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COMPUTER SIMULATION OF SOME FIELD-INDUCED PHENOMENA OF MOLECULAR LIQUIDS

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ABSTRACT

Molecular dynamics simulation of a molecular liquid subjected to an intense external field of force is used to detect and describe some new phenomena of the molecular liquid state of matter.

i) Field-induced decoupling, monitored through the field-dependence of the decay envelope of relevant auto-correlation functions. This is the isolation by the field of the molecular motion from the competing influence of its thermal bath.

ii) Field-induced transient acceleration, monitored via decay transients of orientation. This phenomenon provides unambiguous evidence for the non-linear physical nature of the liquid state, in or out of equilibrium.

iii) Rotating frame rotation/translation coupling, another intrinsically non-linear phenomenon.

These are described in terms of reduced model theory, developed by Grigolini et al.

INTRODUCTION

In a series of papers [1-8] we have pioneered the computer simulation of field-induced phenomena in liquids. The presence of an extra variable (torque due to the external field) provides us with major new insights which have recently been corroborated analytically by Grigolini et al. [7,8,9] using a generally valid non-linear theory of the molecular liquid state. Two of the new phenomena detected and explained so far are:

i) field-induced decoupling [5,7,9] (at equilibrium in the presence of a field with energy $\leq kT$);

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ii) field-induced transient acceleration [2,8,9] (after the removal of a strong field at $t = 0$).

In case (i) above, a dynamical variable such as $\underline{\omega}$, the molecular angular velocity, is isolated (or decoupled) by the field from the effects of its thermal bath, so that the decay of the oscillation envelope of the autocorrelation function $\langle\underline{\omega}(t).\underline{\omega}(0)\rangle/\langle\omega^2\rangle$ varies with field strength, as predicted analytically by Grigolini [10], and slows as the field strength increases. This new phenomenon is basically non-Markovian in statistical nature, and appears also in the field of vibrational dephasing, as simulated by Oxtoby et al. [11].

In case (ii), the decay of the fall transient after the instantaneous removal (at $t = 0$) of field (energetically) equivalent to $\geq kT$, is accelerated considerably with respect to that of the orientational auto-correlation function at equilibrium. In more precise terms a fall transient such as $\langle e_{AZ}(t)\rangle$ decays considerably faster than the equilibrium, field-off, a.c.f. $\langle\underline{e}_A(t).\underline{e}_A(0)\rangle$. Here $\underline{e}_A$ is a unit vector in an axis of the molecule. This violates the fluctuation-dissipation theorem [9] and is a phenomenon which can be explained only with a non-linear general theory of the liquid state. The non-linear analytical approach of Grigolini et al. [6-9] is in detailed agreement with the computer simulations of Evans [1-5] and both sources point towards the existence of a hitherto undetected fall transient phenomenon that could be measured experimentally using the great power of mode locked lasers with sub picosecond time resolution. Its existence implies that the physics of the molecular liquid state has a basically non-linear structure, in or out of equilibrium. The classical Langevin equation [9]:

$$\dot{\underline{\omega}}(t) = -\gamma\underline{\omega}(t) + \underline{f}(t), \qquad (1)$$

a linear approximation, is unable to account for the field acceleration effect, and is also (for the same reason) unable to describe the range of new rotation/translation coupling phenomena [4,5] recently discovered by computer simulation [12].

The generally valid theoretical framework developed by Grigolini [9] reduced model theory (RMT) is a formally rigorous theory, based on well-defined operations of projection into sub-spaces of the total relevant Hilbert space. It reduces to the equations of phenomenological theory in well-defined limiting forms, but provides additional constraints which these simple models must obey. The methods of RMT determine the structure of the simple models, such as Langevin's equation, which are therefore particular cases of RMT. The correct non-linear generalisation of Langevin's equation is determined by RMT to be, in the simplest case [7-9]:

$$\dot{\underline{\omega}}(t) = -\gamma\underline{\omega}(t) + \gamma'\underline{\omega}^3(t) + \underline{f}(t) \qquad (2)$$

where γ' is a non-linear friction coefficient. Eqn. (2) is a limiting form of the non-linear itinerant oscillator. More generally, all the odd powers of $\underline{\omega}(t)$ appear in eqn. (2). This has been solved in another context by Suzuki [13] who showed it to be utterly different in its mathematical properties to the classical eqn. (1). Using Suzuki's results Grigolini [8] has reproduced the key field-induced transient acceleration effect detected by Evans [2] using computer simulation. The fact that eqn. (2) can and eqn. (1) cannot account for this effect means that the nature of the molecular liquid state, in or out of equilibrium, is fundamentally non-linear. In general γ and γ' of eqn. (2) evolve into memory functions whose properties are also defined by RMT [14-18].

