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GROUP THEORETICAL STATISTICAL MECHANICS OF NEMATOGENIC AND CHOLESTERIC LIQUID CRYSTALS

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The principles of group theoretical statistical mechanics have been applied to the molecular dynamics of nematogens and cholesterics, with point groups $C_{\infty v}$, $D_{\infty h}$, C_{∞} and D_{∞}. The effect of alignment with an external static electric field is discussed in terms of new ensemble averages that take the symmetry of the applied field and make swarm averages directly visible in the laboratory frame (X, Y, Z). The symmetry arguments lead to experimentally observable effects and to characteristic ensemble averages of swarm dynamics which should be reproducible numerically by computer simulation.

1. Introduction

The principles of group theory [1–3] have recently been shown to be applicable [4–8] to thermodynamic ensemble averages at equilibrium, and in a steady state subjected to shear. It has been shown that an ensemble average, $\langle\ \rangle$, over a physical property or product of properties such as a time correlation function exists if it reduces as the totally symmetric representation (tsr) of the appropriate point group [1–3]. In the laboratory frame (X, Y, Z), this is the $D_g^{(0)}$ representation [1–3] of the rotation/reflection point group $R_h(3)$. In the frame (x, y, z) of the molecule fixed point group it is the tsr of the point group itself. In the presence of fields, such as the static electric field, $\boldsymbol{E}$, extra ensemble averages are allowed depending on the field symmetry itself [5]. The electric field allows, to first order, averages of $D_u^{(1)}$ symmetry in frame (X, Y, Z). To second order, the field E^2 allows averages of symmetry

$$D_g^{(0)} + D_g^{(2)}.$$

In a shearing field which causes a shear strain of the type $\partial v_X/\partial Z$ for example, where v_X is the strain velocity, new time asymmetric cross correlation functions are observed [4] with the (traceless) D symmetry

$$D_g^{(1)} + D_g^{(2)}.$$

The shearing field makes visible directly in the laboratory frame (X, Y, Z) time antisymmetric ensemble averages of $D_g^{(1)}$ symmetry [4] and time symmetric ensemble averages of $D_g^{(2)}$ symmetry. Examples are [4] the velocity cross correlation functions

$$\langle v_X(0)v_Z(t)\rangle = -\langle v_X(t)v_Z(0)\rangle \quad (D_g^{(1)}),$$

$$\langle v_X(0)v_Z(t)\rangle = \langle v_X(t)v_Z(0)\rangle \quad (D_g^{(2)}).$$

The new cross correlation function between orthogonal atomic velocity components seen in the computer simulation [4] of an atomic ensemble subjected to this type of shear is a weighted sum of the above, giving the new and unexpected result

$$\langle v_X(0)v_Z(t)\rangle \neq \langle v_X(t)v_Z(0)\rangle.$$

The effect of this type of shear stress on nematogens and cholesterics is of widespread interest and is explored in this paper, which is intended to extend the application of group theoretical statistical mechanics (GTSM) to the molecular dynamics in liquid crystals. In the unaligned nematogenic phase, for exam-

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ple, the director axis [9–13] forms a frame of reference (x_D, y_D, z_D) with two axes of the frame, say x_D and y_D mutually perpendicular to the director axis z_D. The swarm axes form a right-handed frame for consistency of definition when dealing with chiral molecules. The extra time cross correlations set up by the presence of molecular alignment along the director vector are calculated with symmetry arguments, both for electrically dipolar and non-dipolar liquid crystal molecules. Both in dipolar and non-dipolar nematogens, the number of extra cross-correlations help to synchronise the molecular dynamics. In the presence of an aligning field, such as $\boldsymbol{E}$ or E^2, the director frame becomes virtually coincidental with the laboratory frame (X, Y, Z) and the complete aligned liquid crystal specimen ceases to have the isotropic three-dimensional symmetry $R_h(3)$, taking on $C_{\infty v}$ symmetry for example for dipolar molecules in a field $\boldsymbol{E}$. The extra correlation functions and pair distribution functions that previously existed only in frame (x_D, y_D, z_D) but vanished in the overall isotropic, unaligned, nematogenic sample now survive ensemble averaging, and accompany the appearance of macroscopic birefringence.

