Z. Phys. B - Condensed Matter 41, 165–176 (1981)

Condensed Matter
Zeitschrift für Physik B


# Probability Diffusion in Non-Markhovian, Non-Gaussian Molecular Ensembles: A Theoretical Analysis and Computer Simulation

P. Grigolini* and M. Ferrario**
Gruppo Nazionale di Struttura della Materia del C.N.R.,
Istituto di Fisica, Universita di Pisa, Italy

M.W. Evans
Department of Chemistry, University College of Wales, Aberystwyth, Wales

Received July 21, 1980

A theoretical generalisation of the Fokker/Planck equation for atomic and molecular diffusion is compared with the results of a molecular dynamics simulation of a triatomic molecule of $C_{2v}$ symmetry. The molecular dynamics results are non-Markhovian and non-Gaussian in nature, markedly so in the case of the centre of mass linear velocity **V**. This may be ascertained by simulating the long-time limit of the three dimensional kinetic energy autocorrelation function $\langle \mathbf{V}^2(t)\,\mathbf{V}^2(0)\rangle/\langle \mathbf{V}^2(0)\,\mathbf{V}^2(0)\rangle$, which falls well below the theoretical Gaussian value of 3/5. By expressing the Mori continued fraction as a multidimensional Markhovian chain of differential equations and expressing this in turn as a non-Gaussian probability-diffusion equation of the Kramers/Moyal type it is possible to account for the simulation results in a qualitative fashion.

## I. Introduction

Non-Markhovian behaviour can be regarded as being a physical property pertinent to a wide variety of phenomena. According to general theories of relaxation [1] memory effects are exhibited by any relaxation process where a clearcut separation between the microscopic time scale and the macroscopic one is not possible. Relevant examples are provided, for example, by *EPR* spectroscopy [2], ultrafast vibrational relaxation [3] and molecular motion [4] both in liquids.

It should be stressed, however, that non-Markhovianicity is not to be regarded as a real difficulty in itself. Indeed, any stochastic process concerning a variable $y$ can be described by the following transition probability

$$P_y(y, t\,|\,y_0, 0) = [(1-\Psi_y^2(t))\,\pi\alpha]^{-\frac{1}{2}} \times \exp[-(y-y_0\,\Psi_y(t))^2/(\alpha(1-\Psi_y^2(t))] \quad (1)$$

where

$$\Psi_y(t) = \langle y(0)\,y(t)\rangle/\langle y(0)\,y(0)\rangle \quad (2)$$

and the symbol $\langle\ldots\rangle$ denotes stochastic averaging [5] Equation (2) can be obtained without any recourse to Markhovian assumptions. Gaussianicity, in fact, is the only physical property required to obtain the transition probability of (1).

It is interesting to notice that (1) is the kind of equation which allowed Adelman [6], Fox [7] and Davies and Evans [8] to build up their generalised Fokker-Planck equations.

However, in the recent literature one can find several stimuli to reject the Gaussian assumption. Fox [5, 9] shows that critical fluctuations are not Gaussian. In his recent work on this subject he found an equilibrium distribution which is the exponential of a quartic form. It is evident that his result, when related to a linear Langevin equation, should involve stochastic forces of non-Gaussian nature.

Though this problem is fairly general in that it involves, for instance, phenomena such as the non-

* Present address: Institute of Molecular Biophysics, State University of Florida, Tallahassee, Florida, USA
** Present address: Department of Chemistry, University College of Wales, Aberystwyth, Wales SY23 1NE, U.K.

0340-224X/81/0041/0165/$02.40

Boltzmann fluorescence distribution observed recently by Roodhart and Wegdam [10] in this work we shall focus our attention on processes described by the generalised Langevin equation

$$\frac{d}{dt}\mathrm{A}(t)=i\Omega_0\,\mathrm{A}(t)-\int_0^t \Phi(t,\tau)\,\mathrm{A}(\tau)+\mathrm{f}(t). \tag{3}$$

In Sect. II the results of a computer simulation experiment are described. They clearly show that the relaxation dynamics of some triatomic liquid molecules requires the rejection of the Gaussian assumption concerning $\mathrm{f}(t)$ of (3). Correlation function such as $\langle \mathbf{V}^{2n}(0)\,\mathbf{V}^{2n}(t)\rangle$, in fact, are found attaining their equilibrium well below the Gaussian limit.
The usual treatment of (3) [6–8] has to be modified. Due to the difficulties of dealing with non-Markhovian relaxation processes a new approach is attempted in Section IIIa and a general form for non-Gaussian, non-Markhovian Fokker-Planck equations is proposed.
Then, in Sect. IIIb, this equation is specialized to describe the translational diffusion process of one component of the velocity of the molecules.
Finally in Section IV the monodimensional diffusion equation is solved and the results are related to the three dimensional case by using the fact that the space is isotropic and that the three components are not statistically correlated. Various degrees of non gaussianicity are inspected and the results show themselves to be in qualitative agreement with the former ones obtained with the molecular simulation.

## II. Non-Gaussianicity in Liquids

When the stochastic variable $y$ is the velocity $\mathbf{V}$ of a molecule with mass $M$, the parameter $\alpha$ appearing in (1) may be written as

$$\alpha=2KT/M,$$

where $K$ and $T$ denote the Boltzmann constant and the temperature, respectively. In such a case (1) becomes (250) of [4]. Berne and Harp [4] by exploiting this equation, provided the following expressions in three dimensions:

$$\varepsilon_{2G}(t)=\langle \mathbf{V}^2(0)\,\mathbf{V}^2(t)\rangle/\langle \mathbf{V}^4(0)\rangle=\tfrac{3}{5}\,[1+\Psi_v^2(t)], \tag{4}$$

$$\varepsilon_{4G}(t)=\langle \mathbf{V}^4(0)\,\mathbf{V}^4(t)\rangle/\langle \mathbf{V}^8(0)\rangle$$
$$=[\tfrac{225}{945}+\tfrac{600}{945}\,\Psi_v^2(t)+\tfrac{120}{945}\,\Psi_v^4(t)]. \tag{5}$$

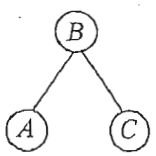
The meaning of these formulae is that higher-order correlation functions can be expressed in terms of the usual correlation function $\Psi_v(t)$, provided that the relaxation phenomenon is assumed to be Gaussian. In this case, however, $\varepsilon_{2G}(t)$ should reach 3/5 and $\varepsilon_{4G}(t)$ go to 225/945.
The results provided by our computer simulation show that such is not the case.
Evidence for non-Gaussian behaviour in molecular liquids has previously been presented by Rahman [11] in his classical simulation of argon and by Berne and Harp [4] who used a modified Stockmayer potential to simulate carbon monoxide, based on a Lennard-Jones form for the dispersive and repulsive form. In this section we report some new molecular dynamics simulations which strongly suggest that polyatomic asymmetric tops behave dynamically in a non-Gaussian manner. The evidence is presented in two ways. Firstly we simulate the following functions; which vanish in the Gaussian limit:

$$a_n=\langle \mathbf{X}^{2n}\rangle/(C_n\langle \mathbf{X}^2\rangle^n)-1;\quad n=1,2,3,4.$$

where $\langle\ldots\rangle$ means an average at each time step over the number of molecules used (108). We have:

$$C_n=1.3.5\ldots(2n+1)/3^n.$$

Here $\mathbf{X}$ is a molecular vector such as the linear centre of mass velocity ($\mathbf{V}$), angular momentum ($\mathbf{L}$), atomic coordinates ($\mathbf{r}$) or unit vectors ($\mathbf{I}_{A,B,C}$) along the principal inertia axes ($I_A, I_B, I_C$).
Secondly we simulated the moment auto-correlation functions $\langle \mathbf{X}^{2n}(t)\,\mathbf{X}^{2n}(0)\rangle/\langle \mathbf{X}^{2n}(0)\,\mathbf{X}^{2n}(0)\rangle$ whose Gaussian limits can be calculated analytically.
The algorithm used is a $3\times3$ atom-atom Lennard-Jones potential and a two-step predictor corrector method developed by Singer and Renaud [12]. The equation of motion for 108 triatomics of $C_{2v}$ symmetry were solved using periodic boundary conditions and the resulting data stored on 9 track magnetic tape of the CDC 7600 computer of U.M.R.C.C. The data were subsequently analysed in twenty minute segments of real time. The molecule used may be described as follows:




with $AB=BC=10^{-10}$ m, $m_A=2.5\times10^{-25}$ kgm, ${}^{L}ABC=60°$, $m_B=m_A=m_C$, with Lennard-Jones parameters $\sigma=3.0\times10^{-10}$ m, $\varepsilon/k=173.5$ K. One time step $=10^{-14}$ s $=0.01$ ps.
The temperature of the sample was set at 220 K (or 100 K), the molar volume being $10^{-4}$ m$^3$. The functions $a_N$ were calculated over a time span of 3,000 time steps, at each step averages being taken over the 108 molecules. An initial 3,000 time steps were run

