DECOUPLING EFFECTS IN COMPUTER SIMULATION OF LIQUID-STATE MOLECULAR DYNAMICS

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Decoupling effects in liquid-state molecular dynamics are unambiguously proven by computer simulations. These can be described as the weakening of the dissipative interaction between the system of interest (e.g. molecular angular velocity) and its thermal bath caused by an intense external field of force. The new phenomenon may be used to confirm or challenge the validity of simple models of the liquid state of molecular matter and provide information on the microscopic time scale.

1. Introduction

The process of excitation has been shown [1,2] to have a profound influence on the relaxation of non-markoffian systems. This influence can be exerted in both the excitation (field turned on) (i) and decay regimes (field turned off) (ii). As a major effect concerning case (ii) we recall that one of us [3] showed Abbott and Oxtoby's computer simulation of vibrational relaxation [4] to be an "experimental" proof that the increase in the time duration of the exciting pulse results in washing out the oscillatory decay behaviour of a strongly non-markoffian system. This, being reinforced by the agreement with the results of more recent "experiments" [5,6], poses a tremendous challenge to true experimentalists, in that the required ultrafast excitation pulses are not yet available. Fortunately [1] the effect of the excitation of large intensity is to decouple the non-markoffian systems from their thermal baths [2,3,7,8] so as to make strong excitation pulses completely equivalent to the ultrafast ones.

Since Grigolini's remarks are based on the "reduced" model theory (RMT) [7–11], this effect, which should provide a suggestion of basic importance to experimentalists, is not confined to the field of vibrational relaxation (in this field this effect has been confirmed by Bagchi and Oxtoby's computer simulation [5]). The RMT, in fact, when applied to multiplicative stochastic processes such as those of refs. [4–6], was proven [10] to be equivalent to the celebrated stochastic Liouville equation (SLE) approach of Kubo [12], though in an improved version taking the back-reaction from the system onto the bath [11] into account. The SLE has successfully been applied, therefore, to account for decoupling phenomena in both case (i) [8] and (ii) [3,5,6]. When applied to liquid-state molecular dynamics, the RMT has been proven [13] to result in a rigorous theoretical justification for the itinerant oscillator, which has been widely applied by Evans and co-workers [8,14]. Therefore, decoupling effects should also be exhibited in this field of investigation.

In the absence of experimental data, Evans, in a series of five papers [15–19], has studied the effect of strong excitations on liquid molecular dynamics by computer simulation (note that the "experiments" of Oxtoby and co-workers [4–6] are a semistochastic simulation rather than a true computer simulation). One major aim of this paper is to show that Evans' computer simulations [19] provide further evidence of the decoupling effect.

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2. Decoupling effects in the quasi-markoffian case

The simplest scheme roughly mimicking Evans' "experiment" [19] reads

$$dC(t)/dt = -\int_0^t \varphi(t-\tau)C(\tau)d\tau + i\omega_1 C(t), \qquad (1)$$

where the frequency $\omega_1 = \mu E/I$ (μ and I denote the dipole and the moment of inertia of the tagged molecule) simulates the effect of the torque applied to each molecule of the sample. Eq. (1) can also be written as follows:

$$d\tilde{C}(t)/dt = -\int_0^t \exp[-i\omega_1(t-\tau)]\varphi(t-\tau)\tilde{C}(\tau)d\tau;$$

$$\tilde{C}(t) = \exp(i\omega_1 t)\,C(t). \qquad (2)$$

Let us assume $\varphi(t) = \varphi_0 \exp(-\gamma_a t)$ and γ_a to be so large as to justify the markoffian assumption. Then, on coming back to the original frame of reference, we have

$$dC(t)/dt = [i\Omega(\omega_1) - \Gamma(\omega_1)]\,C(t), \qquad (3)$$

where

$$\Omega(\omega_1) = \omega_1 + \omega_1\varphi_0/(\omega_1^2 + \gamma_a^2), \qquad (4)$$

