

GROUP THEORETICAL STATISTICAL MECHANICS OF THE EVANS EFFECTS

PHASE CHANGES PRODUCED BY INHOMOGENEOUS ELECTRIC AND MAGNETIC FIELDS

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The effects first observed by G.J. Evans are explored in terms of the symmetry of ensemble averages, using the principles of group theoretical statistical mechanics (GTSM). The effects include phase changes brought about by inhomogeneous electric and/or magnetic fields, all of whose gradients are included in the treatment in a multipole expansion of the force differential across the interface between a molecular crystal and a molecular liquid. It is shown by GTSM that the force differential is generated by extra vector components which are sustained in the laboratory frame by the symmetry of the molecular crystal but which vanish in the liquid. In this way the symmetry of the former is continuously imparted to the latter.

1. Introduction

One of the effects first observed by Gareth J. Evans [1–5] is a phase change brought about by the application of an inhomogeneous electric field across the interface between the two phases. We refer to these important phenomena as the “Evans effects”. Evans himself modestly referred to the electric field effect as the inverse Costa Ribeiro effect because it is in some senses the opposite [1–5] of the generation of an electric potential across a phase interface first reported by Costa Ribeiro [6].

The Evans effects are observed [1–5] across a boundary between two phases, one of whose symmetries is different from the $R_h(3)$ point group of an isotropic molecular or atomic ensemble. Thus, there appear to be no Evans effects across the interface between a liquid and a gas, for example. They were reported [1–5] by Evans not only for inhomogeneous electric fields, but also for inhomogeneous magnetic fields. There appears to be also an analogous influence of electromagnetic fields in the presence of magnetic fields. These observations appear to be both fundamentally important and practically useful, and amount to far more than just the inverse of the (electric) Costa Ribeiro effect.

In this paper we use the three principles of group theoretical statistical mechanics (GTSM)

[7–12] to propose a mechanism for crystal/liquid phase changes brought about by externally applied inhomogeneous electric and magnetic fields, all of whose gradients exist in general in frame (X, Y, Z) of the laboratory. In section 2, the principles are briefly recounted, and applied in section 3 using a multipole expansion of the linear force differential cross the ideal (defect free) crystal to liquid interface. The 32 possible point groups of a molecular crystalline lattice are typified by the lattices of most and least symmetry, respectively the cubic and triclinic crystal point groups, for which some details of the calculation are appended. It is concluded that an Evans effect is made possible by force components which are sustained in general by the point group symmetry of the crystal lattice, but which vanish in the point group $R_h(3)$ of an isotropic molecular liquid. The force components in the crystal are not all balanced across the interface by those in the liquid, and as a result the interface moves in to the phase of lesser symmetry (the liquid).

2. The principles of group theoretical statistical mechanics

This new branch of statistical mechanics rests on three principles [7–12], with which the well-

developed methods of point group theory [13–15] are applied to ensemble averages. The principles allow conclusions to be drawn on the basis of symmetry alone. They have already provided valuable new insights in, for example, micro-rheology, forecasting the existence of fundamental indicator cross correlation functions, confirmed by computer simulation [16], shear induced light scattering from atomic ensembles [17], and other computer simulated and previously unknown phenomena such as thermal conductivity from combined shear and elongational stress [18]. They also anticipate the existence of shear induced spectroscopies of various kinds based on new types of asymmetric (irreversible) indicator ccf's [19–21]. One of these is shear induced dielectric spectroscopy [19]. The asymmetric ccf's are in general non-Markovian, non-linear and irreversible, and the symmetry principles apply equally in linear and non-linear response theory, to field-free equilibrium, field-applied steady states, and transient processes induced by the application of external fields. In non-linear optics they anticipate the existence of several new birefringence phenomena [22–25]; for the nematic, cholesteric and smectic phases of liquid crystals they define non-vanishing ensemble averages in the laboratory, director, and molecular frames of reference [26–28]. In the molecular frame of isotropic ensembles they confirm data available from extensive computer simulation [29, 30].