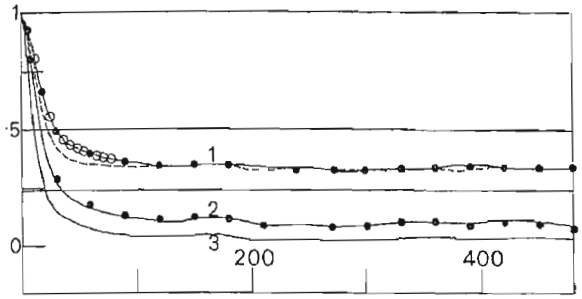



Fig. 1. Moment autocorrelation functions of velocity from a molecular dynamics simulation (see text), 220 K.
(1) ——— $\langle \mathbf{V}^2(t)\,\mathbf{V}^2(0)\rangle\,\langle \mathbf{V}^2(0)\,\mathbf{V}^2(0)\rangle$ 3,000 time steps
• • $\langle \mathbf{V}^2(t)\,\mathbf{V}^2(0)\rangle\,\langle \mathbf{V}^2(0)\,\mathbf{V}^2(0)\rangle$ 1,500 time steps
---- $\langle \mathbf{V}_x^2(t)\,\mathbf{V}_x^2(0)\rangle/\langle \mathbf{V}_x^2(0)\,\mathbf{V}_x^2(0)\rangle$ the monodimensional case, 3,000 time steps. $3-D$ Gaussian level = 0.6, $1-D$ level = 0.333.
(2) ——— $\langle \mathbf{V}^4(t)\,\mathbf{V}^4(0)\rangle/\langle \mathbf{V}^4(0)\,\mathbf{V}^4(0)\rangle$ 3,000 time steps
• • 1,500 time steps
(3) ——— $\langle \mathbf{V}^6(t)\,\mathbf{V}^6(0)\rangle/\langle \mathbf{V}^6(0)\,\mathbf{V}^6(0)\rangle$
Ordinate: $C(t)$; Abscissa: time steps

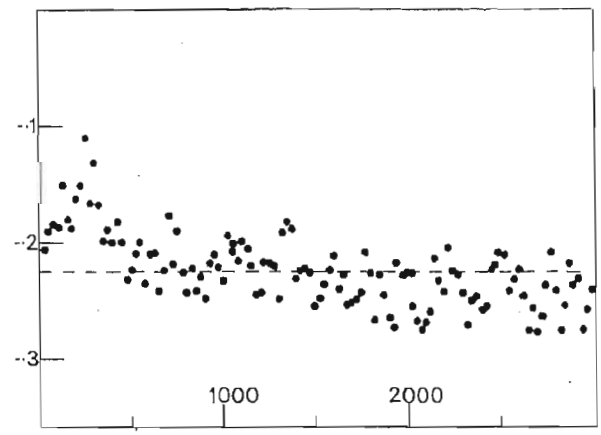



Fig. 2. $a_2$ function for $\mathbf{l}_c$, illustrating a drift. --- Mean level. Ordinate: $C(t)$; Abscissa: time steps

and the dynamical data at the end of this run used to restart a further simulation over a further 3,000 step time-span.

The autocorrelation functions were calculated using a running time average over a 3,000 time-step span, and checked using average over a 3,000 time-step span, and checked using a 1500 time-step span for consistency and statistical noise level. Some of these checks are illustrated in Figs. 1 to 5. Simulations were carried out for the following **X**:

*(i)* $\mathbf{l}_A$, a unit vector along the least principal moment of inertia axis.

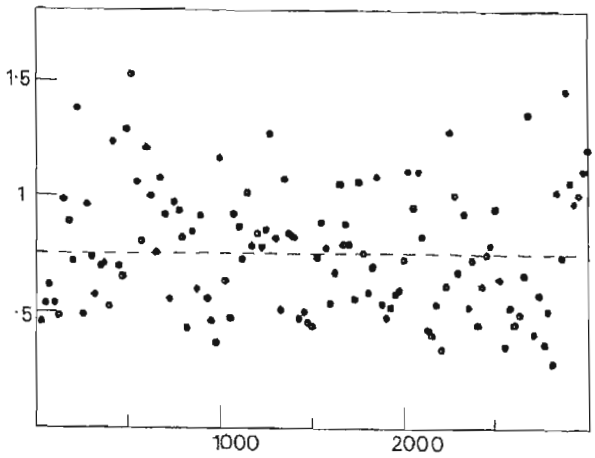



Fig. 3. As for Fig. 2, velocity in $3-D$, V

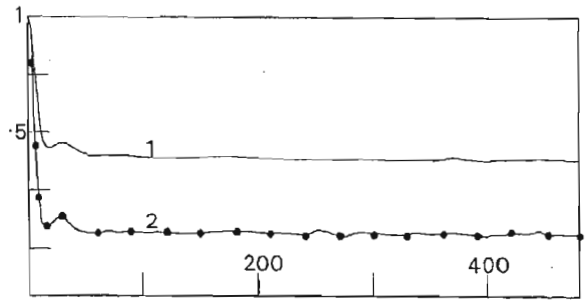



Fig. 4.
(1) $\langle \mathbf{T}_q^2(t)\,\mathbf{T}_q^2(0)\rangle/\langle \mathbf{T}_q^2(0)\,\mathbf{T}_q^2(0)\rangle$
(2) ——— $\langle \mathbf{T}_q^4(t)\,\mathbf{T}_q^4(0)\rangle/\langle \mathbf{T}_q^4(0)\,\mathbf{T}_q^4(0)\rangle$ 3,000 time steps
• • 1,500 time steps
Ordinate: $C(t)$; Abscissa: time steps

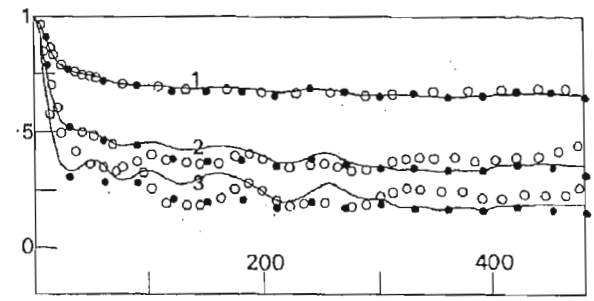



Fig. 5.
(1) $\langle \mathbf{V}^2(t)\,\mathbf{L}^2(0)\rangle/\langle \mathbf{V}^2(0)\,\mathbf{V}^2(0)\rangle$ 3,000 time steps
• • 1,500 time steps
∘ ∘ $\langle \mathbf{L}^2(t)\,\mathbf{V}^2(0)\rangle/\langle \mathbf{L}^2(0)\,\mathbf{L}^2(0)\rangle$ 3,000 time steps (consistency check).
(2) The same for the fourth moment functions.
(3) Sixth moment functions.
Ordinate: $C(t)$; Abscissa: time steps

Table 1. $a_n$ For Various X: Molecular Dynamics Simulation[a] at 220 K

| X | $a_2$ | $a_3$ | $a_4$ |
|---|---|---|---|
| $l_A$ | −0.25 ±0.024 | −0.55 ±0.032 | −0.78±0.026 |
| $l_C$ | −0.225±0.03 | −0.515±0.045 | −0.74±0.039 |
| $r_A$ | −0.29 ±0.016 | −0.60 ±0.022 | −0.81±0.017 |
| $r_B$ | −0.285±0.016 | −0.59 ±0.022 | −0.81±0.018 |
| L | 0.26 ±0.15 | 0.83 ±0.72 | 1.96±2.41 |
| V | 0.75 ±0.27 | 2.55 ±1.50 | 6.54±6.57 |
| $T_q$ | 0.56 ±0.32 | 2.19 ±2.21 | 6.75±11.70 |

[a] ±(standard deviation)

*(ii)* $l_B$, and $l_C$.
*(iii)* $r_A$, $r_B$ and $r_C$, the atom position vectors.
*(iv)* L, the resultant molecular angular momentum, defined with respect to the laboratory frame.
*(v)* The centre of mass linear velocity, V.
*(vi)* The resultant molecular torque, $T_q$, in the laboratory frame of reference.