In this paper we aim to use a very strong field to illustrate cases (i) and (ii) by computer simulation for a 3 x 3 Lennard-Jones atom-atom potential roughly representing the real liquid CH_2Cl_2 at 293 K, with techniques developed for this purpose by Evans [1-5]. In this high field region new phenomena reveal themselves clearly. In addition to (i) and (ii) we report some autocorrelation functions which seem to corroborate, for the first time, the non-adiabatic fluctuation-dissipation theory recently developed by Chatzidimitriou-Dreissman and Lippert [19,20]. This was motivated by the criticism of the accepted adiabatic theory put forward by van Vliet [21] and van Kampen [22]. The field strengths used in our computer simulation are just within range of those provided by modern mode-locked lasers (energy flux $\doteq 10^{12} Js^{-1}cm^{-2}$; electric field strength of the laser = $10^8 V\ cm^{-1}$; i.e. power transferred per mole per unit in one picosecond $\doteq 10^3 kT$; $\alpha E^2/kT \doteq \mu E/kT \doteq 1$ to 100). The field induced transient acceleration could be detected using sub-picosecond time resolution. The resolution need not be so fine to detect the effect of case (i), which is an equilibrium (but field-on) phenomenon.

Computer simulation Algorithm

This is based on the listing TR12, supplied originally to the author by Singer [23]. An external field of force is applied to the 108 molecules in the usual m.d. box as described elsewhere [1-5]. The force field may be electric, magnetic, electromagnetic, mechanical or other. By varying the field strength ($\underline{E}$) Evans reproduced the Langevin functions [2,4] from linear response to saturation. With an energy ratio of the type $\mu E/kT$ (electric or magnetic torque $\underline{\mu} x \underline{E}$) the classical Langevin function L(a) is simulated precisely

[2]. It is also possible to compute the higher order Langevin functions of the type defined by Kielich [24]. The equivalent functions for $b = \alpha E^2/kT$, have also been simulated by Evans [4] and reproduce precisely the analytical results by Kielich [24]. Here α is the effective (scalar) molecular polarisability. It is clear that the method could be extended to the Langevin functions $L(c)$, where $c = \gamma_0 E^3/kT$, γ_0 being the effective (scalar) molecular hyperpolarisability and so on.

Having tested the algorithm in this way it is then possible to simulate the whole range of dynamical autocorrelation functions at equilibrium in the field-on case, and to produce picosecond scale rise and fall transients in response to the instantaneous switching on and off of the external field. The non-adiabatic fluctuation-dissipation theorem of Chatzidimitriou-Dreissman et al. [19,20] predicts that the fundamental equation:

$$\frac{-d^2}{dt^2}\langle \underline{e}_A(t) . \underline{e}_A(0)\rangle = \langle \dot{\underline{e}}_A(t) . \dot{\underline{e}}_A(0)\rangle \tag{3}$$

is no longer obeyed at equilibrium. This can be tested directly by high-field simulation, because in this limit the non-adiabatic nature of the system should be at its most pronounced.

The simulations were carried out with Lennard-Jones parameters reported elsewhere [25] using an input state point of 293 K, 1 bar. Rise transients were measured after the instantaneous application of a field equivalent energetically to 175 kT. The system was allowed to equilibrate in the presence of this field and several autocorrelation functions were computed in this condition. The fall transient after the removal of the field was evaluated and compared with the equilibrium orientational a.c.f. of the relevant vector $\underline{e}_A$. This procedure reveals clearly the acceleration of the decay transient induced by the intense external field.

RESULTS AND DISCUSSION

The CH_2Cl_2 molecule is, fortuitously, an inertial symmetric top [26], with two principal moments of inertia almost equal and considerably bigger than the third. Its rotational diffusion is, in consequence, highly anisotropic, with $\langle \underline{e}_A(t).\underline{e}_A(0)\rangle$ decaying considerably faster than $\langle \underline{e}_B(t).\underline{e}_B(0)\rangle$ in the field off case [26]. Here $\underline{e}_A$ is a unit vector in the C_{2v} axis and $\underline{e}_B$ a unit vector in the perpendicular axis through the centre of mass - the axis of the smallest principal moment of inertia.

