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Macroscopic and molecular symmetries of unconventional nematic phases

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The effects of the molecular symmetry on macroscopic properties of conventional and unconventional nematic phases are investigated theoretically. These effects concern: (1) the form of the molecular orientation fluctuations, (2) the thermodynamic behavior and the list of stable ordered phases, (3) the effective symmetry of the molecules in the ordered phases. The order-parameter consists of tensors forming the main harmonics of the fluctuation distribution. In conventional models (valid for uniaxial molecules) a single tensor is sufficient while unconventional models (valid for less symmetric molecules) need several tensors with the same rank. We analyze the qualitative differences arising when the number of equivalent tensors varies. We show how to work out complete models in the general case, and to calculate the sequences of stable phases and the corresponding effective molecular symmetries. This yields, for each molecular group and each tensor rank, a complete classification and a deep insight into the structure of thermotropic nematics. This work generalizes the approach we have applied to polar nematics recently observed in polyester compounds and to unconventional uniaxial and biaxial phases of bent-core materials.

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I. INTRODUCTION

Although nematics are known for more than one century [1], they presently display a remarkably poor polymorphism. Indeed, only the cylindrically-symmetric uniaxial [2] and the orthorhombic biaxial [3] states have yet been unambiguously evidenced. Moreover, in thermotropic liquid crystals the biaxial phase has been clearly confirmed only in 2003 [4]. This poverty is particularly puzzling since the set of all possible nematic phases coincides with the infinite set of three-dimensional (3D) point groups. On the other hand, the mesogenic molecules present a rich variety of symmetries, which are not directly related with the observed cylindrical and orthorhombic macroscopic groups. The observed uniaxial and biaxial phases result from the spontaneous onset of nonzero components of a *single* symmetrical second-rank traceless tensor (for brevity, we shall say throughout this paper that these components "condense"). Moreover, they are the only phases that can be theoretically obtained with this tensor. The corresponding "conventional" order parameter may be any physical second-rank tensor as, for instance, averaged molecular-scale properties (dielectric or magnetic susceptibilities), intermolecular-scale properties (optic tensor), or fluctuation parameters such as the quadrupolar statistical coefficient $P_2=\langle 3\cos^2\theta-1\rangle$[5]. In contrast, "unconventional" nematics are associated with the onset of either one tensor with rank $L_0\neq 2$ or of several combined tensors.

When the order parameter is a single vector [$L_0=1$], an unconventional uniaxial polar phase is stabilized [6]. In a recent theory of biaxial polar nematics [7] we have shown that several vectors should be involved in the ordering process when the molecular symmetry is low, yielding in addition monoclinic and triclinic ferroelectric states. Other nematics predicted in Ref. [8] for $L_0=2,3,4$ are uniaxial, cubic, tetragonal, trigonal, orthorhombic, or monoclinic. It has been suggested [9] that hexagonal nematics can appear between homogeneous uniaxial and two-dimensional (2D) translationally-ordered phases. Tetrahedral [10] and icosaedral [11] nematics associated with third- and fifth-rank tensors have also been theoretically investigated. The observation of nematics with such unconventional symmetries is a long standing and yet unsuccessful experimental challenge. Reference [12] shows that dipolar interactions between disk-shaped molecules can stabilize the uniaxial ferroelectric nematic phase. A spontaneous polarization was first reported in the lyotropic cholesteric phase of polypeptide polymer and benzyl [13], and more recently [14] in monoclinic nematic phases. Monoclinic [15], rhombic [16], tetragonal [17], and cubic [18] structures have also been claimed to interpret various observations and proposed for applications. However, neither the symmetries nor the nematic characters of the corresponding unconventional phases are clearly established.

In the phenomenological approach the stable phases and their macroscopic symmetries (G_{Nem}) are determined by the rank of the tensor order parameter, whereas their relations with the molecular symmetry (G_{mol}) are usually overlooked. In order to question the validity of this approach, let us first discuss the oversimplified pedagogical presentation of nematic phases: "In the isotropic phase the molecules are completely disordered, whereas below the critical temperature they all align parallel to a given direction," in such a way that G_{Nem} coincides with G_{mol}. This simple point of view, in which all the orientational fluctuations are frozen at the transition, qualitatively works, for instance, in the biaxial phase of orthorhombic micelles [$G_{\mathrm{Nem}}=G_{\mathrm{mol}}=D_{2h}$]. It would work also with cylindrically-symmetric molecules in the uniaxial phase [$G_{\mathrm{Nem}}=G_{\mathrm{mol}}=D_{\infty h}$]. However, it is not adapted to real uniaxial nematics which are always formed with less symmetric molecules. Indeed, the orientational ordering is then incomplete, and the unfrozen fluctuations play a crucial role to prevent the formation of more asymmetric ordered states.

This fact is well known in the conventional uniaxial nematic phases [19]. In such systems, asymmetric sticklike molecules turn isotropically around their main axis so as to form cylindrically-symmetric "effective molecules" (that we shall denote by "subunits" throughout this paper), which align parallel to each other in the uniaxial phase. Although this more refined example illustrates the role played by the unfrozen fluctuations, its simplicity remains rather misleading. Indeed, at first sight it may be thought that the cylindrical symmetry of the subunit is a consequence of the macroscopic uniaxiality. This statement is wrong, since the subunit remains cylindrical even in the orthorhombic biaxial phase. Accordingly, in order to account for the full complexity of this issue, one has to consider in fact three independent symmetry levels: The actual molecular symmetry G_{mol}, the effective molecular symmetry G_{eff}, and the macroscopic symmetry G_{Nem}. At frequencies smaller than the molecular rotation frequency, the behavior of the system is determined only by G_{Nem} and G_{eff}. Thus, the nematic phase is characterized not only by its macroscopic group, but also by its effective molecular symmetry. Even though one considers only the most likely types of nematics (uniaxial, biaxial, polar), this yields a wide diversity of possible behaviors. This diversity is actually limited by the fact that several molecular groups lead to the same behavior when they yield the same effective symmetry. All the corresponding groups form then a "molecular class." For instance, the cylindrical subunit of the conventional model arises for molecules with point groups in the "uniaxial" class $\{C_n, C_{nv}, D_n, \ldots, n>2\}$. A complete classification needs thus, fortunately, to work out only a rather small number of classes for each nematic ordering mechanism.

In order to show how the three groups are related in the general case, one has to investigate in detail the structure of the order-parameter space spanned by the symmetry-breaking components of the orientational distribution function. Indeed, for a given rank L_0, this structure depends completely on the molecular symmetry. A key feature of this space is the number of distinct tensors of the same rank L_0 that it contains. This number, which has a deep statistical meaning (several equivalent tensors are commonly used in order to analyze experimental data such as NMR or Raman spectra [21]), is also equal to the number of independent molecular tensors that are permitted by the molecular symmetry group G_{mol}. For instance, a cylindrically symmetric molecule permits a single tensor of each rank, whereas a molecule with no symmetry permits $(2L_0+1)$ L_0th-rank tensors. This number, which we denote by "tensor multiplicity," is an important invariant of the theory, and it controls many unconventional properties of a given system. For instance, the list of stable phases depends on the tensor multiplicity. Finally, the effective molecular symmetry depends on the macroscopic group in the same way as the macroscopic group depends on the molecular symmetry. In particular we find that the list of possible macroscopic groups induced by a given tensor coincides with that of possible effective groups, even though the effective symmetry is usually distinct from the macroscopic symmetry in a given phase. Although the whole story may seem rather intricate, it obeys quite regular laws relying only on the molecular symmetry and on the rank of the order parameter. Along this line, we shall present the methods yielding, for any nematic model (i.e., any value of L_0):

(1) The number of tensors needed for a complete description of the molecular fluctuations (tensor multiplicity), on the one hand, and for a complete thermodynamic treatment of the Isotropic→Nematic transition (order-parameter multiplicity), for all molecular symmetry groups.

(2) The lists of phases (and the corresponding macroscopic point groups) that are stabilized for various values of the multiplicities, i.e., for various molecular groups.

(3) The effective molecular symmetry in each phase and for all types of molecules, together with the resulting classification of the actual molecular groups according to the type of subunit they can give rise to.

As an example, let us sketch the analysis of "standard" nematics ($L_0=2$). In the class of tetrahedral and cubic molecules (optically isotropic), no second-rank tensor is permitted, and no nematic ordering can occur. With cylindrical molecules, one *single copy* of the tensor is sufficient to account for the molecular fluctuations, which permits to stabilize the uniaxial and biaxial phases. We have recently shown [20] that this *conventional model* holds in the class of molecules characterized by a preferred rotation axis of order >2 (e.g., with $G_{\mathrm{mol}}=C_{3h}$). All these molecules yield the same effective cylindrical symmetry ($G_{\mathrm{eff}}=D_{\infty h}$) in both the uniaxial ($G_{\mathrm{Nem}}=D_{\infty h}$) and biaxial ($G_{\mathrm{Nem}}=D_{2h}$) phases. Oppositely, in a class of less symmetric molecules (e.g., bent-core molecules with $G_{\mathrm{mol}}=C_{2v}$), *several copies* of the second-rank tensor are permitted, and qualitative differences with the conventional model emerge. The first difference is the possibility of stabilizing monoclinic (C_{2h}) and triclinic (C_i) nematics below the biaxial state when various copies are not parallel. The second difference is the lowering of the effective molecular symmetry, which is then either orthorhombic (D_{2h}), monoclinic (C_{2h}), or triclinic (C_i), even in the uniaxial phase. The list of possible macroscopic symmetries coincides thus with the list of possible effective molecular symmetries. We shall see that this simple result can be generalized to all the nematics.

This paper establishes the building rules of phenomenological nematic models, yielding whenever it is possible, thermodynamic and statistical completeness. In Sec. II we present the algebraic methods relating macroscopic and molecular symmetries to the form of the statistical distribution. They provide the "tensor multiplicities," which control the unconventional character of the various models. In Sec. III we investigate the effects of the molecular symmetry on the thermodynamic aspects of the phenomenological models, and we show how they determine, in each case, the list of stable phases. Section IV is devoted to the determination of the effective symmetry groups and of the corresponding molecular classes. We review the various relationships between the macroscopic and the actual and effective molecular groups predicted within our approach. In Sec. V we show the equivalence between our statistical definition of the order parameter and that based on physical molecular tensors. In this respect we discuss in detail a popular model of unconventional third-rank nematics in bent-core systems.

II. SYMMETRY OF THE FLUCTUATIONS

A number of physical properties characterizing nematics depend only on the statistical distribution of molecular orientations at the equilibrium. It is well known that the form of this distribution is strongly constrained by the macroscopic symmetry of the nematic phase. In fact, the microscopic symmetry group of the molecules plays also an important role. Since the difference between these two types of symmetry operations is usually overlooked, this section aims at establishing the way both symmetries act in the classical formalism of distribution functions, and its effects on the equilibrium form of the distribution. The latter can be summarized by two simple rules that we shall call *external* and *internal selections*, which will turn out to have deep structural and thermodynamic consequences in the following sections.

In order to describe accurately the molecular fluctuations in molecular liquid system, we define rigorously the distribution function $P(\omega,\sigma)$ in Appendix A. $P(\omega,1)$ stands for the (normalized) number of right-handed molecules oriented in space by the set of Euler angles $\omega=\{\alpha,\beta,\gamma\}$, whereas $P(\omega,-1)$ holds for left-handed molecules. The distribution is modified by the rotations with respect to the laboratory axes, but also by the rotations of the molecules with respect to their own reference frames. Let us now describe quantitatively the action of these two types of symmetry transformations, which determine many equilibrium properties of nematic systems.

A. Internal and external symmetries

We call "external symmetries" the usual point transformations turning the molecules with respect to the laboratory axes. All the molecules are then turned in the same way in the laboratory frame $\Sigma_0=\{\mathbf{i},\mathbf{j},\mathbf{k}\}$. Let R_Ω^{ext} be such an external rotation defined by the set of Euler angles collectively denoted by Ω. It transforms a molecular frame initially oriented by the rotation R_ω with respect to Σ_0 into a frame oriented by $R_\Omega R_\omega$, and P into the new distribution $P'=[R_\Omega^{\mathrm{ext}}P]$. Writing, for convenience, $P(\omega,\sigma)$ as $P(R_\omega,\sigma)$ one has then

$$P'(R_\omega,\sigma)=[R_\Omega^{\mathrm{ext}}P](R_\omega,\sigma)=P(R_\Omega^{-1}R_\omega,\sigma). \tag{1}$$

The external space inversion I^{ext} changes only the handedness of the molecules (see Appendix A), hence it transforms σ into $-\sigma$ and Ω into Ω. Therefore, the action of I^{ext} onto P yields a new distribution $P'=[I^{\mathrm{ext}}P]$ defined by

$$P'(R_\omega,\sigma)=[I^{\mathrm{ext}}P](R_\omega,\sigma)=P(R_\omega,-\sigma). \tag{2}$$

External symmetries are not sufficient to describe the orientational order since they are not related to the molecular symmetries, which play a key role for selecting the actual distribution function and the corresponding order parameter. So, we introduce a second type of transformations acting on P. Such "internal operations" transform all the molecules within their own reference frames [20,23]. For instance, in a system where one molecule has its Z axis along the laboratory direction Oz, and a second molecule with its Z axis along Ox, then a twofold internal rotation around OZ turns the first molecule by an angle π around Oz and the second molecule by the same angle around Ox [Fig. 1(a)].

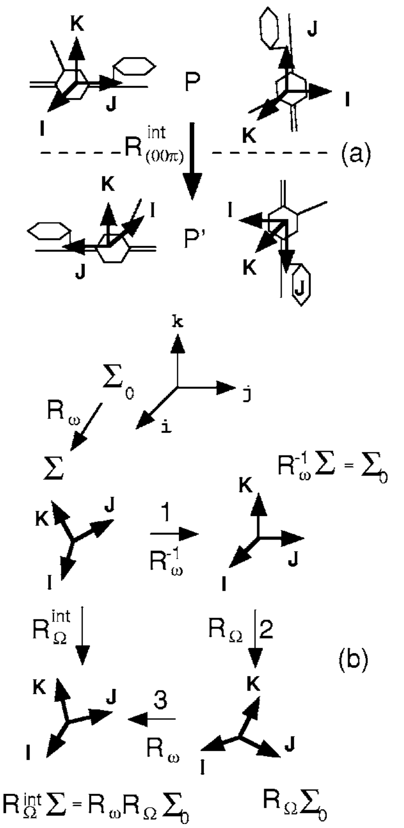

FIG. 1. (a) Action of an internal twofold rotation $R_{00\pi}^{\mathrm{int}}$ around $\mathbf{K}$ on a statistical set composed of two molecules. The initial distribution P is transformed into $P'=R_{00\pi}^{\mathrm{int}}P$. Since the sets associated with P and P' are different, P is not invariant under $R_{00\pi}^{\mathrm{int}}$. (b) Action of an internal rotation R_Ω^{int} onto a frame Σ oriented by the rotation R_ω with respect to the laboratory frame Σ_0. In step 1, Σ is put parallel to Σ_0 (or equivalently the laboratory frame is turned parallel to Σ). In step 2, Σ is turned by the external rotation R_Ω (or equivalently by an internal rotation in the turned laboratory frame). Step 3 reverses step 1 (or equivalently the laboratory frame is back to its initial orientation). The final internally-rotated state is thus oriented with respect to Σ_0 by the rotation $R_\omega R_\Omega$ after the internal rotation R_Ω^{int}, while it is oriented by $R_\omega R_\Omega$ after the external rotation R_Ω^{ext}.

It may be seen that R_Ω^{int} transforms the molecular frame $\Sigma=R_\omega\{\mathbf{i},\mathbf{j},\mathbf{k}\}$ into $(R_\omega R_\Omega)\{\mathbf{i},\mathbf{j},\mathbf{k}\}$ [Fig. 1(b)]: First, apply the rotation R_ω^{-1} to Σ in order to make it parallel to $\{\mathbf{i},\mathbf{j},\mathbf{k}\}$. Afterward, rotate it by R_Ω and then come back with R_ω to the initial observer. The resulting frame is then $(R_\omega R_\Omega)\{\mathbf{i},\mathbf{j},\mathbf{k}\}$. So, the action of R_Ω^{int} on P yields the new distribution $P'=[R_\Omega^{\mathrm{int}}P]$ given by

$$P'(R_\omega,\sigma)=[R_\Omega^{\mathrm{int}}P](R_\omega,\sigma)=P(R_\omega R_\Omega^{-1},\sigma). \tag{3}$$

The internal space inversion I^{int} transforms the molecular frame $\{\mathbf{I},\mathbf{J},\mathbf{K}\}$ into $\{-\mathbf{I},-\mathbf{J},-\mathbf{K}\}$, exactly as I^{ext} does. Thus, one finally gets

$$I^{\mathrm{int}}=I^{\mathrm{ext}}. \tag{4}$$

From now on we shall simply denote this inversion by I.

