NON-GAUSSIAN DISTRIBUTIONS IN COMPUTER TRIATOMICS

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A molecular dynamics simulation of 108 triatomic molecules of C_{2v} symmetry reveals markedly non-gaussian statistical distributions of vectors such as the centre-of-mass linear velocity, molecular angular momentum, positional and orientational coordinates. The results are reproduced qualitatively in the case of linear velocity by a straightforward extension of the Fokker–Planck equation.

1. Introduction

In this letter we report the results of a computer simulation of the molecular dynamics of 108 triatomic molecules of C_{2v} symmetry with the aim of determining whether or not the artificial system is statistically gaussian. Rahman [1] has reported non-gaussian behaviour in a well-known simulation of argon, Berne and Harp [2] for CO (with a modified Stockmayer potential), and Evans et al. [3] for N_2 (atom–atom Lennard-Jones potential). Here we use a 3 X 3 atom–atom Lennard-Jones potential within the framework of an algorithm developed by Singer and Renaud [4].

The statistics are investigated using autocorrelation functions (ACFs) and moment functions. The former decay to an asymptotic long-time limit which can be calculated analytically given the statistical distribution. For example, the rotational kinetic energy ACF, which is important in vibrational relaxation [2], decays to 0.5 of its initial value and the translational kinetic energy ACF to 0.6, given a gaussian distribution of velocity and angular velocities. In this simulation we find for the first time a significant negative departure from these kinetic energy ACF limits. The moment functions can be defined collectively as

$$a_{2n} = \langle x^{2n}\rangle / k_n \langle x^2\rangle^n - 1, \quad n = 1, 2, 3, \ldots \quad , \qquad (1)$$

where $k_n = 3^n/1 \times 3 \times 5 \times \ldots \times (2n+1)$. The averages $\langle x\rangle$ themselves vanish over a sufficiently extended simulation, as shown in fig. 1 for the torque component T_x.

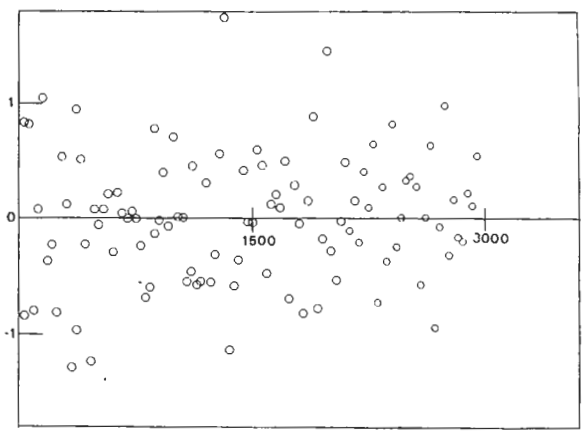

Fig. 1. A plot of mean torque component $\langle T_x\rangle$ against the number of time-steps at 220 K. The mean value is very close to zero, as indicated by the horizontal level.

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This is the case where non-gaussianicity is the most pronounced. All the a_{2n} vanish for a gaussian distribution of x, given $\langle x \rangle = 0$ at thermodynamic equilibrium. We have simulated a_{2n} for a number of x vectors, including the centre-of-mass linear velocity $\boldsymbol{v}$, the molecular angular momentum $\boldsymbol{L}$, the torque $\boldsymbol{T}_q$, the atomic coordinates $\boldsymbol{r}_{1,2,3}$ of each molecule and for unit vectors $\hat{\boldsymbol{e}}_{A,B,C}$ along each principal moment of inertia axis. In no case do the a_{2n} functions vanish, so that the statistics are non-gaussian for all vectors. Berne and Harp have commented on the sensitivity of such non-gaussian results to the number of molecules used in the simulation. For economic reasons we are restricted to 108 molecules at present.

2. Computational details

These will be published in full by Renaud and Singer [4]. The equations of motion for 108 triatomics of C_{2v} symmetry (ABA) are solved using periodic boundary conditions and a two-step predictor/corrector method (University of Manchester Regional Computer Centre, CDC 7600). The conditions under which the runs were made are summarised in table 1.