Similar considerations are developed for cholesterics, where the relevant point groups are chiral. They isolate the set of non-vanishing time cross-correlation functions and radial distribution functions [14] which occur exclusively in cholesterics.

A shearing field makes possible the existence in the laboratory frame of new time asymmetric ensemble averages [4]. Shearing would tend to align the director, as with electric fields, but this time would also allow averages of $D_g^{(1)}$ type (antisymmetric in the indices X and Z, and related to shear induced vorticity) and $D_g^{(2)}$ (symmetric in the indices X and Z, and related to shear induced deformation) to exist in frame (X, Y, Z). Here we make the simple ansatz that averages equivalent to these D symmetries in the field-free liquid crystal that exist in the absence of the field only in frame (x_D, y_D, z_D) become visible in frame (X, Y, Z) when the liquid crystal is sheared.

2. Basic symmetry arguments, the principles of group theoretical statistical mechanics

In the unaligned nematogen, or cholesteric phase [15], group theoretical arguments can be used in the three frames (X, Y, Z), (x_D, y_D, z_D), and (x, y, z), respectively the laboratory, director, and molecule fixed frames of reference. In the frame of reference (X, Y, Z) of the unaligned sample the relevant point group is $R_h(3)$ of isotropic three-dimensional space. The irreducible representations are $D_g^{(0)}$ (scalar), $D_u^{(0)}$ (pseudoscalar), $D_u^{(1)}$ (polar vector) and $D_g^{(1)}$ (pseudo or axial vector). Higher-order tensors are designated $D_u^{(2)}$, $D_g^{(2)}$, and so on. The point group of the director frame is $C_{\infty v}$ for a dipolar nematogen and $D_{\infty h}$ for a non-dipolar nematogen. The irreducible representations are those of these point groups, whichever is appropriate. The director slowly meanders through the laboratory frame but has these point group symmetries over a well defined region of three-dimensional space which is large [10] in comparison with molecular dimensions but small in comparison with the volume occupied by the macroscopic sample. In theory, the director point group may have any symmetry, but in nematogens there is alignment in one axis only (z_D). This feature is absent in isotropic molecular liquids such as water, and in nematogens vanishes at the nematic–isotropic transition temperature. Thus, a nematic phase is distinguished by extra ensemble averages (for example dynamic time correlation functions and static radial pair distribution functions) in the director frame of reference. This paper sets out to explore these in some detail. Finally in the molecule fixed frame (x, y, z) of the point group character tables, the relevant point group and irreducible representations are those of the molecular symmetry itself, and these govern the ensemble averages in (x, y, z) according to the rules [4–8] of GTSM.

Principle (1), Neumann's principle [16–18]. The scalar components of the equilibrium thermodynamic ensemble average $\langle \mathbf{ABC}... \rangle$ over the general tensor product **ABC**... exist in the laboratory frame (X, Y, Z) if they contain individually the totally symmetric representation $D_g^{(0)}$ of the three-dimensional rotation reflection group $R_h(3)$ of isotropic space [2].

Principle (2). These scalar components exist in the molecule fixed frame (x, y,) if they contain individually the totally symmetric representation of the molecular point group.

Principle (3). An applied external force field pro-

motes the existence of extra ensemble averages whose symmetry is that of the applied field.