$$\Gamma(\omega_1) = \gamma_a\varphi_0/(\gamma_a^2 + \omega_1^2). \qquad (4')$$

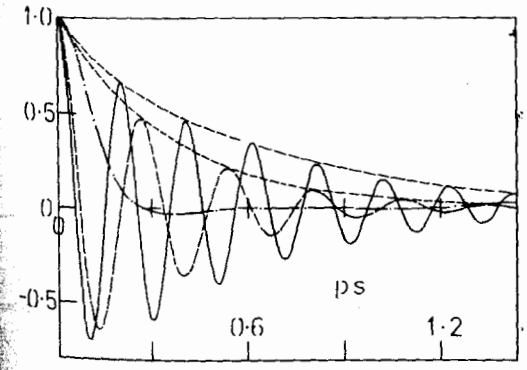

Fig. 1. The behaviour of the correlation function $\langle \boldsymbol{\omega}_T \cdot \boldsymbol{\omega}_T(t)\rangle / \langle \omega_T^2 \rangle$ [19] at several values of the field intensity. – . – . – equilibrium correlation function; – – – $\omega_1^2 = 17.5\ kT/I$; —— $\omega_1^2 = 35\ kT/I$. The correlation function has been evaluated in the laboratory frame.

Since γ_a is finite (the system, therefore, has to be regarded as being quasi-markoffian rather than markoffian) the decay of the oscillation envelope becomes slower as the frequency ω_1 increases. Note the qualitative agreement with the "experimental" results of fig. 1.

3. Effects of thermal bath excitation

The remarks of section 2 remind us that decoupling effects basically depend on the fact that the real systems are not rigorously markoffian. However, when they are significantly non-markoffian we have to release the implicit assumption of section 2 that the memory kernel is unaffected by the external excitation (note that the applied torque of ref. [19] acts on both tagged and untagged molecules).

Let us simulate, for simplicity, the computer "experiment" on dichloromethane [19], with a liquid sample consisting of disks with moment of inertia I constrained to move on a planar surface and colliding with each other. Each disk has an electric dipole μ in one of its diameters. Dipolar interaction, of course, contributes to the total interaction among the disks of the sample. When using the Mori basis set [2,8], the equation of motion

$$d\theta/dt = iL_0\theta, \qquad (5)$$

where θ is the orientation angle of the tagged molecule and L_0 the liouvillian of the model system, can approximately [2,8] be replaced by

$$df_0/dt = f_1,$$

$$df_1/dt = -\Delta_0^2 f_0 + f_2,$$

$$df_2/dt = -\Delta_1^2 f_1 + f_3,$$

$$df_3/dt = -\Delta_2^2 f_2 - \gamma f_3 + F(t), \qquad (6)$$

where $f_0 \equiv \theta, f_1 \equiv \omega \equiv \dot{\theta}$. Note that in the absence of external field, $\Delta_0 = 0$.

In the presence of this we have to add to iL_0, eq. (5), the following interaction

$$\mathcal{L}_1 \equiv iL_1 = -(E\mu/I)\sum_i \sin\theta_i \approx -\omega_1^2 \sum_i \theta_i. \qquad (7)$$

θ_i is the angle between the ith dipole and the direc-

tion of the electric field. The linear approximation is justified when $\langle\omega^2\rangle \ll \omega_1^2$.