In Table 1 we summarise the mean levels of $a_n$, i.e., the mean of the $a_n$ calculated at each of 3,000 time steps (30 ps) of the simulation run.

Some of the results of the simulation are illustrated in Figs. 1 to 5. There are significant deviations from Gaussian statistics for each vector **X**. As far as the authors are aware this is the first attempt to compute $a_n$ for vectors other than the centre of mass or atomic mean square displacement. The $a_2$ functions for $l_A$, $l_B$, $r_A$, $r_B$ and $r_C$ are clearly non zero and negative, and constantly so within the limitations of the statistical noise. The $a_2$ function for $l_C$ illustrates what appears to be a drift as the simulation proceeds. However we have contented ourselves with a calculation of the mean level.

The $a_4$ functions for velocity (V) and torque ($T_q$) (Figs. 3, 4) fluctuate much more about a mean value (see table) significantly, this time, above the zero level of Gaussian statistics.

The functions most accessible to a reasonably tractable analytical analysis are

$$\langle V^{2n}(t)\,V^{2n}(0)\rangle/\langle V^{2n}(0)\,V^{2n}(0)\rangle,$$

the moment autocorrelation functions of the three dimensional linear velocity (Fig. 1). In three dimensions these are interestingly different from the same type of functions calculated by Berne and Harp [4] for CO and Evans et al. [13, 14] for $N_2$ in that they reach a steady long-time limit at a value much lower than that expected from a Gaussian analysis of the statistics (0.6). This is illustrated in Fig. 1. The 1,500 time-step run for the fourth moment (Fig. 1) agrees satisfactorily with the 3,000 time step run, so that it is very unlikely that the deviation from Gaussianicity is due to statistical noise. Figure 1, however, shows that the component function $(1-D)\langle V_x^2(t)V_x^2(0)\rangle$ is more closely Gaussian (see below). Turning our attention to the other moment functions for which Gaussian limits are available analytically at present, the angular momentum autocorrelation functions, our simulations (Fig. 6) show up positive and negative deviations, unlike the consistently positive ones discussed for CO by Berne and Harp and for $N_2$ by Evans et al. This work will be reported in more detail elsewhere. The component autocorrelation function $\langle L_y^2(t)L_y^2(0)\rangle/\langle L_y^2(0)\,L_y^2(0)\rangle$ is illustrated in Fig. 6, the Gaussian limit in 3-$D$ being 0.5 in this case (appendix).

The torque-moment autocorrelation functions (Fig. 4) reach satisfactorily smooth long-time plateau values as do $\langle l_c^{2n}(t)l_c^{2n}(0)\rangle/\langle I_c^{2n}(0)l_c^{2n}(0)\rangle$ (Fig. 7). The statistical noise level is illustrated for $\langle T_q^4(t)\,T_q^4(0)\rangle/\langle T_q^4(0)\,T_q^4(0)\rangle$ in Fig. 4. Finally, in Fig. 5, we illustrate the mixed autocorrelation functions

$$\langle L^{2n}(t)\,V^{2n}(0)\rangle/\langle L^{2n}(0)\,V^{2n}(0)\rangle$$

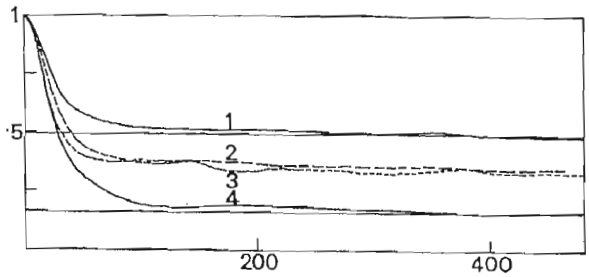



Fig. 6. Molecular dynamics simulation at 100 K of the angular momentum moment a.c.f.s.
(1) $\langle L^2(t)\,L^2(0)\rangle/\langle L^2(0)\,L^2(0)\rangle$ $(3-D)$
(2) $\langle L_x^2(t)L_x^2(0)\rangle/\langle L_x^2(0)L_x^2(0)\rangle$ $(1-D)$ 2,000 time steps
(3) $\langle L_y^2(t)L_y^2(0)\rangle/\langle L_y(0)L_y^2(0)\rangle$ $(1-D)$
(4) $\langle L^4(t)L^4(0)\rangle/\langle L^4(0)L^4(0)\rangle$ $(3-D)$
Ordinate: $C(t)$; Abscissa: time steps

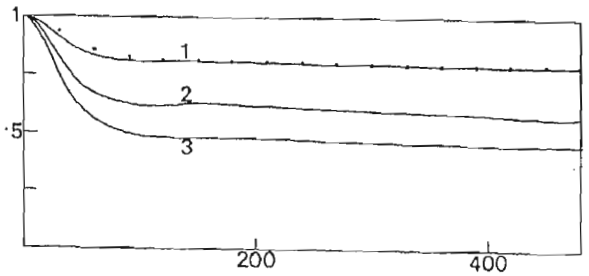



Fig. 7. Molecular dynamics simulation at 220 K of the orientational moment a.c.f.s, vector $l_c$
(1) $\langle l_C^2(t)l_C^2(0)\rangle/\langle l_C^2(0)l_C^2(0)\rangle$ 3,000 time steps,
• • 1,500 time steps
(2) fourth moment; (3) sixth moment.
Ordinate: $C(t)$; Abscissa: time steps

for 1,500 and 3,000 time-step averaging sequences. The noise increases the higher the moments used, but for $\langle L^{2n}(t)\mathbf{V}^{2n}(0)\rangle/\langle L^{2n}(0)\mathbf{V}^{2n}(0)\rangle$ the result is satisfactory. Unfortunately no analytical Gaussian limits are known for these functions at present, but we hope to calculate them shortly. This requires a theory of asymmetric top roto-translation.

The most interesting implication of the simulation results is that the stochastic force appearing in any version of the Langevin equation is also non-Gaussian. This point is dealt with analytically in Sect. 4, where we have reproduced the major features of the simulation results in the case of linear velocity, in $1-D$ and $3-D$.

It will be interesting in future to increase the number of particles in the simulation to evaluate the effect on $a_n$ and moment autocorrelation functions, if any, of periodic boundary conditions.

## III. A Theoretical Approach to the Study of Relaxation Phenomena Involving Both Non-Gaussian and Non-Markhovian Behaviour

The Mori approach [15, 16] allows the replacement of the Liouville equation

$$i\frac{d}{dt}\rho(t)=L\rho(t) \tag{6}$$

with the generalised Langevin equation given by (3) where

$$i\Omega_0=(PiL\mathbf{A},\mathbf{A}^+)(\mathbf{A},\mathbf{A}^+)^{-1} \tag{7}$$

$$\Phi(t,\tau)=(PiL\exp[(1-P)iL(t-\tau)]\cdot(1-P)iL\mathbf{A},\mathbf{A}^+)(\mathbf{A},\mathbf{A}^+)^{-1}$$

$$=-(\mathbf{f}(t),\mathbf{f}(\tau)^+)(\mathbf{A},\mathbf{A}^+)^{-1} \tag{8}$$

and

$$\mathbf{f}(t)=\exp[(1-P)iLt](1-P)iL\mathbf{A}. \tag{9}$$

The previous expressions are based on the projection operator $P$ defined by

$$P\mathbf{G}=(\mathbf{G},\mathbf{A}^+)(\mathbf{A},\mathbf{A}^+)^{-1}\mathbf{A}. \tag{10}$$

A suitable scalar product of the two variables $\mathbf{F}$ and $\mathbf{G}$ must be defined. We denote such a scalar product with the symbols $(\mathbf{F},\mathbf{G}^+)$.

Adelman [6], Fox [7], Davies and Evans [8] have derived the Fokker-Planck equation associated with (3) in the case where the random force $\mathbf{f}(t)$ is assumed to be Gaussian. The result of the previous section indicates that such an assumption is not satisfied in the context of molecular dynamics. On the other hand, the Kramers-Moyal expansion [17, 18] affords some information on the general structure of the Fokker-Planck equation provided that the stochastic process be Markhovian. This equation, in principle, may be valid even in the case of non-Gaussian processes. The main idea of this paper is therefore that of replacing the generalised Langevin equation, (3), with a multi-dimensional Markhovian chain of equations. By using the suggestions provided by the Kramers-Moyal exposition it is then possible to obtain the corresponding Fokker-Planck equation without using Gaussian distributions.