The molecular motion at equilibrium under the 175 kT field is illustrated in Figs. (1) to (4) in terms of $\langle\underline{e}_A(t).\underline{e}_A(0)\rangle$; $\langle\dot{\underline{e}}_A(t).\dot{\underline{e}}_A(0)\rangle/\langle\dot{e}_A{}^2\rangle$; $\langle\underline{e}_B(t).\underline{e}_B(0)\rangle$ and $\langle\dot{\underline{e}}_B(t).\dot{\underline{e}}_B(0)\rangle/\langle\dot{e}_B{}^2\rangle$. Figs. (1) and (2) show that eqn. (3) seems to be violated for the motion of the axis $\underline{e}_B$, therefore supporting the hypothesis of Chatzidimitriou-Dreissman and Lippert [19] for the orientational motion associated with the small amount of inertia. This autocorrelation function is made up of a basically exponential decay superimposed upon which is a slow oscillation together with a fast oscillation of much shorter period.

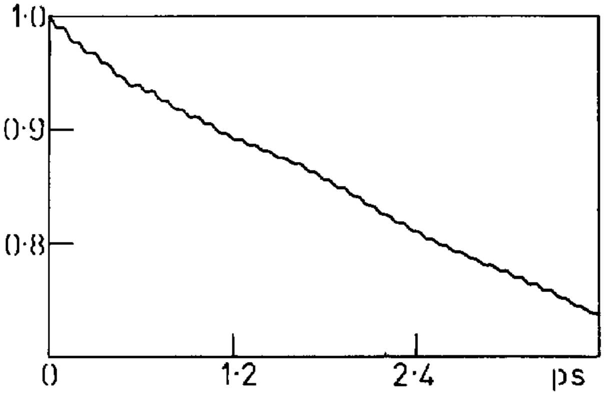


Fig. 1. Orientational a.c.f. $\langle\underline{e}_B(t).\underline{e}_B(0)\rangle$ under a 175 kT field applied to $\underline{e}_A$.
<u>Ordinate</u>: C(t); <u>Abscissa</u>: time/ps.

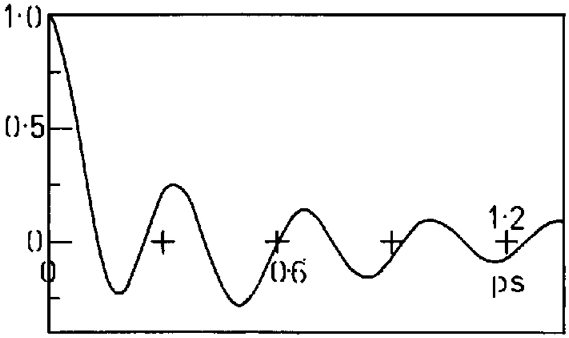


Fig. 2. As for Fig. 1 rotational velocity a.c.f. $\langle\dot{\underline{e}}_B(t).\dot{\underline{e}}_B(0)\rangle/\langle\dot{e}_B^2\rangle$.
<u>Ordinate</u>: C(t); <u>Abscissa</u>: time/ps.

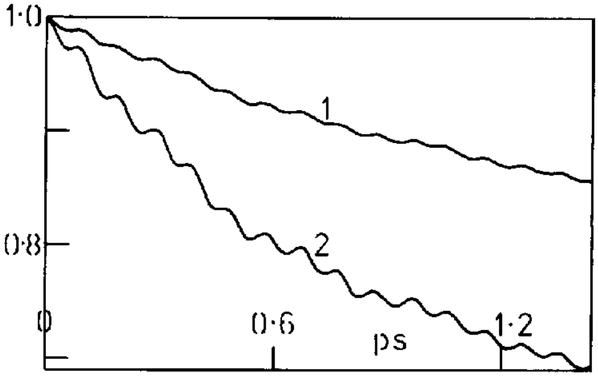


Fig. 3. (1) $<\underline{e}_A(t).\underline{e}_A(0)>$; (2) $\frac{1}{2}<3(\underline{e}_A(t).\underline{e}_A(0))^2 - 1>$.
Ordinate: C(t); Abscissa: time/ps.

