

Symmetry of ensemble averages in smectic liquid crystals

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Group-theoretical statistical mechanics is applied to determine the number of non-vanishing ensemble averages in the point groups of smectic liquid crystals, modelled on the 32 possible crystallographic point groups supplemented by linear symmetries. Assuming that the thermodynamic average exists according to the number of irreducible representations in each point group that are totally symmetric—a basic principle of group-theoretical statistical mechanics—it is possible to conclude whether or not that average exists at thermodynamic equilibrium. The conclusion is valid within the point-group symmetry of the liquid crystal. The number of ensemble averages supported by the smectic point group, exemplified by the time correlation functions, decreases from triclinic to monoclinic to orthorhombic to trigonal to tetragonal to hexagonal to cubic. Within each of these major classifications, the pattern of non-vanishing correlation functions and other ensemble averages has its own distinctive signature, based on point-group theory. By choosing the correlation functions that are known Fourier transforms of spectra, this type of analysis leads to a convenient method of determining how spectra are affected by the type of smectic point-group symmetry. The analysis leads to an appreciation of the differences in allowed ensemble averages between the various smectic point groups and molecular and other types of liquid. The treatment can be extended straightforwardly to consider the effects of external fields.

1. Introduction

Recent work has shown that the symmetry of the director in nematic and cholesteric liquid crystals falls into one of four point groups, two achiral (nematic) and two chiral (cholesteric) [1]. The molecular dynamics within this local point-group symmetry may then be explored systematically with the newly developed principles [2-5] of group-theoretical statistical mechanics (GTSM). In smectic liquid crystals the relevant point-group symmetries are similar to those of the 32 point groups of solid molecular crystals, described by the following 7 major classifications: triclinic, monoclinic, orthorhombic, trigonal, tetragonal, hexagonal and cubic. Each of these major classifications supports a number of point-group symmetries, which cover all known crystal symmetries. Molecules crystallise within these point groups, forming an underlying structure classified by 230 space groups. However, the external symmetry and physical appearance of a molecular crystal

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falls into one of the point groups. Similarly, the physical properties of a smectic liquid crystal may be explored with a point-group description [1] of the local structure, which distinguishes it from an isotropic molecular liquid. In principle, the point-group symmetry within the smectic phase may be any symmetry, but in order to construct a systematic approach to the problem of smectic local ordering, we assume in this paper that the smectic symmetry can be described by the 32 crystallographic point groups supplemented by the 4 point groups of the nematic and cholesteric liquid crystals. We therefore provide symmetry data for 36 point groups, any one of which may provide a framework [1] for the application of GTSM and the determination of non-vanishing ensemble averages of the molecular dynamics within the local point-group symmetry. Many such averages exist at the local level, but disappear if the smectic sample is isotropic on the macroscopic scale of a laboratory sample. If the smectic liquid crystal maintains the point-group anisotropy at this level, and is anisotropic overall, then the ensemble averages survive averaging in the laboratory frame (X, Y, Z) as well as in the local frame of the point group, which we denote by (x_D, y_D, z_D) .

The difference between solid molecular crystals and liquid crystals with three-dimensional anisotropy is not easy to define. De Vries [6] has pointed out that the most significant difference is that in the solid crystal any alkyl chains at the ends of the molecule have very little disorder, or none at all, whereas in a liquid crystal that has three-dimensional anisotropy these chains are slightly disordered. The difference in local point group symmetry seems to be minimal. For example, the smectic H phase of BBFA (4-n-butyloxybenzal-4-ethylaniline) is a liquid and not a solid molecular crystal because there is no transmission of phonon modes through the smectic liquid crystal, which is capable of flow. Translational coupling is much weaker than rotational coupling. When the two compete, as in structures with optically active molecules, the translational correlation is destroyed so as to achieve a more favourable rotational arrangement. A molecular-crystal structure of an optically active compound has a single three-dimensional lattice, but that of a three-dimensional smectic phase becomes twisted if the molecules are optically active, similarly to a cholesteric phase [1]. Three-dimensional anisotropic liquid crystals may be mixed in all proportions, in contrast with molecular crystals. If translational order disappears, there is no three-dimensional order at all.

Smectic liquid crystals and solid molecular crystals therefore differ essentially in translational order. In smectic liquid crystals there is still a residual point-group symmetry, however, although translational space-group symmetry may have been partially or completely destroyed.

The difference between a smectic liquid crystal and an isotropic molecular liquid can be expressed in terms of extra ensemble averages supported by the former within definable local point-group symmetries. In the isotropic molecular liquid, these are absent, its point group in three dimensions is $R_h(3)$, the three-dimensional rotation-reflection group [7], whose irreducible representations are the D representations

$$D_g^{(0)}, D_g^{(1)}, \dots \quad \text{and} \quad D_u^{(0)}, D_u^{(1)}, \dots,$$

where the superscripts denote the order of the spherical harmonics and the subscripts the signature under parity inversion. One of the principles of GTSM, developed recently by Whiffen [3] and Evans [4, 5], states that the ensemble average of statistical mechanics exists within $R_h(3)$ if its D representation includes the totally