Principle (1) shows that in the unaligned nematic phase, the sample being overall isotropic despite the meandering director, the existence of any thermodynamic ensemble average is governed by the presence or absence of $D_g^{(0)}$ in its scalar components. Thus, the thermodynamic average over a scalar exists because its representation is simply $D_g^{(0)}$ itself, but that over a polar or axial vector, respectively $D_u^{(1)}$ and $D_g^{(1)}$ will vanish. Time autocorrelation functions of the general type $\langle \boldsymbol{A}(t)\cdot\boldsymbol{A}(0)\rangle$ will always exist because if A is polar or axial the product of symmetry representations [1–3]

$$\Gamma(\boldsymbol{A})\Gamma(\boldsymbol{A}) = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} \tag{1}$$

contains $D_g^{(0)}$ once. This represents the trace $\langle \boldsymbol{A}(0)\cdot\boldsymbol{A}(t)\rangle$. On the other hand, the time cross correlation function $\langle \boldsymbol{A}(t)\cdot\boldsymbol{B}(0)\rangle$ between a polar vector $\boldsymbol{A}$ and axial vector $\boldsymbol{B}$ vanishes in the unaligned nematic in frame (X, Y, Z) because

$$\Gamma(\boldsymbol{A})\Gamma(\boldsymbol{B}) = D_u^{(0)} + D_u^{(1)} + D_u^{(2)} \tag{2}$$

does not contain $D_g^{(0)}$. For this reason the time cross correlation function (ccf) $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$ vanishes for all t in frame (X, Y, Z) of the unaligned nematic. However, the time ccf between a polar vector $\boldsymbol{A}$ and a different polar vector $\boldsymbol{C}$ exists in frame (X, Y, Z) because

$$\Gamma(\boldsymbol{A})\Gamma(\boldsymbol{C}) = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}. \tag{3}$$

Thus the time ccf $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\mu}(0)\rangle$ for example exists [19] in frame (X, Y, Z), where $\boldsymbol{v}$ is the molecular centre of mass linear velocity, $\boldsymbol{\mu}$ is the molecular dipole moment, and $\boldsymbol{\omega}$ is the molecular angular velocity. Similar considerations apply to pair distribution functions [14,20] and the newer type of angularly resolved pair distribution function [14]. The molecular structure and dynamics of the unaligned nematogen are determined by principle (1) in combination with computer simulation and the theory of diffusion.

The director defines a region of three-dimensional space which is described by the point groups $C_{\infty v}$ and $D_{\infty h}$ respectively, depending on whether the individual molecules are dipolar or non-dipolar. This region is referred to conveniently as the "swarm". Thermodynamic ensemble averages may be constructed inside the swarm, bringing principle (2) into operation, but in frame (x_D, y_D, z_D).

2.1. The $C_{\infty v}$ swarm

This applies to electrically dipolar nematogen molecules, the vast majority. Mapping [1,2] the irreducible representations of a scalar, vector, and so on from $R_h(3)$ to $C_{\infty v}$ gives

$$D_g^{(0)} \rightarrow \Sigma^+, \quad D_u^{(0)} \rightarrow \Sigma^-,$$

$$D_g^{(1)} \rightarrow \Sigma^- + \Pi, \quad D_u^{(1)} \rightarrow \Sigma^+ + \Pi,$$

$$D_g^{(2)} \rightarrow \Sigma^+ + \Pi + \Delta, \quad D_u^{(2)} \rightarrow \Sigma^- + \Pi + \Delta,$$

$$D_g^{(3)} \rightarrow \Sigma^- + \Pi + \Delta + \Phi,$$

$$D_u^{(3)} \rightarrow \Sigma^+ + \Pi + \Delta + \Phi.$$

The totally symmetric irreducible representation [1–3] in the $C_{\infty v}$ swarm is Σ^+. Using principle (2) it can be shown that extra cross correlation functions exist inside the swarm that vanish in (X, Y, Z). For example, one independent element of $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$ exists because the product of representations inside the $C_{\infty v}$ point group

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega}) = (\Sigma^+ + \Pi)(\Sigma^- + \Pi)$$
$$= \Sigma^+ + 2\Sigma^- + 2\Pi + \Delta \tag{4}$$

contains the tsr Σ^+ once. Using this point group's character table [1–3] shows that this is

$$\langle v_{xD}(t)\omega_{yD}(t)\rangle = -\langle v_{yD}(t)\omega_{xD}(0)\rangle. \tag{5}$$

