INTRODUCTION

In the first two parts of this series, we have been concerned with the computer simulation of liquid anisotropy induced by a static electric field or for force equilibrated in. In this paper we explore the dispersion of the induced anisotropy caused by an alternating field of force applied unidirectionally to the liquid sample. The angular frequency $\omega$ of this field is varied from static to $10^3$ rad/s, equivalent to polarized electromagnetic radiation of far infrared frequencies. As in parts I and II, we use an asymmetric trigonal in the simulation of $C_{60}$ symmetry. The direction of the torque on each of 108 such molecules is assumed to be defined by

$$\mathbf{e}_q \times \mathbf{E},$$

where

$$\mathbf{E} = \mathbf{E}_{\text{cos} \omega t}.$$  

Here $\mathbf{e}_q$ is a unit vector in the $C_{60}$ molecule, $\mathbf{E}$ is the external field defined by $\text{Eq. (2)}$. The $t$ is taken as the time step of the molecular dynamics algorithm in ps. As part simulation proceeds, $\omega$ varies from 0 to about 10 ps. As $\omega$ is sufficiently high, the rise and fall transients of the anisotropy induced by a sufficiently large $\mathbf{E}$ will be dispersed by the cos $\omega t$ factor of Eq. (2). If we imagine an electric dipole moment along $\mathbf{e}_q$, then Eqs. (1) and (2) define the interaction of this electric dipole with electromagnetic radiation with Maxwell's wave vector $\mathbf{k}$ taken as vanishingly small compared with the inverse of the box length. A physical analogy is the development of permittivity anisotropy and its dispersion in an alternating electric field. In practical terms, if we want to increase $\omega$ to $10^3$ rad/s, we would have to use powerful laser radiation at sub-millisecond frequencies to induce the anisotropy. This is not yet entirely achievable but might well be in the near future with the rigid development in technique now taking place (e.g., chopped synchrotron radiation). As usual, this simulation is introduced as a numerical guide for basic theoretical development and not as machine experiment.

The effect similar to the one described by the simulation in this paper could be observed by using a tunable CW CO$_2$ laser ($\omega = 10^4$ Hz) to induce birefringence in a highly dipolar biopolymer such as polyl-$\gamma$-benzyl-$\epsilon$-caprolactam (PBLG), whose infrared spectrum contains bands that could be used to extract its rotovibrational anisotropic nature. The change in the infrared spectrum carried by the laser induced birefringence could be monitored at right angles. Bands (i.e., correlation functions) near the C=O frequency would show the dispersion effects as the laser is tuned. The cooling would have to be very efficient to maintain the initial temperature of the sample.

SOME THEORETICAL REMARKS

The theory, for example, of the Kerr effect in an alternating electric field is confined to the case where the field is weak, and has been reviewed by Kielch. In this case linear response theory is applicable and two processes can be classified according to the value of $\omega$:

- If $\omega$ is much smaller than the characteristic frequency $\omega_0$ of oscillations of the molecule, the field will have a restoring effect causing a dipolar polarization of the medium. If the oscillating, orienting field is made stronger, this polarization effect approaches saturation, and linear response theory is no longer applicable.
- If $\omega$ is much larger than $\omega_0$, no orientation of the electric dipoles can set in, so the field causes no polarization of the dipole kind, but solely electron distortional polarization. This is analogous with the situation in the case of polarization linear in the alternating field strength, considered by Debys. Analytical, the problem of nonlinear molecular relaxation is complicated, and its solution is restricted to molecules of axial symmetry only.

If the system is acted on by an alternating field $\mathbf{E}_{\text{cos} \omega t}$, the orientation of molecules is dependent on certain times of relaxation which are functions of the molecularly effective viscosity of the medium, the temperature, and the geometrical shape of the molecules. The system is then described by a diffusion equation with the field $\mathbf{E}$ written as the sum

$$\mathbf{E} = \sum_{\mathbf{k}} \mathbf{E}_{\mathbf{k}, \text{exp}(\mathbf{u}_{\mathbf{k}})},$$

with the summation extending over all positive and negative frequencies $\omega_{\mathbf{k}}$ and $\mathbf{E}_{\mathbf{k}}$, denoting in general a complex field amplitude. Kielch has worked out second order the effect of an alternating field on the statistical distribution function $f_l (l \in \text{the solid angle})$ when the energy of interaction with the system takes the form

$$U = -\mu \mathbf{E} - \mathbf{E} \cdot \mathbf{E}.$$  

Here $\mu$ is the permanent molecular dipole moment and $\mathbf{E}$ the molecular polarizability tensor. In this paper we...
condense ourselves to interactions of the form $Q_0 = -\mu E$
only and calculate the relevant transients governed by the Langevin functions (part II).