symmetric representation (TSR) $D_g^{(0)}$ at least once. Essentially, this is a statement of Neumann's Principle [7-9] in the language of point-group theory. Further axioms extend this [10] to ensemble averages in the molecule-fixed frame (x, y, z) and the local (director) frame [1] (x_D, y_D, z_D) of nematic and cholesteric liquid crystals. Others extend consideration [11] to applied fields, such as electric, magnetic, electromagnetic or shearing fields [12-14] (strain-rate tensor). A particularly useful application of GTSM has recently been made [15] to Couette flow in simple (atomic) liquids, where the Weissenberg effect was explained for the first time in terms of fundamental cross-correlation functions (CCFs) between velocity components generated by the applied strain rate. The methods of GTSM have been successful in providing a symmetry classification [3-6] for available computer simulations of molecular dynamics in liquids, in particular the pattern of CCFs set up in both frames (X, Y, Z) and (x, y, z) at isotropic equilibrium and at field-on equilibrium [11]. Using non-equilibrium statistical-mechanics computer simulation, the cross-correlations predicted by GTSM have been found to be sensitive probes of non-Newtonian effects [16] such as shear thickening and thinning, convective and structural turbulence and, in electrorheology, of the effect of electric fields on colloids. When dealing with isotropic liquids at equilibrium, GTSM shows these [4] to be non-Gaussian in general, corroborating the evidence slowly emerging from computer simulation [17-20] that liquid-state statistical mechanics is in general non-Markovian and non-Gaussian. GTSM has recently also uncovered the phenomenon [21] of time dissymmetry in CCFs such as those of velocity. This has been explained by the fact that such cross-correlations are due to a combination of time-antisymmetric components of $D_g^{(1)}$ symmetry representing vorticity, and symmetric tensor components of $D_g^{(2)}$ symmetry representing deformation. The evidence is therefore quickly accumulating that GTSM is a powerful and essentially simple new method of investigating the dynamics of atoms and molecules in different ensemble environments.

In this paper we apply these methods to investigate ensemble averages such as time correlation functions [22] (Fourier transforms of frequency spectra) in the smectic liquid-crystal environment, characterised by 35 point groups. In section 2 the symmetry of the D representations is mapped [2] from $R_h(3)$ to each point group, and a table constructed of the symmetry of representative ensemble averages, showing which averages may exist in the frame (x_D, y_D, z_D) of the smectic environment but which disappear in the isotropic liquid. Among these are scalar components of the time CCF $\langle \omega(t) \mathbf{v}(0) \rangle$ between the molecular angular velocity ω and linear velocity \mathbf{v} , which can therefore be present in a suitable smectic environment and help to define the structure and dynamics of the liquid crystal. This CCF always vanishes by symmetry in isotropic liquids, and is therefore one of the characteristics of the smectic to isotropic phase change. Many other characteristics of this nature emerge from the analysis. Section 3 is a discussion of the major results and section 4 contains suggestions for further work, including simulations of the smectic environment and its closely related molecular-crystalline counterpart.

2. Mapping from $R_h(3)$ to the 36 point groups

We assume that the local smectic environment is modelled closely by the 32 crystallographic point groups, together with the point groups that characterise the nematic and cholesteric liquid-crystal phases. Each point group is defined with

respect to the frame (x_D, y_D, z_D) and has its own set of irreducible representations in this frame. Thus, for cubic (O_h) symmetry, the principles of GTSM state that thermodynamic averages exist in the frame (x_D, y_D, z_D) , governed by this local cubic symmetry, provided that the symmetry representations of the ensemble averages contain at least once the TSR of this cubic point group. This is the A_{1g} irreducible representation. This result is independent of the molecular symmetry within the point group. (Analogously, GTSM states that the ensemble averages in an isotropic environment exist if their symmetry representations contain the TSR $D_g^{(0)}$ of the point group $R_h(3)$, irrespective of the molecular symmetry.)

In general we must define the irreducible representation of the quantity being averaged in the $R_h(3)$ point group and then in the relevant local smectic point group. If for example the latter is the tetragonal D_{2d} (or $\overline{4}2m$ in the Hermann-Mauguin international notation), the relevant TSR is the irreducible representation A_1 . GTSM implies the powerful result that any thermodynamic ensemble average within the local smectic point group D_{2d} of the frame (x_D, y_D, z_D) may exist in this frame if this irreducible representation contains A_1 . This is a powerful result because it is wholly independent of any residual space-group structure in the smectic liquid crystal. Proceeding on these grounds, it is possible to link the symmetry of ensemble averages in the liquid and smectic liquid crystal by mapping the irreducible representation of the quantities being averaged from the point group $R_h(3)$ to D_{2d} . For ease of development, it is convenient to divide quantities into scalars, pseudoscalars, polar and axial vectors, and higher-order tensors. A scalar is characterised by the TSR in any point group. The irreducible representation of the pseudoscalar in $R_h(3)$ is $D_u^{(0)}$, which is odd under parity reversal, but still a zeroth-order quantity with no directional property. This representation maps on to B_1 of the point group D_{2d} . In chiral point groups C_n, D_n, T, O the irreducible representations of both the scalar and pseudoscalar map on to the TSR of the point group, so that ensemble averages over both scalars and pseudoscalars can exist in chiral point groups at the local level in smectic liquid crystals. There are two distinct liquid-crystal enantiomorphs.

