Computer simulation of liquid anisotropy. IV. Terms to second order in the external field of force

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The method of molecular dynamics computer simulation is extended to deal with liquid anisotropy induced by the interaction of an external electric (or magnetic) field with anisotropy of polarizability. The resulting Langevin functions follow accurately the analytical results of Kielich. The new method is applied to extract the details of rotation/translation interaction in a moving frame of reference. The appropriate first order correlation functions are much more oscillatory in the presence of a strong external field.

INTRODUCTION

In the fourth part of the series[1–3] we extend our consideration to the torque experienced by a molecule due to anisotropy of polarizability.[4] This is to second order in the external (electric or magnetic) field, and is the mechanism operable in the Kerr effect[5] on nondipolar molecules. The methods employed are described in I of this series, and the same caveat is given, namely, we are not looking to reproduce in detail the properties of real molecular systems, but rather using the molecular dynamics simulation method as a numerical guide-line to a difficult analytical[6] (and experimental[7]) problem. The analytical difficulty lies in describing rise transients without the luxury of Markovian ideas and of linear response, and in describing the molecular dynamics (via a.c.f.'s) themselves when the ensemble is subject to an intense external field of force. The experimental probelems can be overcome by the use of electromagnetic fields (e.g., pulses of megawatt mode-locked laser radiation).

THEORETICAL REMARKS

The torque on a gaseous (or isolated) dipolar molecule as a function of applied electric field $\mathbf{E}_0$ may be written as $\mathbf{m}\times\mathbf{E}_0$, where $\mathbf{m}$ is the total dipole moment, which may be expanded as:

$$\mathbf{m}=\mu+\alpha.\,\mathbf{E}_0+\tfrac{1}{2}\beta:\mathbf{E}_0\mathbf{E}_0+\tfrac{1}{6}\gamma:\mathbf{E}_0\mathbf{E}_0\mathbf{E}_0+\cdots. \tag{1}$$

Here μ is the field-off (permanent) dipole moment, α the polarizability tensor, β the first hyperpolarizability, γ the second and so on.

If $\mathbf{E}_0$ is not very large, then in energetic terms the μ part of the right-hand side of Eq. (1) predominates. In the condensed phases, where the interaction of molecules is the important feature, $\mathbf{m}$ is supplemented by terms arising from the fields of other molecules, and the internal field $\mathbf{E}(t)$ at any molecule at a given t is different from $\mathbf{E}_0$. The field $\mathbf{E}(t)$ fluctuates with time and therefore so does $\mathbf{m}$.

In the first and second parts of this series we have used the technique of molecular dynamics computer simulation to investigate the development of anisotropy with, effectively, $\mathbf{m}=\mu$ and $\mathbf{E}=\mathbf{E}_0$. In this case the electrically induced torque, $-\mu\times\mathbf{E}_0$ can be simulated with the equivalent mechanical torque $-\mathbf{e}_A\times\mathbf{E}_0$, where $\mathbf{e}_A$ is a unit vector along the molecular A axis of inertia, coincident with the dipole axis, and $\mathbf{E}_0$ is the externally applied field of force. In this way we avoid the complication $\mathbf{E}_0\neq\mathbf{E}(t)$ because each of the 108 molecules used experiences in the simulation the same $\mathbf{E}_0$, a constant in time. We can use this method with Lennard-Jones atom–atom interaction, i.e., those of the simplest type.[8] In this paper we have incorporated, additionally, point-charge interactions between the molecules, which are rough facsimiles of the asymmetric top CH_2Cl_2.

The problem we tackle in IV is how to investigate the development of liquid anisotropy with a torque of the form

$$(\alpha\cdot\mathbf{E}_0)\times\mathbf{E}_0 \tag{2}$$

and to investigate the dependence of the relevant order parameters[1–3]: $\langle\varepsilon_{AZ}^{2n}\rangle$ on E_Z^2. Here E_Z is the Z component of $\mathbf{E}_0$ in the laboratory frame. The angled brackets $\langle\,\rangle$ denote a simple arithmetic average over 108 molecules. At the same time we wish to avoid, for the present, those aspects of the problem which involve the nonpair additive interaction of molecular polarizability.[9] This is a hugely complicated, but secondary, problem, comparable in this respect with that of the internal field.[10]

In II, we have shown[2] that our mechanical torque method reproduces accurately the Langevin functions which describe the statistical bias of molecular orientation induced by an external field (which may be electric, electromagnetic (II), or magnetic, or mechanical in nature).