Equations (1)–(4) show that external and internal rotations commute. The group containing both types of transformations can thus be written as the product

$$G = \mathrm{SO}(3)^{\mathrm{int}} \otimes \mathrm{SO}(3)^{\mathrm{ext}} \otimes I \tag{5}$$

where the groups $\mathrm{SO}(3)^{\mathrm{int}}$ and $\mathrm{SO}(3)^{\mathrm{ext}}$ contain the internal and external rotations, respectively, and the group I is generated by I. Much care is necessary when using Eqs. (1) and (3), for they obey two distinct combination rules: $R_\omega^{\mathrm{ext}} R_\Omega^{\mathrm{ext}} = (R_\omega R_\Omega)^{\mathrm{ext}}$ and $R_\omega^{\mathrm{int}} R_\Omega^{\mathrm{int}} = (R_\Omega R_\omega)^{\mathrm{int}}$. The free energy of the mixture is invariant under any external operation while, in general, it is not invariant under internal operations since they modify the structure of the distribution. Strictly speaking, internal transformations are not dynamical symmetries, except, of course, when they belong to G_{mol}.

This symmetry analysis is intimately connected with the expansion of $P(R_\omega, \pm 1)$ into Euler spherical functions [24]

$$P(R_\omega, \sigma) = \sum_{L=0}^{\infty} \sum_{m=-L}^{L} \sum_{m'=-L}^{L} P_{mm'}^{L+} D_{mm'}^{L}(\omega) + P_{mm'}^{L-} \sigma D_{mm'}^{L}(\omega), \tag{6}$$

where the functions $D_{mm'}^{L}(\omega)$ are defined from the transformation properties of the spherical harmonics Y_m^L [27]: $R_\omega Y_L^m = \Sigma_{p=-L}^{L} D_{pm}^{L}(\omega) Y_L^p$. We call "fluctuation coefficients" the components $P_{mm'}^{L,\pm}$ of P. Let us denote by Γ_L a tensor of rank L, i.e., a set of $2L+1$ functions (or components) with appropriate transformation properties under rotations. When the tensor is even with respect to space inversion I it is denoted by Γ_L^+, and by Γ_L^- when it is odd (e.g., Γ_1^- is a polar vector and Γ_1^+ an axial vector). Since the rotation can be either internal or external, one has to deal with external as well as internal tensors. The $(2L+1)^2$ functions $\{D_{mm'}^L\}$, or equivalently the $(2L+1)^2$ components $\{P_{mm'}^{L,\pm}\}$, appearing in Eq. (6) for a given L consists of a set of $(2L+1)$ internal tensors of rank L, on the one hand, and a set of $(2L+1)$ external tensors, on the other hand. This means that the functions $P_{mm'}^{L,\pm}$ transform as the tensor components T_m under external rotations and as $T_{m'}$ under internal rotations. The simultaneous presence of internal and external tensors, on the one hand, and the fact that they share the same components, on the other hand, play an important role in the forthcoming analysis.

Averaging $D_{mm'}^L$ over P provides the statistical meaning of the fluctuation coefficients

$$P_{mm'}^{L+} = \frac{2L+1}{16\pi^2} \langle D_{mm'}^{L} \rangle,$$

$$P_{mm'}^{L-} = \frac{2L+1}{16\pi^2} \langle \sigma D_{mm'}^{L} \rangle, \tag{7}$$

where the brackets indicate statistical averages: $\langle F(\omega,\sigma)\rangle = \Sigma_{\sigma=\pm 1} \int\int\int F(\omega,\sigma) P(\omega,\sigma) d\omega$. For instance, $P_{00}^{0,+} = \langle 1 \rangle / 16\pi^2 = 1/16\pi^2$ and $P_{00}^{0,-} = \langle \sigma \rangle / 16\pi^2 = (C_R - C_L)/16\pi^2$ (where C_R and C_L are right- and left-handed concentrations, respectively). Equations (7) show that the fluctuation coefficients $P_{mm'}^{L,\pm}$ can be measured by means of diffusion experiments.

Equation (6) is valid for any macroscopic and molecular symmetry group. Moreover, when these groups are triclinic $[C_1]$, all the coefficients $P_{mm'}^{L,\pm}$ take finite values. Contrariwise, when the groups contain nontrivial elements a number of these coefficients identically vanish. The selection of the surviving coefficients is presented by Zanoni in Ref. [25] for second- and fourth-rank even tensors $[\Gamma_2^+$ and $\Gamma_4^+]$. The following paragraph is devoted to the presentation of the selection procedure for external as well as internal symmetries in the general case.

B. Internal and external selections

The general form of the distribution function is given by Eq. (6). However, for a given molecule and in a given nematic phase, many coefficients must vanish in this distribution, due to the internal symmetries of the molecular point group and to the external symmetries of the macroscopic point group. We present now successively the corresponding selection procedures that we shall systematically use throughout the remainder of this paper.

Due to the molecular symmetry, the distribution P must satisfy the set of the constraints

$$g^{\mathrm{int}} P = P, \quad g^{\mathrm{int}} \in G_{\mathrm{mol}} \tag{8}$$

for all generators g^{int} of G_{mol}. They restrict the number of independent external tensors $\Gamma_L^{\mathrm{ext},\pm}$ appearing in P. This number may then be smaller than $(2L+1)$, and it may even be zero for the most symmetric molecules. We shall call this procedure: the "internal selection". It consists in restricting the number of copies of a given $\Gamma_L^{\mathrm{ext},\pm}$ in P, resulting from the constraints (8).

The construction of the restricted expansion may be achieved by linear projection. Each component P_L of $P = \Sigma_{L=0}^{\infty} P_L$ associated with a single value of L being separately invariant under G_{mol}, P_L reads

$$P_L = \left(\frac{1}{g} \sum_{g^{\mathrm{int}} \in G_{mol}} g^{\mathrm{int}} \right) \sum_{m=-L}^{L} \sum_{m'=-L}^{L} [P_{mm'}^{L+} D_{mm'}^{L}(\omega) + P_{mm'}^{L-} \sigma D_{mm'}^{L}(\omega)], \tag{9}$$

where g is the number of operators in G_{mol}.

We denote "tensor multiplicity" the number $n_0^{\pm}$ of independent surviving copies of $\Gamma_L^{\mathrm{ext},\pm}$ in P_L. It is given by the classical formula [26]

$$n_0^{\pm} = \frac{1}{g} \sum_{g^{\mathrm{int}} \in G_{mol}} (\pm)^{\kappa_{g^{\mathrm{int}}}} \frac{\sin(2L+1)\varphi_{g\ \mathrm{int}}/2}{\sin \varphi_{g\ \mathrm{int}}/2}, \tag{10}$$

where φ_g^{int} is the angle of g^{int} and $\kappa_{g^{\mathrm{int}}}=0$ for rotations, while φ_g^{int} is the angle of Ig^{int} and $\kappa_{g^{\mathrm{int}}}=1$ otherwise. We shall say that the tensor of rank L and parity ± is "forbidden" when $n_0^{\pm}=0$. The corresponding molecules cannot lead to the formation of the nematic phases associated with the condensation of this tensor. This defines a class of molecules that we denote by "isotropic class," which depends on L.

More generally, let us denote by n_0 the number of independent surviving copies of a given external tensor in P_L. In a chiral system the parent symmetry is $\mathrm{SO}(3)^{\mathrm{ext}}$ so that $\Gamma_L^{\mathrm{ext},+}$ and $\Gamma_L^{\mathrm{ext},-}$ are equivalent (e.g., polar Γ_1^- and axial Γ_1^+ vectors). In this case the tensors $\Gamma_{\mathrm{L}}^{\mathrm{ext}}$ are labeled by the tensor rank L

TABLE I. Polar $[n_0^-]$ and axial $[n_0^+]$ vector multiplicities permitted by internal selection for various molecular classes.

G_{mol}	n_0^+	n_0^-
C_1	3	3
C_i	3	0
C_s	1	2
C_n $(n\geqslant 2)$	1	1
C_{nv} $(n\geqslant 2)$	0	1
C_{nh}, $S4$, $S6$	1	0
D_n, D_{nh} $(n\geqslant 2)$	0	0
D_{2d}, T, O, $\mathrm{T_d}$, $\mathrm{T_h}$, $\mathrm{O_h}$		

only (e.g., the vector Γ_1). In achiral systems the parent group is O(3) so that $\Gamma_L^{\mathrm{ext},+}$ and $\Gamma_L^{\mathrm{ext},-}$ are no longer equivalent. Equation (10) shows that for chiral molecules one has always

$$n_0^+ = n_0^-.$$

If the system is optically pure one has in addition $P_{mm'}^{L,+} = \pm P_{mm'}^{L,-}$, so that

$$n_0 = n_0^+ = n_0^-$$

represents the number of copies of Γ_L^{ext}. Contrariwise, in a chiral mixture $P_{mm'}^{L,+}$ and $P_{mm'}^{L,-}$ are independent, so that

$$n_0 = n_0^+ + n_0^-.$$

In a racemic mixture n_0 represents either the number n_0^+ of copies of $\Gamma_L^{\mathrm{ext},+}$ when one considers, for instance, the nematic phase induced by the condensation of an even tensor of rank L, or the number n_0^- of copies of $\Gamma_L^{\mathrm{ext},-}$ for an odd tensor. For achiral molecules n_0^+ may be different from n_0^-.

Table I indicates the multiplicities n_0^+ and n_0^- of vector nematics $[L=1]$ for various molecular groups. More than one copy of an axial (resp. polar) vector arise only for C_1^{int} and C_i^{int} (resp. C_s^{int}). The groups containing D_2^{int} or T^{int} forbid both vectors. Table II presents the multiplicities for second-rank tensors $[L=2]$. These tensors are forbidden only for the optically isotropic groups $G_{\mathrm{mol}}=T$, O, T_d, T_h, O_h, etc. The minimal tensors allowed by these groups are presented in Table III.

Analogous constraints coming from the macroscopic symmetry restrict the number of independent *internal* tensors $\Gamma_L^{\mathrm{int},\pm}$ appearing in P_L. We shall refer to the corresponding procedure as the *external selection*. The distribution being invariant under G_{Nem}, P_L must satisfy the following *external conditions*:

$$g^{\mathrm{ext}} P_L = P_L, \quad g^{\mathrm{ext}} \in G_{\mathrm{mol}} \tag{11}$$

for all the generator g^{ext} of G_{Nem}. P_L can thus be obtained by external projection

TABLE II. Second-rank odd $[n_0^-]$ and even $[n_0^+]$ tensor multiplicities permitted by internal selection for various molecular classes.

G_{mol}	n_0^+	n_0^-
C_1	5	5
C_i	5	0
C_s	3	2
C_{2h}	3	0
C_{2v}	2	1
D_{2h}	2	0
D_2	2	2
C_n, D_n $(n>2)$	1	1
D_{nh}, C_{nh}, C_{nv} $(n>2)$	1	0
D_{3d}, $S6$		
$S4$	1	2
T, O, T_d, T_h, O_h	0	0

$$P_L = \left(\frac{1}{g_{\mathrm{Nem}}} \sum_{g^{\mathrm{ext}} \in G_{\mathrm{Nem}}} g^{\mathrm{ext}} \right) \sum_{m=-L}^{L} \sum_{m'=-L}^{L} [P_{mm'}^{L+} D_{mm'}^{L}(\omega) + P_{mm'}^{L-} \sigma D_{mm'}^{L}(\omega)]. \tag{12}$$

The number $n_0'^{\pm}$ (internal tensor multiplicity) of surviving tensors $\Gamma_L^{\mathrm{int},\pm}$ in Eq. (12) is given by

$$n_0'^{\pm} = \frac{1}{g_{\mathrm{Nem}}} \sum_{g^{\mathrm{int}} \in G_{\mathrm{Nem}}} (\pm)^{\kappa_{g^{\mathrm{int}}}} \frac{\sin(2L+1)\varphi_{g^{\mathrm{int}}}/2}{\sin \varphi_{g^{\mathrm{int}}}/2}. \tag{13}$$

Hence, Tables I–III give also the internal multiplicities, provided that one replaces the molecular group by the macroscopic symmetry group.

For obtaining the actual distribution when G_{mol} and G_{Nem} are given, both projectors must be applied to P_L. These projectors act linearly in Eqs. (9) and (12). They can be found explicitly by using the transformation properties of the Euler functions

$$R_{\Omega}^{\mathrm{ext}} D_{mm'}^{L} = \sum_{p=-L}^{L} D_{pm}^{L}(R_{\Omega})^{*} D_{pm'}^{L},$$

$$R_{\Omega}^{\mathrm{int}} D_{mm'}^{L} = \sum_{p=-L}^{L} D_{pm'}^{L}(R_{\Omega}^{-1}) D_{mp}^{L}.$$

TABLE III. Minimal tensor rank (L) for tetrahedral and cubic molecular symmetries. For each permitted even $(n_0^+=1)$ and odd $(n_0^-=1)$ tensor, the corresponding effective group G_{eff} is indicated in the fourth row.

G_{mol}	T	T_d	T_h	O	O_h
rank	$L=3$	$L=3$	$L=3$	$L=4$	$L=4$
(n_0^+,n_0^-)	(1,1)	(0,1)	(1,0)	(1,1)	(1,0)
G_{eff}	T_h, T_d	—, T_d	T_h, —	O_h, O	O_h, —

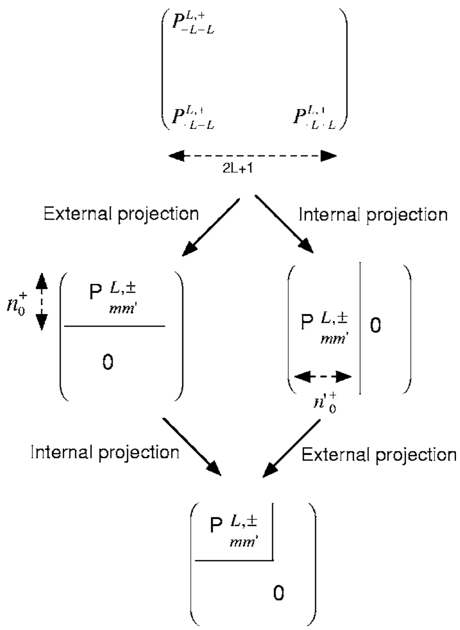

FIG. 2. Action of internal and external selections (projections) on the matrix of fluctuation coefficients $P^{L,+}_{mm'}$ associated with a single tensor rank L and parity, say $+$. Internal projection cancels a number of columns whereas external projection cancels a number of rows in the matrix. More precisely, the projections make linearly dependent a number of rows or of columns. After a linear transformation independent of the coefficients, the fluctuation matrix takes the form (with zero rows and columns) indicated in the figure.

The number of independent odd and even surviving coefficients in P_L after the two selections is given by $n_0^+n_0^- + n_0'^+n_0'^-$. For practical calculations and a more direct understanding of the whole algebra presented above, it proves convenient to visualize the action of the projectors on the matrices of fluctuation coefficients (Fig. 2). Before the selections, all the coefficients are nonzero. After the internal selection a number of columns vanish, whereas after the external selection a number of rows vanish (or, more precisely, become dependent).

III. ISOTROPIC-NEMATIC TRANSITION

The formalism developed in the previous section has immediate consequences on the thermodynamic description of the Isotropic→Nematic phase transition associated with a given tensor order parameter. On the one hand, external symmetries permit to find the free energy controlling the thermodynamic behavior at the transition. On the other hand, the selection imposed by the molecular symmetry yields additional physical features. The first one is the determination of molecular symmetries not compatible with the considered transition. Second, for compatible molecules the internal selection determines the list of possible stable phases. It is a fundamental result of our analysis to state that this list changes with the molecular symmetry. For instance, with a classical second-rank tensor, the molecular symmetry groups C_3, C_{3v}, C_4, etc., yield only the conventional uniaxial and biaxial nematic phases. Contrariwise, with less symmetric molecules or micelles additional monoclinic and triclinic phases can be stabilized. This result holds for all tensors. Thus, the set of possible stable phases depends not only on the rank and parity of the order parameter, but also on the symmetry of the molecules. With the most symmetric molecules the ordering mechanism is impossible, whereas the number of stable phases increases when the molecular symmetry decreases. For a given tensor, this behavior leads us to introduce one of the key concepts in our analysis, the "SG (subgroups) sequence," which contains the list of groups corresponding to the phases stabilized for a given molecular symmetry class.

A. Extended order parameter

In isotropic liquids all the $P^{L,\pm}_{mm'}$ with $L>0$ vanish in Eq. (6), and the distribution depends only on σ

$$P(\sigma) = \frac{1+\sigma(C_R - C_L)}{8\pi^2} \tag{14}$$

with $C_R = C_L = 1/2$ in achiral systems. The order parameter inducing the Isotropic→Nematic phase transition associated with a given tensor of rank L_0 and parity ±, consists of the set of fluctuation coefficients $P^{L_0,\pm}_{mm'} = \langle(\sigma)D^{L_0}_{mm'}\rangle$ $(-L_0 \leqslant m, m' \leqslant L_0)$, which generalize the well known quadrupolar order parameter $S = \langle 1 - 3\cos^2(\theta)\rangle$ characterizing the conventional Isotropic→Uniaxial transition.

