A FRUITFUL FIELD OF APPLICATION OF THE "REDUCED" MODEL THEORY: COMPUTER SIMULATION OF RELAXATION AFTER STRONG EXCITATION

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It is shown that the major result of a "computer experiment" on the transient regime after strong excitation can be accounted for completely by using the non-linear extension of the "reduced" model theory (RMT).

1. Introduction

In a recent paper [1], Evans raised a question on the range of validity of the fluctuation–dissipation relationship

$$\Delta_A(t) = C_A(t), \tag{1}$$

where

$$\Delta_A(t) = \langle A(t)\rangle / \langle A(0)\rangle, \tag{2}$$

$$C_A(t) = \langle A(t)A(0)\rangle_{\rm eq} / \langle A^2\rangle_{\rm eq}. \tag{2'}$$

Note that the autocorrelation function $C_A(t)$ is evaluated at equilibrium, whereas $\Delta_A(t)$ is a transient property requiring preliminary excitation of the variable of interest A. Evans [1] investigated that problem by monitoring via computer simulation the time behaviour of a liquid sample after the instantaneous removal of a strong external field of force E. He found that at the point $\mu E/kT = 12$, $\Delta_A(t)$ decays considerably faster than $C_A(t)$ [1]. Here μ is the dipole of the tagged molecule and μE is the energy associated with the field of force E. A in that case is the component of the dipole along the z-axis (see fig. 1 of ref. [1]).

The major aim of the present short note is to show that these results can be explained within the framework of the "reduced" model theory [2,3], provided that non-linearity be properly taken into account.

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2. Linear and non-linear systems far from equilibrium

Under a wide range of conditions [4,5] the fundamental equation of motion

$$\mathrm{d}A/\mathrm{d}t = \mathrm{i}LA \tag{3}$$

can be recast in the general form

$$\mathrm{d}A/\mathrm{d}t = \lambda A - \int_0^t \varphi_A(t-\tau)A(\tau)\mathrm{d}\tau + F_A(t). \tag{4}$$

Let us make a first significant assumption (i):

$$\langle F_A(t)\rangle = 0. \tag{5}$$

By a simple Laplace transform, from eq. (4) we have,

$$\Delta_A(t) = \mathcal{F}_A(t), \tag{6}$$

where

$$\mathcal{F}_A(t) = \mathcal{L}^{-1}\{s - \lambda + \hat{\varphi}_A(s)\}, \tag{7}$$

and $\hat{\varphi}_A(s)$ denotes the Laplace transform $\mathcal{L}\{\varphi_A(t)\}$. A further basic requirement for eq. (1) to be valid is then that (ii) $\varphi_A(t)$ is a genuine equilibrium property. However, Zwanzig [4] has shown that in the non-linear case $\varphi_A(t)$ also depends on the variable of interest A. This means that if we excite that variable, we can destroy the basic condition (ii) thereby preventing $\Delta_A(t)$ from being identified with the equilibrium property $C_A(t)$ as implied by eq. (1).

Previous investigation on non-markoffian excitation–relaxation processes [2,6] were mainly concerned with cases satisfying condition (ii). The reason why excitation has an influence on the decay process is then the breakdown of (i) via excitation, with profound consequences on relaxation when the time scale of $F_A(t)$ is not well separated from that of the variable of interest. In this paper, on the contrary, we isolate for the first time the novel effect coming from the breakdown of assumption (ii).

3. The non-linear version of the standard second-order Mori truncation [7]

Because of the fact that the breakdown of (ii) must be traced back to non-linearity [4], we are naturally led to replace eq. (8) of ref. [2] with

$$\dot{\theta} = \omega,$$

$$\dot{\omega} = -k \sin[N(\theta - \psi + \xi)] - \omega_1^2 \sin\theta,$$

$$\dot{\psi} = \nu,$$

$$\dot{\nu} = x \sin[N(\theta - \psi + \xi)] - \omega_2^2 \sin\psi - \Gamma_\nu \nu + f(t). \qquad (8)$$

This version of the non-linear itinerant oscillator [8] shares with the models of refs. [9,10] the physically appealing property of rotation via jumps, though in a form compatible with the decoupling effects of ref. [2]. ξ is the average value of the angle between real and "virtual" dipole when no external field is present.