$\begin{align*}
L_1 & = \int \exp(2\theta \cos \phi) \sin \phi \, d\phi \\
L_2 & = \int \exp(2\theta \cos \phi) \sin^2 \phi \, d\phi \\
L_3 & = \int \exp(2\theta \cos \phi) \sin \phi \cos \phi \, d\phi
\end{align*}$

where $\mu = \mu_0 \cos \omega \cos \theta$. We have

$\begin{align*}
L_1 & = -\frac{\theta}{\mu} L_2 (\theta) \\
L_2 & = -\frac{\mu}{2} L_2 (\theta) \\
L_3 & = -\frac{\mu}{2 \cos \theta} L_2 (\theta)
\end{align*}$

and so on.

Each $L_n$ is time dependent and varies with the frequency $\omega$ of the incoming radiation. The features of each $L_n$ are determined therefore by the molecular dynamical details in a wholly different fashion from the case of a static incoming electric field such as that provided by a capacitor. In the latter case each $L_n$ is determined solely by the energy ratio $\mu_0 \omega / \kappa T$.

With sufficiently strong frequency dependent fields it is possible to observe dispersion of diellectric saturation, dispersion in the nonlinear response area, and dispersion in the linear response area of the Langevin functions. These effects are simulated below with a saturating field in Figs. 1-4. We also investigate the equivalent effects on one of the sets of response transients we used in part I to construct $L_n$ and on some relevant equilibrium autocorrelation functions of interest.

DETAILS OF THE SIMULATION METHOD

The conditions of the simulation run are described in parts I and II. The molecular dynamics simulation runs were carried out isothermally; in effect, the sample was constrained at the same temperature by re-

scaling with the field applied. This produces the discontinuities in Figs. 1-4. The saturating field strength used in this paper corresponds to $E_0 / kT = 12.0$ in the static case ($\omega = 0$). At an initial equilibrium state, defined by $n_0$, an external torque $\eta_0 \times E_0 \cos \omega t$ is applied to the $\eta_0$ vector of each of the 100 $\eta_0$ molecules in the sample. Over the next 1000 or so time steps ($t = 10^7$) the averages $\langle \theta \rangle$ behave as illustrated in Figs. 1-3. Here $\phi$ is a positive integer, $L_0$ is the $L_0$ (lab frame) component of $\theta$, $\omega$, $\ldots$, the field is applied along the $z$ axis and $\langle \rangle$ denotes a simple average over the 108 molecules at each time step. Note that the transients can be smoothed considerably by repeating the buildup starting at different initial $n_0$ and averaging out the noise to leave the signal. This requires several different runs but is necessary when we wish to deal with smaller perturbation in energy terms than $kT$. This is very often the case experimentally (sufficiently the linear response region of the Langevin function).

RESULTS AND DISCUSSION

In Fig. 1 we illustrate $\langle \eta_0 \rangle$ for $\omega = 0.10^{17}$, $10^{18}$, and $10^{19}$ rad/s. These frequencies take us through the dispersion region because the molecular dynamics simulation takes place (parts I and II) on a picosecond time scale. In nonlinear dielectric spectroscopy, dispersion may be observable at frequencies as low as $10^{12}$ Hz. The peak at $10^{13}$ rad/s in Fig. 1 illustrates the development of the rise transient [curve (1)] to a plateau at $0.9$. This is near the saturation point of the Langevin function (part II). In an alternating field at frequencies below about $10^{12}$ rad/s, this plateau value

FIG. 1. Transients $(\eta_0)$ for $E_0 / kT = 12.0$. (1) $\omega = 10^{17}$ rad/s; (2) $10^{18}$ rad/s; (3) $10^{19}$ rad/s.


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would remain essentially unaffected. However, as $\omega$ approaches the far infrared/microwave region, the movement of the molecules in response to the strong external alternating field of force (whatever its origin) produces the effects illustrated in Fig. 1 as curves (2) to (6). The transients $\psi_1(\omega_0,t)$ now oscillate with the field angular frequency $\omega$. The form of each transient is the result of a competition between the aligning field and the thermal opposition. The transient oscillations are not simple in form and are relatively long lived in comparison with the rise time in the static field. The amplitude of $\psi_1(\omega_0,t)$ (positive or negative) decreases as the field frequency increases, but interestingly, even at $\omega = 10^8$ rad/s, where the molecules can no longer follow every oscillation, a longer lived alteration in $\psi_1(\omega_0,t)$ persists [curve (4)]. The mean amplitude of the latter is, however, very small, and is buried in the noise of the simulation run.

