are orthogonal. Equations (B1) and (B2) readily imply Eq. (14) in the text.

APPENDIX C: ELLIPSOIDS

Here we solve Eqs. (18a) and (18b) for an ellipsoid. In the representation (13), an ellipsoid Ω is described by a mapping $u(\boldsymbol{e})$ such that

$$\boldsymbol{u} \cdot \mathsf{E}\boldsymbol{u} = 1 \quad \text{and} \quad \boldsymbol{u} = u(\boldsymbol{e})\boldsymbol{e}, \tag{C1}$$

where E is a positive definite symmetric tensor. It readily follows from (C1) that

$$u(\boldsymbol{e}) = \frac{1}{\sqrt{\boldsymbol{e} \cdot \mathsf{E}\boldsymbol{e}}}. \tag{C2}$$

Since $\nabla_s \boldsymbol{e} = \mathbf{I} - \boldsymbol{e} \otimes \boldsymbol{e}$, we obtain from (C2) that

$$\nabla_s u = u\boldsymbol{e} - u^3 \mathsf{E}\boldsymbol{e},$$

and so, by (14), we arrive at

$$\boldsymbol{\nu}(\boldsymbol{e}) = \frac{\mathsf{E}\boldsymbol{e}}{|\mathsf{E}\boldsymbol{e}|}. \tag{C3}$$

By (C3), Eq. (18b) becomes

$$\frac{\mathsf{E}'\boldsymbol{e}'}{|\mathsf{E}'\boldsymbol{e}'|} = -\frac{\mathsf{E}\boldsymbol{e}}{|\mathsf{E}\boldsymbol{e}|}, \tag{C4}$$

where

$$\mathsf{E}' := \mathsf{R}\mathsf{E}\mathsf{R}^{\mathsf{T}}.$$

Since E' is invertible, the solution to Eq. (C4) is

$$\boldsymbol{e}' = -\frac{\mathsf{E}'^{-1}\mathsf{E}\boldsymbol{e}}{|\mathsf{E}'^{-1}\mathsf{E}\boldsymbol{e}|},$$

and then (18a) becomes

$$u^* \boldsymbol{e}^* = \frac{\boldsymbol{e}}{\sqrt{\boldsymbol{e} \cdot \mathsf{E}\boldsymbol{e}}} + \frac{\mathsf{E}'^{-1}\mathsf{E}\boldsymbol{e}}{\sqrt{\mathsf{E}'^{-1}\mathsf{E}\boldsymbol{e} \cdot \mathsf{E}\boldsymbol{e}}},$$

from which we obtain both u^* and $\boldsymbol{f}^*$, though expressed by rather complicated formulas.

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