Field-Induced Acceleration of Fall Transients in Chiral Molecular Liquids: a Computer Simulation

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Abstract

Rise and decay transients of molecular orientation are simulated by computer for the enantiomers and racemic mixture of supercooled liquid fluorochloroacetonitrile. The rise transients are easily distinguishable in these three low temperature liquids and show a pronounced field dependence as predicted analytically by Morita from the Smoluchowski/Debye equation. An original result of this investigation is that the fall transients are accelerated considerably at constant temperature with respect to the equilibrium field-off orientational autocorrelation function. This is fundamental evidence for the use of non-linear Kramers equations for the description of molecular dynamics in the liquid state of matter at equilibrium.

1. Introduction

In this letter I report, using computer simulation, a new effect caused by the application of strong external force fields to an ensemble of chiral molecules in the liquid state. This effect is investigated through the field dependence of rise and fall transients of the type $\langle e_{2Z} \rangle$ where $\mathbf{e}_2$ is a unit vector in the frame of the principal molecular moments of inertia and e_{2Z} a projection in the Z axis of the laboratory frame of reference. The original result of the investigation is that the fall transients decay much more quickly with time than the equivalent equilibrium autocorrelation function $\langle \mathbf{e}_2(t) \cdot \mathbf{e}_2(0) \rangle$. This violates the fluctuation–dissipation theorem of statistical mechanics [1]. The result cannot be explained by theories of molecular diffusion, based on the diffusion of probability density, without the presence of a non-linear potential term in the relevant stochastic partial differential equation of motion, making it a Kramers equation [2–4]. More generally, the acceleration of the fall transient – which I term the de-excitation effect – provides strong support for the reduced model theory of molecular dynamics developed from the Liouville equation by Grigolini [4] and co-workers. This theory is valid both in the equilibrium and transient condition and in its simplest form leads to an approximate analytical description based on non-linear Langevin equations of the type [5]:

$$\dot{\boldsymbol{\omega}} = -\gamma \boldsymbol{\omega} + \gamma'\langle \omega^2(t) \rangle \boldsymbol{\omega} + \mathbf{F}(t) \tag{1}$$

where $\boldsymbol{\omega}$ is the molecular angular velocity, γ the friction coefficient, and $\mathbf{F}(t)$ a stochastic angular acceleration term. This equation is valid only for small deviations from linearity, measured through a non-vanishing γ'. Equation (1) is a limiting form of the cosinal itinerant oscillator theory of Coffey and co-workers [6].

2. Algorithm and method

The algorithm has been developed from a listing [7] based on integrating numerically the equation of motion for 108 chiral molecules; the enantiomers and racemic mixture of fluorochloroacetonitrile. The site–site pair potential is described in the accompanying paper. The effect of an arbitrarily strong external field is simulated by an extra torque term inserted in the forces loop of the algorithm [8]. For an electric field this takes the form $-\mu \times \mathbf{E}$ where μ is the net molecular dipole moment and $\mathbf{E}$ the external electric force field. The rescaling routine of the computer simulation algorithm is used to bring the temperature back to the input level at constant volume: 133 K. The rotational and translational temperatures can become very high immediately after the instantaneous application of the external field. At constant volume the pressure must therefore become very high and the total energy temporarily positive. I have verified that the rate of temperature rescaling has little effect on the characteristics of the rise transient. The temperature is reduced to 133 K within 0.5 to 1.0 ps after field application. Field-on equilibrium is therefore attained at this temperature, which is the same as that at field-off equilibrium.

At field-on equilibrium the total energy is negative, but the potential energy is considerably higher than that at field-off equilibrium (Table I).

Fall transients from field-on to field-off equilibrium are obtained by removing the external field instantaneously. When the field is switched off there is no abnormal temperature fluctuation, so that the self-adjustment of the aligned molecular liquid sample takes place isothermally (i.e. at constant mean temperature T). In the simulations reported here the field is kept on long enough to ensure that the rise transient has reached its maximum, plateau level, i.e., its limiting value at $t \to \infty$. This ensures that the acceleration of the fall transient is not due to insufficient alignment in the field-on ("preparation") stage.

3. Results and discussion

Figure 1 shows that the rise transients for the R and S enantiomers are mirror images. The sign of the transient is reversed, and this provides a simple method of distinguishing in the laboratory frame between the dynamics of enantiomers and racemic mixture in the presence of the electric field. This is potentially important for the direct measurement of roto-translational cross-correlation functions (see accompanying paper). The time dependence of the rise transients for the R or S liquids shows a strong field dependence. In the first approximation this can be described by the Debye diffusion equation, as shown by Morita [9]. This author provides an exact solution of the Debye equation in terms of a continued fraction [10]. Characteristic (1/e) rise times from the simulation of the R rise transient have been compared with Morita's solutions, and are

Table 1. *Selection of thermodynamic data at field-on and field-off equilibrium*

$\mu E/kT$	Liquid	Mean trans. kinetic energy/kJ mole^{-1}	Mean Rot. kinetic energy/kJ mole^{-1}	Potential energy/kJ mole^{-1}	Total energy/kJ mole^{-1}
50.0	RS	1.72	1.82	−30.54	−27.01
10.0	S	1.78	1.79	−30.83	−27.27
2.0	R	1.81	1.80	−43.51	−39.90
0.0	R	1.70	1.74	−48.33	−44.89

in general much shorter, illustrating the importance of inertial effects.