The functions a_{2n} were calculated over a total range of 3000 time steps at 220 K, and 2000 time steps at 100 K, averaging using every third (recorded) value, taken from magnetic tape. Autocorrelation functions of the form

$$C_n(t) = \langle x^{2n}(t) x^{2n}(0) \rangle / \langle x^{2n}(0) x^{2n}(0) \rangle \qquad (2)$$

were built up using a running time average over the total available time steps, and checked using a 1500 (or 1000) time step span for consistency and to estimate the statistical noise level. A typical result is illustrated in fig. 2.

3. Results and discussion

In table 2 we summarise the mean levels over 3000 steps of a_{2n} (n = 1, 2, 3) for various x, together with the standard deviations. The gaussian level is zero in each case.

The level of the a_{2n} function for $\hat{\boldsymbol{e}}_C$ seems to drift as the simulation proceeds but as in the other case we have contented ourselves with a calculation of the mean level and standard deviation. The a_{2n} functions for velocity $\boldsymbol{v}$, angular momentum $\boldsymbol{L}$ and torque $\boldsymbol{T}_q$

Table 1
Thermodynamic conditions and other details

A. Thermodynamic conditions

set temperature (K)	molar volume (m^3)	Lennard-Jones parameters ϵk^{-1} (K)	σ (m)
200 100	10^{-4}	173.5	3×10^{-10}

B. Simulation details

time steps (total)	duration of one time step (s)	recording interval	allowable temp. drift (K)	number of time steps initially rejected
5000	1×10^{-14}	every 3 steps	±25	2000 (220 K) 3000 (100 K)

C. Molecular details

bond length (m)	included angle (deg)	mass of A atoms (kg)	mass of B atoms (kg)
1×10^{-10}	60	2.5×10^{-25}	2.5×10^{-25}

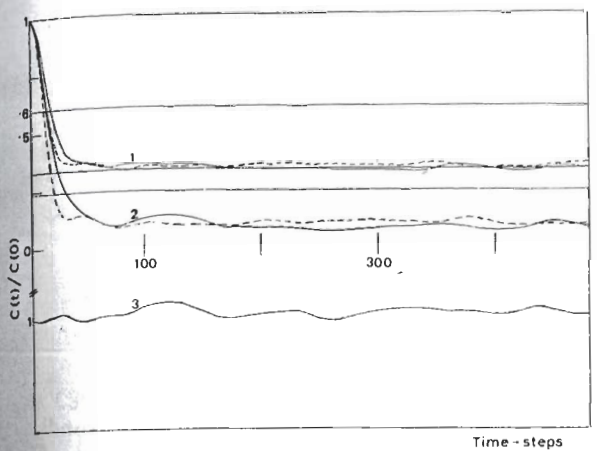

Fig. 2. Moment autocorrelation functions simulated at 100 K (2000 time-step total averaging), ——: (1) $\langle v^2(t)v^2(0)\rangle / \langle v^2(0)v^2(0)\rangle$, (2) $\langle v^4(t)v^4(0)\rangle / \langle v^4(0)v^4(0)\rangle$ (in 3 dimensions both), (3) $\langle v_x^2(t)v_y^2(0)\rangle / \langle v_x^2(0)v_y^2(0)\rangle$, – – –: (1) $\langle v_x^2(t)v_x^2(0)\rangle / \langle v_x^2(0)v_x^2(0)\rangle$, (2) $\langle v_x^4(t)v_x^4(0)\rangle / \langle v_x^4(0)v_x^4(0)\rangle$.

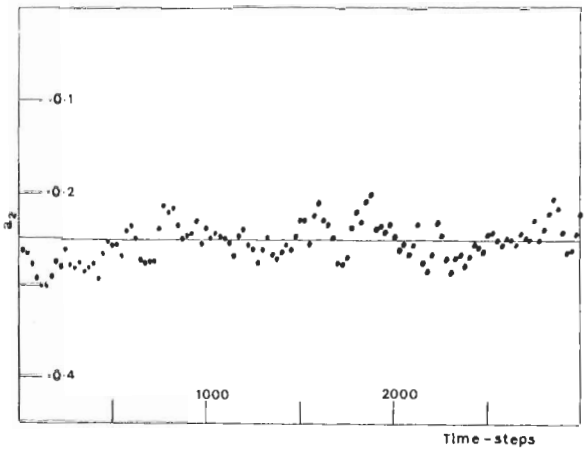

Fig. 3. a_2 for the $\hat{e}_A$ vector, plotted every few time-steps. Gaussian level = 0.

