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NON-GAUSSIAN EFFECTS IN THE COMPUTER SIMULATION OF DICHLORO METHANE

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ABSTRACT

It has recently been suggested that non-linearity implies that the statistics governing the transient behaviour of translational correlation functions of the motion cannot be Gaussian. A computer simulation of CH_2Cl_2 under EMLG pilot project conditions shows that rotational as well as translational motion exhibits strong dynamical non-Gaussian features. It is shown that these effects cannot be ascribed to the non-linear drift appearing in the Markoffian version of the Euler-Langevin equation. This strongly supports an investigation line based on the research of a hidden non-linear dissipation coupling.

INTRODUCTION

It has recently been suggested that a non-linear extension of the "reduced" model theory (RMT) [1,2] can account for the major findings of the computer simulation of molecular dynamics [3,4]. Grigolini and co-workers found that this approach explains both the non-diffusional slope property and non-Gaussian behaviour [3,4]. Note that refs. 3 and 4 concern the translational case. When dealing with the rotational case a new problem arises. The structure of the Euler-Langevin equation is itself non-linear thereby leading, in principle, to a non-Gaussian behaviour for the angular velocity. However, this kind of non-Gaussian behaviour in a sense is trivial in that it is traced back to a well-known deterministic structure, whereas the main aim of the RMT [1,2] is to detect hidden non-linearity within the context of the dissipation interaction between the variable of interest (in the present case the angular velocity ω or the angular momentum J) and its thermal bath. According to the RMT [1,2] the non-Markoffian nature of the variable of interest is simulated by a deterministic

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coupling with a set of "virtual" variables undergoing the influence of fluctuation and dissipation Markoffian in nature. The latest version of the RMT [3,4] is based on the non-linear character of this deterministic coupling, thereby exhibiting a misleading similarity with the non-linear drift of the Euler-Langevin equation.

Tha main aims of this paper are: (i) To prove that rotational dynamics is not Gaussian (see next Section); (ii) To show that such a non-Gaussianicity cannot be ascribed to the non-linear structure of the Euler-Langevin equation (see last Section). This is tantamount to assessing that the methods of [3,4] can be extended to the rotational case thereby offering the RMT a wider field of application.

Computer Simulation of Transient Non-Gaussian Behaviour

The molecular dynamics algorithm used is TETRA, at EMLG pilot project state points for CH_2Cl_2, i.e. 293 K and 177 K at 1bar. The computational details, those of intermolecular potential and experimental checking, are fully reported elsewhere [5]. Note that indications of non-Gaussian behaviour have been reported previously using molecular dynamics simulation, by Rahman [6] for argon, Berne and Harp [7] for CO, and Evans et al. [8] for N_2 in the liquid and high temperature glass. Grigolini et al. [9] reported such behavour in an artifical triatomic of C_{2v} symmetry using the algorithm TRI2, and Balucani et al. [3] have also reported non-Gaussian effects in computer argon. The effects are present therefore in six different algorithms, six different potentials, and with differing box sizes, different state points and numbers of sample molecules. They are therefore unlikely to be artifacts of the molecular dynamics method.

The algorithm TETRA for CH_2Cl_2 uses 108 molecules with a sophisticated site-site interaction potential and using it Evans and Ferrario [5] have produced a wide variety of spectra suitable for the comparison with experimental data of the EMLG pilot project. In some cases TETRA produces information otherwise virtually unobtainable, either experimentally or theoretically. An example is $\langle J(t).J(t)\ J(0).J(0)\rangle$, where J is the molecular angular momentum. Another is $\langle v(t).v(t)\ v(0).v(0)\rangle$, where v is the centre of mass linear velocity; and yet another is the cross-term a.c.f.'s $\langle J(t).J(t)\ v(0).v(0)\rangle$ or $\langle v(t).v(t)\ J(0).J(0)\rangle$. Provided:

i) transient statistics are Gaussian;

ii) $\langle J(0).J(0)\rangle$ is statistically independent of $\langle v(0).v(0)\rangle$ (i.e. equipartition);

these a.c.f.'s may be interrelated analytically. In this case:

$$\frac{\langle v(t).v(t)\ v(0).v(0)\rangle}{\langle v^4(0)\rangle} = \frac{3}{5}\left(1 + \frac{2}{3}\ \frac{\langle v(t).v(0)\rangle^2}{\langle v^2(0)\rangle^2}\right) \qquad (1)$$

$$\frac{\langle J(t).J(t)\ J(0).J(0)\rangle}{\langle J^4(0)\rangle} = \frac{(I_1 + I_2 + I_3)^2 + 2\sum_{i=1}^{3} I_i^2\ \chi_i^2\ (t)}{(I_1 + I_2 + I_3)^2 + 2\ (I_1^2 + I_2^2 + I_3^2)} \qquad (2)$$

where $\chi_i(t) = \langle J_i(t)J_i(0)\rangle/\langle J_i^2(0)\rangle$, and:

$$J = J_i i + J_2 j + J_3 k \qquad (3)$$

where i, j and k are unit vectors and J_1, J_2 and J_3 are components of J in the molecule frame.

In eq.(2) I_1, I_2 and I_3 are the three principal moments of inertia of CH_2Cl_2, defined about the axes of i, j and k respectively.

The computer results are compared with those of eqs.(1) and (2); in figs.(1) and (2). They are clearly non-Gaussian in the interval t=0 to equilibrium ($t \to \infty$) The predictions of eqs.(1) and (2) are plotted as the dashed curves. The maximum deviation in each case occurs at around 0.3 ps after t=0.

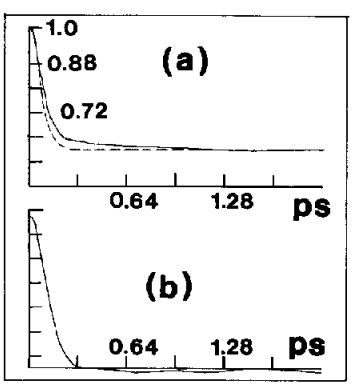


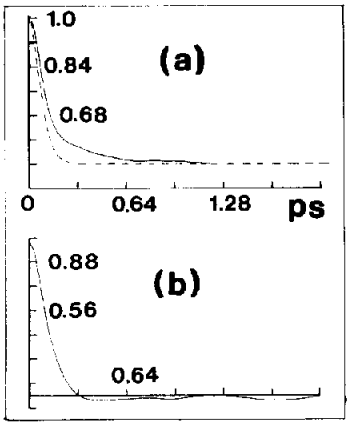
Figure (1)

(a) ——— $\langle v(t).v(t)\ v(0).v(0)\rangle/\langle v^4(0)\rangle$, computer simulation.

----- Gaussian statistics, i.e. $\frac{3}{5}\left(1 + \frac{2}{3}\ \left(\frac{\langle v(t).v(0)\rangle}{\langle v^2(0)\rangle}\right)^2\right)$

(b) $\langle v(t).v(0)\rangle/\langle v^2\rangle$, computer simulation.

Ordinate : normalized a.c.f. ; Abscissa : time/ps



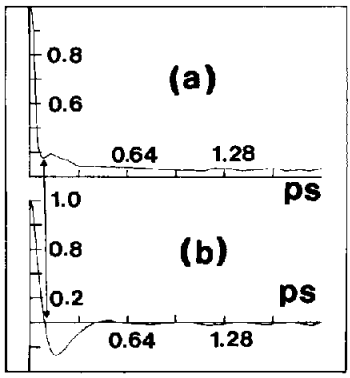


Figure (2)

(a)——— $\langle J(t).J(t)\ J(0).J(0)\rangle/\langle J^4(0)\rangle$, computer simulation.

----- Gaussian result , see text.

(b) $\langle J(t).J(0)\rangle/\langle J^2\rangle$, computer simulation.