Principle (1) is the Neumann or Curie principle expressed in the language of group theory [7–12]. It operates in the laboratory frame (X, Y, Z). Principle (2) is its equivalent in the molecule fixed frame (x, y, z) of the literature point group character tables, and evolved out of work by Whiffen [29] and the present author [7–12]. Principle (3) is a simple but powerful cause effect theorem defining the effect of causal external fields on an ensemble. It is equally valid for linear and non-linear response and for all conceivable fields of force. Principle (1) states that the thermodynamic ensemble average $\langle ABC \dots \rangle$ of the atomic or molecular variables A, B, C, \dots exists in frame (X, Y, Z) if the product of their individual symmetry representa-

tions contains at least once the totally symmetric representation of the point group of the ensemble at field free thermodynamic equilibrium. Principle (2) states that this average exists in the molecule fixed frame (x, y, z) if the product of representations in the point group of the molecule contains the totally symmetric representation of that point group at least once. Principle (3) states that in the steady state in the presence of an applied field of force, or in the transient condition immediately following the imposition or removal of such a force field, new ensemble averages may appear whose symmetry is that of the applied field.

The application of these principles requires definitions of the appropriate point groups and their irreducible representations from point group theory, and this is possible [7–12, 29] in the isotropic molecular liquid condition and also in the 32 point groups of the ideal (defect free) molecular crystals, ranging from triclinic to cubic [31].

3. Multipole expansion of the external force fields, inhomogeneous electric field

It is assumed that the electric field applied to the crystal/liquid interface is in general inhomogeneous [1–5], so that all gradients exist in the laboratory frame (X, Y, Z). The linear force imparted to the liquid and crystal parts of the interface is assumed in consequence to take the general form

$$\langle \mathbf{F} \rangle_{\text{liq}} = a \langle q\mathbf{E} \rangle + \hat{V}(b \langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle + c \langle \mathbf{Q} \nabla \nabla \mathbf{E} \rangle + d \langle \boldsymbol{\Omega} \nabla \nabla \nabla \mathbf{E} \rangle + \dots)_{\text{liq}}, \quad (1)$$

$$\langle \mathbf{F} \rangle_{\text{crys}} = \langle a_1 q \mathbf{E} \rangle + \hat{V}(\langle b_1 \boldsymbol{\mu} \nabla \mathbf{E} \rangle + \langle c_1 \mathbf{Q} \nabla \nabla \mathbf{E} \rangle + \langle d_1 \boldsymbol{\Omega} \nabla \nabla \nabla \mathbf{E} \rangle + \dots)_{\text{crys}}, \quad (2)$$

where $\langle \rangle$ denote thermodynamic ensemble averaging [32–34]. Here a, b, c, \dots are scalar constants. The first term on the right-hand side involves net charge, q , if present, and the others

multiply the appropriate molecular multipole moments and field gradients. Here μ is the permanent molecular dipole moment (a three component vector), Q is the permanent molecular quadrupole moment (a nine component tensor), Ω is the permanent molecular octupole moment (a 27 component tensor), and so on. The notation ∇E stands for the complete product of the gradient vector ∇ and electric field vector, with nine components in general, $\nabla\nabla E$ has 27 components in general, and so on. Thus, the complete product of dipole moment and complete field gradient has 27 scalar components. The product $\nabla\nabla\nabla E$ has 81 scalar components, and so on. These complete (n -order tensor) products can be decomposed into independent vector parts in each point group using the rules of group theory. In eqs. (1) and (2), the operator \hat{V} implies a sum of independent vector components of each n -order tensor product. It can be shown by GTSM that there are always more vector components in the crystal part of the interface than in the liquid. As a consequence, there is a linear force differential across the interface, i.e. there are more non-vanishing components in the solid than in the liquid, and the interface is forced into the liquid. The crystal grows [1–5] under the influence of the external inhomogeneous field. More generally the phase whose symmetry allows the greater number of vector force components grows at the expense of the other. Thus, a nematic grows at the expense of an isotropic, a crystal at the expense of a nematic, and so on. When the symmetries of two phases reduce to the same point group, there is no symmetry effect (e.g. gas and liquid). This agrees qualitatively with observation [1–5]. In atomic ensembles (e.g. the interface between crystalline and liquid helium) charge has to be present for the Evans effect to occur, because there are no multipoles. In interfaces of carbon tetrachloride molecules, the first effective multipole is the octupole, and in sulphur hexafluoride systems the molecular hexadecapole moment. In the absence of charge the electric Evans effect is therefore a potentially valuable measure of the appropriate molecular multipole moment multiplied with the appropriate field gradients.