### *III.a. Replacement of the Mori Equation with a Markhovian Chain of Variables*

The progression outlined above may be accomplished by applying the results obtained by Mori in Ref. [19]. Mori showed that it is possible to build up a chain of variables $\mathbf{f}_j$, $j=1,\ldots,N$, defined by the following equations.

$$\mathbf{f}_0=\mathbf{A}, \tag{11}$$

$$\mathbf{f}_j=iL_j\mathbf{f}_{j-1}, \tag{12}$$

$$L_j=(1-P_{j-1})L_{j-1}, \tag{13}$$

$$L_0=L, \tag{14}$$

$$P_j\mathbf{G}=(\mathbf{G},f_j^+)(\mathbf{f}_j,\mathbf{f}_j^+)^{-1}\mathbf{f}_j. \tag{15}$$

Then it is possible to write the Laplace transform of $\Phi(t)$ in the following way.

$$\hat{\Phi}(z)=\cfrac{\mathbf{1}}{z\mathbf{1}-i\Omega_0+\cfrac{\mathbf{1}}{z\mathbf{1}-i\Omega_1+\cfrac{\mathbf{1}}{z\mathbf{1}-i\Omega_2+\cdots+\cfrac{\mathbf{1}}{z\mathbf{1}-i\Omega_N+\hat{\beta}_N(z)}\Delta_{N-1}^2}\Delta_2^2}\Delta_1^2} \tag{16}$$

where

$$i\Omega_{j-1}=(iL\mathbf{f}_j,\mathbf{f}_j^+)(\mathbf{f}_j,\mathbf{f}_j^+)^{-1}, \tag{17}$$

$$\Delta_{j-1}^2=-(iL\mathbf{f}_{j+1},\mathbf{f}_j^+)(\mathbf{f}_j,\mathbf{f}_j^+)^{-1}. \tag{18}$$

Mori suggests that the chain of variables may be truncated at the $N$th order by assuming that $\beta_N(z)$ may be replaced by the constant matrix $\gamma_N$.

We shall use this result in order to demonstrate that (3) may be replaced by the following one

$$\frac{d}{dt}\mathbf{v}(t)=\Lambda\mathbf{v}(t)-\Gamma\mathbf{v}(t)+\mathbf{F}(t) \tag{19}$$

where

$$\mathbf{v}(t)=\begin{pmatrix}\mathbf{v}_1(t)\\ \mathbf{v}_2(t)\\ \vdots\\ \mathbf{v}_N(t)\end{pmatrix}$$

and

$$\mathbf{F}(t)=\begin{pmatrix}\mathbf{0}\\ \mathbf{0}\\ \vdots\\ \Gamma_N(t)\end{pmatrix} \tag{20}$$

are $n\times N$ dimensional column vectors. The friction grand-matrix $\Gamma$ is a $n\times N$ dimensional square matrix endowed with the following form:

$$\Gamma=\begin{pmatrix}0\ 0\ \dots\ \dots\ 0\\ 0\ \dots\quad \cdot\ \cdot\\ \vdots\ \cdot\ \cdot\quad \cdot\ \cdot\\ 0\ \dots\quad 0\ \gamma_N\end{pmatrix}. \tag{21}$$

Equations (4) to (6) describe a $n\times N$ dimensional Markhov process in that the second fluctuation dissipation theorem may be expressed through the usual form:

$$\langle\mathbf{F}(t)\rangle=\mathbf{0}$$
$$\langle\mathbf{F}(t)\,\mathbf{F}(s)\rangle=[\Gamma\langle\mathbf{v}(0)\,\mathbf{v}^+(0)\rangle+\langle\mathbf{v}(0)\,\mathbf{v}^+(0)\rangle\,\Gamma^+]\delta(t-s) \tag{22}$$

Note that the previous equation implies only Markhovianicity in that we have not made any assumption about higher-order moments. No Gaussian assumption is made.

We can now define the first component of $\mathbf{v}$ as being the component of interest. Each component $\mathbf{v}_j$ can be obtained by applying to $\mathbf{v}$ the projection operator $\mathbf{P}_j^M$ defined in the following matricial form:

$$(\mathbf{P}_j^M)_{km}=\delta_{jk}\,\delta_{jm}\mathrm{I};\qquad j,k,m=1,2,\dots,N. \tag{23}$$

The component of interest may be obtained by applying to $\mathbf{v}$ the projection operator $\mathbf{P}_1^M$. If this is applied to (19) following ref. (20) we obtain:

$$(\mathbf{P}^M=\mathbf{P}_1^M,\ \mathbf{P}^M\mathbf{F}=0,\ \mathbf{P}^M\Gamma=\mathbf{0},\ \mathbf{Q}^M=1-\mathbf{P}^M)$$
$$\frac{d}{dt}\mathbf{P}^M\mathbf{v}(t)$$
$$=\mathbf{P}^M\Lambda\mathbf{P}^M\mathbf{v}(t)+\mathbf{P}^M\Lambda\exp\mathbf{Q}^M(\Lambda-\Gamma)t\,\mathbf{Q}^M\mathbf{v}(\mathbf{0})$$
$$+\int_0^t\mathbf{P}^M\Lambda\exp\mathbf{Q}^M(\Lambda-\Gamma)(t-s)\,\mathbf{Q}^M(\Lambda-\Gamma)\,\mathbf{P}^M\mathbf{v}(s)\,ds$$
$$+\int_0^t\mathbf{P}^M\Lambda\exp\mathbf{Q}^M(\Lambda-\Gamma)(t-s)\,\mathbf{Q}^M\mathbf{F}(s)\,ds. \tag{24}$$

We note that (24) is similar to (3) provided that the stochastic force includes both the second and the third term on the r.h.s. of (24). Since in (3) $\Phi$ and f are related through the second fluctuation-dissipation theorem (24) may replace (3) provided that the two respective memory 'kernels' are shown to be equal. There is no contradiction then in assuming that the stochastic force of (24) is equal to that of (3).

We show now that the 'memory kernels' are equal provided that:

$$(\Lambda)_{jk}=(iL\mathbf{f}_j,\mathbf{f}_k^+)(\mathbf{f}_k,\mathbf{f}_k^+)^{-1}$$
$$(\Gamma)_{jk}=(\hat{\gamma}\mathbf{f}_j,\mathbf{f}_k^+)(\mathbf{f}_k\,\mathbf{f}_k^+)^{-1}. \tag{25}$$

The memory kernel of (3), by exploiting the fact that the set of variables $\mathbf{f}_j$ is assumed to be complete can be written as:

$$\phi(t,s)=((iL-\hat{\gamma})\,\mathbf{A},\mathbf{f}_k^+)(\mathbf{f}_k,\mathbf{f}_k^+)^{-1}$$
$$\cdot(\exp[(1-\mathbf{P})(iL-\hat{\gamma})(t-s)](1-\mathbf{P})\,\mathbf{f}_k,\mathbf{f}_j^+)(\mathbf{f}_j,\mathbf{f}_j^+)^{-1}$$
$$\cdot((iL-\hat{\gamma})\,\mathbf{f}_j,\mathbf{A}^+)(\mathbf{A},\mathbf{A}^+)^{-1} \tag{26}$$

the operator $\hat{\gamma}$ resums the contribution of the variables $\mathbf{f}_l$, $l>N$. In (26) and in the following summation on repeated indices is understood.