A polar vector (e.g. velocity) is represented in $R_h(3)$ by $D_u^{(1)}$, meaning that it is odd under parity reversal and has first-order directional properties. An axial vector, on the other hand, is represented by $D_g^{(1)}$, which is even under parity reversal. An example of a polar vector is molecular linear velocity \mathbf{v} . Molecular angular velocity is an axial vector. The irreducible representations $D_u^{(1)}$ and $D_g^{(1)}$ respectively map onto $B_2 + E$ and $A_2 + E$ of the point group D_{2d} . These do not contain the point group's TSR, and in consequence no ensemble average over a polar or axial vector can exist in the frame (x_D, y_D, z_D) of the local smectic point group D_{2d} .

In local smectic point groups where the TRS appears as part of the irreducible representation in the point group of a polar or axial vector quantity, the thermodynamic average in the local frame of reference (x_D, y_D, z_D) may exist, provided that it is positive under time-reversal symmetry. Examples are listed in the table.

Second-rank tensor quantities are characterised in $R_h(3)$ by $D_g^{(2)}$ or $D_u^{(2)}$ and are second-order directional quantities that are even or odd under parity reversal.

There is a useful relation between D quantities in the point group $R_h(3)$ that is given by the Clebsch-Gordan Theorem

$$D^{(n)}D^{(m)} = D^{(n+m)} + \dots + D^{(|n-m|)} \quad (1)$$

This is also applicable in the point groups of smectic liquid crystals because the sum of D representations maps on to the same sum in the smectic point group. Thus, if

Table.

| Point group | Scalar ($D_0^{(0)}$) | Scalar ($D_0^{(1)}$) | Vector ($D_0^{(1)}$) | Vector ($D_0^{(1)}$) | $D_0^{(1)}D_0^{(1)} = D_0^{(1)}D_0^{(1)}$ $= D_0^{(0)} + D_0^{(1)} + D_0^{(2)}$ | No. | No. | Local symmetry |
|--------------------------|---------------------------|---------------------------|----------------------------|----------------------------|--|-----|-----|---------------------------|
| C_1 (1) | A | A | $3A$ | $3A$ | $9A$ | 9 | 9 | Triclinic |
| $C_1(S_2)$ ($\bar{1}$) | A_g | A_u | $3A_g$ | $3A_u$ | $9A_u$ | 9 | 0 | Triclinic |
| C_2 (2) | A | A | $A + 2B$ | $A + 2B$ | $5A + 4B$ | 5 | 5 | Monoclinic |
| C_{1h} (m) | A^1 | A^{11} | $A^1 + 2A^{11}$ | $2A^1 + A^{11}$ | $4A^1 + 4A^{11}$ | 5 | 4 | Monoclinic |
| C_{2h} (2/m) | A_g | A_u | $A_g + 2B_g$ | $A_u + 2B_u$ | $5A_g + 4B_u$ | 5 | 0 | Monoclinic |
| C_{2v} (2mm) | A_1 | A_2 | $A_2 + B_1 + B_2$ | $A_1 + B_1 + B_2$ | $2A_1 + 3A_2 + 2B_1 + 2B_2$ | 3 | 2 | Orthorhombic |
| D_2 (232) | A_1 | A_1 | $B_1 + B_2 + B_3$ | $B_1 + B_2 + B_3$ | $3A_1 + 2B_1 + 2B_2 + 2B_3$ | 3 | 3 | Orthorhombic |
| D_{2h} (mmmm) | A_{1g} | A_{1u} | $B_{1g} + B_{2g} + B_{3g}$ | $B_{1u} + B_{2u} + B_{3u}$ | $3A_{1g} + 2B_{1g} + 2B_{2g} + 2B_{3g}$ | 3 | 0 | Orthorhombic |
| C_3 (3) | A | A | $A + E$ | $A + E$ | $3A + 3E$ | 2 | 2 | Trigonal |
| C_{3v} (3m) | A_1 | A_2 | $A_2 + E$ | $A_1 + A_2 + 3E$ | $A_1 + 2A_2 + 3E$ | 2 | 1 | Trigonal |
| D_3 (32) | A_1 | A_1 | $A_2 + E$ | $A_2 + E$ | $2A_1 + A_2 + 3E$ | 2 | 2 | Trigonal |
| D_{3d} (3m) | A_{1g} | A_{1u} | $A_{2g} + E_g$ | $A_{2u} + E_u$ | $2A_{1g} + A_{2g} + 3E_g$ | 2 | 0 | Trigonal |
| S_6 (3) | A_g | A_u | $A_g + E_g$ | $A_u + E_u$ | $3A_g + 3E_u$ | 3 | 3 | Trigonal |
| C_4 (4) | A | A | $A + E$ | $A + E$ | $3A + 2B + 2E$ | 3 | 3 | Tetragonal |
| C_{4v} (4mm) | A_1 | A_2 | $A_2 + E$ | $A_1 + E$ | $2A_1 + A_2 + B_1 + B_2 + 2E$ | 2 | 1 | Tetragonal |
| C_{4h} (4/m) | A_g | A_u | $A_g + E_g$ | $A_u + E_u$ | $3A_g + 2B_u + 2E_u$ | 2 | 0 | Tetragonal |
| D_4 (422) | A_1 | A_1 | $A_2 + E$ | $A_2 + E$ | $2A_1 + A_2 + B_1 + B_2 + 2E$ | 2 | 2 | Tetragonal |
| D_{4h} (4/mmm) | A_{1g} | A_{1u} | $A_{2g} + E_g$ | $A_{2u} + E_u$ | $2A_{1g} + A_{2g} + B_{1g} + B_{2g} + 2E_g$ | 2 | 0 | Tetragonal |
| D_{2d} (42m) | A_1 | B_1 | $A_2 + E$ | $B_2 + E$ | $2A_1 + A_2 + B_1 + B_2 + 2E$ | 2 | 1 | Tetragonal |
| S_4 (4) | A | B | $A + E$ | $B + E$ | $3A + 2B + 2E$ | 3 | 2 | Tetragonal |
| C_6 (6) | A | A | $A + E_1$ | $A + E_1$ | $3A + 2E_1 + E_2$ | 3 | 3 | Hexagonal |
| C_{6h} (6mm) | A_1 | A_2 | $A_2 + E_1$ | $A_1 + E_1$ | $A_1 + 2A_2 + 2E_1 + E_2$ | 2 | 1 | Hexagonal |
| C_{3h} (6) | A^1 | A^{11} | $A^1 + E^{11}$ | $A^{11} + E^1$ | $3A^1 + 2E^1 + E^{11}$ | 3 | 0 | Hexagonal |
| C_{6h} (6/m) | A_g | A_u | $A_g + E_{1g}$ | $A_u + E_{1u}$ | $3A_g + 2E_{1g} + E_{2u}$ | 3 | 0 | Hexagonal |
| D_6 (622) | A_1 | A_1 | $A_2 + E_1$ | $A_2 + E_1$ | $2A_1 + A_2 + E_2 + 2E_1$ | 2 | 2 | Hexagonal |
| D_{3h} (6m2) | A_1^1 | A_1^1 | $A_2^1 + E^1$ | $A_2^1 + E^1$ | $2A_1^1 + A_2^1 + E^1 + 2E^{11}$ | 2 | 0 | Hexagonal |
| D_{6h} (6/mmm) | A_{1g} | A_{1u} | $A_{2g} + E_{1g}$ | $A_{2u} + E_{1u}$ | $2A_{1g} + A_{2g} + 2E_{1g} + E_{2u}$ | 2 | 0 | Hexagonal |
| O_h (m3m) | A_1 | A_2 | T_1 | T_2 | $A_2 + T_2 + E + T_1$ | 1 | 0 | Cubic |
| T (23) | A_{1g} | A_{1u} | T_{1g} | T_{1u} | $A_{1g} + T_{1g} + E_g + T_{1u}$ | 1 | 0 | Cubic |
| T_h (m3) | A_g | A_u | T_g | T_u | $A_g + E_g + 2T_u$ | 1 | 0 | Cubic |
| O (434) | A_1 | A_1 | T_1 | T_1 | $A_1 + E + T_1 + T_2$ | 1 | 1 | Cubic |
| $C_{\infty v}$ | Σ^+ | Σ^- | $\Sigma^- + \Pi$ | $\Sigma^+ + \Pi$ | $2\Sigma^- + \Sigma^+ + 2\Pi + 4$ | 2 | 1 | Linear dipolar |
| $C_{\infty h}$ | Σ^+ | Σ^- | $\Sigma + \Pi$ | $\Sigma + \Pi$ | $3\Sigma + 2\Pi + 4$ | 3 | 3 | Linear dipolar chiral |
| $D_{\infty h}$ | Σ_g^+ | Σ_g^- | $\Sigma_g^+ + \Pi_g$ | $\Sigma_g^- + \Pi_g$ | $2\Sigma_g^- + \Sigma_g^+ + 2\Pi_g + 4_u$ | 2 | 0 | Linear non-dipolar |
| $D_{\infty d}$ | Σ^+ | Σ^- | $\Sigma^- + \Pi$ | $\Sigma^- + \Pi$ | $2\Sigma^- + \Sigma^+ + 2\Pi + 4$ | 2 | 2 | Linear non-dipolar chiral |