To simplify our calculation we shall assume ν to be an infinitely fast variable, thereby providing

$$\dot{\theta} = \omega,$$

$$\dot{\omega} = -k \sin(N\Delta) - \omega_1^2 \sin\theta,$$

$$\dot{\Delta} = -(x/\Gamma_\nu)\sin(N\Delta) + \omega - (\omega_2^2/\Gamma_\nu)\sin[N(\theta + \xi - \Delta)] + f(t)/\Gamma_\nu,$$

$$\Delta \equiv \theta - \psi + \xi, \qquad (9)$$

which is the non-linear extension of the second-order Mori truncation [7]. In the absence of external field, a simplified picture approximately equivalent to that of eq. (9) can be obtained, provided that Δ be assumed to be much faster than ω. This assumption allows the adiabatic elimination procedure (AEP) developed within the context of the RMT [3,11] to be applied. It is then possible to show that the long-time behaviour of eq. (9) is roughly equivalent to that provided by the following markoffian, but non-linear, Langevin equation [3,12,13]

$$\dot{\omega} = -\gamma\omega + \gamma'\omega^3 + F(t), \qquad (9')$$

where (we disregard the Γ^{-3} contributions to γ)

$$\gamma = kN\langle\cos(N\Delta)\rangle/\Gamma \qquad (9'')$$

$$\gamma' = (kN^3/6)\langle\cos(N\Delta)\rangle/\Gamma^3, \qquad (9''')$$

$$\Gamma \equiv xN/\Gamma_\nu. \qquad (9'''')$$

The calculations used to arrive at eq. (9′) are basically the rotational counterpart of those described in detailed way in the work of ref. [3], which, in turn, can be regarded as being an application to molecular dynamics of the approach developed in ref. [12]. The detailed discussion of how the non-gaussian stochastic force $F(t)$ is related to $f(t)$ (which is understood to be gaussian) will be given in a more extended report.

In section 4 we shall basically rely on eq. (9′) to account for the major result of Evans' "experiment" [1].

4. Discussion of the "experimental" results

We shall assume θ to be a slow variable compared with ω. Then by using again the AEP [3,11,12] we obtain for the probability distribution of the variable θ, $\sigma(\theta;t)$, the following generally valid equation of motion

$$\frac{\partial\sigma(\theta;t)}{\partial t} = \sum_{n=2}^{\infty} \int_0^t ds\, \varphi_n(t,s) \frac{\partial^n \sigma(\theta;s)}{\partial\theta^n}. \qquad (10)$$

Since θ has been assumed to be almost markoffian, the higher-order derivatives should not play an important role. This allows us to obtain the diffusion equation:

$$\partial\sigma(\theta;t)/\partial t = D(t)\, \partial^2\sigma(\theta;t)/\partial\theta^2, \qquad (11)$$

where

$$D(t) \equiv \int_0^t ds\,[\langle\omega(t)\,\omega(s)\rangle - \langle\omega(t)\rangle\langle\omega(s)\rangle]\,. \qquad (12)$$

Due to the overall symmetry constraints on a non-rotating molecular liquid sample, $\langle\omega(t)\rangle = \langle\omega(s)\rangle = 0$ even in the transient region.

We have to face a final difficulty consisting in evaluating (in the fall-transient regime) the non-stationary correlation function

$$\varphi(t,\tau) \equiv \langle\omega(t)\,\omega(t-\tau)\rangle$$

$$\equiv \int d\omega d\Delta (e^{\Gamma_0^+\tau}\omega)\,\omega\sigma_B(\omega,\Delta;t). \qquad (13)$$

Γ_0 is the Fokker–Planck operator of the (ω, Δ) system and

$$\sigma_B(\omega,\Delta;t) = K\,e^{\Gamma_0 t}$$

$$\times \int d\theta\, \exp\{[k\cos(N\Delta)/N + \omega_1^2\cos\theta$$

$$+ \omega_2^2\cos(\theta + \xi - \Delta) - \tfrac{1}{2}\omega^2]/\langle\omega^2\rangle_{eq}\}, \qquad (14)$$

i.e. the state of the (ω, Δ) system at a time t far from the sudden removal of the field, K is a suitable normalization factor and $\langle\omega^2\rangle_{eq}$ denotes the equilibrium value of $\langle\omega^2\rangle$, which is independent on whether or not the external field is present.