Since the number of independent coefficients $P^{L_0,\pm}_{mm'}$ in $P^{\pm}_{L_0}$ [see Eq. (9)] is determined by internal as well as by external selections, the properties of the transition should be also strongly affected by the molecular symmetry. We have shown in the previous section that external and internal symmetries play very similar roles in the description of the fluctuations. Nevertheless, this duality is limited when one considers thermodynamic effects. Indeed, the Landau free energy $F(P^{\pm}_{L_0})$ [27], which accounts for the phase transition, is invariant under the external symmetries of the parent phase $(S)O(3)^{\mathrm{ext}}$, but only under the internal symmetries of G_{mol}, which is much smaller than $(S)O(3)^{\mathrm{int}}$. Furthermore, some external symmetries are broken at the transition while internal symmetries can never decrease. Therefore, in the forthcoming analysis of the Isotropic→Nematic transition, internal and external operations appear at different levels.

In the free energy $F(P^{\pm}_{L_0})$, the form of $P^{\pm}_{L_0}$ [see Eq. (9)] is restricted only by the molecular symmetry (the macroscopic symmetry results from minimization of F and cannot be imposed *a priori*). We have shown in Sec. II that, as a consequence of the internal selection, $P^{\pm}_{L_0}$ represents in fact $(2L_0+1)n_0^{\pm}$ independent coefficients $P^{L_0,\pm}_{mm'}$ (or linear combinations of the $P^{L_0,\pm}_{mm'}$), so that the number of variables in F changes with the molecular symmetry [see Eq. (10)]. Then, various molecules can yield thermodynamically distinct models. More formally, these coefficients form n_0 (n_0^+, n_0^-, or $n_0^+ + n_0^-$) copies of the tensor $\Gamma = \Gamma^{\mathrm{ext},(\pm)}_{L_0}$ characterized by its rank (L_0) and (when the system is achiral) its parity (±). In the conventional theory of phase transitions this multiplicity is physically irrelevant because a single copy of Γ is sufficient to describe the main thermodynamic features of the transition. However, this is no longer true when the symmetry broken at the transition is continuous (see e.g, Ref. [22]), as it is the case at the Isotropic → Nematic phase transition. Indeed, in this case the possibility of stabilizing states where the various copies are not "parallel" drastically modifies the nature of the transition. In particular, additional low-symmetry phases can then be stabilized. Increasing the number of copies increases the number of stable phases, until the minimal symmetry associated with Γ (technically its "kernel"), denoted by K, appears in the list of stable phases. The number n_Γ of copies necessary for obtaining K, called the "order-parameter multiplicity," never exceeds the dimension d_Γ of Γ

$$n_\Gamma \leqslant d_\Gamma = 2L + 1. \tag{15}$$

A method for computing the multiplicity n_Γ is given in Appendix B.

To summarize, one has shown that two integer numbers characterize a given nematic model: (i) The tensor multiplicity n_0, which provides the number of independent tensors permitted by the molecular symmetry. (ii) The order-parameter multiplicity n_Γ, which states how many tensors are necessary to achieve a complete symmetry breakdown. Comparing these two numbers provides thus a classification of the various models with respect to the list of low-symmetry phases that can be stabilized:

(1) Fully-extended models $[n_0 = n_\Gamma]$.
(2) Over-extended models $[n_0 > n_\Gamma]$.
(3) Under-extended models $[n_0 < n_\Gamma]$.

Under-extended models cannot provide the maximal set of low-symmetry phases whereas over-extended models contain several redundant copies of Γ, which are not useful for completing the symmetry breakdown. The type of model is not an arbitrary ingredient of the theory, since the molecules forming the system impose it. Nevertheless, some freedom remains to the phenomenologist, according to the goals of the theory. When the molecule yields an over-extended model, many physical properties can be safely determined by using only the corresponding fully-extended model obtained by suppressing a part of the initial independent degrees of freedom. Furthermore, when only the most symmetric stable phases foreseen with this tensor are observed, an under-extended model may also be sufficient.

However, in this latter case one has to be careful. Indeed, even in this case, fully- and under-extended models are not completely equivalent. For instance, in the under-extended nematic conventional model $[L_0 = 2+, n_0 = 1, n_\Gamma = 2]$ (uniaxial molecules), a four-phase Landau point is predicted in the uniaxial-biaxial phase diagram while it disappears in the fully-extended model with $n_0 = 2$ (bent-core molecules or orthorhombic micelles) [20]. This absence of a Landau point is a striking property of the fully-extended model associated with low molecular symmetries. Considering in this case the approximate conventional under-extended model is sufficient to describe a number of properties of these systems, e.g., the list and symmetries of the observed stable phases, the order of the transitions, etc., but it fails to account for key features of the phase diagram such as the absence of a Landau point.

As stated above, the sequence of stable phases increases when the distribution function contains more copies of the tensor order parameter, i.e., when n_0 increases. The minimal sequence, containing only the group $(\mathrm{S})\mathrm{O}(3)^{\mathrm{ext}}$ of the isotropic phase, corresponds to the trivial case $n_0 = 0$ indicating that the corresponding tensor is forbidden by the molecular symmetry. The sequence associated with $n_0 = 1$ begins with $(\mathrm{S})\mathrm{O}(3)^{\mathrm{ext}}$ and terminates with G_L, the group of the lowest symmetric phase obtained in the conventional approach taking into account a single copy of Γ (the biaxial D_{2h} group in the conventional model with Γ_2^+). The maximal sequence, which contains K as its last element, is obtained for fully- and over-extended models. One can associate with each sequence of stable phases (i.e., with each value of n_0 between 0 and n_Γ) the corresponding sequence of subgroups that we shall denote by "SG sequence" thereafter (the SG sequences for tensors with rank 1,2,3,4 are presented in Figs. 5–8 of Appendix C). All the external symmetry groups of the stable phases associated with a given tensor belong therefore necessarily to the maximal external SG sequence. Reciprocally, any group G_i in the maximal sequence is characterized by the minimal value of n_0 permitting to stabilize it. This number, denoted by $\bar{a}(G_i)$, is referred to as the "group parametricity" of G_i. Appendix B presents methods for calculating the SG sequences and the $\bar{a}(G_i)$.

Table IV displays the order-parameter multiplicities n_Γ for low-rank tensors, together with the corresponding external SG sequences and group parametricities. It shows, for instance, that with an odd second-rank tensor (Γ_2^-) one has $\bar{a}(C_2) = 2$, so that at least two tensors are necessary to stabilize the monoclinic phase $(G_{\mathrm{Nem}} = C_2^{\mathrm{ext}})$. Hence, this phase cannot be stabilized in achiral systems consisting of molecules with the following internal symmetries: C_n, D_n, D_{nh}, C_{nv} $(n > 2)$, D_{3d}, S_6, S_4, T, O, T_d, T_h, and O_h because (see Table III) they all have $\mathrm{n}_0 = n_0^- < 2$. On the other hand, in a chiral mixture with the same order parameter (Γ_2), one has still $\bar{a}(C_2) = 2$, but now molecules with symmetries C_n or $D_n (n > 2)$ permit this phase (because $n_0 = n_0^+ + n_0^- = 2$), except in optically pure systems $(n_0 = n_0^+ = n_0^- = 1)$. Let us notice that the content of these tables for tensor ranks 1,2,3,4 is very quickly and easily obtained by using the diagrams presented in Appendix C. Obtaining similar results with tensors of rank higher than 4 is a matter of a few minutes of calculation. However, this table contains the central information of our work, which permits to determine not only the list of stable phases for each order parameter, but also, as we shall show in the following sections, the effective symmetry groups in each phase and for each permitted molecular symmetry.

B. Polar nematics

Let us consider as a typical example the nematic phases stabilized when the order parameter is a polar vector (Γ_1^- or Γ_1 in achiral and chiral systems, respectively). In the conventional theory [6] taking into account a *single vector*, only the uniaxial polar phase is stabilized with a point group C_∞^{ext} (chiral case) or $C_{\infty v}^{\mathrm{ext}}$ (achiral case). We have recently generalized this theory to systems consisting of monoclinic molecules [7], which permit several vectors and yield additional

TABLE IV. SG sequences associated with low-rank tensor order parameters. d_Γ is the dimension of the tensor representation and n_Γ its multiplicity. Column 4: Symmetry of the liquid phase ($\bar{a}=0$). Column 5: Symmetry groups accessible with a single tensor ($\bar{a}=1$). Column 6: With two tensors ($\bar{a}=2$). Column 7: With three tensors ($\bar{a}=3$). Gathering all the groups lying in one row provides the maximal SG sequence associated with the corresponding tensor. The nonmaximal SG sequences are obtained by gathering only the groups in the first, first and second, etc. columns. When one of these tensors condenses as a primary order parameter, the macroscopic (G_{Nem}) and effective microscopic (G_{eff}) symmetry groups can only take values within the corresponding sequences. $X=\{C_1,C_2,C_S,C_3,D_2,C_4,C_{2v},S_4,D_4,\mathrm{D}_3,C_{3h},C_{3v},D_6,D_{3h},C_{4v},O,D_{2d},D_\infty,\}$, $Y=\{C_i,C_{2h},D_{2h},C_{2v},S_6,D_{4h},D_{3d},O_h,D_{\infty h}\}$, $Z=\{C_1,C_2,D_2,C_3,D_3,C_4,D_4,D_\infty\}$, $B=\{C_i,C_{2h},S_6,T_h,C_{\infty h}\}$, $A=\{C_1,C_2,C_S,C_3,C_{2v},C_{3v},C_{3h},S_4,D_{3h},T_d,C_{\infty v}\}$ and $C=\{C_1,C_2,C_3,T,D_\infty\}$.

Γ	d_Γ	n_Γ	$\bar{a}=0$	$\bar{a}=1$	$\bar{a}=2$	$\bar{a}=3$
Vector Γ_1	3	2	SO(3)	C_∞	C_1	—
2-tensor Γ_2	5	2	SO(3)	D_∞, D_2	C_2, C_1	—
3-tensor Γ_3	7	1	SO(3)	C	—	—
4-tensor Γ_4	9	1	SO(3)	Z	—	—
Polar vector Γ_1^-	3	3	O(3)	$C_{\infty v}$	C_S	C_1
Axial vector Γ_1^+	3	2	O(3)	$C_{\infty h}$	C_i	—
Odd 2-tensor Γ_2^-	5	2	O(3)	D_∞, D_{2d}	C_2, C_1	—
Even 2-tensor Γ_2^+	5	2	O(3)	$D_{\infty h}$, D_{2h}	C_{2h}, C_i	—
Odd 3-tensor Γ_3^-	7	1	O(3)	A	—	—
Even 3-tensor Γ_3^+	7	1	O(3)	B	—	—
odd 4-tensor Γ_4^-	9	1	O(3)	X	—	—
Even 4-tensor Γ_4^+	9	1	O(3)	Y	—	—

ordered phases. We are going to consider now the possibilities corresponding to all the molecular groups. In the general case the distribution P reads at the first harmonic approximation

$$P(\alpha,\beta,\gamma,\sigma)=\frac{1}{8\pi^2}\{1+\vec{\mathrm{U}}_\sigma\,.\,\vec{\mathrm{I}}(\alpha,\beta,\gamma)+\vec{\mathrm{V}}_\sigma\cdot\vec{\mathrm{J}}(\alpha,\beta,\gamma)+\vec{\mathrm{W}}_\sigma\cdot\vec{\mathrm{K}}(\alpha,\beta,\gamma)\},\tag{16}$$

where the Cartesian components of the three basic vectors,

$$\vec{\mathrm{I}}=(\cos\beta\cos\alpha\cos\gamma-\sin\alpha\sin\gamma,\cos\beta\cos\alpha\sin\gamma+\sin\alpha\cos\gamma,\sin\beta\cos\alpha),$$

$$\vec{\mathrm{J}}=(\cos\beta\sin\alpha\cos\gamma+\cos\alpha\sin\gamma,\cos\beta\sin\alpha\sin\gamma-\cos\alpha\cos\gamma,\sin\beta\sin\alpha),$$

$$\vec{\mathrm{K}}=(-\cos\alpha\sin\beta,\sin\alpha\sin\beta,\cos\beta),$$

are proportional to the nine Euler spherical functions $D^1_{mm'}$ appearing in the expansion (6). Consequently, the Cartesian components of the macroscopic vectors $\vec{U}_\pm$, $\vec{V}_\pm$, and $\vec{W}_\pm$, are proportional to the fluctuation coefficients $P^{1,\pm}_{mm'}$. The vectors $\vec{U}_+ + \vec{U}_-$, $\vec{V}_+ + \vec{V}_-$, and $\vec{W}_+ + \vec{W}_-$ transform as polar vectors $[\Gamma_1^-]$ while $\vec{U}_+ - \vec{U}_-$, $\vec{V}_+ - \vec{V}_-$, and $\vec{W}_+ - \vec{W}_-$ transform as axial vectors $[\Gamma_1^+]$. Thus, in achiral systems with triclinic molecules the extended order parameter consists of the three vectors $\vec{U}_+ + \vec{U}_-$, $\vec{V}_+ + \vec{V}_-$, and $\vec{W}_+ + \vec{W}_-$, while it consists of the full set of six vectors in chiral mixtures. However, the internal selection reduces these numbers when the molecular symmetry increases.

In the chiral case, one finds $n_\Gamma=2$ and the maximal SG sequence is then $\{\mathrm{SO}(3)^{\mathrm{ext}},C_\infty^{\mathrm{ext}},C_1^{\mathrm{ext}}\}$ (see third row of Table IV). In this case $n_0=n_0^+ + n_0^-$ for polar and axial vectors are equivalent in chiral systems, except for optically pure systems where $n_0=n_0^+=n_0^-$. Since $n_0=0$ for the apolar molecules with symmetries D_n^{int}, T^{int}, and O^{int} (because $n_0^+=n_0^-=0$ as one sees in Table I), the macroscopic polar order is then forbidden. Table I indicates also that no chiral molecule can lead to the conventional case ($n_0=1$) yielding the shorter sequence $\{\mathrm{SO}(3)^{\mathrm{ext}},C_\infty^{\mathrm{ext}}\}$. The fully-extended model ($n_0=2$) permitting the triclinic phase $[C_1^{\mathrm{ext}}]$ is realized for the molecular groups C_n^{int} ($n\geqslant 2$). The over-extended model is associated only with triclinic molecules $[C_1^{\mathrm{int}}]$. For optically pure systems, molecules with symmetry C_n^{int} yield the conventional model ($n_0=1$) whereas no molecule yields the fully-extended model.

In the achiral case $n_\Gamma=3$ and the maximal SG sequence is $\{\mathrm{O}(3)^{\mathrm{ext}},C_{\infty v}^{\mathrm{ext}},C_{\mathrm{s}}^{\mathrm{ext}},C_1^{\mathrm{ext}}\}$ (see sixth row of Table IV). C_{nh}^{int}, S_4^{int}, S_6^{int}, C_n^{int}, and C_s^{int} molecules lead to the conventional case ($n_0^-=1$ in Table I) yielding the sequence $\{\mathrm{O}(3)^{\mathrm{ext}},C_{\infty v}^{\mathrm{ext}}\}$. No molecule corresponds to the model $n_0=2$ associated with the sequence $\{\mathrm{O}(3)^{\mathrm{ext}},C_{\infty v}^{\mathrm{ext}},C_s^{\mathrm{ext}}\}$. The fully-extended model $n_0=3$ permitting the triclinic phase is realized only for the triclinic groups $C_{\mathrm{i}}^{\mathrm{int}}$ and C_1^{int}.

The previous polar models allow simple geometrical pictures of the SG sequences and group parametricities (Fig. 3). When all the vectors forming the extended order parameter are parallel, the phase is uniaxial and the symmetry is that of a single vector: $C_{\infty v}^{\mathrm{ext}}$ or C_∞^{ext}. A single vector is thus sufficient

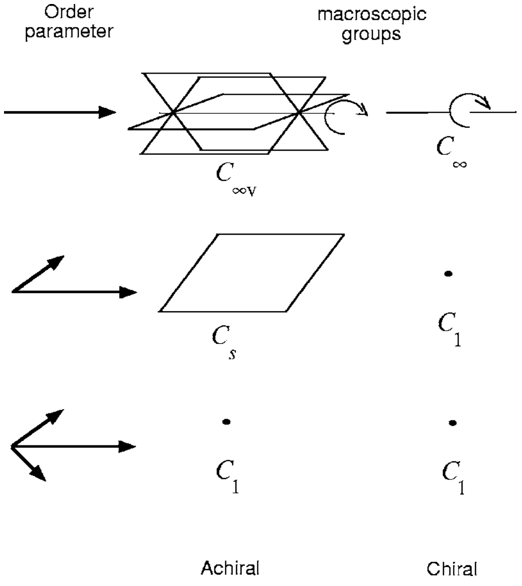

FIG. 3. Symmetry groups of the polar vector model. When the model contains a single vector, or several parallel vectors (first row) the macroscopic group G_{Nem} is $C_{\infty v}$ (achiral case) or C_∞ (chiral case). When the model contains two vectors, or many vectors in a single plane (second row), the symmetry of the achiral case is reduced to one mirror plane (C_S), or it becomes triclinic (C_1) in the chiral case. With three vectors (third row), the symmetry is triclinic in both cases.

to stabilize this phase. When all the vectors are coplanar but not parallel, the symmetry is that of the plane generated by these vectors (group which leaves invariant all the vectors of this plane): C_1^{ext} (chiral case) or C_s^{ext} (achiral case). At least two vectors are necessary. When three vectors are not coplanar in the achiral case, there is no symmetry that leaves them all invariant, and the triclinic phase $[C_1^{\mathrm{ext}}]$ appears.