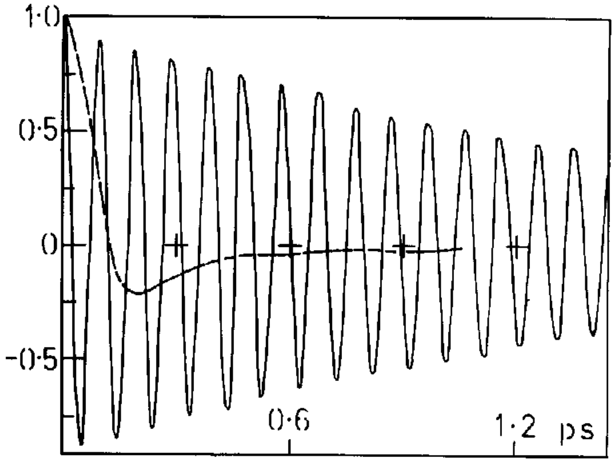


Fig. 4. — $<\dot{\underline{e}}_A(t).\dot{\underline{e}}_A(0)>/<\dot{e}_A^2>$, field-on. - - - - Field-off.
The decoupling effect clearly increases the lifetime (—) in the field-on case.
Ordinate: C(t); Abscissa: time/ps.

The oscillation period of $<\dot{\underline{e}}_B(t).\dot{\underline{e}}_B(0)>/<\dot{e}_B{}^2>$ is different (Fig. (2)) from either of those of Fig. (1).

The equivalent pictures for $<\underline{e}_A(t).\underline{e}_A(0)>$ and $<\dot{\underline{e}}_A(t).\dot{\underline{e}}_A(0)>/<\dot{e}_A^2>$ (Figs. (3) and (4)) are different, in that the oscillation period remains constant.

Eqn. (3) seems to be obeyed accurately. The first rank orientational a.c.f. $<\underline{e}_A(t).\underline{e}_A(0)>$ attains a level of about 3/5 as $t \to \infty$ because $<e^2_{AZ}> \doteqdot 0.98$; $<e^2_{AY}> = 1/3 = <e^2_{AX}>$ at equilibrium; the external, Z-axis, field being intense enough to almost saturate the Langevin function associated with the average $<e^2_{AZ}>$. Similarly, the second-rank a.c.f. $P_2(\underline{e}_A)$ does not decay to zero as $t \to \infty$.

The long-lived envelope of the rotational velocity auto-correlation function in Fig. (4) illustrates phenomenon (i) of the introduction. The oscillations themselves are purely an effect of the torque on $\underline{e}_A$ due to the strong external field of force $\underline{E}$. The rate of decay of these oscillations, on the other hand, is the result of the competition between this torque and that of the molecular ensemble or thermal bath. Grigolini et al. [7,9,10] have shown that this envelope-decay is field-strength dependent. Models of the liquid state which violate the EMT structure [9] do not have this field dependence. Among these are the Langevin equation (1) and the well-jumping model recently published by Praestgaard and van Kampen [27].

The envelope of the lab. frame angular velocity a.c.f. (Fig. (5)) is long-lived with respect to the same a.c.f. at equilibrium in the field-off case. The rotational velocity a.c.f. and angular velocity a.c.f., in Figs. (4) and (5) respectively, behave very similarly. In consequence, if it were possible to detect, free of complications, a far infra-red spectrum of a liquid subjected

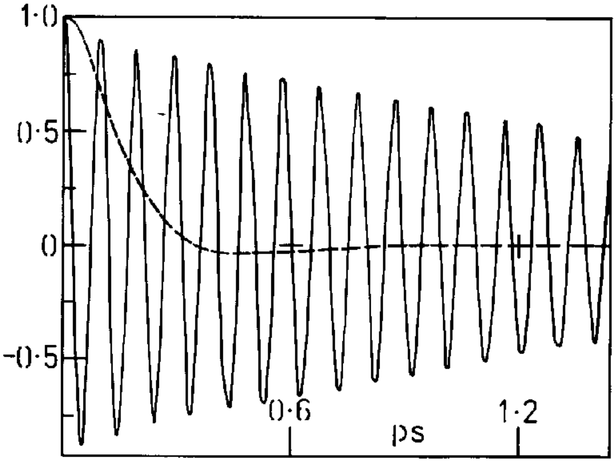


Fig. 5. As for Fig. 4 the molecular angular velocity a.c.f. $<\underline{\omega}(t).\underline{\omega}(0)>/<\omega^2(0)>$. Ordinate: C(t); Abscissa: time/ps.

to intense mode-locked laser pulse trains its Fourier transform would produce the curve of Fig. (4) and by implication the oscillatory angular velocity a.c.f. of Fig. (5). This would give us major new experimental insights to the molecular liquid state of matter.