To evaluate this non-stationary correlation function we shall assume the variable ω to be much slower than the "virtual" variable Δ. This allows us to envisage a simplified approach to the evaluation of the transient correlation function of eq. (13) as follows. In the short-time region soon after the sudden removal of the external field, Δ gets its equilibrium distribution thereby determining a change of the ω-distribution from its equilibrium state. By neglecting this short-time contribution to $\varphi(t,\tau)$, we can write

$$\varphi(t,\tau) = K' \int d\omega d\Delta (e^{\Gamma_0^+\tau}\omega)\,\omega$$

$$\times \exp(-\omega^2/2\langle\omega^2(0)\rangle)\,\sigma_{eq}(\Delta), \qquad (15)$$

where K' is a suitable normalization factor, $\sigma_{eq}(\Delta) \propto \exp[k\cos(N\Delta)/N\langle\omega^2\rangle_{eq}]$ and $\langle\omega^2(0)\rangle$ denotes the value of $\langle\omega^2(t)\rangle$ at the time T far from the sudden removal of the external field when this average value attains its largest deviation from $\langle\omega^2\rangle_{eq}$. It is, therefore, understood that this has to be regarded as being the new origin of time (note that T is much shorter than the relaxation time of the variable ω). Throughout the analysis of this section, a parameter of basic importance will be

$$R \equiv \langle\omega^2(0)\rangle - \langle\omega^2\rangle_{eq}\,. \qquad (16)$$

The absolute value of this parameter strongly depends on the intensity of the "virtual" dipole. Via numerical evaluation, we could also assess that for positive values of R to be obtained, non-vanishing values of ξ are required. This can be understood on physical ground when remarking that for $\xi = 0$ strong fields do not change the average value of the angle between real and "virtual" dipole, while preventing large fluctuations around this mean value from taking place. The field-on equilibrium distribution is, therefore, associated with values of the corresponding potential energy smaller than those in the absence of field. When assuming, for example, that $N = 1$, $\xi = \pi$, the effect of strong fields is to reduce the angle between real and "virtual" dipole from π to 0, thereby resulting in an effect which is the reverse of that above described. This makes it possible to obtain positive values for R.

If our attention is focused on the slow re-equilibration process of ω, by using the results of the AEP mentioned in section 3 we can replace eq. (15) with

$$\varphi(t,\tau) = \int d\omega\,\omega(e^{\Gamma_{ad}^+\tau}\omega)\exp(-\omega^2/2\langle\omega^2(t)\rangle), \qquad (17)$$

where Γ_{ad} is the effective operator to be associated (according with the AEP) with eq. (9′). To explicitly evaluate the dependence on time of $\langle\omega^2(t)\rangle$ we can use the following mean-field approximation to eq. (9′):

$$\dot\omega = -\gamma\omega + \gamma'\langle\omega^2(t)\rangle\omega + F(t), \qquad (18)$$

and solve that by following Suzuki [4]. This results in

$$\langle\omega^2(t)\rangle = \frac{\langle\omega^2\rangle_{eq} + R(\gamma + \langle\omega^2\rangle_{eq}\gamma')\,e^{-2\gamma t}/(\gamma - R\gamma')}{1 + R\gamma' e^{-2\gamma t}/(\gamma - R\gamma')}\,. \qquad (19)$$

It is possible to show that in the case of strong non-linearity (large γ') and/or significant excitation (large positive values of R) eq. (19) results in a sort of locking of the process of exchange of energy between ω and its thermal bath (fig. 1). This, in turn, makes faster the decay of $\langle\cos\theta(t)\rangle$ according to eq.