In the simplest case the torque of Eq. (2) may be rewritten, for each molecule, as[11]:

$$-E_Z^2(\alpha_2-\alpha_1)\sin\theta\cos\theta\mathbf{u}, \tag{3}$$

where θ is the angle between the field direction (z) and $\mathbf{e}_A$. α_1 and α_2 are components of α along and perpendicular to $\mathbf{e}_A$. We assume that the two components of α perpendicular to $\mathbf{e}_A$ are equal to α_2, i.e., that in terms of polarizability, the molecule is a symmetric top. In Eq. (3) $\mathbf{u}$ is a unit vector defining the direction of the imposed torque.

By definition,

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$$\cos\theta = \frac{\mathbf{e}_A \cdot \mathbf{E}_0}{|\mathbf{e}_A|\,|\mathbf{E}_0|} = e_{AZ}\,E_Z/|E_0| = e_{AZ}, \tag{4}$$

$$\sin\theta u = \frac{\mathbf{e}_A \times \mathbf{E}_0}{|\mathbf{e}_A|\,|\mathbf{E}_0|} = \mathbf{e}_A \times \mathbf{E}_0/|\mathbf{E}_0| = \mathbf{i}\,e_{AY} - \mathbf{j}\,e_{AX}, \tag{5}$$

where $\mathbf{i}$ and $\mathbf{j}$ are unit vectors. Therefore the torque is

$$-E_Z^2(\alpha_2 - \alpha_1)(\mathbf{i}\,e_{AZ}\,e_{AY} - \mathbf{j}\,e_{AZ}\,e_{AX}). \tag{6}$$

for each molecule at each instant t. In Eq. (6), $\mathbf{i}$ is an unit vector in the X direction of the laboratory frame and $\mathbf{j}$ in the Y direction. Clearly, the elements of Eq. (6) are defined with respect to the static (lab) frame of reference.

LANGEVIN FUNCTIONS

Kielich[4] has calculated the Langevin functions corresponding to a torque of this type, where $\mathbf{E}_0$ is either an electric or a magnetic field. The torque produces the results

$$\langle e_{AZ}^{2n+1}\rangle = 0; \quad \langle e_{AZ}^{2n}\rangle \neq 0 \tag{7}$$

for positive integral n, i.e., its effect is detectible only through even order averages (over) e_{AZ}^{2n}. *The computer simulation should*[2] *reproduce the analytical results exactly.* Defining

$$q = \frac{(\alpha_2 - \alpha_1)}{2kT} E_Z^2, \tag{8}$$

Kielich produces ($q \equiv |q|$):

$$L_1(\pm q) = 0, \tag{9}$$

$$L_2(\pm q) = \mp\frac{1}{2q} \pm \frac{1}{2q^{1/2} I(\pm q)}, \tag{10}$$

$$L_3(\pm q) = 0 \tag{11}$$

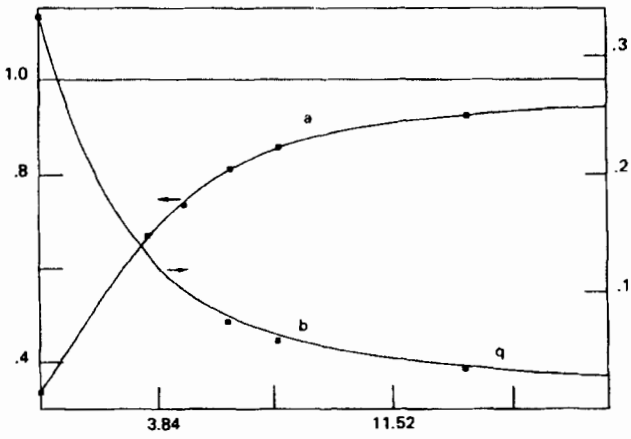

FIG. 1. (a) Second order Kielich function $L_2(q)$. ⊛ Computer simulation; —— analytical result; (b) as for (a); $L_2(-q)$ ordinate scale on right. Ordinate: $\langle e_{AZ}^2\rangle$.