fluctuate much more about a mean value, significantly above the zero level. The values in table 2 were built up by averaging over the 108 molecules every third time step from 2000 or 3000 to 5000, and finally averaging over the number of time steps used. A typical run is illustrated in fig. 3.

The autocorrelation functions most accessible to a fairly tractable analysis based on an extension of the Fokker–Planck method are those for linear centre-of-mass velocity and centre-of-mass position. This is because we are not to contend with the complexities of the Euler equations. The simulated moment ACFs of v (fig. 2) are interestingly different from the same type calculated by Berne and Harp [2] for CO and Evans et al. [3] for N_2, in that in three dimensions they reach a steady long-time limit at a value much *lower* than that expected from a gaussian analysis of the statistics. The 1500 time-step run for the fourth moment agrees satisfactorily with the 3000 time-step runs so that it is unlikely that the deviation from gaussianicity is due to statistical noise. The component functions $\langle v_{x,y,z}^{2n}(t)v_{x,y,z}^{2n}(0)\rangle$ (in one dimension) reach a limit of approximately 1/3 this time in accord with the analytical value of 1/3.

Table 2
The moment functions [a] a_{2n} (n = 1, 2, 3) at 100 K and 220 K

x	T = 220 K			T = 100 K		
	a_2	a_4	a_6	a_2	a_4	a_6
v	0.75 ± 0.27	2.55 ± 1.50	6.54 ± 6.57	0.81 ± 0.32	2.91 ± 2.17	8.26 ± 10.63
L	0.26 ± 0.15	0.83 ± 0.72	1.96 ± 2.41	0.27 ± 0.16	0.85 ± 0.79	1.97 ± 3.00
T_q	0.56 ± 0.32	2.19 ± 2.21	6.75 ± 11.70	0.23 ± 0.15	0.73 ± 0.65	1.61 ± 2.04
$\hat{e}_A$	−0.25 ± 0.24	−0.55 ± 0.032	−0.78 ± 0.026	−0.24 ± 0.024	−0.53 ± 0.034	−0.76 ± 0.029
$\hat{e}_B$				−0.25 ± 0.022	−0.55 ± 0.03	−0.77 ± 0.024
$\hat{e}_C$	−0.225 ± 0.03	−0.515 ± 0.045	−0.74 ± 0.039	−0.23 ± 0.021	−0.53 ± 0.03	−0.76 ± 0.025
r_A	−0.29 ± 0.016	−0.60 ± 0.022	−0.81 ± 0.017	−0.28	−0.59	−0.80
r_B	−0.285 ± 0.016	−0.59 ± 0.022	−0.81 ± 0.018	−0.28	−0.58	−0.53
$r_{c.m.}$				−0.33 ± 0.056	−0.65 ± 0.07	−0.85 ± 0.053

[a] ± standard deviation of 3000 time steps at 220 K, 2000 time steps at 100 K.

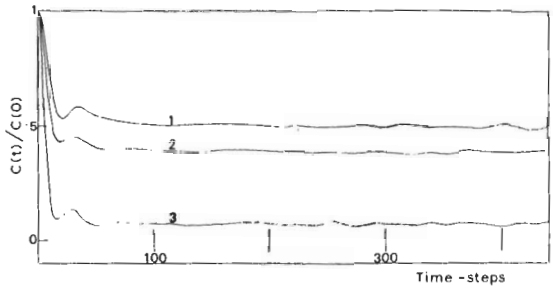

Fig. 4. (1) $\langle T_q^2(t)T_q^2(0)\rangle/\langle T_q^2(0)T_q^2(0)\rangle$ at 100 K, (2) $\langle T_q^2(t)T_q^2(0)\rangle/\langle T_q^2(0)T_q^2(0)\rangle$ at 220 K, (3) $\langle T_q^4(t)T_q^4(0)\rangle/\langle T_q^4(0)T_q^4(0)\rangle$.