we extend our consideration of ensemble averages to time correlation functions that are averages over products of vectors, we have, for example,

$$\Gamma(\mathbf{v})\Gamma(\boldsymbol{\omega}) = D_{\mathbf{v}}^{(1)}D_{\boldsymbol{\omega}}^{(1)} = D_{\mathbf{v}}^{(0)} + D_{\mathbf{v}}^{(1)} + D_{\mathbf{v}}^{(2)} \quad (\mathbf{R}_h(3)) \quad (2a)$$

$$= (B_2 + E)(A_2 + E) = A_1 + A_2 + 2B_1 + B_2 + 2E \quad (\mathbf{D}_{2d}) \quad (2b)$$

This shows that the D representation of the time correlation tensor generated by the tensor product of molecular linear and angular velocity is a sum of three *ungerade* D representations in the molecular-liquid point group $\mathbf{R}_h(3)$. The time correlation function vanishes for all t in the isotropic liquid because its complete D representation does not include $D_{\mathbf{g}}^{(0)}$. In the \mathbf{D}_{2d} smectic point group, however, this is not the case, because the irreducible representation of the CCR $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$ is the sum $A_1 + A_2 + 2B_1 + B_2 + 2E$, which includes the TSS A_1 once. GTSM therefore implies that one element of $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$ may exist in the \mathbf{D}_{2d} point group of the smectic liquid crystal. This result may be checked in principle with molecular-dynamics computer simulation.