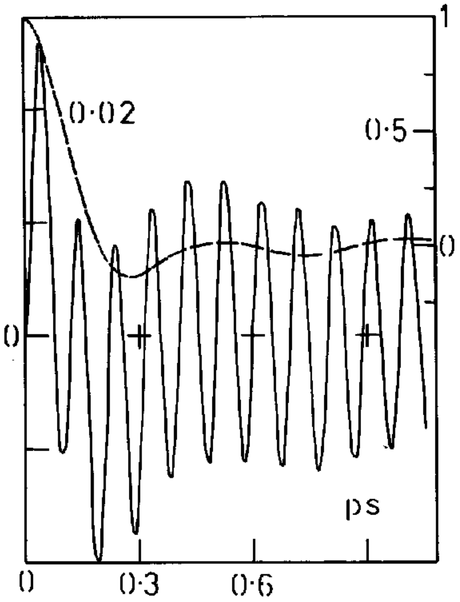
The field-on orientation autocorrelation functions (e.g.$\langle \underline{e}_A(t).\underline{e}_A(0)\rangle$) decay faster than their field-off equivalents as a direct consequence [9] of the decoupling effect on $\langle \underline{\omega}(t).\omega(0)\rangle/\langle \omega^2(0)\rangle$. The effect of a strong external field on the dielectric loss curve, for example, is therefore to shift its peak to higher frequencies, and to distort the frequency dependence of the classical Debye curve [9].

Rotation-Translation Coupling

The development of eqn. (1) into the non-linear type of eqn. (2) has profound conseuqences. One of these is the capability to describe field-induced transient acceleration (vide infra). A second is the ability to describe, within the same overall RMT framework, the subtle and fascinating effects of molecular rotation on molecular translation and vice-versa. We have developed the method originally due to Ciccotti et al. [12] for several types of molecular symmetry [28]. The effects are revealed in a rotating frame of reference through matrices of the type $\langle \underline{v}(t)\underline{\omega}^T(0)\rangle$, where $\underline{v}$ is the centre of mass velocity and $\underline{\omega}$ the molecular angular velocity in this frame of reference (the principal moment of inertia frame). By symmetry in a C_{2v} molecule of the type with which we are dealing here, only two of the elements survive [25].

In Figs. (6) and (7) we illustrate these elements, (3,2) and (2,3) respectively, at equilibrium under a 175kT field. Note that these are not mirror images [5]. The computer noise level can be judged from the symmetry constraint at t = 0, where both functions should vanish. The normalisation factors are $\langle v_3^2\rangle^{\frac{1}{2}}\langle \omega_2^2\rangle^{\frac{1}{2}}$ and $\langle v_2^2\rangle^{\frac{1}{2}}\langle \omega_3^2\rangle^{\frac{1}{2}}$ respectively. In Fig. (6) we note that the contour of the oscillations in (3,2) follows that of $\langle v_3(t)v_3(0)\rangle/\langle v_3^2\rangle$, where v_3 is the third component of $\underline{v}$ in the rotating frame. The a.c.f. $\langle \omega_2(t)\omega_2(0)\rangle/\langle \omega_2^2\rangle$ in this frame is highly oscillatory, much more so than the other two component a.c.f.'s illustrated in Fig. (8). The elemental a.c.f. (3,2) of Fig. (6) therefore follows quite closely the difference $\langle v_2(t)v_2(0)\rangle/\langle v_2^2\rangle - \langle \omega_3(t)\omega_3(0)\rangle/\langle \omega_3^2\rangle$, multiplied by an amplitude factor.

Ferrario [29] has demonstrated that phenomenological equations of rototranslation which are linear in structure, even when written in the correct rotating frame [5], produce $\langle \underline{v}(t)\underline{\omega}^T(0)\rangle = \underline{0}$ for all t and for all elements.