This type of ccf vanishes in frame (X, Y, Z). This is one member of the set of non-vanishing ccfs inside the swarm whose members all vanish in (X, Y, Z). Thus any attempt to describe molecular dynamics inside a swarm with computer simulation must produce the result (5). The swarm volume is bigger than the molecular dynamics "cube" itself, and spontaneous swarm formation under the right conditions can be measured through the spontaneous appearance of the result (5). This ccf element will vanish for all t if the swarm disappears for some reason, for example at the nematic (or cholesteric) to isotropic phase change. This gives a simple test for the occurrence of a liquid crystal in computer simulation.

There are many other differences between swarm dynamics and those in (X, Y, Z). For example, time

autocorrelation functions (acfs) become anisotropic

$$\langle \mu_{z_D}(t)\mu_{z_D}(0)\rangle \neq \langle \mu_{x_D}(t)\mu_{x_D}(0)\rangle = \langle \mu_{y_D}(t)\mu_{y_D}(0)\rangle, \quad (6)$$

$$\langle \omega_{z_D}(t)\omega_{z_D}(0)\rangle \neq \langle \omega_{x_D}(t)\omega_{x_D}(0)\rangle = \langle \omega_{y_D}(t)\omega_{y_D}(0)\rangle. \quad (7)$$

Under some circumstances, thermodynamic averages may exist in the swarm over polar vectors such as $\dot{\boldsymbol{v}}$ or $\dot{\boldsymbol{\mu}}$ which have positive time reversal symmetry. This again can be picked up by computer simulation, and signifies that the swarm can have a net linear acceleration inside the macroscopic unaligned nematogen, measured with respect to the frame (x_D, y_D, z_D). These net accelerations vanish in frame (X, Y, Z).

2.2. The $D_{\infty h}$ swarm

This refers to electrically non-dipolar molecules which form a nematic phase. An example is hexaphenyl (linear end to end arrangement of phenyl groups). In this case the irreducible representations of $R_h(3)$ map onto $D_{\infty h}$ as follows:

$$D_g^{(0)} \rightarrow \Sigma_g^+, \quad D_u^{(0)} \rightarrow \Sigma_u^-,$$

$$D_g^{(1)} \rightarrow \Sigma_g^- + \Pi_g, \quad D_u^{(1)} \rightarrow \Sigma_u^+ + \Pi_u,$$

$$D_g^{(2)} \rightarrow \Sigma_g^+ + \Pi_g + \Delta_g, \quad D_u^{(2)} \rightarrow \Sigma_u^- + \Pi_u + \Delta_u,$$

$$D_g^{(3)} \rightarrow \Sigma_g^- + \Pi_g + \Delta_g + \Phi_g,$$

$$D_u^{(3)} \rightarrow \Sigma_u^+ + \Pi_u + \Delta_u + \Phi_u.$$

There are fewer new ensemble averages specific to the $D_{\infty h}$ swarm. For example, there can be no ccfs between $\boldsymbol{v}$ and $\boldsymbol{\omega}$ because the product of symmetry representations

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega}) = (\Sigma_g^- + \Pi_g)(\Sigma_u^+ + \Pi_u) = \Sigma_u^+ + 2\Sigma_u^- + 2\Pi_u + \Delta_u \quad (8)$$

does not contain the group tsr Σ_g^+. It is more difficult therefore for the molecular dynamics to be synchronised in a $D_{\infty h}$ swarm, which helps to explain why there are far fewer observed to date. However, the results of type (6) and (7) are retained in this type of swarm, the relevant products of representations containing in each case two occurrences of the tsr. Computer simulation must be able to pick up this result when attempting to describe the molecular dynamics within a non-dipolar swarm, e.g. one made up of long rods. In the $D_{\infty h}$ swarm the mean molecular angular acceleration vanishes, but the mean molecular linear centre of mass acceleration exists. In general, the set of non-vanishing ensemble averages in frame (x_D, y_D, z_D) of this swarm contains fewer members than in the $C_{\infty v}$ swarm.