2.1. Time-reversal symmetry†

Time-reversal symmetry is defined in this context as the operation $(\mathbf{q}, \mathbf{p}) \rightarrow (\mathbf{q}, -\mathbf{p})$, which leaves positions unchanged but reverses momenta. Parity reversal is the operation $(\mathbf{q}, \mathbf{p}) \rightarrow (-\mathbf{q}, -\mathbf{p})$. When dealing with scalars and pseudoscalars, the ensemble average over these quantities must be unchanged (i.e. positive) under time reversal. When dealing with vectors, however, some are positive under time reversal, such as the electric field \mathbf{E} , the position vector \mathbf{r} , the linear acceleration $\dot{\mathbf{v}}$, the angular acceleration $\dot{\boldsymbol{\omega}}$ and the acceleration due to gravity \mathbf{g} . Others are negative under time reversal, such as the magnetic field \mathbf{B} , the linear velocity \mathbf{v} , the angular velocity $\boldsymbol{\omega}$ and the electromagnetic-field propagation vector \mathbf{k} . A thermodynamic ensemble average over a vector that is negative under time reversal vanishes, but one that is positive may exist if the vector is also positive under parity reversal in the isotropic-liquid point group $\mathbf{R}_h(3)$. In the local smectic-phase point groups, however, the latter requirement is not necessary, and the thermodynamic ensemble average exists provided that it is carried out over a vector that is positive under time reversal and provided that the irreducible representation of that vector includes the TSR of the point group. Thus the average $\langle \mathbf{r} \rangle$, for example, may exist in the point group \mathbf{C}_{3v} of the trigonal class, because the vector's irreducible representation in the point group is $A_1 + E$. The latter includes the TSR A_1 once. From GTSM, one independent ensemble average exists over a polar with positive time-reversal symmetry. An example is $\langle \mathbf{r} \rangle$. Other examples in this local smectic point group are $\langle \dot{\mathbf{v}} \rangle$ and $\langle \dot{\boldsymbol{\omega}} \rangle$. This may again be investigated with computer simulation. In the tetragonal local smectic point group \mathbf{D}_{2d} , however, all these ensemble averages should vanish by GTSM.

When dealing with time correlation functions, the time-reversal arguments must be applied with care to each individual case. The pitfalls of the procedure may be illustrated with reference to the simple time CCR of the type $\langle \mathbf{A}(t)\mathbf{A}(0) \rangle$ [22]. If \mathbf{A} represents linear velocity \mathbf{v} , for example, the product within the averaging brackets $\langle \rangle$ is overall negative under time reversal. However, this type of time correlation function clearly does not vanish for all t since it is simply the time derivative of $\langle \mathbf{A}(t)\mathbf{A}(0) \rangle$. It exists according to the elementary theory of correlation function in

† See [9, 17].

reversible thermodynamic equilibrium [22]. It is itself a function that is a time derivative, and is intrinsically negative under time reversal. More generally, the class of time correlation functions that are time derivatives of other correlation functions have an existence for $0 < t < \infty$ despite the fact that the product of the two quantities inside the averaging brackets may in itself appear negative under time reversal.

Bearing in mind these considerations of time reversal, mappings of some D representations form the point group $R_n(3)$ are given in the table for 36 local smectic point groups. Column one of the table contains the name of the point group in Schönflies and Hermann–Mauguin notations (the latter in parentheses). Column two is the representation of the scalar in the point group (i.e. the TSR), column three contains the symmetry representation of the pseudoscalar, column four that of the axial vector and column five that of the polar vector. Columns six and seven map products of D representations onto each point group. Columns eight and nine give the number of independent ensemble averages expected in the local smectic point group for representative time correlation-functions, column eight for the rotational velocity correlation tensor and column nine for the angular-linear velocity cross-correlation tensor. Both tensors are defined in the frame (x_D, y_D, z_D) of the local smectic point group. Finally, column ten records the crystal class of the point group if it were being used to describe solid molecular crystals.

Note that in isotropic molecular liquid environments only one independent ensemble average (the trace) is expected in column eight, and none in column nine, evidencing by GTSM a considerable difference between the local molecular dynamics of smectic liquid crystals and isotropic molecular liquids.

Some examples of the symmetry of the correlation functions in columns eight and nine are as follows.

2.2. Local smectic point group $C_{1h}(m)$

Rotational-velocity autocorrelation function (ACF).

The irreducible representation of the rotational-velocity correlation tensor in the point group C_{1h} is

$$\begin{aligned} \Gamma(\dot{\boldsymbol{\mu}}(t))\Gamma(\dot{\boldsymbol{\mu}}(0)) &= (2A^1 + A^{11})(2A^1 + A^{11}) \\ &= 4A^1A^1 + 2A^1A^{11} + 2A^{11}A^1 + A^{11}A^{11} \\ &= 5A^1 + 4A^{11}, \end{aligned} \quad (3)$$

showing five occurrences of the TSR in the product of representations of the correlation tensor. Thus five independent ensemble averages may exist in the local smectic frame of reference (x_D, y_D, z_D) . The individual products that give A^1 in (3) are (i) $4A^1A^1$ and (ii) $A^{11}A^{11}$. The others give A^{11} . Referring to the point-group character table for C_{1h} , we find that A^1 represents the Cartesian components x_D and y_D of the local smectic frame of reference. The A^{11} entry represents z_D . The product $4A^1A^1$ therefore represents four independent components of the rotational-velocity correlation tensor:

$$\langle \dot{\mu}_{x_D}(t)\dot{\mu}_{x_D}(0) \rangle, \quad \langle \dot{\mu}_{y_D}(t)\dot{\mu}_{y_D}(0) \rangle, \quad \langle \dot{\mu}_{x_D}(t)\dot{\mu}_{y_D}(0) \rangle, \quad \langle \dot{\mu}_{y_D}(t)\dot{\mu}_{x_D}(0) \rangle.$$

The fifth component $\langle \dot{\mu}_{zD} \dot{\mu}_{zD}(0) \rangle$ comes from $A^{11}A^{11}$. The complete symmetry of the correlation tensor in the local smectic frame of reference is therefore

$$\langle \dot{\boldsymbol{\mu}}(t)\dot{\boldsymbol{\mu}}(0) \rangle = \begin{bmatrix} a & d & 0 \\ e & b & 0 \\ 0 & 0 & c \end{bmatrix}, \quad C_{1h} \text{ (m)},$$

and the five independent elements are recorded in the table.