The simplest complete phase diagrams corresponding to the previous models result from the minimization of the free energy F, which depends on the 1, 2, or 3 vectors forming under- or fully-extended order parameters. In models with a single vector $\vec{U}$, the free energy depends only on the quadratic invariant $\vec{U}\cdot\vec{U}$, hence it reads $F=\Phi(\vec{U}\cdot\vec{U})$ where Φ is a polynomial of order at least two. With two vectors one has Φ $(\vec{U}\cdot\vec{U},\vec{V}\cdot\vec{V},\vec{V}\cdot\vec{U})$, and Φ $(\vec{U}\cdot\vec{U},\vec{V}\cdot\vec{V},\vec{W}\cdot\vec{W},\vec{W}\cdot\vec{U},\vec{U}\cdot\vec{V},\vec{W}\cdot\vec{V})$ with three vectors. Examples of the corresponding phase diagrams can be found in Refs. [6,7].

Finally, in over-extended models the n_0-n_Γ additional (secondary) vectors are always "parallel" to the primary n_Γ vectors. The simplest free energy accounting for this situation reads

$$F=\Phi(\vec{U}_1,\ldots,\vec{U}_{n_\Gamma})+\sum_{i=n_\Gamma+1}^{n_0}\sum_{j=n_\Gamma+1}^{n_0}\alpha_{ij}\vec{U}_i\cdot\vec{U}_j+\sum_{j=1}^{n_\Gamma}\sum_{i=n_\Gamma+1}^{n_0}\beta_{ij}\vec{U}_i\cdot\vec{U}_j,$$

where Φ $(\vec{U}_1,\ldots,\vec{U}_{n_\Gamma})$ is the fourth-order free energy of the underlying fully-extended model. F being quadratic in the additional vectors $\vec{U}_j$, their equilibrium values are easily determined vs $\vec{U}_1,\ldots,\vec{U}_{n_\Gamma}$. Inserting these values in F provides then an effective free energy whose form coincides with that of the fully-extended model Φ (with renormalized phenomenological parameters). Let us notice that, within the phenomenological point of view, the splitting between the sets of primary ($j=1\rightarrow n_\Gamma$) and secondary ($i=n_\Gamma+1\rightarrow n_0$) vectors is arbitrary.

IV. EFFECTIVE MOLECULAR SYMMETRY

It is well known that in the conventional uniaxial-nematic phase rodlike molecules turn around their main axis so as to form effective cylindrically-symmetric microscopic objects. Three erroneous statements are currently put forward to describe this rotation: (i) the microscopic cylindrical symmetry is a consequence of the macroscopic symmetry of the uniaxial phase, (ii) the molecular rotation is a prerequisite for the formation of the uniaxial phase, and (iii) all the molecules giving rise to this phase exhibit this internal rotation. In fact, we have shown in Ref. [20] that, (i) the molecular cylindrical symmetry persists also in the orthorhombic biaxial phase, (ii) the molecular rotation is a consequence of the ordering process, not its cause, and (iii) low-symmetry molecules (e.g., orthorhombic bent-core mesogens) have an effective molecular symmetry lower than cylindrical, even in the uniaxial cylindrically-symmetric phase. We are going to generalize these results to unconventional nematics made with any type of molecules. Thus, we shall be able to determine, on using a simple method, the effective symmetry of a given molecule in any nematic phase stabilized after condensation of a tensor with arbitrary given rank. The rather subtle reasoning yielding this method mixes group theory and structural stability considerations that we shall describe qualitatively. The main ingredient of this reasoning is the "molecular class," which refines the notion of SG sequence introduced in the previous section. However, let us note (for not discouraging the readers) that the calculation of effective groups and the physical discussion of its consequences (carried out in the last part of this section) can be achieved without referring to the theoretical basis of the method.

In a given nematic phase the equilibrium distribution P is invariant under external as well as internal symmetries. They generate respectively the "macroscopic group" G_{Nem} and the "effective molecular group" G_{eff} of the system [20]. The actual molecular group G_{mol} is a subgroup of G_{eff}, which coincides with it only in the simplest cases. In the general case G_{eff} contains additional operations with respect to the actual symmetry of the molecules. The presence of such operations means that, in the corresponding statistical set, whenever one finds one molecule with a given orientation, one finds also one molecule turned by any additional transformation of G_{eff}. Moreover, each turned orientation has the same statistical weight as the initial orientation. This led us [20] to define a composite statistical object, referred to as the "subunit," which plays in P the role of an effective molecule with symmetry G_{eff} (in the case when $G_{\mathrm{mol}}=G_{\mathrm{eff}}$ the subunit coincides with one molecule). Strictly speaking, the subunit is a statistical subset containing $|G_{\text{eff}}|/|G_{\text{mol}}|$ molecules, built by applying to one of them all the elements of G_{eff}. Roughly speaking, the subunit is an average molecule, usually more symmetric than the actual molecule. Since P is invariant under G_{eff}, it is then more convenient to describe it as consisting of subunits. For instance, in the conventional uniaxial nematic with $G_{\text{mol}}=C_{3h}^{\text{int}}$, the effective group is cylindrically symmetric ($G_{\text{mol}}=D_{\infty h}^{\text{int}}$). Hence, one can describe this nematic state as a distribution of cylindrical subunits, approximately parallel to the macroscopic optic axis. In many physical respects this system behaves as an "ideal" nematic made with microscopic cylinders.

This section reveals how to determine the effective symmetry and analyzes the possible relationships between G_{mol}, G_{eff}, and G_{Nem}. Simple pictures of nematics suggest the following strongly and weakly "naive" relations:

$$G_{\text{mol}} = G_{\text{eff}} = G_{\text{Nem}} \quad (\text{strong}),$$

$$G_{\text{mol}} \subseteq G_{\text{eff}} \subseteq G_{\text{Nem}} \quad (\text{weak}), \tag{17}$$

which hold, for instance, in the isotropic phase or in nematics when all the molecules are parallel [in Eqs. (17), one does not distinguish internal from external operations]. The reality is not always so simple, as shown by the case of the conventional biaxial phase with tetragonal molecules [$G_{\text{mol}}=C_{4v}^{\text{int}}$]. Its macroscopic symmetry is D_{2h}^{ext} and the naive relationships (17) are obviously violated, since the *necessary condition* $G_{\text{mol}}[C_{4v}] \subseteq G_{\text{Nem}}[D_{2h}]$ is not satisfied. The molecules are then not parallel, otherwise the macroscopic symmetry would be also tetragonal [C_{4v}^{ext}]. We arrive thus at the important conclusions that, in general, (i) the molecular orientations remain nontrivially disordered, and (ii) this disorder yields distinct symmetry properties at distinct time and length scales: G_{Nem} at macroscopic scales, G_{mol} at microscopic and fast time scales, and G_{eff} at microscopic length scale and at time scale slower than the typical fluctuation time of one molecule.

In the following paragraphs we define the two main notions allowing us to calculate the effective groups, namely the internal SG sequence and the molecular classes. In the last paragraph we discuss the corresponding concrete possibilities and their physical interpretations that arise with the lowest-rank-tensor order parameters.

A. Internal SG sequence

Let us consider a nematic phase whose order parameter is a tensor of rank L_0. Close to the isotropic phase, the improper secondary order parameters with $L \neq L_0$ can be neglected, and $P \approx P_0 + P_{L_0}^{(\pm)}$. In order to determine the effective molecular group within this approximation, we are helped by the evident duality relating external and internal operations. Indeed, the reasoning which leads from the actual molecular group to the macroscopic symmetries of the SG sequence, summarized in Table IV, is analogous to that leading from the macroscopic symmetry to the possible effective molecular groups. This is because the P_{L_0} space has exactly the same structure with respect to internal as well as to external transformations. In particular, the SG sequences of stable macroscopic groups have internal analogs, which we shall denote by *internal SG sequences*. The internal sequences depend on $n_0'^{\pm}$, which on its turn depends on G_{Nem}. The minimal SG sequence={(S)O(3)} is obtained when $n_0'^{\pm}=0$ (i.e., for a macroscopic group belonging to the isotropic class), and the maximal SG sequence when $n_0'^{\pm}=n_\Gamma$ (triclinic class). The SG sequence associated with $n_0'^{\pm}$ provides all the possible internal symmetries of $P_{L_0}^{\pm}$ when it contains $n_0'^{\pm}$ internal tensors of rank L_0. Of course, if one takes into account the internal selection, then only those groups of the sequence containing G_{mol} can be, in fact, effective groups for this molecule.

The internal and external SG sequences coincide. Despite this apparent analogy, there remains a deep difference between the roles of external and internal groups. Indeed, only *the lowest effective group* in the internal sequence (i.e., the symmetry of the generic position in the order-parameter space) can be physically stable [because the free energy is not invariant under $\text{O}(3)^{\text{int}}$]. This provides the method for finding the effective molecular group:

In a phase with macroscopic symmetry G_{Nem}, G_{eff} is the smallest group in the internal SG sequence associated with $n_0'^{\pm}$ [see Eq. (13)] which, in addition, contains G_{mol}.

As an example, let us consider the standard nematic phases ($L_0=2+$). The SG sequences are {O(3), $D_{\infty h}$, D_{2h}, C_{2h}, and C_{i}} for $n_0^+ \geqslant 2$ (resp. $n_0'^+ \geqslant 2$), {O(3), $D_{\infty h}$, D_{2h}} for $n_0^+=1$, and {O(3)} for $n_0^+=0$. The possible stable nematic phases are thus uniaxial, biaxial, monoclinic, and triclinic whereas the possible effective groups are $D_{\infty h}^{\text{int}}$, D_{2h}^{int}, $C_{\infty h}^{\text{int}}$, and D_i^{int}.

—In the uniaxial phase [$G_{\text{Nem}}=D_{\infty h}^{\text{ext}}$], $n_0'^+=1$ and only two effective molecular groups are possible: $D_{\infty h}^{\text{int}}$ and D_{2h}^{int}. With tetragonal molecules [$G_{\text{mol}}=C_{4v}^{\text{int}}$], D_{2h}^{int} does not contain C_{4v}^{int} and the effective molecular group is cylindrically symmetric [$G_{\text{eff}}=D_{\infty h}^{\text{int}}$], even in the biaxial phase. With orthorhombic [$G_{\text{mol}}=C_{2v}^{\text{int}}$], monoclinic [$G_{\text{mol}}=C_s^{\text{int}}$], and triclinic [$G_{\text{mol}}=C_i^{\text{int}}$] molecules, the subunit is orthorhombic [$G_{\text{eff}}=D_{2h}^{\text{int}}$].

—In the biaxial, monoclinic, and triclinic phases, $n_0'^+ \geqslant 2$, and the four effective symmetries are possible. For tetragonal molecules, $D_{\infty h}^{\text{int}}$ contains C_{4v}^{int} and again $G_{\text{eff}}=D_{\infty h}^{\text{int}}$, but the monoclinic and triclinic phases cannot be stabilized ($n_0^+=1$). As stated above, the naive relation is violated since $G_{\text{Nem}}[D_{2h}] \subseteq G_{\text{eff}}[D_{\infty h}]$. With orthorhombic, monoclinic, and triclinic molecules, the three phases can be stabilized. With orthorhombic molecules one finds $G_{\text{eff}}=D_{2h}^{\text{int}}$, with monoclinic molecules one finds $G_{\text{eff}}=D_{2h}^{\text{int}}$, whereas for triclinic molecules the subunit remains triclinic [C_i^{int}].

One sees that the effective molecular group and the macroscopic group do not necessarily coincide, though they both always belong to the same maximal SG sequence. For instance, the uniaxial phase ($D_{\infty h}^{\text{ext}}$) can be composed of orthorhombic subunits (D_{2h}^{int}) (e.g., in bent-core systems [20] $G_{\text{mol}}=C_{2v}^{\text{int}}$), whereas the biaxial phase (D_{2h}^{ext}) can be composed with cylindrical subunits ($D_{\infty h}^{\text{int}}$) (e.g., with $G_{\text{mol}}=C_{4v}$).

B. Molecular classes

Fortunately, it is not necessary to work out the previous analysis with all the possible molecular groups separately.

Indeed, generalizing the preceding examples leads naturally to a repartition of the molecular groups in equivalence classes. By definition, such a class contains all the G_{mol} associated with a given value of $n_0^{\pm}$ and giving rise in addition to a common effective group (a more formal definition of the classes is given in Appendix B together with a method for computing them). This does not mean that the molecules in one given class exhibit the same effective group in all the stable phases. Indeed, the effective group may change when the system undergoes a phase transition changing its macroscopic symmetry, but it remains the same for all the molecules in the class for each phase. One sees immediately that the maximal SG sequence consists of the most symmetric groups of each class. The classes with $n_0^{\pm} < n_\Gamma$ cannot lead to the K phase. In this phase, all the molecules in any permitted class take the effective symmetry corresponding to the most symmetric group in this class. The molecules belonging to the same class behave thus as subunits having the symmetry of the maximal group in the class, yielding thereby the same measurable physical features. In more symmetric phases two differences arise. (i) More classes permit this phase. (ii) The SG sequence is restricted so that the least symmetric effective groups possible when $G_{\mathrm{Nem}} = K$ become impossible. The least symmetric classes have then the same effective group. All the groups in a class have the same $n_0^{\pm}$, but the converse statement is not necessarily true. For instance, for $L_0 = 3$, the groups having $n_0^{-} = 2$, namely C_{3h}^{int}, S_4^{int}, C_{3v}^{int}, and C_{2v}^{int} split into four distinct one-element classes. The SG sequences and molecular classes are represented in Appendix C for even and odd tensors with rank $\leqslant 4$.

In order to show how one proceeds to a complete classification, let us consider again the standard nematics with $L_0 = 2+$. Their five classes are represented in Fig. 4(a). In the isotropic class $n_0^{+} = 0$ and no such molecule can provoke the nematic ordering. All the groups with $n_0^{+} = 1$ belong to the class of uniaxial molecules [i.e., yielding $G_{\mathrm{eff}} = D_{\infty h}^{\mathrm{int}}$], namely $G_{\mathrm{mol}} = C_n^{\mathrm{int}}$, D_n^{int}, D_{nv}^{int}, D_{nh}^{int}, $C_{nv}^{\mathrm{int}}(n>2)$, D_{2d}^{int}, D_{3d}^{int}, S_4^{int}, and S_6^{int}, and lead to the *conventional model* [21,20] of nematics, which permits only the uniaxial and biaxial phases. Oppositely, the orthorhombic ($n_0^{\pm} = 2$), monoclinic ($n_0^{\pm} = 3$), and triclinic ($n_0^{\pm} = 5$) molecular classes yield the full set of stable phases. In the isotropic phase, all the classes merge into a single set for which the effective group is always O(3). The uniaxial phase is permitted by all the classes except the isotropic one. Since in this phase $n_0'^{+} = 1$, only uniaxial and orthorhombic subunits can exist. Therefore, the molecules in the uniaxial class have cylindrically-symmetric subunits ($G_{\mathrm{eff}} = D_{\infty h}^{\mathrm{int}}$) whereas the three other classes have orthorhombic subunits ($G_{\mathrm{eff}} = D_{2h}^{\mathrm{int}}$). In the biaxial phase one has $n_0'^{+} = 2$, so that the four effective symmetries can exist. Thus, the molecules in each possible class yield a subunit with the maximal element of the class. The monoclinic and triclinic phases can arise only with molecules in the three last classes. Since $n_0'^{+} > 2$ in these phases, all the effective symmetries can again exist and each remaining class yields a subunit with the maximal element of the class.