By expanding the exponential between the square brackets and applying (25) we obtain:

$$(\exp[(1-P)(iL-\hat{\gamma})(t-s)](1-P)\,\mathbf{f}_k,\mathbf{f}_j^+)(\mathbf{f}_j,\mathbf{f}_j^+)^{-1}$$
$$=\sum_{r=0}^{\infty}\frac{(t-s)^r}{r!}((1-P)\,\mathbf{f}_k,\mathbf{f}_{m_1})$$
$$\cdot(\mathbf{f}_{m_1},\mathbf{f}_{m_1}^+)^{-1}((iL-\hat{\gamma})\,\mathbf{f}_{m_1},\mathbf{f}_{l_1}^+)(\mathbf{f}_{l_1},\mathbf{f}_{l_1}^+)^{-1}$$
$$\cdot((1-P)\,\mathbf{f}_{l_1},\mathbf{f}_{m_2}^+)(\mathbf{f}_{m_2},\mathbf{f}_{m_2}^+)^{-1}\dots$$
$$\cdot((iL-\hat{\gamma})\,\mathbf{f}_{m_r},\mathbf{f}_{l_r}^+)(\mathbf{f}_{l_r},\mathbf{f}_{l_r}^+)^{-1}$$
$$\cdot((1-\mathbf{P})\,\mathbf{f}_{l_r},\mathbf{f}_j^+)(\mathbf{f}_j,\mathbf{f}_j^+)^{-1}=\sum_{r=0}^{\infty}\frac{(t-s)^r}{r!}$$
$$\cdot(1-\mathbf{P}^M)_{km_1}(\Lambda-\Gamma)_{m_1l_1}\dots$$
$$\cdot(\Lambda-\Gamma)_{m_rl_r}(\mathbf{1}-\mathbf{P}^M)_{l_rj}$$
$$=\exp\{(1-\mathbf{P}^M)(\Lambda-\Gamma)(t-s)\}\,(\mathbf{1}-\mathbf{P}^M) \tag{27}$$

The matrix $\Gamma$ has to be inserted in order to take into account the suggestion by Mori of replacing $\beta_N(z)$ with a constant matrix $\gamma_N$. The memory kernel of (26) can then be written in the same way as the 'memory kernel' of (24).

After showing that we can focus our attention on the Markhovian Langevin equation (19) we can easily find the associated equation using the van Kampen lemma [21]:

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial\mathbf{v}_i}(\Lambda_{ij}-\Gamma_{ij})\,\mathbf{v}_jP+\Gamma_wP=\Gamma_DP \tag{28}$$

where $\Gamma_w$ is the Markhovian-diffusion operator concerning the last variable of the Markhovian chain, $\mathbf{v}_N$.

Fox and Uhlenbeck [22] provided the method of constructing the Fokker-Planck equation even for a multidimensional variable such as $\mathbf{v}_N$. However they exploited the Gaussian properties of the stochastic force. In the next section we shall try to build up the operator $\Gamma_w$ in the non-Gaussian case.

### *III.b. The Markhovian Fokker-Planck Equation in the Non-Gaussian Case*

We would like to recall that (28) has been obtained without any Gaussian assumption. However, (28) can be applied only when a suitable analytical expression for the diffusion operator $\Gamma_w$ is available.
In this section we shall give some useful suggestions about a practicable approach to build up the explicit expression for $\Gamma_w$.
For the sake of simplicity we shall assume that the last variable of the chain is a monodimensional variable $w$, which satisfies the Markhovian Langevin equation

$$\frac{d}{dt}w=-\beta w+f(t). \tag{29}$$

It is well known [17, 18] that the Markhovian Fokker-Planck equation is endowed with the general form

$$\frac{\partial}{\partial t}P(w,t|w_0,0)=\sum_{n=1}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n[\mu_w^n P(w,t|w_0,0)] \tag{30}$$

which is fully equivalent to the master equation

$$\frac{\partial}{\partial t}P(w,t|w_0,0)=\int dw^1\,P(w^1,t|w_0,0)$$
$$\cdot W(w|w^1)-P(w,t|w_0,0)\,W(w^1|w) \tag{31}$$

provided that

$$\mu_w^n=\int dw^1(w^1-w)^n\,W(w|w^1). \tag{32}$$

Note that (30) when limited to the first two terms is the usual Fokker-Planck equation. By using a mathematical model for the transition operator $W$ it is possible to evaluate any moment $\mu_w^n$. Unfortunately, the model used in [23] for example is of a Gaussian kind.
As a consequence we suggest a correction to the usual Fokker-Planck equation

$$\frac{\partial}{\partial t}P=\Gamma_0 P=\left[-\frac{\partial}{\partial w}\mu_w^1(w)+\tfrac{1}{2}\frac{\partial^2}{\partial w^2}\mu_w^2(w)\right]P(w,t|w_0 0) \tag{33}$$

whose general form is

$$\Gamma_1 P=\sum_{n=3}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial w}\right)^n[\mu_w^n P(w,t|w_0,0)] \tag{34}$$

by truncating the summation of (34) and giving $\mu^n(w)$ simple analytical expressions.
An alternative approach to build up $\Gamma_w$ is the one of exploiting the moments of the stochastic force $f(t)$, since the $\mu_w^n(w)$ can be evaluated through the stochastic average $\langle\ldots\rangle$ as follows.

$$\mu_w^n(w)=\langle\Delta w^n\rangle/\Delta t. \tag{35}$$

If we assume that the moments of the stochastic force are products of functions and the first moments of the stochastic force vanish, any moment $\mu_w^n(w)$ except the first one, which is

$$\mu_w^1(w)=-\beta w, \tag{36}$$

depends on the stochastic force through the general formula

$$\mu_w^n(w)=\lim_{\Delta t\to 0}\int_t^{t+\Delta t}dt_1\int_t^{t+\Delta t}dt_2\ldots$$
$$\cdot\int_t^{t+\Delta t}dt_n\langle f(t_1)f(t_2)\ldots f(t_n)\rangle/\Delta t. \tag{37}$$

It is easy then to show that in the Gaussian case

$$\mu_w^n(w)=0\qquad n>3. \tag{38}$$

In order to avoid using a Gaussian distribution, we can reasonably assume that:

$$(\Delta^2=\langle w^2\rangle)\quad\langle f(t_1)f(t_2)\ldots f(t_n)\rangle$$
$$=n!\,\varepsilon_n\Delta^n\beta\,\delta(t_1-t_2)\,\delta(t_2-t_3)\ldots\delta(t_{n-1}-t_n)$$
$$+(\text{Gaussian contribution}).$$

As a consequence we have ($\varepsilon_2=1$)

$$\Gamma_0=\beta\left(\frac{\partial}{\partial w}w+\Delta^2\frac{\partial^2}{\partial w^2}\right), \tag{39}$$

$$\Gamma_1=\beta\left\{\varepsilon_3\Delta^3\frac{\partial^3}{\partial w^3}+\varepsilon_4\Delta^4\frac{\partial^4}{\partial w^4}+\ldots\right\}. \tag{40}$$

The parameters $\varepsilon_3,\varepsilon_4$ have to be taken as being small perturbation parameters in such a way as to slightly modify the result provided by $\Gamma_0$. However, it is evident that Gaussianicity is destroyed by the presence of $\Gamma_1$.
A point which is not yet well understood is the possibility of obtaining non-vanishing higher order moments $\mu_w^n(w)$ through the Gaussian model of [23]. This issue will be clarified in future work. We limit ourselves here to recall that a Gaussian distribution is no longer a solution of the Fokker-Planck equation when a few terms of (34) are taken into account.
The 'non-Markhovian' non-Gaussian Fokker-Planck equation reads (when the Mori truncation is performed at second-order)

$$\frac{\partial}{\partial t}P(v,w,t|v_0,w_0,0)$$
$$=\left\{\omega\left(\frac{\partial}{\partial v}w-\frac{\partial}{\partial w}v\right)+\beta\left[\frac{\partial}{\partial w}w+\Delta^2\frac{\partial^2}{\partial w^2}\right.\right.$$
$$\left.\left.+\varepsilon_3\Delta^3\frac{\partial^3}{\partial w^3}\varepsilon_4\Delta^4\frac{\partial^4}{\partial w^4}+\ldots\right]\right\}P(v,w,t|v_0,w_0,0)=\Gamma_d P. \quad (41)$$

Formally, when the Wigner-Moyal diffusion operator is replaced in (28) we obtain a non-Gaussian, non-Markhovian extension of the Fokker-Planck equation.

## IV. Solution

To solve the generalised Fokker-Planck equation we expand the diffusion operator $\Gamma_d$ of (41) over a convenient basis set provided by the direct products of Hermite polynomials [24].

$$F_{n,m}(v,w)=C(n,m)\,He_n(v)\,He_m(w)\exp\left[-\frac{v^2+w^2}{2\Delta^2}\right] \quad (42)$$

where $C(n,m)$ is the opportune normalizing factor defined by the following scalar product.

$$\frac{1}{2\pi}\int F_{nm}(v,w)\,F_{n'm'}(v,w)\exp\left[\frac{v^2+w^2}{2\Delta^2}\right]dv\,dw=\delta_{nn'}\,\delta_{mm'}. \quad (43)$$

So we have:

$$C(n,m)=(n!\,m!)^{1/2}. \quad (44)$$

Using recursion formulae for the Hermite polynomials [4] we reduce the problem to that of solving a matrix equation:

$$\dot{\mathbf{X}}=\mathbf{AX}$$

by diagonalising $A$. This is a matrix expression for the diffusion operator $\Gamma_d$ on the basis set (42) with the scalar product (43).