2.3. The C_∞ swarm

This is found in an unaligned cholesteric phase [9,15] made up of chiral dipolar molecules. The D representations map onto the following in the point group C_∞:

$$D_g^{(0)} \text{ and } D_u^{(0)} \rightarrow \Sigma,$$

$$D_g^{(1)} \text{ and } D_u^{(1)} \rightarrow \Sigma + \Pi,$$

$$D_g^{(2)} \text{ and } D_u^{(2)} \rightarrow \Sigma + \Pi + \Delta,$$

$$D_g^{(3)} \text{ and } D_u^{(3)} \rightarrow \Sigma + \Pi + \Delta + \Phi.$$

These mappings show that the cholesteric C_∞ swarm has more intrinsic non-vanishing ensemble averages in the frame (x_D, y_D, z_D) than the nematic $C_{\infty v}$ swarm. For example, the product of representations

$$\Gamma(\boldsymbol{v})\Gamma(\boldsymbol{\omega}) = (\Sigma + \Pi)(\Sigma + \Pi) = 3\Sigma + 2\Pi + \Delta \quad (9)$$

shows that there are three independent elements in the swarm frame of a ccf such as $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$. Reference to the C_∞ point group character table [1–3] shows these to be

$$\langle v_{z_D}(0)\omega_{z_D}(t)\rangle \neq \langle v_{y_D}(0)\omega_{y_D}(t)\rangle = \langle v_{x_D}(0)\omega_{x_D}(t)\rangle,$$

$$\langle v_{x_D}(0)\omega_{y_D}(t)\rangle = -\langle v_{y_D}(0)\omega_{x_D}(t)\rangle. \quad (10)$$

This cholesteric swarm also allows the existence of off-diagonal elements of time acfs, the overall symmetry being the same pattern as (10), two independent diagonal elements and one independent off-diagonal. All ccf elements change sign from one enantiomorph to the other. A computer simulation of a cholesteric swarm would be expected to reproduce these results. At the cholesteric to isotropic phase transition the set of ccf elements of type (10) all dis-

appear with the director and the swarm frame, and this is another test for computer simulation.

2.4. The D_∞ swarm

This is a cholesteric swarm with overall non-dipolar symmetry. The relevant mappings are as follows:

$D_g^{(0)}$ and $D_u^{(0)} \rightarrow \Sigma^+$,

$D_g^{(1)}$ and $D_u^{(1)} \rightarrow \Sigma^- + \Pi$,

$D_g^{(2)}$ and $D_u^{(2)} \rightarrow \Sigma^+ + \Pi + \Delta$,

$D_g^{(3)}$ and $D_u^{(3)} \rightarrow \Sigma^- + \Pi + \Delta + \Phi$,

again providing the opportunity for several new time ccf patterns to develop in the swarm.

3. The molecule fixed frame (x, y, z)

Extra time cross correlations are set up in frame (x, y, z) which are governed by principle (2) and the point group symmetry of the molecule itself. The molecules making up nematogens and cholesterics [9] are often of quite low symmetry, thus allowing many more thermodynamic ensemble averages to become visible at the molecular level which are different from those at the intermediate swarm level and which vanish at the macroscopic level. A computer simulation must be able to produce numerical results which reproduce self-consistently all the symmetry predicted thermodynamic averages in all three frames. Thermodynamically and statistically therefore, the existence of unaligned nematogens and cholesterics is accompanied by the appearance of extra time cross correlations at the swarm and molecular level. Properties specific to such liquid crystals can be traced to these cross correlations, which can therefore be related to these observable properties with computer simulation.