Similar arguments applied to the generic ACF $\langle \mathbf{A}(t)\mathbf{A}(0) \rangle$ show these five independent elements, with the same symmetry pattern. In a molecular crystal this result is related to the number of lattice modes, but in a smectic liquid crystal there are no phonon modes.

The cross-correlation function $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$

The irreducible representation is now

$$\begin{aligned} \Gamma(\mathbf{v})\Gamma(\boldsymbol{\omega}) &= (2A^1 + A^{11})(A^1 + 2A^{11}) \\ &= 2A^1A^1 + A^{11}A^1 + 4A^1A^{11} + 2A^{11}A^{11} \\ &= 4A^1 + 5A^{11}, \end{aligned} \quad (4)$$

showing four occurrences of A^1 . Thus the crystal class supports four independent ensemble averages, which are scalar elements of $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$. Bearing in mind that the linear velocity \mathbf{v} is referred to the Cartesian components X , Y and Z of the C_{1h} point-group character table, and the angular-velocity component $\boldsymbol{\omega}$ by R_x , R_y and R_z , we arrive at the symmetry

$$\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle = \begin{bmatrix} 0 & 0 & a_1 \\ 0 & 0 & b_1 \\ c_1 & d_1 & 0 \end{bmatrix}.$$

Thus four independent elements exist, which all vanish in the equivalent molecular liquid.

2.3. Orthorhombic D_2 (232)

Rotational-velocity ACF

The relevant irreducible representation of the time ACF is

$$\Gamma(\dot{\boldsymbol{\mu}})\Gamma(\dot{\boldsymbol{\mu}}) = (B_1 + B_2 + B_3)(B_1 + B_2 + B_3) = 3A_1 + 2B_1 + 2B_2 + 2B_3, \quad (5)$$

which contains the totally symmetric component three times. From the axioms of GTSM, we can expect three independent ensembles in the local smectic point group D_2 (232), a chiral class. From the point-group character table for D_2 , and using the rules for forming the products of irreducible representations, we have the symmetry

$$\langle \dot{\boldsymbol{\mu}}(t)\dot{\boldsymbol{\mu}}(0) \rangle = \begin{bmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{bmatrix}, \quad D_2.$$

In this case all the off-diagonal elements vanish, leaving three independent diagonal elements. The far-infrared spectrum in the local smectic frame is different for each element.

The CCF $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$

The irreducible representation is

$$\Gamma(\mathbf{v})\Gamma(\boldsymbol{\omega}) = (B_1 + B_2 + B_3)(B_1 + B_2 + B_3) = 3A_1 + 2B_1 + 2B_2 + 2B_3, \quad (6)$$

which again contains A_1 three times and is the same as (5). This is because the D_2 point group is chiral, and $D_g^{(1)}$ and $D_u^{(1)}$ of $R_h(3)$ map on to the same representation in D_2 , i.e. $B_1 + B_2 + B_3$. Using (6) and the Cartesian and R representations in the point-group character table for D_2 leads to the symmetry

$$\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle = \pm \begin{bmatrix} a_1 & 0 & 0 \\ 0 & b_1 & 0 \\ 0 & 0 & c_1 \end{bmatrix}.$$

Thus the three diagonal elements of $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$ exist in the class D_2 (232). These elements change sign in the opposite enantiomer.

2.3. Orthorhombic C_{2v} (2mm)

Rotational-velocity ACF

In this achiral orthorhombic crystal class the irreducible representation is

$$\Gamma(\dot{\boldsymbol{\mu}})\Gamma(\dot{\boldsymbol{\mu}}) = (A_1 + B_1 + B_2)(A_1 + B_1 + B_2) = 3A_1 + 2A_2 + 2B_1 + 2B_2, \quad (7)$$

leading to the symmetry recorded in the table. Three independent diagonal elements exist as in the orthorhombic D_2 .

The CCF $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$

Here the irreducible representation is

$$\Gamma(\mathbf{v})\Gamma(\boldsymbol{\omega}) = (A_1 + B_1 + B_2)(A_2 + B_1 + B_2) = 2A_1 + 3A_2 + 2B_1 + 2B_2, \quad (8)$$

which contains A_1 twice. Reference to the point-group character tables reveals that the two independent elements are off-diagonals, so that the complete matrix symmetry is

$$\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle = \begin{bmatrix} 0 & a_1 & 0 \\ b_1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad C_{2v}.$$

This contrasts with the orthorhombic D_2 (232) crystal class, where only the diagonals of the CCF are visible.