Ordinate : normalized a.c.f. ; Abscissa : time/ps

Figure (3)

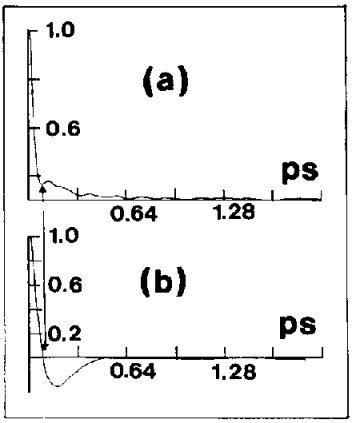
(a) $\langle F(t).F(t)\ F(0).F(0)\rangle/\langle F^4(0)\rangle$, computer simulation.

(b) $\langle F(t).F(0)\rangle/\langle F^2(0)\rangle$, computer simulation.

Ordinate : normalized a.c.f.; Abscissa : time/ps.

The analysis brings the same conclusion for the molecular force F and torque T. In figs.(3) and (4) we mark points where the non-Gaussian nature of the simulation results is clearly apparent, and analytical expressions linking, for example, $\langle F(t).F(t)F(0).F(0)\rangle/\langle F^4(0)\rangle$ to $\langle F(t).F(0)\rangle/\langle F^2(0)\rangle$ are not necessary. However, in Appendix A we sketch their derivation.

Finally, in fig.(5) we illustrate the simulation results for $\langle v^2(t)\ J^2(0)\rangle/\langle v^2\ (0)\rangle\langle J^2\ (0)\rangle$ (and $\langle F^2(t)T_q^{\ 2}(0)\rangle/\langle F^2(0)\rangle\langle T_q^{\ 2}(0)\rangle$). These reflect very clearly the nature of rotation/translation interaction in diffusing CH_2Cl_2. We note that $\langle v^2(0)\rangle$ and $\langle J^2(0)\rangle$ are statistically uncorrelated (whereas $\langle F^2(0)\rangle$ and $\langle T_q^{\ 2}(0)\rangle$ are not). We also note that any analytical theory which purports a description of these functions must produce $\langle v(t).J(0)\rangle=\langle J(t).v(0)\rangle=0$ because of the physics of parity reversal. The derivation of $\langle v^2(t)J^2(0)\rangle/\langle v^2(0)\rangle\langle J^2(0)\rangle$ from $\langle v(t).v(0)\rangle$ and $\langle J(t).J(0)\rangle$ is sketched in Appendix B, where we use two dimensional Gaussian statistics. In conclusion it is clear that the computer



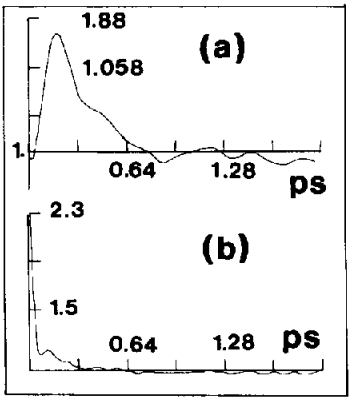


Figure (4)

(a) $\langle T_q(t).T_q(t)T_q(0).T_q(0)\rangle/\langle T_q^4(0)\rangle$, computer simulation.

(b) $\langle T_q(t).T_q(0)\rangle/\langle T_q^2(0)\rangle$, computer simulation.

Ordinate : normalized a.c.f. ; Abscissa : time/ps.

Figure (5)

(a) $\dfrac{\langle v(t).v(t)\ J(0).J(0)\rangle}{\langle v^2(0)\rangle\langle J^2(0)\rangle}$, computer simulation.

Note that $\langle v(t).J(0)\rangle=\langle J(t).v(0)\rangle= 0$ for all t by parity reversal symmetry. This is corroborated in the m.d. simulation. If we assume the p.d.f.'s of v and J to be Gaussian, then this, together with the foregoing parity reversal condition, implies that $\langle v^2(t)\ J^2(0)\rangle=\langle J^2(t)\ v^2(0)\rangle= 0$ theoretically for all t. The existence of the simulated function of fig. (5a) is therefore a strong support for non linear theories of the liquid state.

(b) $\dfrac{\langle F(t).F(t)\ T_q(0).T_q(0)\rangle}{\langle F^2(0)\rangle\langle T_q^2(0)\rangle}$

Note that $\langle F^2(0)\ T_q^2(0)\rangle=\langle F^2(0)\rangle\langle T_q^2(0)\rangle$ and that the force squared and torque squared are statistically correlated.