4. The electrically aligned nematogen

In the aligned nematogen, the director axis no longer meanders in three dimensions, but is locked in one axis, say Z, of the laboratory frame (X, Y, Z) by the torque generated between the molecular dipole moment, $\boldsymbol{\mu}$, and the electric field, E_Z. On the basis of principle (3) the first-order applied electric field of symmetry $D_u^{(1)}$ sets up new ensemble averages of the same symmetry at field-on equilibrium. One example is the time ccf

$$\langle v_X(t)\omega_Y(0)\rangle = -\langle v_Y(t)\omega_X(0)\rangle \,, \tag{11}$$

which becomes directly visible in the laboratory. This was first demonstrated [21–24] for molecular liquids using computer simulation, but has yet to be explored in aligned nematogens and other liquid crystals. The ccf (11) represents the $D_u^{(1)}$ part of the tensor $\langle \boldsymbol{v}(t)\cdot\boldsymbol{\omega}(0)\rangle$ which has

$$D_u^{(0)} + D_u^{(1)} + D_u^{(2)}$$

symmetry. The $D_u^{(1)}$ is the vector part $\langle \boldsymbol{v}(t)\times\boldsymbol{\omega}(0)\rangle$.

The effect of the static electric field E_Z on a nematogen made up of molecules each with the electric dipole moment $\boldsymbol{\mu}$ is to make the frames (x_D, y_D, z_D) and (X, Y, Z) indistinguishable as reference frames for molecular dynamics. This is because the director axis z_D is the laboratory axis Z. The extra ensemble averages that have been shown to exist in, for example, a $C_{\infty v}$ swarm now exist in (X, Y, Z) itself. If the nematogen is only partially aligned the ensemble averages lose some amplitude but are still visible in (X, Y, Z). Similar conclusions are valid for a second-order field E^2, but in this case the field interacts with the polarisability tensor of the molecule, producing orientation, but not alignment. This means that half the aligned molecules have dipoles in one direction, on average, and half in the other. This is described in D language as a sum of $D_g^{(0)}$ and $D_g^{(2)}$ type ensemble averages in frame (X, Y, Z). Mappings of both these D representations on to the $C_{\infty v}$ point group contain the latter's tsr, as is also the case for the other swarm point groups. Thus a field E^2 makes $D_g^{(2)}$ averages of the swarms directly observable in frame (X, Y, Z). (The $D_g^{(0)}$ represents scalars which are frame invariant, i.e. their thermodynamic averages exist in any frame of reference.) In the aligned or oriented state we denote, for convenience, "$C_{\infty v}$ nematogens", constructed from swarms of the same symmetry, and so on.

4.1. The $C_{\infty v}$ nematogen

The mappings given already for this swarm can be utilised directly to find the non-vanishing ensemble averages in frame (X, Y, Z) in the $C_{\infty v}$ nematic. For example, whenever a D representation of group $R_h(3)$ maps onto a $C_{\infty v}$ representation of the aligned nematic that contains the latter group's tsr, extra ensemble averages will appear in frame (X, Y, Z) itself. Thus for example, the averages previously confined to the swarm and described in eqs. (5)–(7) now exist directly in (X, Y, Z),

$$\langle v_X(t)\omega_Y(0)\rangle = -\langle v_Y(t)\omega_X(0)\rangle, \tag{12}$$

$$\langle \mu_Z(t)\mu_Z(0)\rangle \neq \langle \mu_X(t)\mu_X(0)\rangle = \langle \mu_Y(t)\mu_Y(0)\rangle, \tag{13}$$

$$\langle \omega_Z(t)\omega_Z(0)\rangle \neq \langle \omega_X(t)\omega_X(0)\rangle = \langle \omega_Y(t)\omega_Y(0)\rangle. \tag{14}$$

Eq. (12) signals the existence of direct rotation–translation coupling in the aligned nematic which has a considerable effect on the molecular dynamics because of the considerable degree of alignment possible experimentally, even with a weak electric field, of equivalent energy μE_Z much smaller than the thermal energy kT. So far in computer simulations, alignment has been achieved, and ccfs such as (12) observed [21–24], but only through the use of field energies μE_Z about the same as kT. This is because the simulations deal with isotropic molecular liquids such as water. No complete computer simulation of an aligned nematogen is yet available.