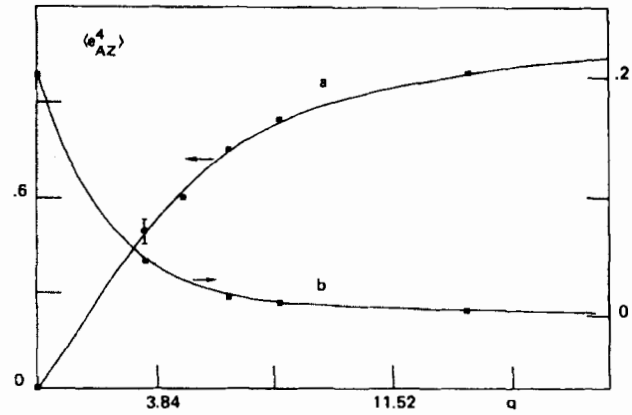

FIG. 2. As for Fig. 1; fourth order functions.

$$L_4(\pm q) = \frac{3}{4q^2} \pm \frac{(2q \mp 3)}{4q^{3/2} I(\pm q)}, \tag{12}$$

where

$$I(\pm q) = e^{\mp q} \int_0^{\sqrt{q}} e^{\pm x^2}\,dx. \tag{13}$$

In our notation $L_1(\pm q)$ describes the q dependence of $\langle e_{AZ}\rangle$, $L_2(\pm q)$ that of $\langle e_{AZ}^2\rangle$, and so on. Equations (9)–(12) are derived on the basis of equilibrium Maxwell/Boltzmann statistics and for small values[4] of q,

$$L_2(\pm q) = \frac{1}{3} \pm \frac{4q}{45} + \frac{8q^2}{945} \mp \frac{16q^3}{14175} + \cdots, \tag{14}$$

$$L_4(\pm q) = \frac{1}{5} \pm \frac{8q}{105} + \frac{16q^2}{1575} \mp \frac{32q^3}{51975} - \cdots. \tag{15}$$

As $E_Z \to \infty$,

$$L_2(+q) \to 1, \quad L_2(-q) \to 0,$$

as do the L_4 functions.

The great advantage of the computer simulation method is that having accurately produced the functions (10) and (12) the molecular dynamics for all E_Z can be investigated in detail without any of the difficulties associated with the analytical theory.[12] Some features of rotation/translation coupling[13] are investigated later in this paper using a moving frame of reference to bring out elements of the first order linear/angular velocity correlation function unobtainable in any way other than computer simulation.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the dependence, respectively, $\langle e_{AZ}^2\rangle$ and $\langle e_{AZ}^4\rangle$ on q, the energy ratio. The computer simulation produces points which have been fitted to the analytical results, Eqs. (10) and (12), using nonlinear least mean squares and numerical quadrature routines in combination. This method produces the energy ratio marked on the abscissae of both figures. Clearly the same result should and has come out of fitting both $\langle e_{AZ}^2\rangle$ and $\langle e_{AZ}^4\rangle$.

As an example of how the Kielich functions[4] are con-

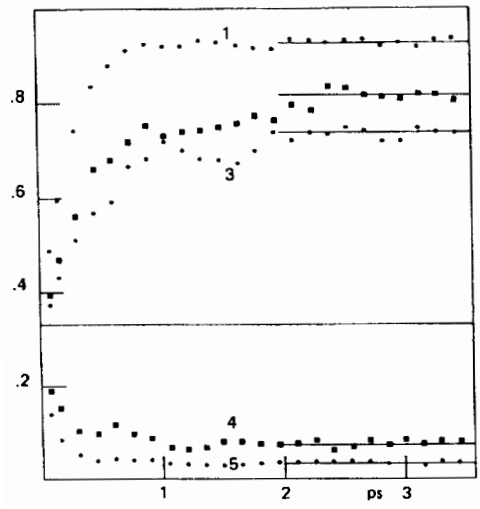

FIG. 3. Rise transients, second order. (1) $q = 13.8$, positive anisotropy; (3) $q = 6.1$, positive anisotropy; (4) $q = 6.1$, negative anisotropy; (5) $q = 13.8$, negative anisotropy.

structed we illustrate in Fig. 3 transient averages $\langle e_{AZ}^2 \rangle$ for positive and negative anisotropy. These are a little noisy, but could be smoothed by using different start times ($t = 0$) and averaging. As they stand they are merely simple averages over 108 molecules taken at each time step of the computer simulation. [The final level attained by each transient is taken for a point on the curve of Fig. 1 (or 2 for $\langle e_{AZ}^4 \rangle$ transients)]. These are field-on transients, and to construct them analytically is a formidable problem, requiring probably as much computer power as was used in formulating this paper.