2.4. Trigonal C_{3v} (3m)

Rotational velocity

The irreducible representation in this case is

$$\Gamma(\dot{\boldsymbol{\mu}})\Gamma(\dot{\boldsymbol{\mu}}) = (A_1 + E)(A_1 + E) = 2A_1 + A_2 + 3E, \quad (9)$$

which contains the TSR twice. One comes from the product $A_1 A_1$ and the other from EE , which signifies the product $(x_D, y_D)(x_D, y_D)$ in the Cartesian representation of the point-group character table. It is well known that this notation implies the equivalence of x_D and y_D . The product implies four rotational-velocity correlation function elements according to GTSM. These four elements are not independent, and are grouped together, being equivalent to one A_1 , generated by the product rule

$$EE = A_1 + A_2 + E.$$

However, from the elementary theory of time correlation functions, we know that

$$\langle \dot{\mu}_{x_D}(t)\dot{\mu}_{x_D}(0) \rangle \neq \langle \dot{\mu}_{x_D}(t)\dot{\mu}_{y_D}(0) \rangle$$

because one is an autocorrelation function, with finite value at $t = 0$, and the other a CCF, which vanishes at $t = 0$. This, together with the independent appearance of $\langle \dot{\mu}_{z_D}(t)\dot{\mu}_{z_D}(0) \rangle$ from $A_1 A_1$ leads to the final symmetry

$$\langle \dot{\mu}_{x_D}(t)\dot{\mu}_{x_D}(0) \rangle = \langle \dot{\mu}_{y_D}(t)\dot{\mu}_{y_D}(0) \rangle \neq \langle \dot{\mu}_{z_D}(t)\dot{\mu}_{z_D}(0) \rangle.$$

The two independent non-vanishing elements are thus

$$\langle \dot{\mu}_{x_D}(t)\dot{\mu}_{x_D}(0) \rangle = \langle \dot{\mu}_{y_D}(t)\dot{\mu}_{y_D}(0) \rangle$$

and $\langle \dot{\mu}_{z_D}(t)\dot{\mu}_{z_D}(0) \rangle$. The further result

$$\langle \dot{\mu}_{x_D}(t)\dot{\mu}_{y_D}(0) \rangle = \langle \dot{\mu}_{y_D}(t)\dot{\mu}_{x_D}(0) \rangle = 0$$

follows from the fact that the irreducible representation (9) allows two and only two independent non-vanishing elements. The symmetry of the complete ACF matrix is thus

$$\langle \dot{\boldsymbol{\mu}}(t)\dot{\boldsymbol{\mu}}(0) \rangle = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}, \quad C_{3v} \quad (3m),$$

and is recorded in the table.

The CCF $\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle$

The relevant irreducible representation is

$$\Gamma(\mathbf{v})\Gamma(\boldsymbol{\omega}) = (A_1 + E)(A_2 + E) = A_1 + 2A_2 + 3E \quad (10)$$

allowing one occurrence of A_1 , and, by GTSM, one independent non-vanishing CCF element. This comes from the product $EE = A_1 + A_2 + E$. The non-vanishing element must therefore be from the four possible generated from $(x_D, y_D)(x_D, y_D)$. There is no independent occurrence of the diagonal element $\langle v_{z_D}(t)v_{z_D}(0) \rangle$ from (10), and therefore the single independent element is

$$\langle v_{x_D}(t)\omega_{y_D}(0) \rangle = -\langle v_{y_D}(t)\omega_{x_D}(0) \rangle. \quad (11)$$

The minus sign [19] comes from the fact that the overall matrix symmetry is odd under parity reversal; the result (11) represents the vector cross-product symmetry, denoted by $D_u^{(1)}$ in the $R_h(3)$ point group. The overall matrix symmetry is thus

$$\langle \mathbf{v}(t)\boldsymbol{\omega}(0) \rangle = \begin{bmatrix} 0 & a_1 & 0 \\ -a_1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad C_{3v} \quad (3m),$$

as in the table.

2.5. The cubic crystal classes

There are five cubic crystal classes of high symmetry [1]. Two of these (T and O) are chiral. Applying the same methods as in section 2.1–2.4 results in the classification in the table, which shows that the diagonal elements are supported for the rotational velocity and other time autocorrelation functions. Cross-correlation functions are supported only in the chiral classes T and O. No more than one independent element appears in each class, i.e. there is no more than one occurrence of the relevant totally symmetric irreducible representation in each local point group. The far-infrared spectrum remains the same along the x_D , y_D and z_D axes of the cubic point group.

3. Discussion of results

The table provides a classification scheme for non-vanishing thermodynamic ensemble averages in the given point-group classification scheme. Each point group may accommodate molecules of independent symmetry, but the overall thermodynamic average is determined by the point-group symmetry alone. We have shown only a few representative thermodynamic ensemble averages in the table, but in general all such averages may be accommodated. For example, if we wish to consider polarisability of a volume element in the isotropic environment, we take the $R_h(3)$ point group and represent the polarisability with the D symmetry $D_g^{(0)} + D_g^{(2)}$, a symmetric second-rank tensor that is even under parity reversal. The overall macroscopic polarisability of a point-group representation of local smectic symmetry may then be investigated according to how many occurrences there are of the TSR in the local point group. The latter's character table may then be used to find out in more detail the nature of the polarisability tensor in the local smectic point group, i.e. which ensemble averages over the polarisability vanish and which exist. If we are investigating pyroelectric symmetry, on the other hand, we note that pyroelectricity has $D_u^{(1)}$ symmetry in $R_h(3)$, and we then map this onto the smectic point group representing local symmetry in the liquid crystal as in the table. This shows that in some local smectic point groups pyroelectric properties are supported in principle while in others they are not, according to whether the totally symmetric representation occurs in the point group. In some cases the pyroelectricity is different along each smectic axis axis (three occurrences of the TSR). For a given point-group symmetry, care must be taken to examine the time-reversal symmetry of the quantity being averaged thermodynamically.