Eqs. (13) and (14) show that the sample is anisotropic in the laboratory frame under the influence of an aligning first-order electric field E_Z. It is therefore birefringent [9]. Our symmetry arguments have therefore consistently reproduced a well-known feature of nematogenic behaviour, especially noticeable [9,11] in dielectric loss and dispersion. The dielectric complex permittivity is essentially [9] the Fourier transform of eq. (13) and is by symmetry and GTSM measurably different in Z, being identical in X and Y. The complex permittivity is the square of the complex refractive index, implying birefringence as observed experimentally [9]. We have shown that this is describable in terms of the point group $C_{\infty v}$ and its irreducible representation.

One interesting implication of symmetry is that the ensemble averages over time – even polar vectors, such as $\langle \dot{\boldsymbol{v}} \rangle$ or $\langle \dot{\boldsymbol{\mu}} \rangle$ which include the tsr of $C_{\infty v}$ must have the possibility of existence in the aligned nematogen of this symmetry. In this case the $D_u^{(1)}$ representation implies a non-vanishing Σ^+, i.e. a non-vanishing linear acceleration or force in the Z axis of the aligned nematogen. The applied E_Z cannot generate the mean acceleration directly, but only through a torque $-\boldsymbol{\mu}\times\boldsymbol{E}_Z$ on each dipolar molecule. The net linear acceleration must come from correlation between molecular rotation and translation, and is an experimental measure of this phenomenon. The net linear acceleration of the aligned sample would result in such effects as a meniscus at the surface of the nematogen as the sample is forced against the electric field generating apparatus, normally an electrode. This meniscus should be measurable with a microscope. Similarly, GTSM predicts the possibility of non-vanishing rotational acceleration, the second time derivative of the dipole moment, implying

$$\langle \ddot{\mu}_Z(t)\ddot{\mu}_Z(0)\rangle \to \langle \ddot{\mu}_Z\rangle^2, \quad t\to\infty, \tag{15}$$

$$\langle \mu_Z(t)\mu_Z(0)\rangle \to \langle \mu_Z\rangle^2, \quad t\to\infty. \tag{16}$$

Eq. (16) implies the existence of a zero frequency (infinite time) component of the dielectric spectrum, as observed [9] experimentally in the Z axis of the aligned nematogen. This is the static permittivity component in axis Z, which becomes different from those in X and Y. A similar effect is expected on the fourth spectral moment [9], which is the Fourier transform, essentially speaking, of eq. (15).

4.2. The $D_{\infty h}$ nematogen

In this case the molecules of the swarm are non-dipolar, but if they are polarisable new thermodynamic averages of total symmetry $\Gamma(E^2)$ appear in frame (X, Y, Z) by principle (3). The sample is oriented along the axis of the applied field, for example the Z axis. In D language

$$\Gamma(E^2) = D_g^{(0)} + D_g^{(2)}. \tag{17}$$

More generally

$$\Gamma(\boldsymbol{EE}) = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}, \tag{18}$$

but the notation E^2 implies $\boldsymbol{E}$ parallel to itself, so that $\boldsymbol{E}\times\boldsymbol{E}$ vanishes and by principle (3) no $D_g^{(1)}$ averages appear in (X, Y, Z). This leaves the other two D terms on the rhs of eq. (17), representing averages of the second-Legendre-polynomial type

$$\tfrac{1}{2}\langle 3[\boldsymbol{A}(t)\cdot\boldsymbol{B}(0)]^2\rangle - 1 \qquad (19)$$

and even-order Langevin functions [9]. In (19) $\boldsymbol{A}$ and $\boldsymbol{B}$ must have the same parity reversal symmetry.

Averages of this kind that had previously been visible only in the swarm frame become visible under the effect of the field in the laboratory frame. In this case they must all be even to parity reversal symmetry. This time there is no net linear acceleration, therefore, and no net dipole $\langle \mu_Z \rangle$.