The theory of transient Kerr effect response for arbitrarily strong driving fields has been discussed by Evans, Ferrario, and Grigolini[12] who considered the time evolution of a Hamiltonian of the form[5]

$$H = H_0 - \tfrac{1}{2} N\alpha E_Z^2 - \tfrac{1}{3}(\alpha_1 - \alpha_2) E_Z^2 \sum_{n=1}^{N} P_2(\cos\theta_i) \quad , \qquad (16)$$

which describes the Kerr effect to powers of E_Z^2. The time evolution of this Hamiltonian is then governed by the Liouville equation[14]:

$$\frac{\partial}{\partial t}\rho(t) = -i\,[H(t),\, \rho(t)]\,, \qquad (17)$$

where $\rho(t)$ is the density matrix. The Hamiltonian $H(t)$ may be written effectively as

$$H(t) = H_0 + H_1(t)\,, \qquad (18)$$

where H_0 describes the isolated molecular ensemble and $H_1(t)$ represents the interaction of the system with an external field. The solution of the equation of motion is particularly difficult because (i) the physical system is no longer invariant to time reversal, so that time-ordered exponential operators must be employed; (ii) the memory kernel of the Moritype equation ($K(t, s)$) is no longer dependent on the difference $(t - s)$ but is a function of the two independent variables t and s; (iii) the Liouville operator $L_1(t)$ associated with $H_1(t)$ is not Hermitian and is not anti-Hermitian.

Grigolini *et al.*[14–17] have, nevertheless, made substantial progress towards the solution of equations such as this,[18–20] and the computer simulation method is immediately useful as a guide for the theoretical analysis. For example the rise times of the transients are clearly q dependent. Paranjape and Coffey[11] and Morita[21–23] have discussed the equivalent times of the fall transients using Markovian statistics and classical Langevin equations. In the case of fall transients we have

$$H_1(t) = 0; \quad t > 0;$$

which simplifies the analysis considerably.

The computer simulation can be made to reveal details which the classical analytical theory of, for example, McConnell[24] or Morita[25] does not consider. A striking example is rotation/translation coupling in a moving frame of reference.

ROTATIONAL–TRANSLATION COUPLING

Following a suggestion of Ciccotti *et al.*[13] we have computed the correlation function of the variates $\mathbf{v}(t)$ (the molecular centre of mass velocity), and $\omega(t)$ the molecular angular velocity in a moving frame of reference defined as follows. Let v_X, v_Y, and v_Z be the components of $\mathbf{v}$, for example, in the lab frame. Define a moving (molecular) frame of reference with respect to unit vectors $\mathbf{e}_A$, $\mathbf{e}_B$, and $\mathbf{e}_C$ along the principal moment of inertia axes of the molecule under consideration. The components of $\mathbf{v}$ in the moving frame are then

$$\begin{aligned} v_A &= v_X e_{AX} + v_Y e_{AY} + v_Z e_{AZ}, \\ v_B &= v_X e_{BX} + v_Y e_{BY} + v_Z e_{BZ}, \\ v_C &= v_X e_{CX} + v_Y e_{CY} + v_Z e_{CZ}, \end{aligned} \qquad (19)$$

and similarly for ω. By applying symmetry rules of parity, time reversal etc., to our C_{2v} symmetry molecule we deduce that the correlation function elements:

$$\langle v_C(t)\omega_B(0)\rangle \text{ and } \langle v_B(t)\omega_C(0)\rangle$$

exist for $t > 0$. All others vanish for all t.

The behavior of these functions without an applied field is illustrated in Fig. 4 where we have computed

$$\frac{\langle v_C(t)\omega_B(0)\rangle + \langle v_C(0)\omega_B(t)\rangle}{2\langle v_C^2(0)\rangle^{1/2}\langle \omega_B^2(0)\rangle^{1/2}}$$

to cut down the computer noise. The noise level can be judged with reference to the $t = 0$ cutoff, which should, by symmetry, be zero. It is clear that the noise is smaller than the signal by a satisfactory amount. Both first order correlation functions oscillate, the (C, B) function attaining a maximum of $+0.22$ and a minimum of -0.04, with an uncertainty of ± 0.01 or thereabouts.

It is clear, therefore, even *before* applying our field E_Z, that the classical theory of rotational Brownian motion, so long accepted as the basis of subjects such as dielectric relaxation, cannot be used to de-

scribe these rototranslational signatures. Again, therefore, as in the case of Alder and Wainwright's[28] discovery of the long negative tail of $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ in the lab frame, the computer simulation method is ahead of *either* the analytical method *or* experimental method.

Ferrario and Evans[27] have constructed and solved a novel type of rototranslational Langevin equation,[15] *written in a moving frame*, to try to account for the basic feature of curves such as those in Fig. 4, but even in this case the ordinate in Fig. 4 is vanishingly small for all t. The classical theory must therefore be abandoned in favor of diffusion equations which take account of the nonlinear nature[19,20] of the interaction between a tagged molecule and its thermal bath.