We limit ourselves to treating one component, $v_x$ of the centre of mass linear velocity vector $\mathbf{V}$ for storage reasons during computation. In the case of liquid phase (isotropic) diffusion the results for the three-dimensional $(3-D)$ case may be easily found as there is no correlation between two different vector components and all the spatial directions are equivalent. From now on we denote by $v_x$ any one component of the total vector. Clearly, in (4) and (5) we refer to the latter.

The Gaussian limits of the moment autocorrelation functions in one dimension (e.g., those for $v_x$) are different from those in $3-D$. Some analytical results for one dimensional diffusion are:

$$\langle v_x(t)\,v_x(0)\rangle=\chi(t), \quad (45)$$
$$\langle v_x^2(t)\,v_x^2(0)\rangle=\tfrac{1}{3}(1+2\chi^2(t)), \quad (46)$$
$$\langle v_x^3(t)\,v_x^3(0)\rangle=\tfrac{1}{15}(9\chi(t)+6\chi^3(t)), \quad (47)$$
$$\langle v_x^4(t)\,v_x^4(0)\rangle=\tfrac{1}{105}(9+72\chi^2(t)+24\chi^4(t)), \quad (48)$$
$$\langle v_x^6(t)\,v_x^6(0)\rangle=\tfrac{1}{693}(15+360\chi^2(t)+900\chi^4(t)+78\chi^6(t)) \quad (49)$$

while for the $a_n$ coefficients:

$$a_n=\langle v_x^{2n}\rangle/(\langle v_x^2\rangle^n\,C_n^{(1)})-1 \quad (50)$$

where

$$C_n^{(1)}=1.3\ldots(2n-1)=(2n-1)!! \quad (51)$$

For Gaussian statistics all $a_n=0$.

The evaluation of the moment autocorrelation function is made following Kubo's method [25] of solving the stochastic Liouville equation. With non-Gaussian statistics the diffusion process has a unique equilibrium state $P_0$, defined by:

$$\Gamma_d P_0(v_x,w_x)=0.$$

The Gaussian equilibrium state $P_0^{(G)}$ is well known:

$$P_0^{(G)}\propto\exp\left\{-\frac{v_x^2+w_x^2}{2\Delta^2}\right\}\propto F_{00}(v_x,w_x) \quad (52)$$

but when the Gaussian assumption is relaxed the equilibrium state $P_0$ becomes a linear super position of the function $F_{nm}(v_x,w_x)$. Once $P_0$ is known the calculation of the correlation of any function $f(v_x,w_x,t)$ may be made through the following formal expression, where in analogy to Dirac's notation we define the normalised zero bra $\langle 0|$ and ket $|0\rangle$ vectors which satisfy the equation $\Gamma_d|0\rangle=0=\langle 0|\Gamma_d$ and $\langle 0|0\rangle=1$. This means:

$$\langle f(v_x,w_x,t)f(v_x,w_x,0)\rangle$$
$$=\langle 0|f(v_x,w_x,0)\,e^{\Gamma_d t}f(v_x,w_x,0)|0\rangle \quad (53)$$

where we have used the fact that the temporal evolution is totally described by the time-translation operator:

$$\mathbf{U}(t)=e^{\Gamma_d t}.$$

Another advantage of this kind of approach is that we can evaluate three-time and higher order correlation functions. The diffusion process when handled this way is in fact Markhovian in nature [24] described by the exponential operator $\mathbf{U}(t)$ in accord with Doob's theorem. We have calculated explicitly the three-time correlation function:

$$\langle v_x(0)\,v_x(t)\,v_x(2t)\rangle=\langle 0|\,v_x\,e^{\Gamma_d t}\,v_x\,e^{\Gamma_d t}\,v_x|0\rangle$$

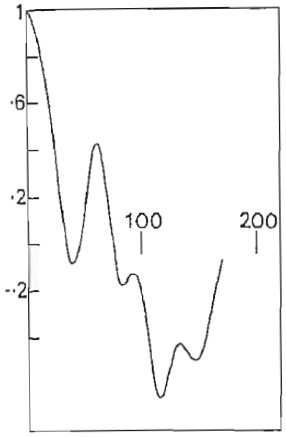



Fig. 8. Simulated three-time autocorrelation function of velocity at 100 K:

$\langle V_x(0)V_x(t)V_x(2t)\rangle/\langle V_x^3(0)\rangle$,

This normalisation is prossible because the denominator is slightly different from zero in the simulation.
Ordinate: $C(t)$; Abscissa: time steps

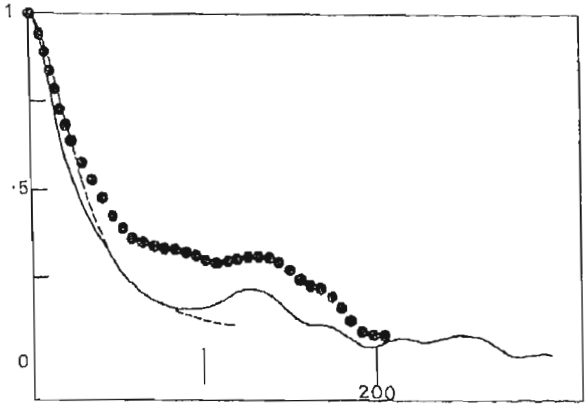



Fig. 9.
——— $\langle L_x(0)L_x(t)L_x(2t)\rangle/\langle L_x^3(0)\rangle$ (3,000 time steps $(=2t)$
• • 1,200 time steps
- - - - $\langle L(t)\cdot L(0)\rangle/\langle L(0)\cdot L(0)\rangle$ for comparison.
Ordinate: $C(t)$; Abscissa: time steps

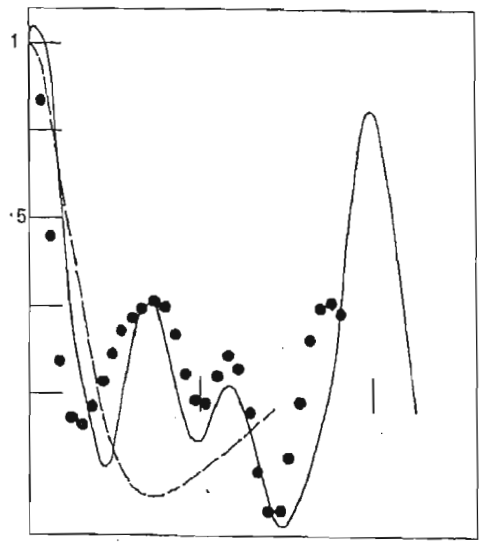



Fig. 10. As for Fig. (9), $T_{qx}$ component of the torque vector $T_q$

which is identically zero for all $t>0$ in a Gaussian process. We have also simulated this function and the results are shown in Fig. 8. The stability of such simulations is open to question. A test of such is illustrated in Figs. 9 and 10 for the angular momentum ($L_x$) three-time function and the torque ($T_x$) equivalent.

We perform our calculation by limiting ourselves to the first non-zero term in the expansion of $\Gamma_1$. We assume that this is the one related to the fourth derivative, i.e., we take $\varepsilon_4 \neq 0$ and $\varepsilon_3, \varepsilon_J = 0$, $J>3$. The parameters $\omega$ and $\gamma$ are derived by fitting the simulated velocity autocorrelation function. The best fit is the one with $\gamma = 9.25\times10^{12}\,s^{-1}$ and $\omega = 6.25\times10^{12}\,s^{-1}$. The numerical solution of the relevant matrix equation was performed on the University of Pisa IBM 360/370 and UMRCC CDC 7600 computers, using perturbation methodology.

Results for the coefficients $a_n$ are summarized in table II for several values of the parameter $\varepsilon_4$. Note that in three dimensions:

$$a_2^{(3d)} = \tfrac{3}{5}a_2^{(1d)}.$$

In Fig. 11 we illustrate the behaviour of the normalised autocorrelation functions $\langle v_x^{2n}(t)v_x^{2n}(0)\rangle/\langle v_x^{2n}(0)v_x^{2n}(0)\rangle$ as calculated from the generalised Fokker-Planck equation as functions of $\varepsilon_4$. The results are in qualitative agreement with the machine simulations of Sect. (II). The $a_n$ functions have the same sign and the limit as $t\to\infty$ of the kinetic energy a.c.f. $(1-D)$ is always below the Gaussian one. Due to the assumptions we made in Sect. III the equilibrium average $\langle v_x^2\rangle$ is unchanged by the non-Gaussian perturbation so we find that in three dimensions:

$$\lim_{t\to\infty}\frac{\langle \mathbf{V}^2(t)\mathbf{V}^2(0)\rangle}{\langle \mathbf{V}^2(0)\mathbf{V}^2(0)\rangle} = \left(\tfrac{5}{3}(1+a_2)\right)^{-1}$$

which implies that for positive $a_2$ the limit of the kinetic energy autocorrelation function is below the Gaussian one.