Note that the sum (17) maps onto

$$2\Sigma_g^+ + \Pi_g + \Delta_g$$

of $D_{\infty h}$. This implies two independent occurrences of this point group's tsr, and two independent types of thermodynamic average in the sample oriented by E^2. This means that the time dependence of the Z, Z component of averages such as (19) is different from those of the Y, Y and X, X components, which are the same. In other words the sample is anisotropic and birefringent, and supports even-order Langevin functions.

5. The electrically aligned cholesteric

5.1. The C_∞ cholesteric

In this cholesteric symmetry, alignment with a first-order electric field produces a unidirectional spiral symmetry along the axis of the applied field, say Z. Ensemble averages that map onto symmetry representations in the C_∞ point group that contain the group's tsr at least once now survive in the frame (X, Y, Z). In this point group the tsr appears in the symmetry representations both of polar and axial vectors. If a vector quantity is also even to time reversal symmetry, its thermodynamic ensemble average might not vanish. The average switches sign from one enantiomer to the other, and must vanish by symmetry only in the racemic mixture [25]. This produces the possibility of observing in the electrically aligned cholesteric net molecular linear acceleration, molecular angular acceleration, and a net molecular rotational acceleration which vanish in the racemic mixture.

5.2. The D_∞ cholesteric

In this case similar considerations apply to orientation by an E^2 field as in the case of $D_{\infty h}$. The second-order field induces averages of type (19), but this time the vectors $\boldsymbol{A}$ and $\boldsymbol{B}$ can have different parity reversal symmetry.

6. The effect of a shearing field

The symmetry of a shearing field has been shown in section 1 and elsewhere [4–8] to consist of a vector component $D_g^{(1)}$ and a tensor component $D_g^{(2)}$. A shear of the type $\partial v_X/\partial Z$ produces by computer simulation [6–8] velocity ccfs between orthogonal molecular Cartesian components X and Z (see section 1).

These D symmetries of the laboratory frame map differently on to the four swarm point groups considered in this paper,

$$\begin{aligned} D_g^{(1)} + D_g^{(2)} &\rightarrow \Sigma^+ + \Sigma^- + 2\Pi + \Delta \quad (C_{\infty v}),\\ &\rightarrow \Sigma_g^+ + \Sigma_g^- + 2\Pi_g + \Delta_g \quad (D_{\infty h}),\\ &\rightarrow 2\Sigma + 2\Pi + \Delta \quad (C_\infty),\\ &\rightarrow \Sigma^+ + \Sigma^- + 2\Pi + \Delta \quad (D_\infty), \end{aligned}$$

and there are two independent occurrences in the C_∞ group, one in each of the others. This distinguishes the symmetry effect of shear on a dipolar cholesteric from the other types considered here. Only in the dipolar cholesteric is the shear induced vorticity transferred to the point group of the swarm. In the other point groups the tsr does not occur in the relevant representation of $D_g^{(1)}$. This will help decide whether shearing an isotropic phase of a liquid crystal induces a phase transition into the nematic or cholesteric phase.

7. Computer simulation, a specific application

One specific application of the symmetry theory is

to test for the appearance of predicted averages in a computer simulation of long rods, or ellipsoids, of $D_{\infty h}$ or $C_{\infty v}$ symmetry. The predicted averages will be immediately useful in deciding whether a transition from an isotropic to a liquid crystal phase has indeed occurred. Long rods are of $D_{\infty h}$ symmetry but the addition of a dipolar term in the potential, with charges and asymmetric mass distribution produces $C_{\infty v}$ symmetry. Liquid crystals and long rod polymers are known to be highly non-Newtonian in response to shear and work is in progress to simulate linear molecules with applied shearing fields with SLLOD and PUT [4,7,19] algorithms and arbitrary applied field strength. This will be a stringent test of the symmetry expectations put forward in this paper.

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