Abscissa ; time/ps.

simulation results are non-Gaussian in nature. This can lend strong support to the research line proposed in 2,3, provided that we succeed in showing that these non-Gaussian features do not depend on the non-linear structure of the Markoffian Euler-Langevin equation. This is the main aim of the next Section.

THEORETICAL EVALUATION

When making the Markoffian assumption on the interaction between and its

thermal bath, the motion of the variable ω in a rotating frame fixed to the molecule is described by the well-known Euler-Langevin equations [2] which read

$$\dot{\omega}_1 = \tau_i \omega_j \omega_k - B_i \omega_i + A_i(t) \equiv - E_i(\omega) + A_i(t) \tag{4}$$

where $\tau_i = (I_k - I_j)/I_i$ and i, j and k are cyclically permuted among 1, 2 and 3. The stochastic forces A_i are assumed to be white Gaussian noises defined by

$$\langle A_i(t_1) A_j(t_2) \rangle = 2\, a_i \delta_{ij} \delta(t_1 - t_2) \tag{5}$$

The equation of motion of a variable of interest f_o is then driven by

$$\dot{f}_o = \alpha_o f_o \tag{6}$$

with

$$\alpha_o = \Gamma^+ \tag{7}$$

$$\Gamma \equiv -\sum_{j=1}^{3} \left(\frac{\partial}{\partial \omega_j} E_j(\omega) - a_j \frac{\partial^2}{\partial \omega_j^2} \right) \tag{8}$$

The main difficulty met when dealing with eq.(6) descends from the non-linear nature of $E_i(\omega)$, which renders this equation equivalent to an infinite hierarchy of linear equations. The algorithm of ref. 10 (which, in turn, is a natural outcome of the theoretical background behind the RMT) allows us to solve this problem via a continued fraction expansion, the virtually infinite parameters of which are straightforwardly evaluated on the basis of a Mori-like theory (see Appendix C).

When evaluating the correlation functions $\langle J_i(0) J_i(t) \rangle$, f_o has to be identified with J_i (i = 1,3), whereas the calculation of

$$\phi(t) \equiv (\langle J^2(0) J^2(t) \rangle - \langle J^2 \rangle^2) / \langle J^4 \rangle \tag{9}$$

implies that f_o be identified with $J^2 - \langle J^2 \rangle$.

To apply this method of calculation, however, we have to rely on suitable values of the friction parameters B_i. These can be determined via a sort of "semiempirical" method as follows. Let us call e_1, e_2 and e_3 the three unit vectors defined by the principal moment of inertia frame in the CH_2Cl_2 molecule. The a.c.f.'s $\langle e_i(0) . e_i(t) \rangle$ (i = 1,3) are found via computer simulation to be almost exponential with damping γ_i. On the other hand, to a first approximation these dampings are shown theoretically (see Appendix C) to be related to the friction parameters B_1 via the following relationship

$$\gamma_i = kT \left(\frac{1}{I_j B_j} + \frac{1}{I_k B_k} \right)^{-1} \tag{10}$$

in cyclic permutation of the indices i,j,k. Eq. (9) allows us to determine the parameters B_i to be used in our theoretical calculation in terms of the "experimental" dampings γ_i.

We are now in a position to illustrate the results of this "exact" calculation. First of all, let us consider the curves of figs. (6) and (7). These have been evaluated by using the dampings B_i provided by eq. (10). The moments of inertia are $I_1 = 2.526\ 10^{-38}$ gm cm^2, $I_2 = 0.262\ 10^{-38}$ gm cm^2, $I_3 = 2.737\ 10^{-38}$ gm cm^2. The friction parameters are $B_1 = B_3 = 18.8$ THz and $B_2 = 49.4$ Hz at T = 177 K and $B_1 = B_3 = 11.7$ THz and $B_2 = 22.0$ THz at T = 293 K. The latter parameters refer to CH_2Cl_2 at 1 bar. We can remark that the distance between the exact $\phi(t)$ and its Gaussian approximation $\phi_G(t)$ is less than $0.5\ 10^{-2}$ throughout the whole range of t.