Figure 2 illustrates the original result of this letter. The fall transients $\langle e_{2Z}\rangle$ fall much more rapidly to zero than the equivalent equilibrium a.c.f. $\langle e_2(t)\cdot e_2(0)\rangle$. The time dependence of the fall transients is also dependent on the field strength applied prior to releasing it. The fall transients approach the equilibrium a.c.f. in time dependence as the applied field strength is decreased to zero. These results are interpreted in the first approximation by the following analysis, developed by Grigolini and co-workers [4] as a branch of their rigorous and generally valid reduced model theory of the molecular liquid state.

4. Analytical theory

In the appendix it is shown that the Debye diffusion equation, a Smoluchowski equation [2], cannot reproduce the acceleration of the fall transients reported in this letter.

The de-excitation effects of Fig. 2 are pronounced, even for values of the energy ratio $\mu E/kT$ near to 1.0. This proves beyond reasonable doubt that Kramers equations with non-linear potential terms are needed for a proper description of liquid state molecular dynamics. It is not sufficient to work with a theory which is non-Markovian [2] but linear, in the sense that the potential term in the diffusion equation is linear. Linear theories produce fall transients identical, when normalised to one at the time origin, with the equilibrium a.c.f. [11, 12].

In the first approximation the adiabatic elimination procedure developed by Grigolini et al. [4] may be used to obtain the following expression for the fall transient from an isolated sample at field-on equilibrium:

$$\langle\cos\theta(t)\rangle = \exp\left(-\int_0^t D(t')\,\mathrm{d}t'\right)\langle\cos\theta(0)\rangle \qquad (2)$$

$$D(t) = \int_0^t \phi(t,\tau)\,\mathrm{d}\tau \qquad \phi(t,\tau) = \langle\omega^2(t)\rangle\,\mathrm{e}^{-(\gamma-\gamma'\langle\omega^2(t)\rangle)\tau}$$

$$\langle\omega^2(t)\rangle = \frac{\langle\omega^2\rangle_{\mathrm{eq}} + R(\gamma+\langle\omega^2\rangle_{\mathrm{eq}}\gamma')\,\mathrm{e}^{-2\gamma t}/(\gamma-R\gamma')}{1+R\gamma'\,\mathrm{e}^{-2\gamma t}/(\gamma-R\gamma')}$$

$$R = \langle\omega^2(0)\rangle - \langle\omega^2\rangle_{\mathrm{eq}}$$

In this series of relations $\langle\omega^2(0)\rangle$ is the equilibrium field-on mean square angular velocity; $\langle\omega^2\rangle_{\mathrm{eq}}$ the field-off equivalent; γ and γ' the linear and non-linear friction coefficients of the non-linear Langevin eq. (1); $\phi(t,\tau)$ denotes the non-equilibrium two-time auto-correlation function of e_2 during the decay process; and $\langle\cos\theta(t)\rangle$ denotes the fall transient. For $R = 0$ this result reduces to Kubo's linear stochastic oscillator [12], for which fall transient and equilibrium orientational a.c.f. are identical. For eq. (2) to work, therefore, requires $R > 0$, i.e., the temperature of the field-on sample, measured through the mean square angular velocity, must be infinitesimally greater than that of the field-off sample. The theory embodied in eq. (2) therefore applies, strictly speaking, to a sample isolated from its surroundings in the sense that it cannot dissipate the temperature increase caused by the field application. The computer simulation and eq. (2) are comparable therefore only for the smaller field strengths. Such a comparison is given in Fig. 2.

The original result of this letter, the field-induced acceleration of the fall transient at constant temperature, implies that the Kramers diffusion equation at field-off equilibrium, as well as

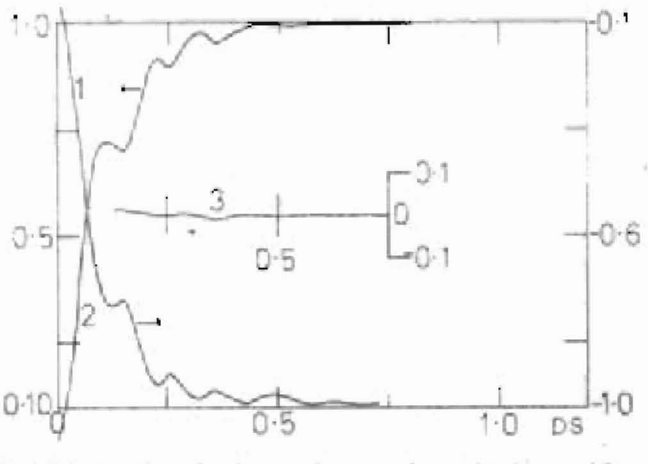

Fig. 1. Rise transients for the enantiomers and racemic mixture of fluorochloroacetonitrile for $\mu E/kT = 50.0$. (1) R; (2) S; (3) RS.