More generally, there is always one class corresponding to $n_0^{\pm} = 0$, and at least another class corresponding to $n_0^{\pm} = 1$. In the former class no order parameter is possible so that this

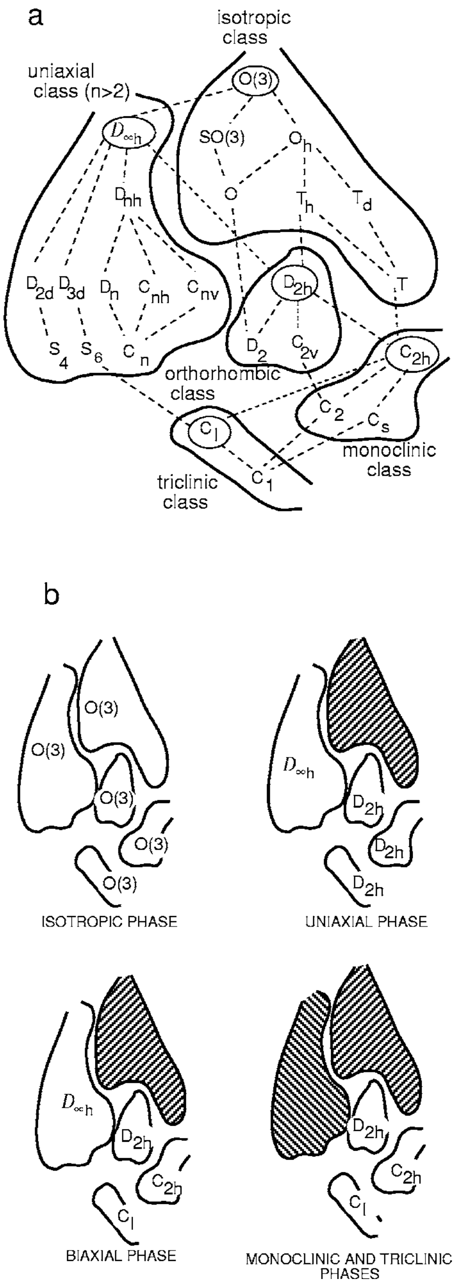

FIG. 4. (a) Classes of subgroups of O(3) when the order parameter is an even second-rank tensor. Some group-subgroup relationships are indicated by broken lines. The five groups of the maximal SG sequence [O(3), $D_{\infty h}$, D_{2h}, C_{2h}, and C_i] are inside ovals. The groups forming the five corresponding classes are surrounded by thick lines. When the symmetry of one molecule belongs to the isotropic class, no standard nematic can be stabilized. Molecules belonging to the class of uniaxial molecules can stabilize the uniaxial and biaxial conventional phases. Molecules belonging to the orthorhombic, monoclinic and triclinic classes can stabilize all the ordered standard phases [$\mathrm{O}(3)^{\mathrm{ext}}$, $D_{\infty h}^{\mathrm{ext}}$, D_{2h}^{ext}, C_{2h}^{ext}, and C_i^{ext}]. The noncrystallographic groups that have not been indicated on the figure all belong to the isotropic class. (b) Effective molecular groups associated with the molecules of each class. When the phase is impossible with the molecules of one class, the class is hatched in gray.

nematic transition cannot occur. We say that the corresponding molecules are forbidden or "isotropic" (since then the subunit remains spherical) for this tensor. In one of the latter classes the subunit is cylindrically symmetric so that we say this class is uniaxial. Let us stress that these definitions of isotropy and uniaxiality are not intrinsic since they depend on the rank and parity of the tensor order parameter. For instance, orthorhombic bent-core molecules with symmetry C_{2v}^{int} are spherical for axial vectors, uniaxial for polar vectors and biaxial for second-rank tensors. Finally there exists always one "triclinic" class containing only $\{C_1\}$ for odd tensors and equal to $\{C_1, C_i\}$ for even tensors.

Notice that, since the SG sequences are formed with the maximal elements of each class, the other groups in a given class can never be effective molecular groups. Correspondingly, the groups that are not in the SG sequence, can also never be the macroscopic symmetries of a stable phase. To summarize, one may apply the subgroup classification to internal as well as to external groups, which provides the following dual rules:

(i) Given the tensor order parameter, only the phases with macroscopic symmetry groups in the maximal (external) SG sequence can be stabilized. Furthermore, with triclinic molecules all the phases in the sequence have an extended domain of stability in the theoretical phase diagram. If the molecule is more symmetric, the lists of possible stable phases are restricted to the corresponding nonmaximal (external) SG sequences associated with the value of $n_0^{\pm}$ given by Eq. (10). The elements of a class, except the maximal element, can never be associated with a stable phase.

(ii) Similarly, any effective molecular group necessarily belongs to the maximal (internal) SG sequence. By varying G_{mol} in the triclinic K phase one stabilizes all the effective groups of this sequence. If the phase is more symmetric, the lists of possible effective groups are restricted to the nonmaximal (internal) SG sequences associated with the corresponding values of $n_0'^{\pm}$ in Eq. (13). The elements of a class, except the maximal element, can never be stable effective groups.

One sees that, in this respect, the main difference between internal and external selections lies in the fact that for generating the various groups in the SG sequences one has to change the external (thermodynamic) parameters for the macroscopic groups, while one has to change the molecular symmetries (chemical parameters) for the effective groups.

C. Symmetry enhancing and symmetry-suppressing fluctuations

The relationships between G_{mol}, G_{eff}, and G_{Nem} provide a useful insight into the symmetry and the nature of the nematic orientational fluctuations. Let us call "internal fluctuations" those that tend to increase the effective group with respect to the actual molecular symmetry. They are responsible on the formation of the subunit. However, this increase in the molecular symmetry does not exhaust the effects of the orientational disorder. The subunit orientation itself can fluctuate and G_{Nem} finally results from these fluctuations. Let us call "external fluctuations" those describing the orientational fluctuations of the subunit. They can be responsible on the enhancement as well as on the breakdown of the macroscopic symmetry with respect to G_{eff}. It is convenient, though quite arbitrary, to think of internal fluctuations as fast dynamical rotations (or jumps), and of external fluctuations as the "slow" spatial disorder of the resulting subunits.

Table V presents the effective molecular groups for uniaxial and biaxial standard and vector nematics. They exhibit five types of group relationship.

(1) The three groups identify with each other and the strongly naive relation, $G_{\text{mol}}=G_{\text{eff}}=G_{\text{Nem}}$, is satisfied. For polar vectors $[L_0=1]$, this happens with triclinic molecules $[G_{\text{mol}}=C_1^{\text{int}}]$ in the triclinic phase, with monoclinic molecules $[G_{\text{mol}}=C_s^{\text{int}}]$ in the biaxial phase, and with cylindrical molecules $[G_{\text{mol}}=C_{\infty v}^{\text{int}}]$ in the uniaxial phase. One may roughly picture such distributions by considering almost motionless parallel molecules. However, this parallelism is not necessary, e.g., in the standard lyotropic biaxial phase $[G_{\text{mol}}=G_{\text{eff}}=G_{\text{Nem}}=D_{2h}]$ the micelles are not parallel since they have six possibilities for aligning their three internal twofold axes with the three macroscopic axes. The resulting statistical set mixes the six corresponding molecular orientations [20]. More generally, a necessary condition for the strongly naive relation to hold for a given L_0, is that G_{mol} belongs to the maximal SG sequence of the fully-extended model. In this case the strongly-naive phase with $G_{\text{Nem}}=G_{\text{mol}}$ is always theoretically possible.

(2) The subunit is more symmetric than the molecule $[G_{\text{mol}}\subset G_{\text{eff}}=G_{\text{Nem}}]$. This happens for instance in the conventional uniaxial phase for tetragonal molecules $[C_{4v}\subset D_{\infty h}=D_{\infty h}]$. Internal fluctuations enhance the subunit symmetry and external fluctuations are qualitatively negligible (have neither symmetry-breaking nor symmetry-enhancing effects).

(3) In other cases one finds the converse situation: $[G_{\text{mol}}=G_{\text{eff}}\subset G_{\text{Nem}}]$. This happens, for instance, in the standard uniaxial phase for orthorhombic molecules $[D_{2h}=D_{2h}\subset D_{\infty h}]$. There are no internal fluctuations whereas external fluctuations enhance the macroscopic symmetry.

In the two previous cases both types of fluctuations lead to an increase of the symmetry. In the first case (uniaxial conventional phase with $G_{\text{mol}}=C_{4v}^{\text{int}}$) the internal fluctuations are associated with an isotropic rotation of the molecule about its fourfold symmetry axis, creating a cylindrical subunit. The subunits are almost parallel and determine the symmetry of the phase. In the second case (uniaxial conventional phase with $G_{\text{mol}}=D_{2h}^{\text{int}}$) the molecules fail to reach an effective cylindrical symmetry because there is not one preferred twofold axis singled out in D_{2h}^{int}.

(4) The case of a strict inclusion relation $[G_{\text{mol}}\subset G_{\text{eff}}\subset G_{\text{Nem}}]$ happens in the standard uniaxial phase for monoclinic molecules $[C_2\subset D_{2h}\subset D_{\infty h}]$. The molecular twofold axis can then be either parallel or perpendicular to the macroscopic optic axis.

Non-naive situations arise when the condition $G_{\text{mol}}\subseteq G_{\text{Nem}}$ is not satisfied. The fourteen such cases found in Table V combine internal *symmetry-enhancing* and external *symmetry-suppressing* fluctuations. For instance, in the triclinic polar phase of a chiral mixture formed with mono-

TABLE V. Effective molecular symmetries in the nematic phases induced by various tensors $\Gamma_L^{(\pm)}$ vs the molecular groups (G_{mol}) permitting these tensors. (a): Polar vector Γ_1^- in an achiral system. (b): Vector Γ_1 in a chiral mixture. (c): Vector Γ_1 in an optically pure chiral system. (d): Even second-rank tensor Γ_2^+. (e): Second-rank tensor Γ_2 in a chiral mixture. (f): Second-rank tensor Γ_2 in an optically pure chiral system.

a	$G_{\mathrm{Nem}}=C_{\infty v}$	$G_{\mathrm{Nem}}=C_S$	$G_{\mathrm{Nem}}=C_1$	
$G_{\mathrm{mol}}=C_1$	$C_{\infty v}$	C_S	C_1	
$G_{\mathrm{mol}}=C_S$	$C_{\infty v}$	C_S		
$G_{\mathrm{mol}}=C_{nv},C_n$	$C_{\infty v}$			
b	$G_{\mathrm{Nem}}=C_{\infty}$	$G_{\mathrm{Nem}}=C_1$		
$G_{\mathrm{mol}}=C_1$	C_1	C_1		
$G_{\mathrm{mol}}=C_n$	C_{∞}	C_{∞}		
c	$G_{\mathrm{Nem}}=C_{\infty}$	$G_{\mathrm{Nem}}=C_1$		
$G_{\mathrm{mol}}=C_1$	C_1	C_1		
$G_{\mathrm{mol}}=C_n$	C_{∞}			
d	$G_{\mathrm{Nem}}=D_{\infty h}$	$G_{\mathrm{Nem}}=D_{2h}$	$G_{\mathrm{Nem}}=C_{2h}$	$G_{\mathrm{Nem}}=C_i$
$G_{\mathrm{mol}}=C_1,C_i$	D_{2h}	C_i	C_i	C_i
$G_{\mathrm{mol}}=C_2,C_S$	D_{2h}	C_{2h}	C_{2h}	C_{2h}
$G_{\mathrm{mol}}=D_2,D_{2h}$	D_{2h}	D_{2h}	D_{2h}	D_{2h}
$C_{n(v,h)},D_{n(h)},D_{2d},D_{3d},S_4,S_6$	$D_{\infty h}$	$D_{\infty h}$		
e	$G_{\mathrm{Nem}}=D_{\infty}$	$G_{\mathrm{Nem}}=D_2$	$G_{\mathrm{Nem}}=C_2$	$G_{\mathrm{Nem}}=C_1$
$G_{\mathrm{mol}}=C_1$	C_1	C_1	C_1	C_1
$G_{\mathrm{mol}}=C_2$	C_2	C_2	C_2	C_2
$G_{\mathrm{mol}}=D_2$	D_2	D_2	D_2	D_2
$G_{\mathrm{mol}}=C_n,D_n$	D_{∞}	D_{∞}	D_{∞}	D_{∞}
f	$G_{\mathrm{Nem}}=D_{\infty}$	$G_{\mathrm{Nem}}=D_2$	$G_{\mathrm{Nem}}=C_2$	$G_{\mathrm{Nem}}=C_1$
$G_{\mathrm{mol}}=C_1$	D_2	C_1	C_1	C_1
$G_{\mathrm{mol}}=C_2$	D_2	C_2	C_2	C_2
$G_{\mathrm{mol}}=D_2$	D_2	D_2	D_2	D_2
$G_{\mathrm{mol}}=C_n,D_n$	D_{∞}	D_{∞}		

clinic molecules $[G_{\mathrm{mol}}=C_2^{\mathrm{int}}]$, the subunit is cylindrically symmetric $[G_{\mathrm{eff}}=C_{\infty}^{\mathrm{int}}]$ but the anisotropy of its fluctuations suppresses the macroscopic uniaxiality. In all cases one gets

$$G_{\mathrm{mol}} \subset G_{\mathrm{eff}} \supset G_{\mathrm{Nem}}. \tag{18}$$

Table V presents two types of such non-naive situations:

(5) The example above of a triclinic polar phase corresponds to the relation $G_{\mathrm{Nem}} \subset G_{\mathrm{mol}} \subset G_{\mathrm{eff}}$.

(6) In six cases there is no inclusion relationship between G_{mol} and G_{Nem}. This happens, for instance, in the standard biaxial nematic phase with $G_{\mathrm{mol}}=C_{4v}^{\mathrm{int}}$ $[G_{\mathrm{eff}}=D_{\infty h}^{\mathrm{int}}, G_{\mathrm{Nem}}=D_{2h}^{\mathrm{ext}}]$. The corresponding naivety breakdown is due to the frustration between molecular and macroscopic groups, which forces symmetry-suppressing fluctuations.

Nevertheless, the fact that one finds then $G_{\mathrm{Nem}} \subset G_{\mathrm{eff}}$ is possibly due to the approximation neglecting improper secondary order parameters [i.e., non-(external) symmetry-breaking higher harmonics (with $L > L_0$) in the expansion of P]. This possibility is justified when the Isotropic → Nematic transition is weakly first order so that the order parameter is not saturated, at least close to the transition line. In the case of a strongly first-order transition, several higher harmonics play a role in the qualitative behavior of the fluctuations, and the effective group depends on the behavior of each P_L, and not only on the primary P_{L_0}. The true effective molecular group is the intersection of the effective groups obtained, by the external selection, for all primary and secondary P_L giving non-negligible contributions to the equilibrium distribution function.

In Appendix C we present the classes and sequences for tensors with rank ⩽4 in achiral systems. They permit anybody to determine immediately the stable phases and the corresponding effective symmetry groups for all the molecules. For tensor of higher ranks, or in chiral systems, the same procedure can be achieved after the (slightly longer) preliminary calculation of the classes, group parametricities and SG-sequences, as described in Appendix B.

V. DISCUSSION

A. Molecular tensors and fluctuation coefficients

In the previous sections, the nematic order parameter has been defined in a rather abstract way as a collection of coefficients arising in the distribution function $P(\omega,\sigma)$. Although such coefficients are familiar in the nematic science, a more intuitive approach in terms of molecular physical quantities (e.g., the molecular polarization) is also useful. In this approach we consider the thermodynamic averaged values of molecular tensors. Indeed, we shall show that all the distribution coefficients can be expressed as combinations of such tensor components (and reciprocally), so that one can deal equivalently with the statistic representation of the nematic state or with its mean-molecular-tensor representation. Moreover, this equivalence permits us to reply to an elementary objection concerning our theory, which deeply relies on the numbering of independent tensors involved in the condensation process: When one considers additional macroscopic mean tensors, such as the mean polarization or susceptibility, the number of tensors can increase unboundedly and the finite tensor multiplicities used in the previous sections become meaningless. This objection fails naturally when one remarks that all these additional tensors are linear combinations of the fluctuations coefficients and, hence, cannot be considered as independent degrees of freedom. Expressing the full theory on using either statistical or mean tensors is a matter of convenience. All the results presented above can be obtained along both ways. In fact, the two presentations are related to two types of classical experiments. On the one hand, the interpretation of x ray, NMR, or Raman spectra lead to using the statistical degrees of freedom, whereas, on the other hand, electric, magnetic, optic, etc. experiments give results in terms of mean molecular tensors.

Let us first introduce a physical interpretation of the fluctuation coefficients $P_{mm'}^{L,\pm}$ in terms of molecular properties, which completes the statistical interpretation given by Eqs. (7). Each molecular tensor can be expanded onto a tensor basis, which is defined in analogy with the 3 *geometrical* molecular vectors $\mathbf{I},\mathbf{J},\mathbf{K}$ (see Appendix D). Let $\Omega_{(m)}^{L+}$ and $\Omega_{(m)}^{L-}$ $(-L\leqslant m\leqslant L)$ be the corresponding complex bases of even and odd tensors. Similarly, $\mathbf{i},\mathbf{j},\mathbf{k}$ denotes the laboratory basis of polar vectors and $\{\omega_{(m)}^{L\pm}\}$ the laboratory bases of Lth-rank tensors. Each basis molecular tensor $\Omega_{(m)}^{L\pm}$ turns with the molecule, so that its $2L+1$ components $\Omega_{(m)}^{L\pm,p}$ on the laboratory basis $\omega_{(p)}^{L\pm}$ can fluctuate. Their statistical mean values $\langle\Omega_{(m)}^{L\pm,p}\rangle$ are related to the fluctuation coefficients by [see Eq. (D11) in Appendix D]

$$\langle\Omega_{(m)}^{L\pm,p}\rangle=\frac{16\pi^2}{2L+1}P_{pm}^{L\pm*}. \tag{19}$$

Every physical tensor carried by the molecule is a linear combination of the $\Omega_{(m)}^{L\pm}$ (e.g., the molecular polarization reads $\vec{p}_0=p_x\mathbf{I}+p_y\mathbf{J}+p_z\mathbf{K}$). Its corresponding components are constant (they depend on the Hamiltonian of the molecule but almost not on the thermodynamic conditions) so that its fluctuations are completely described by Eq. (19). Accordingly, no new thermodynamic degree of freedom is introduced by considering physical molecular tensors, with respect to the set of parameters $\langle\Omega_{(m)}^{L\pm,p}\rangle\propto P_{pm}^{L,\pm}$.