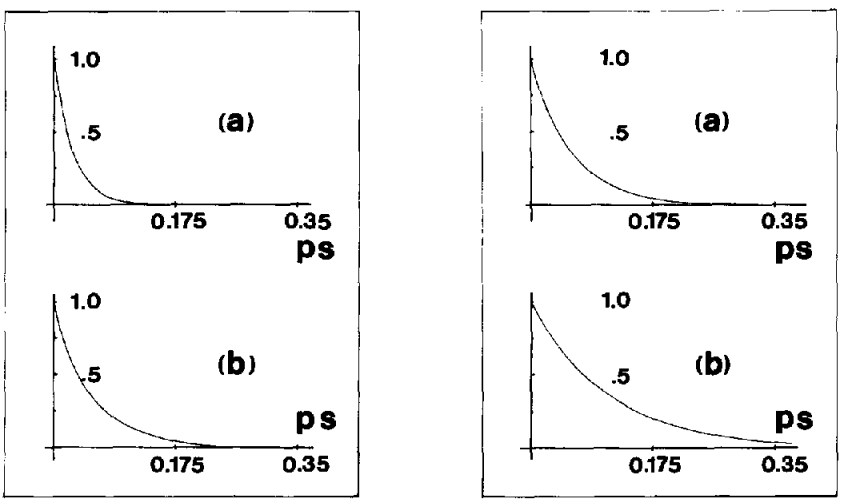


Figure (6)

(a) $\Phi(t)$, calculated. In this scale $\Phi(t)$ coincides with its Gaussian approximation, $\Phi_G(t)$.

(b) $\langle J(t).J(0)\rangle/\langle J^2(0)\rangle$, calculated.

The molecular parameters are those concerning T = 177K.

Ordinate : normalized a.c.f. ; Abscissa : time/ps.

Figure (7)

(a) $\Phi(t)$, calculated. In this scale $\Phi(t)$ coincides with its Gaussian approximation, $\Phi_G(t)$.

(b) $\langle J(t).J(0)\rangle/\langle J^2(0)\rangle$, calculated

The molecular parameters are those concerning T = 293K.

Ordinate : normalized a.c.f. ; Abscissa : time/ps.

A significant non-Gaussian behaviour is exhibited by the curves of fig. (8). However, these curves concern values of the parameters B_1 which are significantly smaller than those provided by eq. (10). Therefore, according to our "semi-empirical" criterion this result has to be rejected.

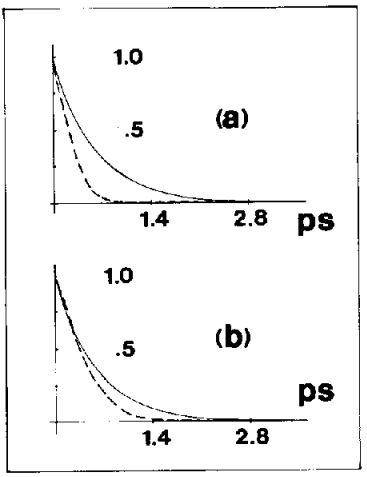


Figure (8)

(a) ——— $\Phi(t)$, calculated.

----- Gaussian result, see text.

(b) ----- $\langle J_1(t).J_1(0)\rangle/\langle J_1^2(0)\rangle$, calculated

——— $\langle J_2(t).J_2(0)\rangle/\langle J_2^2(0)\rangle$, calculated.

The parameters B_i are : $B_1 = B_3 = 1.11$ THz and $B_2 = 2.22$ THz.

Ordinate : normalized a.c.f. ; Abscissa : time/ps.