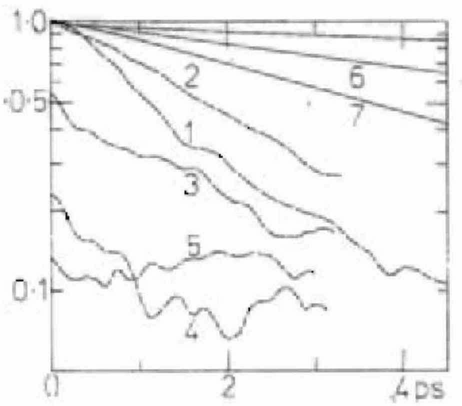

Fig. 2. Equilibrium a.c.f. $\langle e_z(t)\cdot e_z(0)\rangle$ for R; computer simulation. ----, Fall transients, computer simulation after the instantaneous removal of electric fields equivalent to (1) $\mu E/kT = 50.0$; (2) 10.0; (3) 2.0; (4) 1.0; (5) 0.5. (6) ——, Fall transient from eq. (2), calculated for $R = 0.5$ (THz)^2; $\gamma = 30.0$ THz; $\gamma' = 20.0$ (THz)^3; $\langle\omega^2\rangle_{\mathrm{eq}} = 1.0$ (THz)^2. Note that for $(\gamma - R\gamma') \to 0$, the theoretical fall transient must decay infinitely quickly, even for $R \to 0$, the condition of the computer simulation. (7) As for (6), $R = 0.1$ (THz)^2; $\gamma = 30.0$ THz; $\gamma' = 25.0$ (THz)^3, $\langle\omega^2\rangle_{\mathrm{eq}} = 1.0$ (THz)^2.

at field-on equilibrium must contain a non-linear potential term. Smoluchowski equations, or linear Fokker–Planck equations [2], cannot produce the simulated transient acceleration. These non-linear Kramers equations are exemplified by the cosinal itinerant oscillator theory of Coffey and co-workers [2–4, 6].

Finally I mention that the technology is available, in principle, to test the simulation reported in this paper experimentally. Transients can be induced by electromagnetic radiation-laser fields. The power available in picosecond or sub-picosecond pulses from these devices can reach the terrawatt level. Streak camera detection systems can detect rise or fall transients over sub-picosecond intervals. The transients produced in this way would be mixtures (because of the chiral symmetry of the sample) of first and second Legendre averages over orientation [2, 3], and could be observed isothermally with the efficient removal of heating effects. Such lasers are ememplified by VULCAN of the S.E.R.C. Rutherford/Appleton Lab., U.K., or the Los Alamos carbon dioxide laser.

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Appendix

Coffey et al. [2, 11] have shown that the decay transient after the instantaneous removal of a square wave pulse from a liquid sample is given by the Debye diffusion equation (2) as

$$\langle\cos\theta(t)\rangle = \tfrac{1}{3}\left[\gamma_0\left(e^{-(t-t_1)/\tau} - e^{-t/\tau}\right) - \gamma_0^3/5\left(e^{-(t-t_1)/\tau}/3 - \frac{t_1}{2\tau}e^{-t/\tau} - \tfrac{1}{3}e^{-t/\tau} - \tfrac{1}{12}e^{-(t-t_1)/\tau}\right) + O(\gamma^5)\right] \quad \text{(A1)}$$

Here $\gamma_0 = \mu E/kT$, τ is the Debye relaxation time, and t_1 the length of time for which the pulse was applied prior to its removal.

The attainment of field on equilibrium in the computer simulation corresponds to the limiting case $t_1 \to \infty$. In this limit eq. (A1) becomes

$$\langle\cos\theta(t)\rangle \xrightarrow[t_1\to\infty]{} \tfrac{1}{3}\left[\gamma_0 e^{t_1/\tau} - \tfrac{1}{15}\gamma_0^3 e^{t_1/\tau} + \frac{t_1}{10\tau} + \frac{\gamma_0^3}{60}e^{t_1/\tau}\right]e^{-t/\tau} = [\text{const.}]\,e^{-t/\tau} \quad \text{(A2)}$$

Equation (A2) implies that the equilibrium a.c.f. and fall-transient decay identically as the simple exponential $e^{-t/\tau}$. The normalised fall transient in this limit is independent of γ_0 and t_1. The Debye diffusion equation cannot, therefore, produce accelerated transient decay from field-on to field-off equilibrium at constant temperature.

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