It is especially interesting to look at the nature of the (CB) or (BC) elements under an applied field corresponding to $q = 17.5$, i.e., near the saturation level. By our foregoing considerations this is obviously not yet possible *except by computer simulation*. Nevertheless the consideration of such behavior is an important one, because this is a route towards a molecular explanation of what happens when a mesophase is aligned with an electric or magnetic field. In this case it is well known that averages such as $\langle e_{AZ} \rangle \to 0.5$ or so, with a relatively small external field, causing dramatic changes in dynamical features such as those embodied in the Kerr constant,[5] or, if the molecule is dipolar, in the dielectric loss. The molecular dynamics, as opposed to the hydrodynamics,[28] of aligned mesophases have never been satisfactorily explained, and the role of rotation/translation coupling is implicitly important. At $q = 17.5$ the rototranslational functions are illustrated in Fig. 5. Note that these (CB) and (BC) elements are defined again *in the proving frame* [Eq. (19)]. They are much more oscillatory, the (CB) element this time having a positive peak of $+0.12$ and a negative peak of -0.13.

If we take into consideration the fact that cooperativity in the mesophase is known to magnify single molecule properties enormously (e.g., the Kerr constant[5] $\to \infty$) *it is likely that rototranslation is the key to explaining many of the spectral features observable in the aligned (or unaligned) mesophase*. We note, to end with, that such effects have eluded detection up to now because they sometimes manifest themselves *only in the moving reference frame*. Although an electric field breaks time reversal symmetry,[29] it does not affect parity symmetry, and first order mixed autocorrelation functions of linear and angular velocity vanish for all t and E_Z in the laboratory frame of reference. This does *not* mean that the effects of rototranslation average out in the laboratory frame to zero. On the contrary, they are critically important and underlie every type of spectrum whose origins can be traced to molecular diffusion.

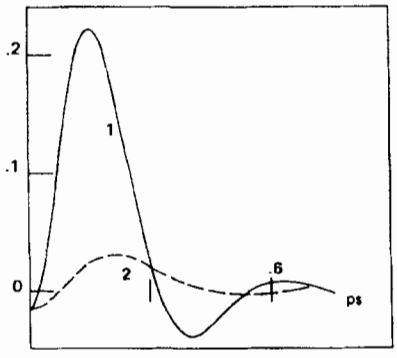

FIG. 4. Mixed linear/angular velocity correlation functions:

(1) $$\frac{\langle v_C(t)\omega_B(0)\rangle + \langle v_C(0)\omega_B(t)\rangle}{2\langle v_C^2\rangle^{1/2}\langle \omega_B^2\rangle^{1/2}},$$

(2) $$\frac{\langle v_B(t)\omega_C(0)\rangle + \langle v_B(0)\omega_C(t)\rangle}{2\langle v_B^2\rangle^{1/2}\langle \omega_C^2\rangle^{1/2}}.$$

These correlation functions are constructed in the moving frame (A, B, C).

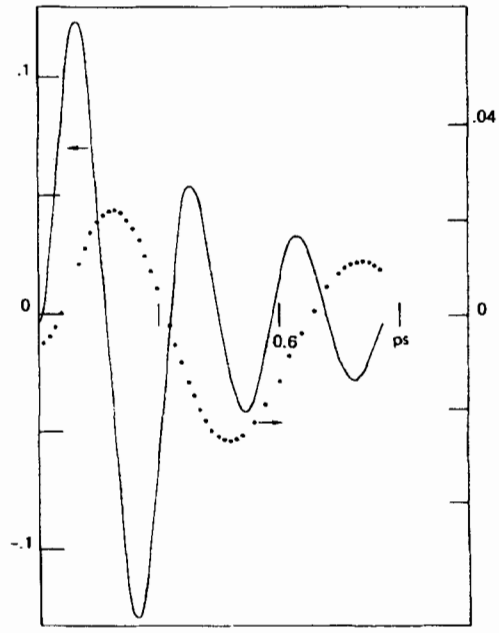

FIG. 5. As for Fig. 4; $q = 17.5\ kT$.

CONCLUSIONS

(1) The method of molecular dynamics simulation has been extended to deal with the development of bulk anisotropy through the interaction of polarizability anisotropy with an external electric field.

(2) The appropriate Langevin functions have been fitted to Kielich's analytical results[4] for first and second order, respectively.

(3) The new method has been used to investigate the interaction of rotation with translation in a moving frame of reference. There are striking differences between the field-off results and those in the presence of a strong external field.

ACKNOWLEDGMENT

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