Some D symmetries of physical quantities are listed below.

- (i) The magnetic dipole is an axial (or pseudo) vector of $D_g^{(1)}$ symmetry.
- (ii) Electric polarisability, thermal and electric conductivity, thermoelectricity, thermal expansion and magnetic susceptibility each have $D_g^{(0)} + D_g^{(2)}$ symmetry in $R_h(3)$.
- (iii) The quadrupole moment has $D_g^{(2)}$ symmetry.
- (iv) The gyration tensor of optical activity has $D_u^{(0)} + D_u^{(2)}$ symmetry.
- (v) The first hyperpolarisability has $D_u^{(1)} + D_u^{(3)}$ symmetry.

- (vi) Piezoelectricity and the electro-optic Kerr effect have $2D_u^{(1)} + D_u^{(2)} + D_u^{(3)}$ symmetry.
- (vii) Elasticity is a symmetric fourth-rank tensor of $2D_g^{(0)} + 2D_g^{(2)} + D_g^{(4)}$ symmetry.

Thermodynamic ensemble averages over all these quantities vanish in the isotropic-liquid environment except for polarisability and elasticity, which contain the $D_g^{(0)}$ representation. In the local smectic point groups, however, new thermodynamic averages may exist that vanish in the laboratory frame if the local (crystal-like) smectic symmetry is not maintained to the macroscopic level. (A key difference between a smectic liquid crystal and a molecular solid crystal is that the same (crystal) point-group symmetry is maintained in the latter from the local to the macroscopic level.) Local ensemble averages may exist in the smectic liquid crystal, depending on the number of occurrences of the appropriate totally symmetric irreducible representation and on the time-reversal symmetry of the quantity being averaged. The molecular electric polarisability and quadrupole moment are both positive under time-reversal symmetry, and extra ensemble averages over these quantities might appear in some of the local point groups. For example, in the orthorhombic class of C_{2v} point-group symmetry the representation $D_g^{(0)} + D_g^{(2)}$ of the electric polarisability maps on to $3A_1 + A_2 + B_1 + B_2$ showing that there are three independent non-vanishing thermodynamic averages over the molecular polarisability in this local point group. These correspond in the Cartesian notation of the point-group character table to X^2 , Y^2 and Z^2 , the three diagonal elements of the polarisability-tensor average. All three become equal in the isotropic molecular liquid. Again, this result is independent of the individual molecular symmetry within the C_{2v} point group. In the monoclinic C_{1h} crystal class $D_g^{(0)} + D_g^{(2)}$ maps on to $4A^1 + 2A^{11}$, meaning that four independent thermodynamic averages over polarisability exist in this class. These are denoted by X^2 , Y^2 , Z^2 and XY in the point-group character table opposite to the A^1 entry, signifying the existence of three independent diagonal thermodynamic averages and one off-diagonal symmetric pair, $XY = YX$. In the molecular liquid only one average exists, the trace of the diagonal averages, which are the same in the three isotropic laboratory axes in the molecular liquid. Group-theoretical statistical mechanics provides a unifying picture of the properties of these ensemble averages together with those of the set of non-vanishing time correlation functions for each local point group.

4. Suggestions for computer simulation

The results obtained in section 2 and discussed in section 3 provide a coherent system of predicting the existence of ensemble averages in the point groups of the table. The numerical values of these averages and the time dependences of the correlation functions must be obtained using additional complementary methods, such as bandshape analysis and molecular-dynamics computer simulation. Not only would this provide a needed and detailed check on the predictions of GTSM applied to smectic liquid crystals, but it would also be a new area of fruitful investigation of liquid-crystal molecular dynamics, extending the range of liquid-state computer simulations.

The methods developed in section 2 can also be extended to deal with the effect of external fields on smectic liquid crystals, using the third principle of GTSM [10].

This states that the symmetry of ensemble averages set up in a molecular environment subjected to an externally applied macroscopic force field is the symmetry of the applied field itself. In an ensemble of atoms subjected to a strain rate of overall symmetry $D_g^{(0)} + D_g^{(1)} + D_g^{(2)}$ recent computer simulation [15, 16, 21] has indeed revealed the existence of new types of ensemble average set up by the field and taking its overall symmetry. These CCFs explain the fundamental origin of the well known Weissenberg effect of rheology [12–14]. Similarly, an electric field of symmetry $D_u^{(1)}$ sets up ensemble averages of this symmetry in the $R_h(3)$ point group, and thus also in the local smectic point groups. The symmetry of the electric-field-induced ensemble average in a given point group is $D_u^{(1)}$, mapped onto its equivalent irreducible representation in the local point group. Similar predictions can be made for other applied macroscopic fields, such as a magnetic field, an electromagnetic field and strain rate, applied to the smectic liquid crystal in the laboratory axes X , Y and Z . These methods, used with computer simulation and experimental spectroscopy, for example [17–20], will reveal a great deal about fundamental and unknown areas of chemical physics.

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