The exponential behaviour exhibited by $\varphi(t)$ in figs. (6) to (8) can easily be accounted for as follows. Let us explicate the expressions for the expansion parameters λ_o, Δ_1, λ_1 (for their meaning see Appendix C). We obtain

$$\lambda_o = -2\sum_i I_i^2 B_i \Big/ \sum_i I_i^2 \tag{11}$$

$$\Delta_1^2 = -4\left[I_1^2I_2^2(B_1-B_2)^2 + I_2^2I_3^2(B_2-B_3)^2 + I_1^2I_3^2(B_1-B_3)^2\right]\left[\sum_i I_i^2\right]^{-1} \tag{12}$$

$$\lambda_1 = -2\left[I_1^2I_2^2(B_1-B_2)(B_1^2-B_2^2) + I_2^2I_3^2(B_2-B_3)(B_2^2-B_3^2) + I_1^2I_3^2(B_1-B_3)(B_1^2-B_3^2)\right]$$
$$\times\left[I_1^2I_2^2(B_1-B_2)^2 + I_2^2I_3^2(B_2-B_3)^2 + I_1^2I_3^2(B_1-B_3)^2\right]^{-1} \tag{13}$$

It is easily seen for all the three groups of values of B_i of figs. (6) to (8)

that $|\lambda_o-\lambda_1|^2 >> |\Delta_i^2$ so that the Mori chain providing $\phi(t)$ is almost exactly truncated at the zeroth order, i.e. $\phi(t) \sim \exp(-\lambda_o t)$.

As far as the non-Gaussian behaviour of the curves of fig. (8) is concerned, we can note that this seems to depend on the fact that the correlation functions $<J_i J_i(t)>$ compared to $\phi(t)$ are much faster that in the cases of figs. (6) and (7).

In conclusion, we are in a position to assert that no significant non-Gaussian effects can be given by eq. (4) for reasonable values of the parameters B_i. Therefore, the strong non-Gaussian properties exhibited by the "experimental" results of figs. (1) to (4) have to be traced back to the dissipative interaction driving ω rather than the drift term. The appearance of rototranslational interactions on the correlation function $<J^2(0)v^2(t)>$, furthermore, leaves open the question whether or not this effect can be related to the same non-linear mechanism which destroys the Gaussian relationship between the two time correlation functions and higher-order ones.

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APPENDIX A: DERIVATION OF ANALYTICAL EXPRESSION FOR HIGHER MOMENT FORCE AND TORQUE AUTOCORRELATION FUNCTIONS

The Gaussian distribution can be written as:

$$\left(\frac{3}{\sigma\sqrt{2\pi}}\right)^{3/2} \exp\left[-\frac{3}{2}\left(\frac{x-m}{\sigma}\right)^2\right] \tag{A1}$$

where m is the mean, σ^2 the variance. In the case of linear centre of mass velocity the probability density function may be defined as:

$$P_v(v,t|v_o,\,0) = \left[\frac{M}{2\pi\kappa T\,(1-\psi^2(t))}\right]^{3/2} \times \exp\left[-\frac{M(v-v_o\psi(t))^2}{2\kappa T\,(1-\psi^2(t))}\right] \tag{A2}$$

where M is the particle mass, and:

$$\psi(t) = <v(t).v(0)>/<v(0).v(0)> \tag{A3}$$

The variance is:

$$\sigma^2 = \frac{3\kappa T}{M}\,(1-\psi^2(t)) \tag{A4}$$

and the mean:

$$m = v_o\psi(t) \tag{A5}$$

v_o being the particle's initial velocity. The required fourth moment is calculated through the relation:

$$\langle v(t).v(t)v_o.v_o\rangle.\langle v^4\rangle^{-1} = \int d^3v \int d^3v_o \; v.v \; v_o.v_o \; P(v,t|v_o,0) \; P(v_o, 0), \tag{A6}$$

where $P(v_o, 0)$ is the equilibrium probability distribution function. Evaluating the integral, we have [7,9] the results of eq. (1). Similarly we can derive [9] eq. (2) for the angular momentum. The integrals for force and torque may be evaluated, but with considerable more difficulty. For Gaussian statistics it is clear that when $\langle F(t).F(0)\rangle$, for example, vanishes, then all $\langle F^{2n}(t)F^{2n}(0)\rangle$ should also vanish at the same instant t. This is not the case in the computer simulation for either the force or the torque (figs. (3) and (4)).