3.1. The isotropic liquid phase

The point group is $R_h(3)$ with the irreducible D representations [7–12]. The n -order tensor ensemble averages on the right-hand side of eq. (1) each have D representations that include m times the irreducible representation $D_u^{(1)}$ of the polar vector average $\langle F \rangle$. These are given as follows [7–12], using the Clebsch–Gordan theorem to multiply D terms:

$$\Gamma(qE) = D_u^{(1)}$$

$$\Gamma(\mu\nabla E) = D_u^{(0)} + 3D_u^{(1)} + 2D_u^{(2)} + D_u^{(3)}$$

$$\Gamma(Q\nabla\nabla E) = 3D_u^{(0)} + 9D_u^{(1)} + 9D_u^{(2)} + 7D_u^{(3)} \\ + 3D_u^{(4)} + D_u^{(5)}$$

$$\Gamma(\Omega\nabla\nabla\nabla E) = 25D_u^{(1)} + \dots$$

Thus the charge-field term contains $D_u^{(1)}$ once, the dipole-field gradient term contains $D_u^{(1)}$ three times, the quadrupole-gradient of the field gradient contains $D_u^{(1)}$ nine times, and the octupole term contains $D_u^{(1)}$ 25 times. These numbers signify the *number of ways* in which a vector can be produced in each term on the right-hand side of eq. (1). The details of how the vector appears from the tensor are given in appendix A. In $R_h(3)$ a vector quantity can always be written as the sum of three scalar components multiplied by the unit vectors i , j , and k in axes X , Y , and Z , respectively. The ensemble is overall isotropic, so that each scalar component is the same on average. There is only one *independent* scalar component of each vector type. This is summarised by the numbers in brackets in table 1. (In the crystal lattices this may no longer be the case, there may be more than one independent scalar components of the vector.)

In general, all the different types of force vectors summarised in table 1 are generated in the molecular liquid by an inhomogeneous electric field and its gradients. The term on the left hand side of eq. (1) is the vector sum of all these components.

Tables 1 and 2

Molecular linear force components in an inhomogeneous electric or magnetic field across a phase interface.

Point group	Phase	$\Gamma(\langle F \rangle)$	No. of independent vectors		
			$\hat{V}(\langle qE \rangle)$	$\hat{V}(\langle \mu \nabla E \rangle)$	$\hat{V}(\langle Q \nabla \nabla E \rangle)$
$R_h(3)$	Liquid	$D_u^{(1)}$	1(1)	3(3)	9(9)
O(434)	Cubic	T_1	1(1)	4(4)	20(20)
$O_h(m3m)$	Cubic	T_{1u}	1(1)	4(4)	20(20)
$T_d(43m)$	Cubic	T_2	1(1)	4(4)	20(20)
$T_h(m3)$	Cubic	T_u	1(1)	7(7)	41(41)
T(23)	Cubic	T	1(1)	7(7)	41(41)
$C_2(1)$	Triclinic	$3A$	1(3)	9(27)	54(162)
$C_1(\bar{1})$	Triclinic	$3A_u$	1(3)	9(27)	54(162)

Note: For a magnetic field, replace E by B , and electric multipoles by magnetic multipoles where appropriate.

3.2. Cubic and triclinic molecular crystals (solid phases)

The exercise above can be repeated for the five cubic and two triclinic crystal lattices using the appropriate point group and the second principle of GTSM applied not to surviving scalar averages, but to surviving vector (force component) averages. The frame (x, y, z) of principle (2) becomes the frame of the crystal lattice. The latter can always be identified with the laboratory frame (X, Y, Z) , and in general [15, 32] there are 32 distinct crystal point groups, ranging from triclinic to cubic. Some details of the calculations are given in appendix B and summarised in table 1.