Equation (19) provides a more intuitive interpretation of the selection rules than that given by Eq. (7). Indeed, the number of independent tensors that a given molecule can physically carry is actually smaller than $2L+1$ and depends on its symmetry (e.g., a uniaxial molecule can carry a single physical polar vector parallel to its rotation axis, otherwise its symmetry would break below uniaxiality). Equation (19) states then that the list of independent molecular physical tensors permitted by the molecular symmetry coincides with the list of fluctuation tensors permitted by the internal selection rule.

For instance, in the case when the order parameter is a polar vector and the molecule is vectorially uniaxial (e.g., $G_{\mathrm{mol}}=C_{nv}$ with $n\geqslant 2$), one finds from Eq. (19) that the internal selection rule yields $\langle\mathbf{I}\rangle=\langle\mathbf{J}\rangle=0$. This result is the macroscopic counterpart of the absence of physical vectors parallel to $\mathbf{I}$ or $\mathbf{J}$ on such molecules. On the other hand, according to the external selection in the uniaxial phase, the macroscopic symmetry $C_{\infty v}^{\mathrm{ext}}$ cancels the components $\langle K_X\rangle$ and $\langle K_y\rangle$ of the remaining macroscopic vector $\langle\mathbf{K}\rangle$. In other words, internal fluctuations first create cylindrical subunits without modifying the molecular polarization $\vec{p}_0=p_0\mathbf{K}$, for it is parallel to the molecular rotation axis. External fluctuations rotate then the subunit about the macroscopic optic axis, reducing the mean polarization $\vec{P}/n=p_0\langle K_z\rangle\mathbf{k}$ with respect to $\vec{p}_0$ $(\langle K_z\rangle\propto P_{00}^{1,-*})$. At saturation $\langle K_z\rangle=1$ so that measuring $\vec{\mathrm{P}}$ provides also the magnitude of $\vec{p}_0$. Conversely, when one knows p_0, measuring $\vec{\mathrm{P}}$ provides $\langle K_z\rangle$ and, hence, the primary first harmonic $P_1=3\langle K_z\rangle\sigma D_{00}^1/16\pi^2$ of the orientation distribution $P(\alpha,\beta,\gamma,\sigma)$.

Thus, beside classical diffusion experiments [21] Eq. (19) provides an alternative macroscopic method for measuring the fluctuation coefficients. For instance, in standard nematics $[L_0=2+]$ measuring the five components of the dielectric susceptibility (even second-rank tensor) at five different frequencies permit to determine the twenty-five relevant coefficients $P_{mm'}^{2,+}$ appearing in the first nonzero harmonics of the distribution. Along this line, an explicit construction of P_2 is presented in Ref. [20] for bent-core molecules. In this case, due to the orthorhombic molecular symmetry (yielding $n_0^+=2$ from the internal selection), only two frequencies are necessary.

To summarize, instead of the fluctuation function P_{L_0}, the order parameter of the Isotropic→Nematic transition can be alternatively defined as a set of measurable mean physical molecular tensors. Indeed, Eq. (19) shows the two approaches are equivalent. In this respect, we shall discuss hereafter unconventional models corresponding to $L_0=3-$.

B. Third-rank tensor model

Lubensky and Radzihovsky [28] have proposed a model of unconventional nematic phases in bent-core systems. It involves one polar vector, one (even) second-rank tensor and one (odd) third-rank tensor as order parameters, which are proportional to the macroscopic averages of the first, second, and third mass moments of a bent-core molecule [$G_{\mathrm{mol}} = C_{2v}^{\mathrm{int}}$]. This model yields a rich polymorphism of complex phases with uniaxial, tetrahedral, orthorhombic, rhombic, and monoclinic symmetries. Some of these phases can arise after the spontaneous onset of the third-rank tensor alone (which in these phases is thus the *primary* order parameter). In this case, the list of stable phases has been determined by Bul'bich [8], giving (using our terminology) the following maximal SG sequence: C_1, C_2, C_S, C_3, C_{2v}, C_{3v}, C_{3h}, S_4, D_{3h}, T_d, $C_{\infty v}$ (we have corrected the list of Ref. [8] by suppressing the group D_{2d} because it belongs in fact to the class of T_d). The corresponding classes are indicated in Appendix C, Fig. 7. It can be seen that in the case of the bent-core symmetry group, C_{2v}^{int}, the tensor multiplicity $n_0^- = 2$, so that the two-tensor model is necessary to describe correctly the orientational fluctuations while the model [28] has a single tensor.

Let us now describe the molecular physical tensors permitted on bent-core molecules. The internal selection applied to such molecules permits one molecular polar vector ($\Omega_{(0)}^{1-} = \mathbf{K}$) along OZ (parallel to the twofold axis) and forbids axial vectors. Two even ($\Omega_{(0)}^{2+}, \Omega_{(2)}^{2+} + \Omega_{(-2)}^{2+}$) and one odd ($\Omega_{(2)}^{2+} - \Omega_{(-2)}^{2+}$) second-rank tensors, and one even ($\Omega_{(2)}^{3+} + \Omega_{(-2)}^{3+}$) and two odd ($\Omega_{(0)}^{3-}, \Omega_{(2)}^{3-} - \Omega_{(-2)}^{3-}$) third-rank tensors are also permitted in the molecule. For instance, the third mass moment used in Ref. [28] can be expressed as the linear combination $\mathrm{m}_0 \Omega_{(0)}^{3-} + m_2(\Omega_{(2)}^{3-} - \Omega_{(-2)}^{3-})$, where m_0 and m_2 are constant characteristics of the molecule. Accordingly, a complete description of the fluctuations needs at least one additional even second-rank and, as stated above, one additional odd third-rank tensors with respect to the model [28]. On the other hand, we have shown (see Appendixes B and C) that all the phases occurring in the third-rank model can be stabilized with a single tensor (i.e., $n_\Gamma = 1$). Thus, although the one-third-rank tensor approach of Ref. [28] is not complete at the viewpoint of fluctuations, it provides a fully-extended thermodynamic model.

Let us now determine the form of the distribution function and some characteristic properties of the tetrahedral and trigonal phases T and $V+3$ predicted by Lubensky and Radzihovsky. The external selection in the tetrahedral T phase [$G_{\mathrm{Nem}} = T_d^{\mathrm{ext}}$] forbids all the macroscopic vectors, the second-rank and the even macroscopic tensors, whereas it permits a single macroscopic odd third-rank tensor ($\omega_{(2)}^{3-} - \omega_{(-2)}^{3-}$). Taking also into account the internal selection, one sees it remains only two odd ($\langle \Omega_{(0)}^{3-} \rangle$ and $\langle \Omega_{(2)}^{3-} - \Omega_{(-2)}^{3-} \rangle$) and one even ($\langle \Omega_{(2)}^{3+} + \Omega_{(-2)}^{3+} \rangle$) order parameters of rank smaller than 4. After setting the threefold axes of T along the diagonal directions of the laboratory frame, one finds: $\langle \Omega_{(0)}^{3-} \rangle = T_0(\omega_{(2)}^{3-} - \omega_{(-2)}^{3-})$ and $\langle \Omega_{(2)}^{3-} - \Omega_{(-2)}^{3-} \rangle = T_2(\omega_{(2)}^{3-} - \omega_{(-2)}^{3-})$. We have shown above that the knowledge of the macroscopic mean tensor values is equivalent to the knowledge of the corresponding harmonics in the distribution function P. Hence, within the third-harmonic approximation the equilibrium distribution reads

$$P = \frac{1}{8\pi^3} + \frac{7\sigma}{16\pi^2}\{\mathrm{T}_2(D_{22}^3 + D_{-2-2}^3 - D_{2-2}^3 - D_{-22}^3) + \mathrm{T}_0(D_{20}^3 - D_{-20}^3)\}. \tag{20}$$

T_0 and T_2 are the two effective components of the order parameter, which vary freely with temperature in T. Since the actual molecular symmetry C_{2v}^{int} belongs to the SG sequence associated with a single odd third-rank tensor (see Appendix C, Fig. 7, Table IV, and Ref. [8]), one has $G_{\mathrm{eff}} = G_{\mathrm{mol}}$. This shows that phase T is weakly naïve, with the following relationships between its characteristic groups: $G_{\mathrm{mol}} = G_{\mathrm{eff}} = C_{2v} \subset T_d = G_{\mathrm{Nem}}$.

Let us now deal with the trigonal subphase of T denoted by $V+3$ in [28]. This phase is non-naive since there is no group-subgroup relationship between $G_{\mathrm{mol}} = G_{\mathrm{eff}} = C_{2v}^{\mathrm{int}}$ and $G_{\mathrm{Nem}} = C_{3v}^{\mathrm{ext}}$. Its macroscopic symmetry permits one macroscopic polar vector, one even second-rank tensor, one even and two odd third-rank tensors. Thus, Eq. (20) provides again the even third harmonics of P, whereas additional vector, second-rank, and odd third-rank terms give its symmetry-breaking contributions with respect to its expression in the tetrahedral phase T. The vector and the axis of the uniaxial optic tensor are directed along the threefold rotation axis of C_{3v}^{ext} (say $\mathbf{i}+\mathbf{j}+\mathbf{k}$). They are given by

$$\langle \Omega_{(0)}^{1-} \rangle = p\{\omega_{(0)}^{1-} + e^{i\pi/4}\omega_{(1)}^{1-} - e^{-i\pi/4}\omega_{(-1)}^{1-}\},$$

$$\langle \Omega_{(2)}^{2+} - \Omega_{(-2)}^{2+} \rangle = \mathrm{C}\{\, i\omega_{(-2)}^{2+} - i\omega_{(2)}^{2+}) + (i-1)\omega_{(1)}^{2+} + (1+\mathrm{i})\omega_{(-1)}^{2+}\},$$

whereas the odd third-rank tensors read

$$\langle \Omega_{(0)}^{3-} \rangle = T_0\omega + T_0'\omega',$$

$$\langle \Omega_{(2)}^{3-} - \Omega_{(-2)}^{3-} \rangle = T_2\omega + T_0'\omega',$$

where

$$\omega = \omega_{(2)}^{3-} - \omega_{(-2)}^{3-},$$

$$\omega' = \sqrt{5}(1-\mathrm{i})\omega_{(3)}^{3-} - \sqrt{3}\omega_{(1)}^{3-} + 8\omega_{(0)}^{3-} + \sqrt{3}\omega_{(-1)}^{3-} - \sqrt{5}(1+\mathrm{i})\omega_{(-3)}^{3-}.$$

Finally, the even third-rank tensor takes the form

$$\langle \Omega_{(2)}^{3+} + \Omega_{(-2\_)}^{3+} \rangle = E\{\omega_{(2)}^{3+} - \omega_{(-2)}^{3+}\}.$$

These expressions together with Eq. (20) provide the selected expansion of P up to the third harmonics vs seven fluctuation coefficients. T_0 and T_2 exist already in the T phase whereas p, C, T_0', T_2', and E form the order parameters associated with the $T \rightarrow V+3$ first-order transition. Let us stress that each of them alone is sufficient to break completely the tetrahedral symmetry.

Let us finally note that in Ref. [28] a number of phases are lacking with respect to the maximal SG sequence of the third-rank tensor, namely those with the macroscopic groups: C_1^{ext}, C_3^{ext}, C_{3h}^{ext}, and S_4^{ext}. This result is puzzling since we have shown that the one-tensor model is fully extended, so that the full set of phases should be stabilized. However, to obtain a phase diagram in which all the phases have extended domains of stability, the free energy expansion of the fully-extended model must, in addition, take into account high-degree polynomials of the tensor components. More precisely, in this model the free energy actually depends on six basic invariant polynomials, the highest invariant being of the sixth degree. Thus, the free energy should be expanded at least to the twelfth degree for stabilizing the least-symmetric phases of the SG sequence. Since the free energy used in Ref. [28] is expanded only up to the fourth degree, the stability domains of some low-symmetry phases collapse within this approximation.

C. Conclusion

Taking into account the molecular symmetry within the phenomenological approach to the nematic phases permits a complete description of the orientation fluctuations together with a rigorous construction of the thermodynamic behaviors at the transition. More particularly, the list of stable phases, and hence the phase diagrams, are strongly dependent of the molecular symmetry. We have shown how to determine this list, and how to build the corresponding Landau model (order-parameter space+invariant polynomials), vs the rank and parity of the tensor order parameter, on the one hand, and the molecular symmetry, on the other hand. This yields a larger variety of models and possible behaviors than what is expected in the conventional theory, which is valid only in a limited class of molecular symmetries. Indeed, in addition to the new phases, stabilized when the internal groups permit several tensors, each phase can appear under various qualitatively distinct "states." Indeed, the physical properties of a nematic system depend not only on its macroscopic group (which defines the phase) but also on the effective molecular symmetry. Accordingly, in a given nematic phase, systems made with molecules that do not belong to the same class correspond to states exhibiting qualitatively distinct physical properties. They can be experimentally distinguished provided the experimental set up is sensitive to molecular properties averaged at the appropriate time and space scales.

This diversity is accounted for by only three integer numbers: The tensor multiplicities $n_0^{\pm}$ and $n_0'^{\pm}$, on the one hand, and the order-parameter multiplicity n_Γ, on the other hand, which can be computed by simple algorithmic procedures. Knowing these numbers is sufficient to determine the list of stable phases and the possible effective molecular symmetries resulting from a given model. In this respect our work provides the building rules on which relies any phenomenological model of nematics, which can be easily applied to any type of tensor with any molecular symmetry. So, we have not really attempted, as in our previous papers [7,20] to work out extensively concrete examples. Instead, we have illustrated our methods by superficially discussing some aspects of the classical vector, second-rank and third-rank models. Among the general results demonstrated here, let us note the fact that the effective molecular symmetries and the possible macroscopic symmetries associated with a given tensor belong to a common class of groups, namely the maximal SG sequence. However, these two groups do not necessarily coincide in a given system, and the determination of the subunit symmetry needs the molecular classification together with the tensor and order-parameter multiplicities. For instance, the fact that the cylindrically-symmetric subunit in conventional nematics is stable in a limited class of molecules, and that it must be replaced with orthorhombic, monoclinic or triclinic subunits in other cases, is an important and not completely trivial result.

Nematic phases associated with tensors of rank $L_0 \neq 2$ have never been unambiguously reported. Nevertheless, clarifying the properties of such tensors is not only of prospective or academic interest. Indeed, various such tensors appear as secondary order parameters in the rich family of smectic and columnar structures, in which they describe the local orientation and fluctuations of the molecules. For instance, the phase denoted by SmC_P [29] (or R phase in Ref. [30]) in bent-core systems presents a puzzling situation in which the local point groups are C_S, C_{2v}, and C_{2h} according to the position considered in the structure. The position C_{2h} is particularly intriguing because there is no group-subgroup relationship between C_{2h} and the molecular symmetry C_{2v}. The orientational order parameter consists then of one second-rank tensor, one axial and one polar vector [30] varying with position, and the C_{2h} position is obviously nonnaive.

Reliable experimental data concerning unconventional nematics are rather rare. We have already discussed those concerning (possible) polar nematics (L_0=1−, $n_0^-=2$) in polyester compounds [7] and classical (L_0=2+, $n_0^+=2$) bent-core nematic phases [20]. Let us note that almost all the molecules forming classical nematic phases are in fact unconventional, since their symmetry groups seldom belong to the uniaxial class. However, their unconventional character should be weak (i.e., the additional tensor equilibrium values are much smaller than the main tensor) due to the fact that rodlike or disklike molecules have usually an approximate cylindrical symmetry. However, we have shown that qualitative differences emerge with respect to actually conventional molecules. Careful experiments sensitive to the effective molecular symmetry must evidence this unconventional character, as for instance the ordering of the small molecular axes in the uniaxial phase (since the internal cylindrical rotation does not hold for such molecules). Moreover, in the continuously increasing new families of mesogens, there exist surely many that are not approximately cylindrically symmetric and should display strong unconventional properties even in the classical uniaxial phase (as orthorhombic micelles and bent-core molecules).