The analytical three-time autocorrelation function is shown in Fig. 12. It is interesting that this function is oscillatory, and can exceed the normalised value of unity at $t=0$. Its absolute magnitude is small compared with the two-time correlation function.

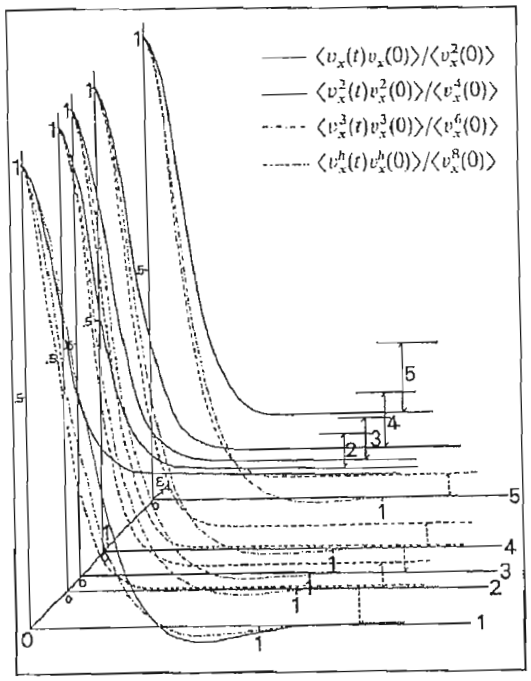



Fig. 11. Two time correlation functions, normalized at $t=0$. The different values of the non-Gaussian parameter $\varepsilon_4$ are: 1. $\varepsilon_4=0.0$. the Gaussian case; 2. $\varepsilon_4=0.4625$; 3. $\varepsilon_4=0.625$; 4. $\varepsilon_4=0.925$; 5. $\varepsilon_4=1.55$. The velocity autocorrelation function does not depend on the actual value $\varepsilon$. The time units are picoseconds. In the figure the differences with the Gaussian case of $\lim_{t\to\infty}\langle v_x^2(t)v_x^2(0)\rangle/\langle v_x^4(0)\rangle$ are explicitly shown by arrows: the dashed arrows, instead, show the $\lim_{t\to\infty}\langle v_x^4(t)v_x^4(0)\rangle$. It is evident that the $\infty$-levels are always below the Gaussian one. Abscissa: time/ps; Ordinate: $C(t)$

Finally we wish to note a relevant feature of our non-Gaussian calculation. The velocity correlation function does not depend on the non-Gaussianicity of the system. This is true also of the absolute value of the average kinetic energy $\frac{1}{2}m\langle v_x^2\rangle$ eq. which is related to the former through the second fluctuation-dissipation theorem (8). This is independent of any Gaussian assumption (Mori [19] and Zwanzig [26]). Non-Gaussianicity affects only the higher $n$-order correlations and averages.

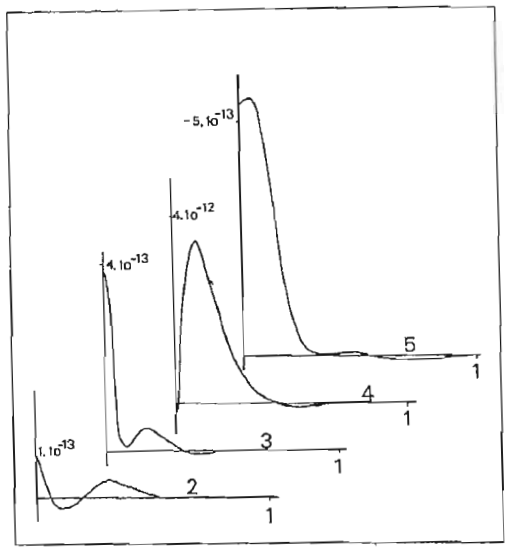



Fig. 12. Three-time correlation function $\langle v_x(0)v_x(t)v_x(2t)\rangle$. Time units are picoseconds, while the intensities are in units of $\Delta^3$. The values of $\varepsilon_4$ are the same as for Fig. 11. The Gaussian case is not plotted as it results in a correlation function which is zero, $\pm\sim10^{-30}$, for any time $t$. Abscissa: time/ps, Ordinate: $\langle v_x(0)v_x(t)v_x(2t)\rangle$

## IV. Concluding Remarks

Both experiments and computer simulations [4, 11] and the results exposed in the present paper, show that the gaussian assumption is not always applicable. The need, therefore, arises to develop a generalized diffusion equation to describe non gaussian features without disregarding the non Markhovian ones too. The proposed equation (41) leads to results which are in qualitative agreement with the computer simulation described in Sect. 2.

Equations (28) and (41) allow us also to exploit the well known Stochastic Liouville Equation (S.L.E.) theory [25, 27, 28] in such a way as to include processes which are both non gaussian and non Markhovian at the same time.

Let

$$\dot{\mathbf{u}}(t)=\mathbf{F}(\mathbf{u}(t),\mathbf{A}(t),t) \tag{54}$$

**Table 2.** Non-Gaussian Parameters

| $\varepsilon_4$ | $\langle v_x^4\rangle$ | $a_2$(1d) | $a_2$(3d) | limit[a] $\langle \mathbf{V}^2(t)\,\mathbf{V}^2(0)\rangle$ (1d) | (3d) | $\langle v_x^6\rangle$ [a] | $a_3$(1d) | $\langle v_x^8\rangle$ [a] | $a_4$(1d) | Limit[a] $\langle v_x^4(0)\times v_x^4(t)\rangle$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 3 | 0 | 0 | 0.333 | 0.6 | 15 | 0 | 105 | 0 | 0.0 |
| 0.4625 | 3.788 | 0.25 | 0.16 | 0.264 | 0.517 | 26.80 | 0.787 | 276.4 | 1.58 | 0.053 |
| 0.625 | 4.064 | 0.355 | 0.21 | 0.246 | 0.496 | 30.96 | 1.06 | 328.5 | 2.13 | 0.053 |
| 0.925 | 4.575 | 0.525 | 0.31 | 0.219 | 0.458 | 38.63 | 1.58 | 435.8 | 3.15 | 0.048 |
| 1.55 | 5.639 | 0.879 | 0.53 | 0.177 | 0.392 | 54.59 | 2.64 | 659.2 | 5.28 | 0.048 |

[a] Normalised at $t=0$

where $\mathbf{A}(t)$ is a stochastic processes described by the generalized Langevin Equation (3). The theory developed in the present paper allows us to build up an elarged set of stochastic variables $[\mathbf{v}_i, i=0, \ldots, N]$, including $\mathbf{A}(t)=\mathbf{v}_0(t)$ in such a way that the contracted dynamics only involving $\mathbf{A}(t)$ is the same as the one of (3). However the probability density $P([\mathbf{v}_i(t)], t)$ describing the enlarged set of variables obeys the Markhov master equation (28). By following the basic idea of S.L.E. theory [25, 27, 28] we notice that the multidimensional variable $[\mathbf{u}(t), \mathbf{v}_i(t), i=1, \ldots, N]$ is again a Markhov process which obeys the master Equation

$$\frac{\partial}{\partial t} P(\mathbf{u}(t), [\mathbf{v}_i(t)], t) = \frac{\partial}{\partial \mathbf{u}} \mathbf{F}(\mathbf{u}(t), [\mathbf{v}_i(t)], t) P + \Gamma_j P \qquad (55)$$

where $\Gamma_j$ retains both the non gaussian and the non markhovian feature of the process $\mathbf{A}(t)$. Equation (55) can be regarded as a generalized S.L.E. avoiding the approximation of Markhovian-Gaussian relaxation for the stochastic variable $\mathbf{A}(t)$.

We are grateful to Professor K. Singer for a listing of the algorithm TRI2. The S.R.C. is thanked for financial support to M.F. and M.W.E. P.G. acknowledges financial support by the U.S. National Institute of Health (Grant No. GM 23942 and Contract No. EY-76-S-05-2690 between the Division of Biomedical and Environmental Research of the Department of Energy and Florida State University).