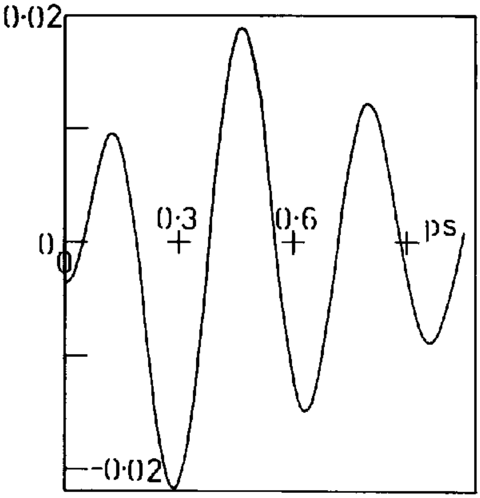
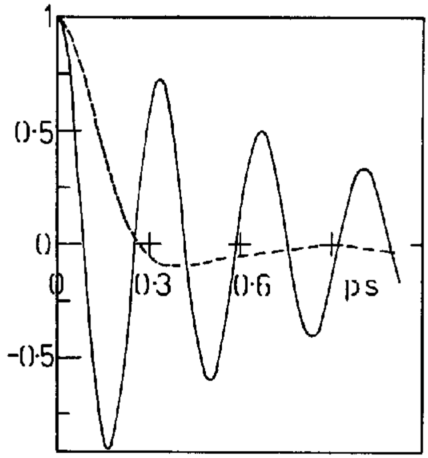


Fig. 6. Rotation/translation coupling in the rotating frame of reference, field-on.
$\frac{\langle v_3(t)\omega_2(0)\rangle}{\langle v_3^2\rangle^{\frac{1}{2}}\langle\omega_2\rangle^{\frac{1}{2}}}$ — — — $\langle v_3(t)v_3(0)\rangle/\langle v_3^2\rangle$ rotating frame.

Ordinates: left: $C(v_3,\omega_2)$ right: $C(v_3)$; Abscissa: time/ps.

Fig. 7. As for Fig. 6, (2,3) r/t element in the rotating frame.
Ordinate: C(t); Abscissa: time/ps.

We therefore arrive at the fundamental law that rototranslational coupling is unambiguous evidence for the validity of Grigolini's non-linear RMT [9]. In other words, functions such as those of Figs. (6) and (7) cannot be described, even qualitatively, without using the precisely defined general mathematical structure of RMT. The very simplest phenomenological description of Figs. (6) and (7) is therefore the correct rototranslational version of eqn. (2). This is of major significance in our understanding of the liquid state which is mostly molecular in nature.



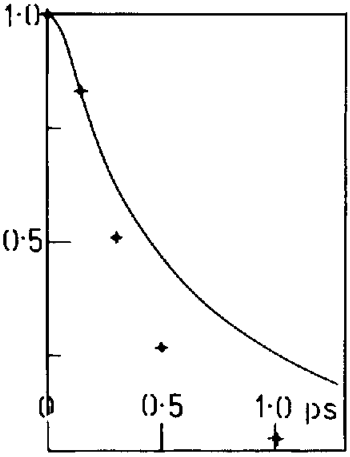


Fig. 8. — $\langle\omega_3(t)\omega_3(0)\rangle/\langle\omega_3^2\rangle$, rotating frame, field-on.

- - - - $\langle\omega_1(t)\omega_1(0)\rangle/\langle\omega_1^2\rangle$, rotating frame, field-on.

Ordinate: C(t); Abscissa: time/ps.

Fig. 9. Field-induced transient acceleration.

— $\langle\underline{e}_A(t).\underline{e}_A(0)\rangle$, field-off.

Decay transient $\langle e_{AZ}\rangle$ after removing the field at t = 0. The transient is normalised to unity at t = 0.

Ordinate: C(t); Abscissa: time/ps.