This table shows that there are always more types of vector components (with their independent scalar types in brackets) sustainable in the crystal lattices than in the liquid ensemble the other side of the interface. As a result, the vector sum of force components is in general different in magnitude and direction on each side of the interface, i.e. there is a resultant force vector *across* the interface, and one phase must be forced into the other by the applied inhomogeneous electric field. The way in which this occurs is governed by principle (3) of GTSM, the symmetry of the resultant force vector is imparted to the phase of lesser symmetry, the liquid.

The exercise may be repeated for tensor components of force gradients, gradients of force gradients, and so on. The complete pattern of

resultant symmetry is imparted to the liquid by principle (3), and the crystal grows into the liquid as observed [1–5], for example, in ice/water. In accordance with these considerations, the liquid has never been observed to expand into the solid lattice; the latter never appears to melt at the interface [1–5].

3.3. Inhomogeneous magnetic field

The force imparted across the crystal/liquid interface by an inhomogeneous magnetic field can be described in general by an expansion analogous to (1) and (2):

$$\langle F \rangle_{\text{liq}} = \hat{V}(\langle a \mu_B \nabla B \rangle + \langle b Q_B \nabla \nabla B \rangle + \langle c \Omega_B \nabla \nabla \nabla B \rangle + \dots)_{\text{liq}} \quad (3)$$

$$\langle F \rangle_{\text{cryst}} = \hat{V}(\langle a_1 \mu_B \nabla B \rangle + \langle b_1 Q_B \nabla \nabla B \rangle + \langle c_1 \Omega_B \nabla \nabla \nabla B \rangle + \dots)_{\text{cryst}} \quad (4)$$

Here μ_B is a permanent molecular magnetic dipole moment assumed to be fixed in time in the molecular frame. Q_B is a permanent, time invariant, molecular magnetic quadrupole moment, Ω_B the octopole moment, and so on. The gradients of the magnetic field are n -order tensors, in analogy with (1) and (2).

The analysis of the magnetic Evans effect [1–5] proceeds as for the electric analogue, using the appropriate irreducible representations in each point group of the magnetic field and its gradients, and the molecular magnetic multipole

moments. Some details are given in appendix C and the exercise summarised in table 2.

4. Discussion

The GTSM analysis given here is quite general, and provides the following indications.

(1) The electric and magnetic Evans effects [1–5] depend on the different symmetries on the liquid and crystalline sides of the interface. If there is no symmetry difference (as in a liquid/gas interface) there is no symmetry effect.

(2) The interface between environments of different point group symmetry is in general forced into that of lesser symmetry. Thus, a crystal grows into a liquid, a smectic into a nematic, a nematic into an isotropic liquid, a crystal into a gas and so on.

(3) The relevant consideration is the point group of the *environment* on either side of the interface, *not* the point group of the molecules themselves. As a consequence, electric and magnetic Evans effects are expected in molecular solutions, suspensions, colloids, aggregates and so forth, provided that the environmental point groups are different on either side of the interface. This appears to provide plenty of scope for inducing industrially interesting effects across an interface such as a membrane, one example being aggregation of colloids. Many other potential applications have been reviewed by Evans in the source literature [1–5].

(4) The mechanism proposed in this communication accounts for dielectrophoresis and electric and magnetic levitation effects [1–5] through the fact that field gradients produce linear force through interaction with the appropriate molecular multipole moment.

(5) These symmetry considerations are unaffected by replacing the multipole moments by sums over those of the N molecules in the ensemble. By doing this we extend our analysis to multi-body properties of the environments on either side of the interface.

(6) When the point groups of distinct environments on either side of an interface are identical, the number of allowed force components is the

same, but the magnitude of the components in either environment may be different in general. Considerations of symmetry alone cannot rule out the possibility of a force differential induced by inhomogeneous electric or magnetic fields across the interface between, for example, a layer of carbon tetrachloride and a layer of water.

(7) The point group analysis can be extended straightforwardly to interactions of electromagnetic fields with environments on either side of the interface, i.e. to the electromagnetic Evans effect. Similarly, we can consider any combination of electric, magnetic and electromagnetic field symmetries.