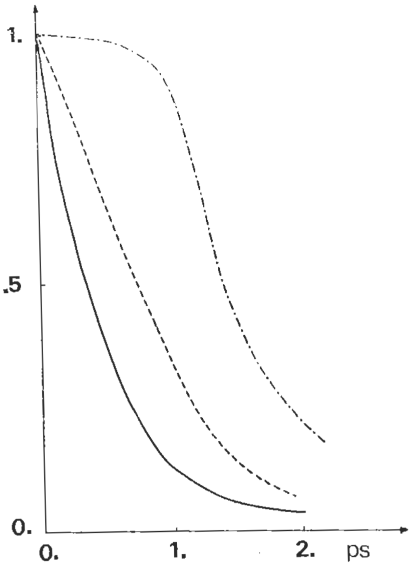

Fig. 1.

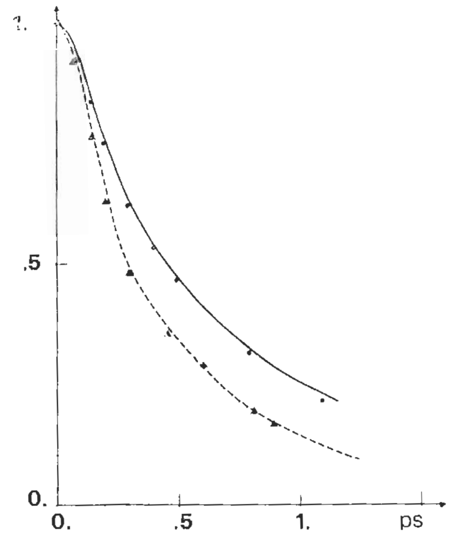

Fig. 2.

(11). We have, in fact, that eq. (17) gives

$$\varphi(t,\tau) = \langle\omega^2(t)\rangle \exp\{-[\gamma - \gamma'\langle\omega^2(t)\rangle]\,\tau\}. \qquad (20)$$

Eqs. (12) and (11) then result in

$$\langle\cos\theta(t)\rangle = \exp\left(-\int_0^t D(t')\,\mathrm{d}t'\right)\langle\cos\theta(0)\rangle \qquad (21)$$

for the fall transient of $\langle\cos\theta(t)\rangle$, where

$$D(t) = \int_0^t \varphi(t,\tau)\,\mathrm{d}\tau. \qquad (22)$$

and $\varphi(t, \tau)$ is defined via eqs. (20) and (19). Note that in the absence of excitation ($R = 0$) eq. (22) reduces to the well-known Kubo result for the stochastic oscillator [15].

Fig. 2 shows that the "experimental effect" of ref. [1] is completely accounted for by the analytical theory of the present paper. Of course, we do not claim for a quantitative agreement, the attainment of which would also require a more detailed discussion of the dependence of R from both ω_2 and ξ, and, perhaps, more accurate "experimental" results.

Finally, we would like to stress that the RMT is a theoretical approach for finding simplified models satisfying the rigorous formal constraints of the general theories of relaxation [6]. This property has been shown to be fundamental for the major findings of Evans' "experiments" [1,2] to be reproduced. The short-time formal constraint [2] prevents us from directly affecting with dissipation the variable of interest thereby accounting for decoupling phenomena. When the "reduced" model is given a non-linear character, the long-time behaviour of the corresponding part of interest is shown to be the same as that resulting from rigorous theories more formal in nature [3]. The slowing down of ω (and thereby, in a complete qualitative agreement with "experiment", the accelerated decay of $\langle\cos\theta(t)\rangle$) are shown to be a natural outcome of the form of this long-time behaviour. A stimulating investigation on the role of the "virtual" dipole should be promoted by our finding that Evans' "experiment" seems to imply non-vanishing values for ξ.

Models of the same kind as that studied in the present paper are currently introduced on a simple phenomenological ground [16]. It should be stressed, however, that within the context of the RMT we found a simple way of exploring the response to strong excitations, whereas the current approaches are restricted to linear response cases [8,16]. Note also that we are in a position to check our analytical theory by an "exact" calculation based on the continued-fraction procedure of ref. [17] which is a further outcome of the theoretical background behind the RMT. Preliminary calculation based on this computational procedure did result in a complete support of the analytical theory developed in the present paper.

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