In principle, as mentioned in the preceding section, features such as these could be investigated in the more accessible linear response region of Langen's function $\psi(\omega_0,t)$ by averaging several transients. As indication of the thermal noise part run in this case is illustrated in Fig. 10, of part II. Davies et al. 7 have shown that saturation of the Langen function is observable by choosing carefully the sample (e.g.) and experimental conditions. The analytical description (as opposed to the present numerical description) of the transients in Fig. 1 requires the use of (i) non- linear response theory, (ii) a full and apt consideration of inertial and memory effects; and (iii) a careful consideration of the validity of the fluctuation-dis sipation theorem (see part II).

In addition to the self-evident fact that transients such as these have first seen the light of day through the use of computer simulation, the method has the added advantage of allowing one an insight into the behavior of these special (equilibrium) features whose time domain equivalents are the correlation functions of $\psi_1$. In particular, we may compute $\langle \psi_1(t) \psi_1(0) \rangle$ and its double time derivative $\langle \psi_1(2t) \psi_1(t) \rangle$, both in the presence of a strong alternating field. These are illustrated in Fig. 4 for $\omega = 10^8$ rad/s.

The higher order transients $\psi_2(\omega_0,t)$ ($n = 2, 3, \ldots$) are of interest in the theory of the Kerr effect, 8 depolarized light scattering from birefringent liquids, 9 spin-epin NMR inhomogeneous nuclear electron scattering, and so on. 10 In principle, all of the relevant theoretical averages for these techniques can be extracted from the computer simulation method described in this paper. In Fig. 3 we illustrate $\psi_1(\omega_0,0)$ and $\psi_1(\omega_0,t)$ for a field of $\omega = 5 \times 10^7$ rad/s. The mean value of $\langle \psi_1(\omega_0,0) \rangle$ is clearly shifted upwards from 0 of this isomorphic sample file (t = 0 value of Fig. 2). The mean value of $\langle \psi_1(\omega_0,t) \rangle$ is, on the other hand, very small although the amplitude is much larger. This suggests, of course, that the second order equilibrium averages (correlation functions) such as $\langle (\psi_1(t) \psi_1(0)) \rangle$ will be affected by the field to a greater degree than first order functions such as $\langle \psi_1(0) \psi_1(0) \rangle$. Using time-resolved spectroscopy, both kinds of transients are observable. The behavior of $\psi_2(\omega_0)$ is further illustrated in Fig. 3 for $\omega = 10^8$ and (rather naively) $10^9$ and $10^6$ rad/s. [The signal can be refined (as above) by making several molecular dynamics runs and averaging out the noise.]

The external field used in this simulation breaks time-reversal symmetry (as pointed out by the referee) and a magnetic field would break parity reversal symmetry, especially if some Lorentz forces were created on charges in the system, e.g., those placed at atomic sites, because this would make the molecule precess along the external magnetic field direction. It is expected that such a simulation would provide insight into new couplings via nonvanishing mixed a, f, f2 such as that of velocity and angular momentum. An applied electric field also means that many-point correlation functions exist in the box of molecules under consideration and given good long computer runs these can also be simulated, thus testing directly theories involving time-ordered exponentials.

We are not using Ewald summation in the present paper but similar studies of long-range forces could be very interesting because of their implications for hydrodynamic theory.

Finally, the amplitude in Fig. 1 for high $\omega$ appears to be random. This could be accounted for by a theory based on amplitude randomness in an externally driven pendulum system. This will be the subject of further work.

CONCLUSIONS

Time resolved transients, reflecting birefringence induced by an alternating field, have been computed numerically for 108 C60, trinitroanisole interacting with a 3x3 atom-atom potential of the Lennard-Jones type.

The dispersion of the induced birefringence with increasing field frequency $\omega$ produces oscillatory transients whose features reflect in detail the effect of the strong aligning field on the molecular dynamics. The mean value of the transients is shifted away from that in the field-off case for $\psi_1(\omega_0,0)$, where $n = 2, 4, 6, \ldots$. This affects the decay of the corresponding equilibrium (field-on) autocorrelation functions.

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