APPENDIX B: THE MIXED-MOMENT A.C.F.'S

Assuming $\langle v^2\rangle$ to be independent, statistically, of $\langle J^2\rangle$, we may evaluate the mixed a.c.f.'s using the two dimensional equilibrium Gaussian distribution:

$$p(X_1, X_2) = \left(\frac{1}{\sigma_{x_1}\sqrt{2\pi}} e^{- X_1^2/2\sigma_{x_1}^2} \right) \times \left(\frac{1}{\sigma_{x_2}\sqrt{2\pi}} e^{- X_2^2/2\sigma_{x_2}^2} \right) \tag{B1}$$

for uncorrelated variables X_1 and X_2. In the case of force squared and torque squared we must use the correlated form :

$$p(Y_1, Y_2) = \frac{1}{2\pi \, \sigma_{Y_1} \, \sigma_{Y_2} \sqrt{1 - \tau^2}} \; \text{xexp} \left[- \frac{1}{2(1 - \tau^2)} \left(\frac{Y_1^2}{\sigma_{Y_1}^2} - \frac{2\tau \, Y_1 \, Y_2}{\sigma_{Y_1} \, \sigma_{Y_2}} + \frac{Y_2^2}{\sigma_{Y_2}^2} \right) \right]$$

where τ is the correlation coefficient and σ_{Y_1} and σ_{Y_2} are the standard deviations of Y_1 and Y_2 respectively. Note, however, that the correlation function of force and torque $\langle F(t).T_q(0)\rangle$ vanishes, whereas $\langle F^2(t)T_q^2(0)\rangle$ of course does not vanish. This is because the parity reversal symmetry of F is different from that of T_q.

Eqs. (B1) and (B2) imply that:

$$\langle v^{2n}(t)J^{2n}(0)\rangle = \langle v^{2n}(0)J^{2n}(t)\rangle = 0 \tag{B3}$$

for all t and n, if v and J are transiently Gaussian in nature. Fig. (5a) is clear evidence of the contrary.

Similarly:

$$\langle F^{2n}(t)T_q^{2n}(0)\rangle = \langle F^{2n}(0)T_q^{2n}(t)\rangle = 0 \qquad (B4)$$

for all t and n for transiently Gaussian F and T_q. This is obviously not the case either analytically or numerically (fig. (5b)).

APPENDIX C

Dupuis' algorithm [11] leads to an easy evaluation of the Mori expansion parameters Δ_i^2 and λ_i [10]. These parameters in turn give the Laplace transform of the correlation function $\Phi(t) = \langle f_o f_o(t)\rangle$ (see eqs.(6) to (8)) this continued fraction expansion :

$$\hat{\Phi}(z) = \cfrac{1}{z + \lambda_o + \cfrac{\Delta_1^2}{z + \lambda_i + \cdots}} \qquad (C1)$$

As far as the time behaviour of $\Phi(t)$ is concerned, its explicit e valuation can straightforwardly [10] be given by:

$$\Phi(t) = \sum_{\pi} \langle 1|\pi\rangle\langle\tilde{\pi}|1\rangle\, e^{E_\pi t} \qquad (C2)$$

where $|\pi\rangle, \langle\tilde{\pi}|$ and E_π are respectively the eigenstates (right and left) and eigenvalues of the matrix A defined as follows:

$$A = \begin{bmatrix} \lambda_o & 1 & 0. & . & . \\ -\Delta_1^2 & \lambda_1 & 1 & . & . \\ 0 & -\Delta_2^2 & \lambda_2 & . & . \\ . & . & . & . & . \\ . & . & . & . & . \end{bmatrix} \qquad (C3)$$

It is interesting to notice that this algorithm can also be applied to the case where the variable of interest is the orientation g. In such a case the equation of motion for the probability density $P(g,\omega)$ is

$$\frac{\partial}{\partial t} P(g,\omega;t) = (-i\omega . J + \Gamma)\, P(g,\omega;t) \qquad (C4)$$

where T is the rotation generator and the operator Γ is defined by eq. (8). When f_o is identified with e_1(i = 1,3) and

$$L_o^{+} = -i\omega . J + \Gamma, \qquad (C5)$$

the zeroth-order of our continued fraction approach is shown to lead to eq. (10).

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