According to ref. [20], if the dynamics of the infinite chain of states simulated by the friction γ and the stochastic force $F(t)$ involves frequencies much larger than ω_1, we can limit ourselves to expanding L_1 on the first four Mori states while assuming γ and F to be unaffected by the field. Let us assume, furthermore, that all these matrix elements vanish but

$$\langle f_1|\mathcal{L}_1|f_0\rangle = -\omega_1^2,$$

and

$$\langle f_3|\mathcal{L}_1|f_0\rangle = \Delta_1^2, \quad \langle f_3|\mathcal{L}_1|f_2\rangle \equiv -\omega_2^2.$$

Then the set of equations (2) is straightforwardly proven to be equivalent to the model of the itinerant oscillator [8,14]

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

$$\dot{\omega} = -\Delta_1^2(\theta - \psi) - \omega_1^2\theta,$$

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

$$\dot{\nu} = \Delta_2^2(\theta - \psi) - \omega_2^2\psi - \gamma\nu + f(t). \qquad (8)$$

When $\gamma \gg \Delta_2$ the counterpart of the microscopic time $1/\gamma_a$ (see section 2) is $\Gamma^{-1} \equiv \gamma/\Delta_2$. Then decoupling effects should be exhibited when $\omega_1 \approx \Gamma$. To get an approximated value of Γ we could use the experiment itself as follows. First of all we have to evaluate the rate of decay of the envelopes of fig. 1 as a function of ω_1. This is approximately a lorentzian [recall eq. (4′)] the linewidth of which provides the approximate expression for Γ. The experimental results of fig. 1 provide $\Gamma = 5(kT/I)^{1/2}$. A fitting procedure of the free relaxation case of fig. 1 obtained by using the constraint that Δ_1^2 be equal to 57.5 kT/I, i.e. the value provided by the computer experiment, resulted in $\Delta_2^2 = 104.5\ kT/I$, $\gamma = 11.8\ (kt/I)^{1/2}$ thereby providing $\Gamma = 8.85\ (kT/I)^{1/2}$. The disagreement can easily be traced back to the fact that in the computer simulation we are far from the conditions justifying the second-order Mori truncation. On the other hand, even the third-order Mori truncation seems to lead to unsatisfactory results when compared with the free-relaxation case (fig. 2). However the agreement with the "experimental" decoupling effect is quantitatively, as well as qualitatively good, when the ratio ω_2^2/ω_1^2 is assumed to be equal to 8.5.

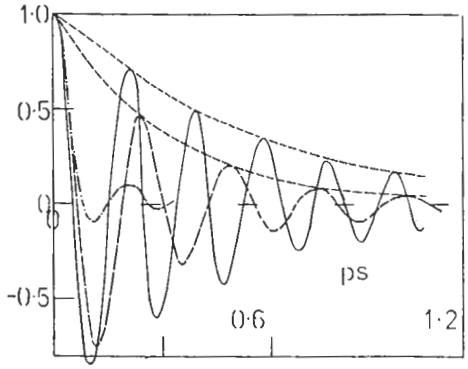

Fig. 2. The behaviour of the correlation function $\langle\omega\omega(t)\rangle/\langle\omega^2\rangle$ (theoretical calculation) for the same values of the fields as in fig. 1. The parameters used are $\Delta_1^2 = 57.5\ \langle\omega^2\rangle$ (provided by the computer simulation); $\Delta_2^2 = 104.5\ \langle\omega^2\rangle$ and $\gamma = 11.8\ \langle\omega^2\rangle^{1/2}$ (both given by a best fitting of the free correlation function). Note that $\langle\omega^2\rangle = \langle\omega_T^2\rangle/2$, where $\langle\omega_T^2\rangle$ is the three-dimensional value provided by the computer simulation [19].

The main conclusion we can draw from these preliminary results is that the RMT theory, while being unable to produce something more than a qualitative agreement with the free relaxation case, however satisfied the basic requirement for the appearance of the novel decoupling effects.