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Appendix A

Vector components of some tensor products

We examine further the three vector components of a tensor product such as $\langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle$ of the text. The symmetry representation of this tensor indicates that it contains three polar vector types. These, written in full, are

$$\text{Type 1: } \langle \boldsymbol{\mu} \times (\nabla \times \mathbf{E}) \rangle \quad \text{or} \\ \langle (\boldsymbol{\mu} \times \nabla) \times \mathbf{E} \rangle \quad (\equiv \hat{V}_1 \langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle)$$

Type 2: $\langle \boldsymbol{\mu}(\nabla \cdot \mathbf{E}) \rangle$ or

$$\langle (\boldsymbol{\mu} \cdot \nabla) \mathbf{E} \rangle (\equiv \hat{V}_2 \langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle)$$

Type 3: $\langle \boldsymbol{\mu}(\nabla \mathbf{E}^T) \rangle$ or

$$\langle (\boldsymbol{\mu} \nabla^T) \mathbf{E} \rangle (\equiv \hat{V}_3 \langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle).$$

$$\hat{V}(\boldsymbol{\mu} \nabla \mathbf{E}) = \hat{V}_1 + \hat{V}_2 + \hat{V}_3.$$

If the applied electric field is inhomogeneous, the three scalar components of each vector type exist and are equal after thermodynamic averaging in an isotropic molecular liquid environment.

Appendix B

Vector components in cubic and triclinic molecular crystals, inhomogeneous electric field

In this appendix we consider some details of the calculations leading to table 1 of the text for one cubic group and one triclinic.

B.1. Cubic crystal point group T_d ($\bar{4}3m$)

The representation of a polar vector in point group T_d ($\bar{4}3m$) is T_2 , and this is found in column two of table 1. This is the irreducible representation of both $\langle \mathbf{F} \rangle$ and $\langle q\mathbf{E} \rangle$ in any molecular crystal with this cubic point group symmetry. The other columns of the table contain the number of times T_2 occurs in the relevant symmetry representations of the higher order tensors at the head of each column. For example, the representation of $\langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle$ is

$$\begin{aligned} \Gamma(\boldsymbol{\mu} \nabla \mathbf{E}) &= T_2 T_2 T_2 = T_2(A_1 + T_1 + E + T_2) \\ &= 3T_1 + 4T_2 + 2E + A_2 + A_1, \end{aligned}$$

which is worked out using the rules for multiplying irreducible representations [13–15] in the point group T_d . This contains T_2 four times, signifying four independent ways in which a vector can be obtained from the tensor $\langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle$ in T_d . There are *four* vector components of linear force generated by $\langle \boldsymbol{\mu} \nabla \mathbf{E} \rangle$ in T_d , compared with only three in the liquid point group $R_h(3)$.

In order to obtain the results of table 1 we have used the fact that the representations in $R_h(3)$ of the molecular dipole, quadrupole, and octupole moments are respectively:

$$\Gamma(\boldsymbol{\mu}) = D_u^{(1)},$$

$$\Gamma(\mathbf{Q}) = D_g^{(0)} + D_g^{(2)},$$

$$\Gamma(\boldsymbol{\Omega}) = D_u^{(1)} + D_u^{(3)},$$

and have mapped [13–15] these representations on to the appropriate crystal point groups.

B.2. Triclinic crystal lattice, C_i (S_2) ($\bar{1}$)

The calculations proceed in the same way, but in this case the three scalar components of each vector are all independent. This is recognised by the numbers in brackets in columns two to four.

Appendix C

Calculations for an inhomogeneous magnetic field

The calculations for table 2 proceed analogously to those for table 1; using the symmetries of the magnetic dipole, quadrupole and octupole, i.e.

$$\Gamma(\boldsymbol{\mu}_B) = D_g^{(1)},$$

$$\Gamma(\mathbf{Q}_B) = D_g^{(0)} + D_g^{(2)},$$

$$\Gamma(\boldsymbol{\Omega}_B) = D_g^{(1)} + D_g^{(3)}.$$

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