Field-Induced Transient Acceleration [2,7,8]

Fig. (9) illustrates the field induced acceleration of the transient $\langle e_{AZ}(t)\rangle$ with respect to the equilibrium field-off a.c.f. $\langle\underline{e}_A(t).\underline{e}_A(0)\rangle$. Grigolini [7,8] has used eqn. (2) to show that in the simplest (2-D) case:

$$\langle e_{AZ}(t)\rangle = \exp\left[-\int_0^t D(t')dt'\right] \tag{4}$$

$$D(t) = \int_0^t \phi(t,\tau)d\tau$$

$$\phi(t,\tau) = \langle\omega^2\rangle_{eq}\exp[-(\gamma-\gamma'\langle\omega^2(t)\rangle)\tau]$$

$$<\omega^2(t)> = \frac{[<\omega^2>_{eq} + \dfrac{R(\gamma+<\omega^2>_{eq}\gamma')e^{-2\gamma t}}{(\gamma - R\gamma')}]}{[1 + \dfrac{R\gamma' e^{-2\gamma t}}{(\gamma - R\gamma')}]}$$

where $R = <\omega^2(0)> - <\omega^2>_{eq}$.

Here $<\omega^2>_{eq}$ is the equilibrium, field-off, mean square angular velocity, γ and γ' the linear and non-linear friction coefficents, $\varphi(t,\tau)$ the non-equilibrium and non-stationary autocorrelation function of molecular angular velocity as the system falls back to equilibrium after the removal of the 175 kT field at t = 0. The parameter R measures the redistribution of mean square angular velocity in this interval. It is possible to show that in the case of strong non-linearity (large γ') and significant, but not necessarily strong excitation, there is a locking of the process of exchange of energy between $\underline{\omega}$ and its thermal bath. This speeds up the decay of $<e_{AZ}(t)>$ as observed by the independent technique developed by Evans [2] using computer simulation. Eqn. (4) is valid only when the γ' parameter is relatively small in comparison with γ because eqn. (2) as used by Grigolini [7,8] is a truncated expansion using the mean-field approximation [13] for $\underline{\omega}^3\gamma'$(i.e. $\omega^3 \doteqdot <\omega^2>\omega$). However, we can obtain good agreement with the computed fall transient using eqn. (4) and $\gamma \geq \gamma' R$.

As the externally applied field-strength ($\underline{E}$) increases, the system responds following Langevin's function [2,4], so that $<e_{AZ}(t)> \to 1$ as $|\underline{E}| \to \infty$. There is a similar saturation effect (to that of Langevin) in the field-induced transient acceleration. In the range of validity of eqn. (4) this may be written as $\gamma > R\gamma'$. The difference $(\gamma - R\gamma')$ becomes infinitesimally small but never vanishes. In this limit $<\omega^2(t)>$ remains at $<\omega^2(0)>$ for a well-defined "plateau-time" after the removal of the field and then suddenly changes very quickly to $<\omega^2>_{eq}$. This process accelerates the transient decay of $<e_{AZ}(t)>$ (Fig. (9)) via eqn. (4). Linear theories of the molecular liquid state, be they Markovian or otherwise, do not produce the field-induced transient acceleration [7]. By using RMT structure, Grigolini has shown that the Suzuki equation (2) is in fact the long-time version of an itinerant-oscillator [9] limit of RMT, whose structure is in two dimensions:

$$\begin{aligned}
\dot{\theta} &= \omega \\
\dot{\omega} &= -\kappa \sin N(\theta-\psi) - \omega_1^2 \sin\theta \\
\dot{\psi} &= \nu \\
\dot{\nu} &= \chi \sin N(\theta-\psi) - \omega_2^2 \sin\psi - \gamma\nu + f(t)
\end{aligned} \qquad (5)$$

This accords with the general constraints of RMT and reduces to eqn. (2) when some simplifying assumptions are made. Work is in progress to solve eqn. (5) numerically (without limiting its validity and without imposing restrictions on the strength of the non-linearity [16]). In this way it is possible to reproduce self-consistently the phenomena (i) and (ii) of the introduction together with the transient non-Gaussian effects observable by computer simulation. This gives us enough information to define the amplitude parameters κ and χ of eqn. (5), the friction γ, number of wells N, and frequency factors ω_1^2 and ω_2^2.

The properties of the simplified version of eqn. (5) (i.e. eqn. (2)), as manifested in field-induced transient acceleration show clearly that non-linear liquid state physics is utterly different from and much richer in content [13] than that which we have been used to with the classical equations epitomised by eqn. (1). The use of a strong external field reveals these new phenomena clearly.

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