Although we have only studied chemically pure systems, our approach extends naturally to mixtures on making P dependent of an additional index associated with the molecular species. It extends also easily to magnetic complex fluids (see, e.g., Ref. [31]) by introducing a new index changing its sign under time-reversal symmetry (as σ changes under the space inversion I). In order to account for flexible molecules, additional internal degrees of freedom must also appear in P. However, in this case the molecular configurations might also undergo symmetry-breaking transformations, which would require a wide deepening of the theory. Moreover, many nematogenic molecules have more than one conformer, some of them with no symmetry. Finally in systems formed with macromolecules, it might be necessary to include new types of molecular symmetries. For instance, in many respects DNA molecules can be considered as one-dimensional infinite objects with an approximate internal helical symmetry, which is not accounted for by a point group.

APPENDIX A

In order to characterize quantitatively the orientation distribution of a mixture consisting of right-handed and left-handed rigid molecules of the same type, let us first rigidly tie a set of orthogonal frames on each molecule in the system. The symmetry group of a chiral molecule $G_{\mathrm{mol}}=\{g_1=e,g_2,\ldots,g_g\}$ contains g rotations. Thus, for consistency one ties g right-handed frames on each right-handed molecule. The orientation of the first frame, denoted by $\Sigma_1=\{\mathbf{I},\mathbf{J},\mathbf{K}\}$, is chosen arbitrarily in the molecule. The other frames tied to the same molecule, denoted by $\Sigma_q=g_q\Sigma_1$ $(q=2,\ldots,g)$, are turned with respect to Σ_1 by the operations g_q of G_{mol}. Likewise, one ties g left-handed frames on each left-handed molecule: $\Sigma_1'=\{-\mathbf{I},-\mathbf{J},-\mathbf{K}\}$, $\Sigma_2'=g_2\Sigma_1'$, etc. For an arbitrary orientation of the molecule in space, the frames orientations are described by g rotation matrices R_ω (or equivalently by their Euler angles $\omega=\{\alpha,\beta,\gamma\}$) which transform the laboratory frame $\Sigma_0=\{\mathbf{i},\mathbf{j},\mathbf{k}\}$ (resp. $\Sigma_0'=\{-\mathbf{i},-\mathbf{j},-\mathbf{k}\}$) into the molecular frames $\Sigma_q=R_\omega\Sigma_0$ (resp. $\Sigma_q'=R_\omega\Sigma_0'$).

In a mixture consisting of $N_0=N_L+N_R$ molecules, one denotes by N_L and N_R the numbers of left- and right-handed molecules respectively. Let $N(\omega,\sigma)d\omega$ $(d\omega=\sin\beta d\alpha d\beta d\gamma)$ be the number of frames characterized by the handedness σ ($\sigma=+1$ or -1 for right- and left-handed frames respectively) and the orientation R_ω. The corresponding statistical distribution $P(\omega,\sigma)=N(\omega,\sigma)/N_0g$ is related to the concentration of left-handed molecules $C_L=N_L/N_0=\iiint P(\omega,-)d\omega$ and to that of right-handed molecules $C_R=N_R/N_0=\iiint P(\omega,+1)d\omega$ ($C_R+C_L=1$ and $C_R=C_L=1/2$ in achiral systems). $P(\omega,-1)/C_L$ is the probability of finding one left-handed molecule with one of its frames oriented by R_ω whereas $P(\omega,+1)/C_R$ is the same probability for one right-handed molecule. For achiral molecules the two types of frame are tied to the same molecule, and the functions $P(\omega,1)$ and $P(\omega,-1)$ become dependent. One defines henceforth the orientations of the left-handed frames with respect to $\Sigma_0'=\{-\mathbf{i},-\mathbf{j},-\mathbf{k}\}$, so that one has $P(\omega,1)=P(\omega,-1)$ when the molecule is centrosymmetric.

APPENDIX B

The conventional order parameter η describing a phase transition spans an irreducible representation Γ [set of matrices associated with the symmetries of O(3)] of the high-symmetry phase. The "kernel" K is defined as the subgroup associated with the identity matrix in Γ [30]. An equilibrium state is represented by a vector in the abstract vector space of the order-parameter components. A vector lying along the general direction in the η space represents the least-symmetric stable phase (denoted by L phase). However, when the broken symmetry is continuous, it may happen that the group G_L of this phase is larger than the kernel. In this case, neighboring general directions have different symmetries. Their groups belong to a continuous class of isomorphic subgroups, the intersection of which coincides with the kernel. Considering now an "extended order parameter" consisting of several *isomorphic copies* of Γ, say $\eta^{(1)}$, $\eta^{(2)}$, $\eta^{(3)}$, etc., opens the possibility of breaking the symmetry beyond G_L. Taking, for instance, $\eta^{(1)}$ and $\eta^{(2)}$ in two distinct general directions in the η space yields a phase whose symmetry group G belongs to the intersection of their groups $[K\subset G\subset G_L]$. Increasing the number of nonparallel copies resumes the process until the kernel is reached ($G=K$ in the K phase). The number n_Γ of copies necessary for achieving this process, called the "order-parameter multiplicity," depends on the representation, but it never exceeds the dimension d_Γ of Γ. Indeed, the linear symmetry group leaving invariant a set of d_Γ nonparallel vectors in the d_Γ dimensional η space leaves all the vectors of this space invariant, and is thus confused with the kernel.

Let us expose now the methods yielding the SG sequences, the classes, the group parametricity $\bar{a}(G_i)$ and the order-parameter multiplicity n_Γ. Consider an Isotropic $\rightarrow$Nematic transition associated with a representation Λ of the symmetry group G_{HS} of the parent phase. Let $\{G_i\}$ be the set of subgroups of G_{HS}. More precisely, each G_i represents a continuous family of conjugate subgroups (e.g., C_S represents the set of all mirror planes whatever their orientations be in space). To each G_i one associates two integers: (i) $\gamma(G_i)$ is the dimension of the family $[\gamma(G_i)=0$ for $G_i=\mathrm{(S)O(3)}$, $\gamma(G_i)=2$ for $G_i=C_S$, C_n, C_{nh}, $S_n(n>1)$, $C_{\infty v}$, D_∞, $D_{\infty h}$, and $\gamma(G_i)=3$ otherwise]. (ii) $\sigma_\Lambda(G_i)$ is the dimension of the order-parameter subspace consisting of vectors whose common symmetry is one given group in the family G_i (this number is independent of the choice of the group in the family). It is equal to the multiplicity of the totally symmetric representation in the decomposition of Λ as a direct sum of irreducible representations of G_i. In the case when Λ is irreducible $\sigma_\Lambda(G_i)$ is given by $n_0^\pm$ in Eq. (10). provided G_{mol} is replaced by G_i in the sum, whereas when Λ is reducible the contributions of each irreducible part must be summed up. Finally, $\pi_\Lambda(G_i)$ is the dimension of the order-parameter subspace comprising vectors representing all the domains of the phase associated with the family G_i. One finds obviously $\pi_\Lambda(G_i)=\sigma_\Lambda(G_i)+\gamma(G_i)$.

Consider the set of G_i associated with a given value of $\sigma_\Lambda(G_i)$. Each one possesses a subset of maximal elements, defined by the fact that they are not subgroups of other groups in the set. To each maximal element is associated one "class," comprising the G_i in the set which are subgroups of this maximal element. The maximal elements form the "SG sequence." Determining the SG sequence is a straightforward algorithmic procedure.

Consider transitions where Λ contains b copies of an irreducible tensor representation Γ: $\Lambda=\Gamma\oplus\cdots\oplus\Gamma=b\Gamma$. Then, $\sigma_\Lambda(G_i)=b\sigma_\Gamma(G_i)=bn_0^\pm$. When $b=0$ the SG sequence is restricted to G_{HS}. When $b=1$ the SG sequence starts at G_{HS} and terminates at G_L. Increasing b inserts new phases in the SG sequences. When K is reached, the SG sequence is called the "maximal SG sequence" of Γ. To each G_i in the maximal

SG sequence one associates its “group parametricity” $\bar{a}(G_i)$ equal to the minimal number of Γ copies in Λ (i.e., b) necessary to stabilize the phase with external symmetry G_i. $\bar{a}(K)$ is the “order-parameter multiplicity” n_Γ. The determination of $\bar{a}(G_i)$ is based on the fact that, if (1) $\pi_\Lambda(G_i) \leqslant \dim(\Lambda)$, and (2) there is no $G_j \supset G_i$ with $\pi_\Lambda(G_i) = \pi_\Lambda(G_j)$, then G_i belongs to the SG sequence of Λ. Hence, the minimal element G_m in the SG sequence of Λ is characterized by: $\pi_\Lambda(G_m) \geqslant \dim(\Lambda)$ while, for any G_p such that $G_m \subset G_p$, one has either $\pi_\Lambda(G_p) < \dim(\Lambda)$ or $\pi_\Lambda(G_p) = \pi_\Lambda(G_m)$. Then, any proper subgroup of G_m is excluded from this sequence.

Let us illustrate the method with polar nematics ($\Gamma = \Gamma_1^-$) in an achiral system. The $\sigma_\Gamma = n_0^\pm$ are given in Table I. The maximal SG sequence contains O(3)$[\sigma_\Gamma = 0]$, $C_{\infty v}[\sigma_\Gamma = 1]$, $C_s[\sigma_\Gamma = 2]$, and $C_1[\sigma_\Gamma = 3]$. Since $\pi_\Gamma(C_{\infty v}) = 1.1 + 2 = 3 = \dim(\Gamma)$ and $\pi_\Gamma(C_s) = 1.2 + 2 = 4 > \dim(\Gamma)$, $C_{\infty v}$ is the minimal element of the first (nontrivial) SG sequence: $\{\mathrm{O}(3), C_{\infty v}\}$. Then, $\pi_{2\Gamma}(C_{\infty v}) = 2.1 + 2 < 6 = \dim(2\Gamma)$, $\pi_{2\Gamma}(C_S) = 2.2 + 2 = 6$ whereas $\pi_{2\Gamma}(C_1) = 2.3 + 0 = 6$, hence C_S is the minimal element of the second SG sequence $\{\mathrm{O}(3), C_{\infty v}, C_S\}$. Finally, since $\pi_{3\Gamma}(C_S) = 3.2 + 2 < 9 = \dim(3\Gamma)$ whereas $\pi_{3\Gamma}(K = C_1) = 3.3 + 0 = \dim(3\Gamma)$, the third sequence is maximal. One finds thus $\bar{a}[\mathrm{O}(3)] = 0$, $\bar{a}(C_{\infty v}) = 1$, $\bar{a}(C_S) = 2$, and $\bar{a}(C_1) = n_\Gamma = 3$. Consider now a third-rank odd tensor ($\Gamma = \Gamma_3^-$). The maximal sequence contains $O(3[\sigma_\Gamma = 0])$, $C_{\infty v}[\sigma_\Gamma = 1]$, $T_d[\sigma_\Gamma = 1]$, $D_{3h}[\sigma_\Gamma = 1]$, $C_{3h}[\sigma_\Gamma = 2]$, $S_4[\sigma_\Gamma = 2]$, $C_{2v}[\sigma_\Gamma = 2]$, $C_3[\sigma_\Gamma = 3]$, $C_2[\sigma_\Gamma = 3]$, $C_S[\sigma_\Gamma = 4]$, and $K = C_1[\sigma_\Gamma = 7]$. Since $\pi_\Gamma(C_S) = 4 + 2 < 7 = \dim(\Gamma)$ whereas $\pi_\Gamma(C_1) = 7 = \dim(\Gamma)$, the first SG sequence is maximal and $n_\Gamma = 1$.

APPENDIX C

We present the SG sequences and molecular classes for tensors of rank $L = 1, 2, 3, 4$ in achiral systems (Figs. 5–8). One class contains the molecular groups having always the same effective symmetry. The elements of one class have also the same value of n_0^+ or n_0^- (or of $n_0'^+$, $n_0'^-$ when the groups are external), which are indicated beside the classes. The maximal elements of all the classes form the maximal SG sequence. This sequence contains the groups corresponding to nematic phases that can be stabilized when one or several Lth-rank tensors condense. The number $\bar{a}$ (group parametricity) of tensors necessary to stabilize the phase associated with one of these groups is indicated beside the group in the sequence. The order-parameter multiplicity n_Γ is the value of $\bar{a}$ corresponding to the kernel, C_1 (odd tensors) or C_i (even tensors). A SG sequence is obtained by keeping only the groups of the maximal SG sequence with $\bar{a} \leqslant$ fixed integer.

The SG sequence can also be used to determine effective molecular groups arising in the nematic phases. Let us take, as an illustrating example, molecules with symmetry C_2^{int} when the order parameter is an even second-rank tensor (Γ_2^+). Figure 6 shows that C_2^{int} belongs to the class $\{C_2, C_s, C_{2h}\}$. This means first that, in all the possible nematic phases, molecules with one of these groups behave equivalently. In particular, they have always the same form of the first harmonic of the distribution function, and the same effective symmetry. Moreover, this effective symmetry is always larger or equal to C_{2h}^{int}. The number of tensors Γ_2^+ arising in the orientational distribution of such molecules is $n_0^+ = 3$ (see Fig. 6). Thus, all the possible stable phases that can be stabilized with 3 tensors are permitted in the phase diagram associated with these molecules. Since the maximum number of tensors (n_Γ) needed to stabilize all the phases (see Fig. 6) is 2 ($\bar{a} = 2$ in the least symmetric phase, C_i^{ext}), such molecules can be associated with the full list of stable phases in the maximal SG sequence: $\{\mathrm{O}(3), D_{\infty h}^{\mathrm{ext}}, D_{2h}^{\mathrm{ext}}, C_{2h}^{\mathrm{ext}}, C_i^{\mathrm{ext}}\}$. In the uniaxial phase with symmetry $D_{\infty h}^{\mathrm{ext}}$, the number of permitted internal tensors is $n_0'^+ = 1$ (see Fig. 6). Hence, the number of independent coefficients in the distribution function P is $n_0^+ \, n_0'^+ = 2$. With $n_0'^+ = 1$, the internal permitted symmetries (see Fig. 6) are $\{\mathrm{O}(3), D_{\infty h}^{\mathrm{int}}, D_{2h}^{\mathrm{int}}\}$ (list of groups in the maximal SG sequence with $\bar{a} \leqslant 1$). All these groups contain $G_{\mathrm{mol}} = C_2^{\mathrm{int}}$. Consequently, the effective symmetry group is the least symmetric in this list, $G_{\mathrm{eff}} = D_{2h}^{\mathrm{int}}$. In the biaxial phase ($G_{\mathrm{Nem}} = D_{2h}^{\mathrm{int}}$), $n_0'^+ = 2$ (yielding four independent parameters in P) and all the groups of the maximal SG sequence are candidate for the effective symmetry of the molecule. Since C_i^{int} does not con-

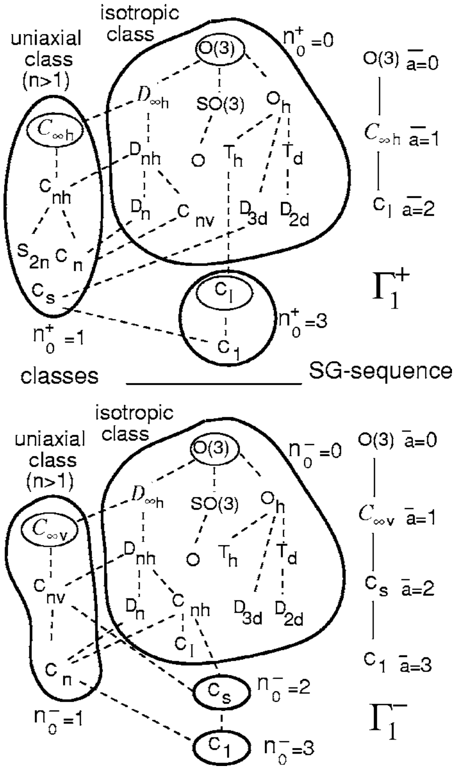

FIG. 5. Molecular classes when the order parameter is an axial (Γ_1^+) or a polar (Γ_1^-) vector. The classes are surrounded by thick lines. The maximal element of each class lies inside an oval. The value of $n_0^\pm$ (or of $n_0'^\pm$) common to all the groups in one class is indicated beside the class. Some group-subgroup relationships are indicated by broken lines. The maximal SG sequence is presented on the right. Each group in this sequence is represented with its group-parametricity, $\bar{a}$. The order parameter multiplicity is $n_\Gamma = \bar{a}(C_1)$ or $\bar{a}(C_i)$. Straight lines represent the group-subgroup relationships between the elements of the maximal SG sequence. The successive nonmaximal SG sequences are formed with all the groups having $\bar{a} \leqslant 0, 1, 2, \ldots, n_\Gamma$.