## Appendix

In this appendix we evaluate the moment function (J = *angular momentum*) $\langle \mathbf{J}^2(t) \mathbf{J}^2(0)\rangle / \langle \mathbf{J}^2(0) \mathbf{J}^2(0)\rangle$ for the rotation in space $(3-D)$ of the asymmetric top. If we assume that the statistical distribution of angular momenta is Gaussian we may write:

$$\langle \mathbf{J}(t)\rangle = 0 \colon \langle \mathbf{J}(t) \mathbf{J}^T(s)\rangle \equiv \chi(t-s)$$

so that the conditional probability function is:

$$P_2(\mathbf{J}_t, t | \mathbf{J}_s, s) \propto \exp\left[-\tfrac{1}{2}(\mathbf{J}_t - \chi(t-s)\mathbf{J}_s)^T \cdot (\langle \mathbf{J}(0)\mathbf{J}^T(0)\rangle - \chi(t-s)\langle \mathbf{J}(0)\mathbf{J}^T(0)\rangle \chi^T(t-s))^{-1} \cdot (\mathbf{J}_t - \chi(t-s)\mathbf{J}_s)\right].$$

If we assume that both $\chi(t)$ and $\langle \mathbf{J}(0)\mathbf{J}^T(0)\rangle$ are diagonal in the same representation (i.e. that the principal moment of inertia dynamic is known) then:

$$\langle \mathbf{J}(0)\mathbf{J}^T(0)\rangle = \begin{bmatrix} kTI_1 & 0 & 0 \\ 0 & kTI_2 & 0 \\ 0 & 0 & kTI_3 \end{bmatrix}$$

where $I_1$, $I_2$ and $I_3$ are the principal moments of inertia, and:

$$\chi(t-s) = \begin{bmatrix} \chi_1(t-s) & 0 & 0 \\ 0 & \chi_2(t-s) & 0 \\ 0 & 0 & \chi_3(t-s) \end{bmatrix}.$$

We have the simple formula:

$$P_2(\mathbf{J}_t, t | \mathbf{J}_s, s) \propto \exp\left\{-\frac{1}{2kT}\left[\frac{(\mathbf{J}_t^{(1)} - \chi_1(t-s)\mathbf{J}_s^{(1)})^2}{I_1(1-\chi_1^2(t-s))} + \frac{(\mathbf{J}_t^{(2)} - \chi_2^2(t-s)\mathbf{J}_2^{(2)})}{I_2(1-\chi_2^2(t-s))} + \frac{(\mathbf{J}_t^{(3)} - \chi_3(t-s)\mathbf{J}_s^{(3)})}{I_3(1-\chi_3^2(t-s))}\right]\right\}$$

Using this expression we may calculate the moment autocorrelation functions by integration over the probability density function, so that:

$$\langle J_1^2(t) J_1^2(0)\rangle = (1+2\chi_1^2(t))(kTI_1)^2$$
$$\langle J_1^2(0) J_1^2(0)\rangle = 3(kTI_1)^2$$
$$\langle J_2^2(t) J_2^2(0)\rangle = (1+2\chi_2^2(t))(kTI_2)^2 \xrightarrow[t\to 0]{} 3(kTI_2)^2$$

$$\langle \mathbf{J}(0)\cdot\mathbf{J}(0)\,\mathbf{J}(0)\cdot\mathbf{J}(0)\rangle = 3(kTI_1)^2 + 3(kTI_2)^2 + 3(kTI_3)^2 + 2(kT)^2(I_1I_2 + I_2I_3 + I_1I_3),$$

$$\langle \mathbf{J}(t)\cdot\mathbf{J}(t)\,\mathbf{J}(0)\cdot\mathbf{J}(0)\rangle = [(1+2\chi_1^2(t))I_1^2 + (1+2\chi_2^2(t))I_2^2 + (1+2\chi_3^2(t))I_3^2 + 2(I_1I_2 + I_2I_3 + I_1I_3)(kT)^2 = (kT)^2[(I_1+I_2+I_3)^2 + 2I_1^2\chi_1^2(t) + 2I_2^2\chi_2^2(t) + 2I_3^2\chi_3^2(t)].$$

Finally:

$$\frac{\langle \mathbf{J}(t)\cdot\mathbf{J}(t)\,\mathbf{J}(0)\cdot\mathbf{J}(0)\rangle}{\langle \mathbf{J}(0)\cdot\mathbf{J}(0)\,\mathbf{J}(0)\cdot\mathbf{J}(0)\rangle} = [(I_1+I_2+I_3)^2 + 2\sum_1^3 I_i^2\chi_i^2(t)]/[(I_1+I_2+I_3)^2 + 2(I_1^2+I_2^2+I_3^2)] \xrightarrow[t\to\infty]{} \left[1 + 2\frac{I_1^2+I_2^2+I_3^2}{(I_1+I_2+I_3)^2}\right]$$

$= 0.5$ for $I_1 = I_2$; $I_3 = 0$, the result of Berne and Harp.

The moment of inertia characteristic of the molecule used in the simulation is such that the limit of 1/2 should be replaced by 1/2.125, a correction insufficient to explain the markedly non-Gaussian characteristics of the simulated moment autocorrelation functions.

## References

1. Zwanzig, R.: Lectures in Theoretical Physics. Brittin, W.E., Downs, B.W., Downs, J. (eds.), Vol. 3, p. 106. New York: Interscience 1965

2. Muus, L.T., Atkins, P.W. (eds.): Electron Spin Relaxation in Liquids. New York: Plenum Press 1972
3. Laubereau, A., Kaiser, W.: Rev. Mod. Phys. **50**, 607 (1978)
4. Berne, B.J., Harp, G.D.: Adv. Chem. Phys. **17**, 63 (1970)
5. Fox, R.F.: Phys. Rep. **48**, 179 (1978)
6. Adelman, S.A.: J. Chem. Phys. **64**, 124 (1975)
7. Fox, R.F.: J. Stat. Phys. **16**, 259 (1977); J. Math. Phys. **18**, 2331 (1977)
8. Davies, A.R., Evans, M.W.: Mol. Phys. **35**, 857 (1978)
9. Fox, R.F.: J. Chem. Phys. **70**, 4660 (1979)
10. Roodhart, L.P., Wegdam, G.H.: Chem. Phys. Lett. **61**, 449 (1979)
11. Rahman, A.: Phys. Rev. **136A**, 405 (1964)
12. Communication. Comput. Phys. Commun. (to be published)
13. Evans, M.W., Evans, G.J., Davies, A.R.: 13th International Conference on Molecular Spectroscopy, Wroclaw, J. Mol. Struct. **46**, 395 (1978)
14. Evans, M.W., Evans, G.J., Davies, A.R.: Adv. Chem. Phys. **44**, (1980)
15. Mori, H.: Prog. Theor. Phys. **33**, 127 (1965)
16. Nordholm, S., Zwanzig, R.: J. Stat. Phys. **13**, 397 (1975)
17. Kramers, H.A.: Physica **7**, 284 (1940)
18. Moyal, J.E.: J. R. Stat. Soc. (London), **B11**, 150 (1949)
19. Mori, H.: Prog. Theor. Phys. **39**, 399 (1965)
20. Platz, O.: In: Electron Spin Relaxation in Liquids. Muus, L.T. Atkins, P.W. (eds.), p. 89. New York: Plenum Press 1972
21. Van Kampen, N.G.: Phys. Rep. **24**, 171 (1976)
22. Fox, R.F., Uhlenbeck, G.E.: Phys. Fluids **13**, 1893, 2881 (1970)
23. Van Kampen, N.G.: Adv. Chem. Phys. **15**, 65 (1969)
24. Ferrario, M., Grigolini, P.: Chem. Phys. Lett. **62**, 100 (1979)
25. Kubo, R.: Adv. Chem. Phys. **15**, 108 (1969)
26. Zwanzig, R.: Annu. Rev. Phys. Chem. **16**, 67 (1965)
27. Van Kampen, N.G.: Phys. Rep. **24C**, 171 (1976)
28. Kubo, R.: J. Phys. Soc. Jpn. **26**, 1 (1969)

P. Grigolini
M. Ferrario
Gruppo Nazionale di Struttura
della Materia del C.N.R.
Istituto di Fisica
Universitá di Pisa
Piazza Torricelli 2
I-56100 Pisa
Italy

M.W. Evans
Department of Chemistry
University College of Wales
Aberystwyth SY 23 INE
U.K.