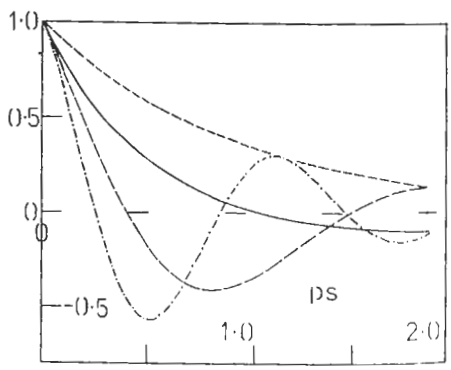

Fig. 3. The behaviour of the correlation function $\langle\omega\omega(t)\rangle/\langle\omega^2\rangle$ (theoretical calculation) corresponding to the model of ref. [23]; $\dot{\theta} = \omega$, $\dot{\omega} = -\gamma\omega - \partial V/\partial\theta$ where $V = V_0[1 - \cos(N\theta)]$ in the presence of the external torque $-\omega_1^2 \sin\theta$. No linear approximation is made in this case. The calculation algorithm used is that of ref. [25] = $\gamma = 6.32\ \langle\omega^2\rangle^{1/2}$; $\langle\omega^2\rangle = 0.1\ \mathrm{ps}^{-2}$; $N = 2$. —— equilibrium correlation function; – – – $\omega_1^2 = 40\ \langle\omega^2\rangle$; – . – . – $\omega_1^2 = 60\ \langle\omega^2\rangle$.

Marin and Grigolini [21] showed that non-linear models such as those modelling the reorientating molecule as jumping from a stable orientation to another one of a multiple well potential [22,23] provide an accurate simulation of the non-gaussian properties of the "experimental" results. However, these models, being basically markoffian, cannot account for decoupling effects (fig. 3). It seems, therefore, that a model satisfying both requirements should be the non-linear version of eq. (8). This model satisfies, in fact, the basic requirements of section 2. Balucani et al. [24], on the other hand, had already shown that this model can also satisfyingly account for the basic features of the free relaxation case.

References

[1] P. Grigolini, Mol. Phys. 31 (1976) 1717.
[2] P. Grigolini, Nuovo Cimento 63B (1981) 174.
[3] P. Grigolini, J. Chem. Phys. 74 (1981) 1517.
[4] R.J. Abbott and D.W. Oxtoby, J. Chem. Phys. 72 (1980) 3972.
[5] B. Bagchi and D.W. Oxtoby, J. Phys. Chem. 86 (1982) 2197.
[6] B. Bagchi and D.W. Oxtoby, J. Chem. Phys. 77 (1982) 1391.
[7] P. Grigolini and A. Lami, Chem. Phys. 30 (1978) 61.
[8] M.W. Evans, G.J. Evans, W.T. Coffey and P. Grigolini, Molecular dynamics (Wiley, New York, 1982) chs. 9,10.
[9] P. Grigolini, Chem. Phys. Letters 47 (1977) 483.
[10] P. Grigolini, Chem. Phys. 38 (1979) 389.
[11] P. Grigolini, J. Stat. Phys. 27 (1982) 283.
[12] R. Kubo, Advan. Chem. Phys. 15 (1969) 101; J. Phys. Soc. Japan 26 (1979) 1.
[13] M. Ferrario and P. Grigolini, J. Math. Phys. 20 (1979) 2567.
[14] M. Evans, G. Evans and R. Davies, Advan. Chem. Phys. 44 (1980) 255.
[15] M.W. Evans, J. Chem. Phys. 76 (1982) 5473.
[16] M.W. Evans, J. Chem. Phys. 76 (1982) 5480.
[17] M.W. Evans, J. Chem. Phys. 77 (1982) 4632.
[18] M.W. Evans, J. Chem. Phys. (1983), to be published.
[19] M.W. Evans, J. Chem. Phys. (1983), to be published.
[20] M. Ferrario and P. Grigolini, J. Chem. Phys. 74 (1981) 235.
[21] P. Marin and P. Grigolini, J. Mol. Struct. 80 (1982) 401.
[22] B. Lassier and C. Brot, Chem. Phys. Letters 1 (1968) 581.
[23] E. Praestgaard and N.G. van Kampen, Mol. Phys. 43 (1981) (1981) 33.
[24] U. Balucani, R. Vallauri, V. Tognetti, P. Grigolini and P. Marin, Z. Physik B49 (1982) 181.