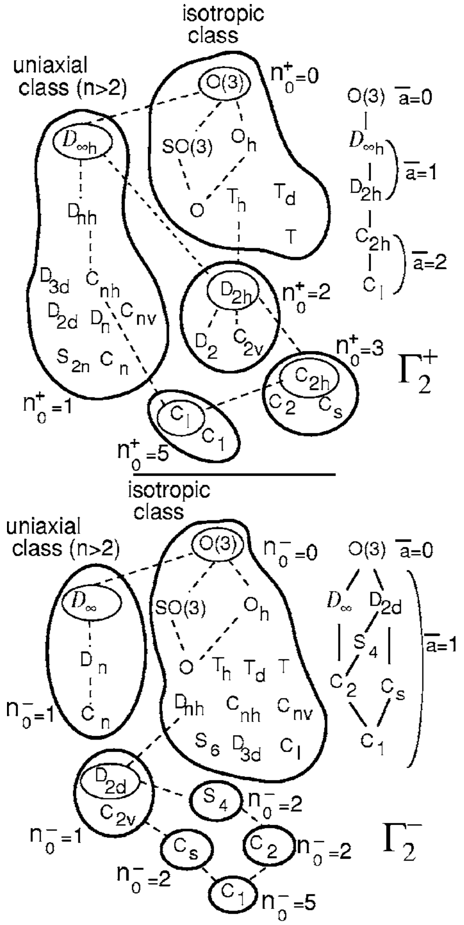

FIG. 6. Molecular classes and maximal SG-sequence when the order parameter is an even (Γ_2^+) or an odd (Γ_2^-) second-rank tensor.

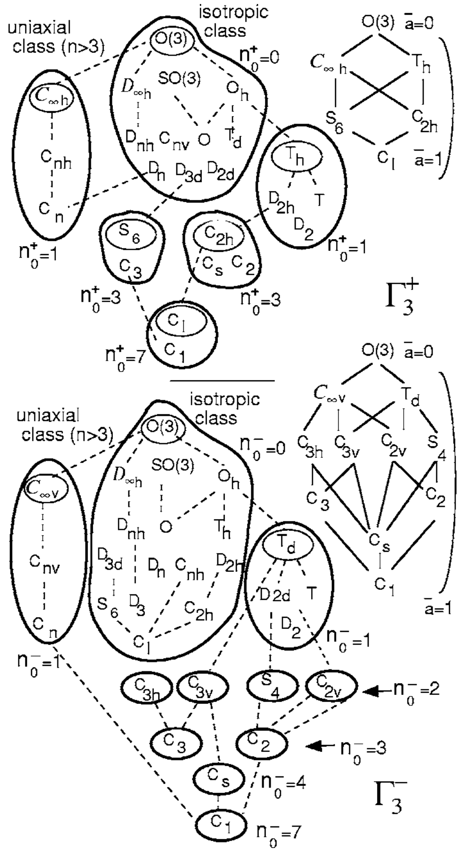

FIG. 7. Molecular classes and maximal SG sequence when the order parameter is an even (Γ_3^+) or an odd (Γ_3^-) third-rank tensor.

tain G_{mol}, the effective group is the least symmetric remaining group in the sequence, namely C_{2h}^{int}. In the monoclinic phase ($G_{\mathrm{Nem}}=C_{2h}^{\mathrm{ext}}$), $n_0'^{+}=3$, and six independent coefficients arise in P, whereas in the triclinic phase ($G_{\mathrm{Nem}}=C_i^{\mathrm{ext}}$), $n_0'^{+}=5$, and ten independent coefficients arise in P. In both cases all the effective groups are possible so that, once again, the actual effective symmetry is C_{2h}^{int}.

Let us now focus on the biaxial phase, and calculate the effective symmetry associated with higher harmonics of P. Since C_{2h}^{ext} contains I, no odd tensor appears in the distribution function. Moreover it forbids also the presence of an axial vector. On the contrary, it permits one third-rank ($n_0^+=1$ in Fig. 7) and three fourth-rank tensors ($n_0^+=3$ in Fig. 8). Figures 7 and 8 show that C_2 molecules belong to the class of C_{2h} for both tensors, so that the effective symmetry cannot decrease below C_{2h}^{int}. With one third-rank tensor the permitted effective groups are not limited in the maximal SG sequence, but since C_{2h} is the least symmetric group of the sequence containing $G_{\mathrm{mol}}=C_2$, the effective symmetry of this harmonic is C_{2h}^{int}. With three fourth-rank tensors the permitted effective groups are neither limited in the maximal SG sequence. Again C_{2h} is the least symmetric group of the sequence containing $G_{\mathrm{mol}}=C_2$, so that the effective symmetry of this harmonic is also C_{2h}^{int}. We conclude that the harmonics up to the fourth order do not modify the effective symmetry C_{2h}^{int} resulting from the primary tensor. In fact, it is obvious that this result holds for all the harmonics since C_{2h}^{int} is generated by C_2^{int} and $I^{\mathrm{int}}=I^{\mathrm{ext}}\in G_{\mathrm{Nem}}$ [see, Eq. (4)].

APPENDIX D

We formalize the relationship between macroscopic tensors $P_{mm'}^{L,\pm}$ and the microscopic basis tensors $\Omega_{(m)}^{L\pm,p}$ carried by one molecule. Let us begin with polar vectors lying on a chiral triclinic molecule $[G_{\mathrm{mol}}=C_1^{\mathrm{int}}]$. The molecular complex vectors $\mathbf{I}_{(m=0,\pm1)}$ $[\mathbf{I}_{(\pm1)}=(\pm\mathbf{I}-i\mathbf{J})/\sqrt{2},\ \mathbf{I}_{(0)}=\mathbf{K}]$ transform under internal rotations as

$$R_\Omega^{\mathrm{int}}\vec{\mathbf{I}}_{(m)}=\sum_{p=-1}^{1}D_{mp}^{1}(R_\Omega^{-1})\vec{\mathbf{I}}_{(p)} \tag{D1}$$

The laboratory basis $\{\mathbf{i}_{(m)}\}$ transforms under external rotations as

$$R_\Omega^{\mathrm{ext}}\vec{\mathbf{i}}_{(m)}=\sum_{p=-1}^{1}D_{mp}^{1}(R_\Omega^{-1})\vec{\mathbf{i}}_{(p)}. \tag{D2}$$

In general the molecule is rotated with respect to its reference orientation (conventionally defined by $\mathbf{I}_{(m)}=\mathbf{i}_{(m)}$) by the external rotation $R_\omega^{\mathrm{ext}}:\mathbf{I}_{(m)}(\omega)=R_\omega^{\mathrm{ext}}\mathbf{i}_{(m)}$. Hence, from Eq. (A2) one finds

$$\vec{\mathrm{I}}_{(m)}(\omega)=\sum_{p=-1}^{1} I^{p}_{(m)}\vec{\mathrm{i}}_{(p)}=\sum_{p=-1}^{1} D^{1}_{mp}(R^{-1}_{\omega})\vec{\mathrm{i}}_{(p)}=\sum_{\mathrm{p}=-1}^{1}\mathrm{D}^{1}_{\mathrm{pm}}(R_{\omega})^{*}\vec{\mathrm{i}}_{(\mathrm{p})}, \tag{D3}$$

where $I^{p}_{(m)}$ are the complex components of $\mathbf{I}_{(m)}$ on the laboratory frame $\{\mathbf{i}_{(p)}\}$. In a chiral mixture the right-handed frames $\{\mathbf{I}_{(m)}\}$ are tied to right-handed molecules whereas the left-handed frames $\{-\mathbf{I}_{(m)}\}$ are tied to left-handed molecules. Let us define $\mathbf{I}_{(m)}(\omega,\sigma)=\sigma\mathbf{I}_{(m)}(\omega)$. After averaging over P one finds

$$\langle I^{p}_{(m)}(\omega,\sigma)\rangle=\langle\sigma D^{1}_{pm}(R_{\omega})^{*}\rangle=\frac{16\pi^{2}}{3}P^{1-*}_{pm}. \tag{D4}$$

Elementary algebra yields the transformation properties of the average molecular vectors

$$R^{\mathrm{int}}_{\Omega}\langle\vec{\mathrm{I}}_{(m)}\rangle=\int\vec{\mathrm{I}}_{(m)}(R_{\omega})P(R_{\omega}R^{-1}_{\Omega})d\omega=\sum_{p=-1}^{1}D^{1}_{mp}(R^{-1}_{\Omega})\vec{\mathrm{I}}_{(p)},$$

$$R^{\mathrm{ext}}_{\Omega}\langle\vec{\mathrm{I}}_{(m)}\rangle=\int\vec{\mathrm{I}}_{(m)}(R_{\omega})P(R^{-1}_{\Omega}R_{\omega})d\omega=R_{\Omega}\langle\vec{\mathrm{I}}_{(m)}\rangle,$$

$$I\langle\vec{\mathrm{I}}_{(m)}\rangle=-\langle\vec{\mathrm{I}}_{(m)}\rangle. \tag{D5}$$

One defines also a complex basis of molecular (resp. laboratory) axial vectors $\mathbf{J}_{(m)}(\omega)$ (resp. $\mathbf{j}_{(m)}$) on the right-handed molecules. Axial vectors do not depend on the molecules handedness, so that $\mathbf{J}_{(m)}(\omega,\sigma)=\mathbf{J}_{(m)}(\omega)$. This leads to

$$\langle J^{p}_{(m)}(\omega,\sigma)\rangle=\langle D^{1}_{pm}(R_{\omega})^{*}\rangle=\frac{16\pi^{2}}{3}P^{1+*}_{pm}, \tag{D6}$$

$\langle\mathbf{I}_{(m)}\rangle$ and $\langle\mathbf{J}_{(m)}\rangle$ transform under rotations according to the same rules [Eqs. (D5)] whereas

$$I\langle\vec{\mathrm{J}}_{(m)}\rangle=\langle\vec{\mathrm{J}}_{(m)}\rangle. \tag{D7}$$

For more symmetric molecules the number of independent molecular vectors is $\leqslant 3$. For instance, when $G_{\mathrm{mol}}=C^{\mathrm{int}}_{2}$ ($\mathbf{K}$ parallel to the twofold axis) no physical vector can arise along $\mathbf{I}$ and $\mathbf{J}$. The number of independent physical vectors is equal to the internal selection multiplicity n^{-}_{0} [Eq. (10) with $L=1$]. $n^{-}_{0}=0$ when G_{mol} is nonpolar (containing C^{int}_{i}, D^{int}_{2}, or T^{int}), $n^{-}_{0}=1$ if G_{mol} contains a single rotation axis, $n^{-}_{0}=2$ when $G_{\mathrm{mol}}=C^{\mathrm{int}}_{S}$, and $n^{-}_{0}=3$ for $G_{\mathrm{mol}}=C^{\mathrm{int}}_{i}$. In the latter case, the three independent physical vectors may be chosen parallel to $\mathbf{I}$, $\mathbf{J}$, and $\mathbf{K}$. When $n^{-}_{0}=2$, one may choose the two vectors parallel to $\mathbf{I}$ and $\mathbf{J}$ (i.e., $\mathbf{K}$ normal to the molecular mirror plane), and when $n^{-}_{0}=1$, one may choose the single physical vector parallel to the rotation axis $\mathbf{K}$. The distribution P being invariant under the internal twofold axis, one has $-\langle\mathbf{I}\rangle=C^{\mathrm{int}}_{2}\langle\mathbf{I}\rangle=\langle\mathbf{I}\rangle$, i.e., $\langle\mathbf{I}\rangle=\mathbf{0}$ and similarly for $\langle\mathbf{J}\rangle$. One thus recovers, in a more transparent way, the results of the internal selection. It remains only 3 vector coefficients in P, corresponding to the components of $\langle\mathbf{K}\rangle$.

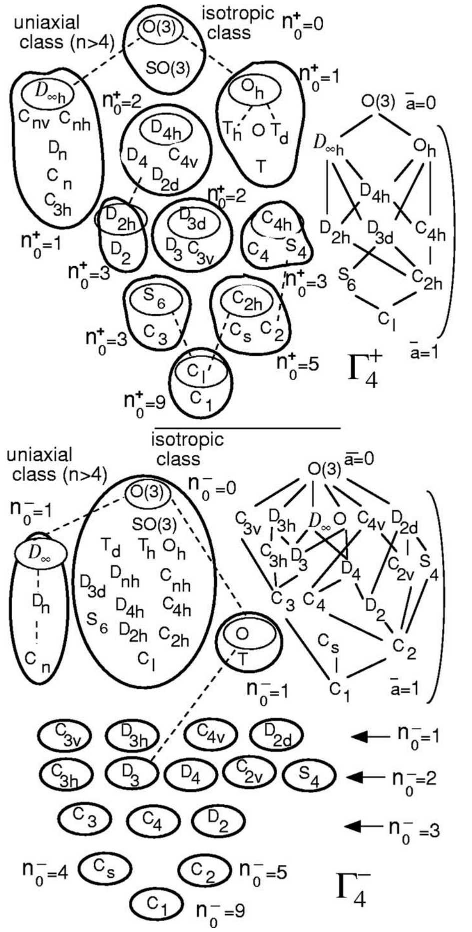

FIG. 8. Molecular classes and maximal SG sequence when the order parameter is an even (Γ^{+}_{4}) or an odd (Γ^{-}_{4}) fourth-rank tensor.

The standard complex basis $\omega^{L+}_{(m)}$ $(-L\leqslant m\leqslant +L)$ in the space of laboratory Lth-rank even contravariant tensors $[\omega^{L+}_{(L)}=\mathbf{j}_{(1)}\otimes\cdots\otimes\mathbf{j}_{(1)},\quad \omega^{L+}_{(m-1)}=\hat{L}_{-}\omega^{L+}_{(m)}/\sqrt{L(L+1)-m(m-1)}]$ transforms as

$$R^{\mathrm{ext}}_{\Omega}\omega^{L+}_{(m)}=\sum_{p=-L}^{L}D^{L}_{mp}(R^{-1}_{\Omega})\omega^{L+}_{(p)},$$

$$I\omega^{L+}_{(m)}=\omega^{L+}_{(m)},$$

$$\omega^{L+}_{(-m)}=(-1)^{m}\omega^{L+*}_{(m)}, \tag{D8}$$

whereas the molecular basis $\Omega^{L+}_{(m)}$ $(\Omega^{L+}_{(L)}=\mathbf{J}_{(1)}\otimes\cdots\otimes\mathbf{J}_{(1)})$ transforms as

$$\Omega^{L+}_{(m)}(R_{\omega})=R^{\mathrm{ext}}_{\omega}\omega^{L+}_{(m)}. \tag{D9}$$

$\Omega^{L+}_{(m)}$ has the same components on the molecular frame $\{\mathbf{I}_{(m)}\}$ as $\omega^{L+}_{(m)}$ has on the laboratory frame $\{\mathbf{i}_{(m)}\}$. Thus

$$R^{\mathrm{int}}_{\Omega}\Omega^{L+}_{(m)}(R_{\omega})=\Omega^{L+}_{(m)}(R_{\omega}R_{\Omega})=\sum_{p=-L}^{L}D^{L}_{mp}(R^{-1}_{\Omega})\Omega^{L+}_{(p)}(R_{\omega}),$$

$$R^{\mathrm{ext}}_{\Omega}\Omega^{L+}_{(m)}(R_{\omega})=\Omega^{L+}_{(m)}(R_{\Omega}R_{\omega})=\sum_{p=-L}^{L}D^{L}_{mp}(R^{-1}_{\omega}R^{-1}_{\Omega}R_{\omega})\Omega^{L+}_{(p)}(R_{\omega}),$$

$$I\Omega^{L+}_{(m)}(R_\omega) = \Omega^{L+}_{(m)}(R_\omega). \tag{D10}$$

Comparing Eqs. (D10) with Eqs. (3) and (1) shows that much care must be paid with the transformation algebra. $\Omega^{L+}_{(m)}$ has the same components on the basis of both left- and right-handed molecules, and we can define $\Omega^{L+}_{(m)}(R_\omega,\sigma) = \Omega^{L+}_{(m)}(R_\omega)$. Along the same way we define a standard basis of odd tensors $\Omega^{L-}_{(m)}(R_\omega,\sigma) = \sigma\Omega^{L-}_{(m)}(R_\omega,\sigma)$. They obey the same rotational properties [Eq. (D8)] as even tensors, but with $I\Omega^{L-}_{(m)} = -\Omega^{L-}_{(m)}$. Equations (D8) and (D9) show that the functions $D^L_{pm}(R_\omega)^*$ and $\sigma D^L_{pm}(R_\omega)^*$ coincide with the components $\Omega^{L+,p}_{(m)}(R_\omega)$ and $\Omega^{L-,p}_{(m)}(R_\omega)$ of $\Omega^{L+}_{(m)}(R_\omega,\sigma)$ and $\Omega^{L+}_{(m)}(R_\omega,\sigma)$ on $\omega^{L+}_{(p)}$ and $\omega^{L-}_{(p)}$, respectively. Thus, one gets after averaging on P and taking Eq. (D10) into account

$$\langle \Omega^{L\pm,p}_{(m)} \rangle = \frac{16\pi^2}{2L+1} P^{L\pm *}_{pm}. \tag{D11}$$

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