The angular momentum ACFs show up a similar kind of negative deviation, unlike the small positive ones discussed by Berne and Harp for CO and Evans et al. for N_2. The torque moment ACFs (fig. 4) reach satisfactorily smooth long-time plateau levels as do the orientational functions. Unfortunately, no analytical level is known for these functions at present but it is noted that the $t \to \infty$ levels at 100 K and 220 K are different, which is once more a sign of non-gaussian statistics.

4. Discussion

The most interesting implication of these results is that the stochastic force appearing in any version of the Langevin equation [5] for molecular and brownian motion is also markedly non-gaussian. This point may be dealt with analytically with a modified form of markovian Fokker–Planck equation derived from the master equation for the conditional two-time probability density function P

$$\partial P(\mathbf{v}, t|\mathbf{v}_0, 0)/\partial t = \int [P(\mathbf{v}', t|\mathbf{v}_0, 0)W(\mathbf{v}|\mathbf{v}') - P(\mathbf{v}, t|\mathbf{v}_0, 0)W(\mathbf{v}'|\mathbf{v})]\, \mathrm{d}\mathbf{v}', \tag{3}$$

i.e.

$$\partial P(\mathbf{v}, t|\mathbf{v}_0, 0)/\partial t = \sum_{n=1}^{\infty} (1/n!)(-\partial/\partial\mathbf{v})^n [\langle \mu_v^n \rangle P(\mathbf{v}, t|\mathbf{v}_0, 0)], \tag{4}$$

provided that:

$$\langle \mu_v^n \rangle = \int \mathrm{d}\mathbf{v}'(\mathbf{v}' - \mathbf{v})^n W(\mathbf{v}'|\mathbf{v}). \tag{5}$$

The physical meaning of eq. (3) can be clarified through the definition of the correlation function of a variable y

$$\langle y y(t)\rangle = \langle y(t) y\rangle = \int \mathrm{d}y_1 \mathrm{d}y_2\, P_1(y_1) P(y_2|y_1, t) y_1 y_2,$$

since $P_1(y)$ is the a priori probability of finding y in the range $(y, y + \mathrm{d}y)$ and $P(y_2|y_1, t)$ is the conditional probability that given y_1 at initial time $t = 0$, it may be found at $t = t$ in the range $(y_2, y_2 + \mathrm{d}y_2)$. Eq. (4), 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 μ_v^n. When the statistics governing the system are gaussian then only the first two terms of eq. (4) are accounted for. By using a correction to the Fokker–Planck equation of the form

$$\Gamma_1 = \sum_{n=3}^{\infty} (1/n!)(-\partial/\partial\mathbf{v})^n [\mu_v^n P(\mathbf{v}, t|\mathbf{v}_0, 0)] \tag{6}$$

and by approximating $\mu^n(\mathbf{v})$ analytically it is possible to reproduce the results of the simulation for $\langle v^{2n}(t)v^{2n}(0)\rangle/\langle v^{2n}(0)v^{2n}(0)\rangle$ analytically. The function $\mu^n(\mathbf{v})$ may be approximated analytically with a Mori continued fraction expansion of the Liouville equation truncated at various orders (or approximants) and interpreted analytically in terms of mechanical models [6] such as the itinerant librator–oscillator [7] or harmonic oscillator [8]. To produce the results of fig. 5 we have used the latter to least mean squares best fit the simulated velocity autocorrelation function. An alternative approach to dealing with non-gaussianicity is through use of the moments of the stochastic force $f(t)$ of the Langevin equation

$$\dot{\mathbf{v}}(t) = -\beta\mathbf{v} + \boldsymbol{f}(t),$$

in its simplest (markovian) form. The moments $\mu^n(\mathbf{v})$ can be evaluated through the stochastic average $\langle\ \rangle$ of the stochastic force $\boldsymbol{f}(t)$ as follows

$$\mu^n(\mathbf{v}) = \lim_{\Delta t \to 0} \langle \Delta v^n \rangle / \Delta t,$$

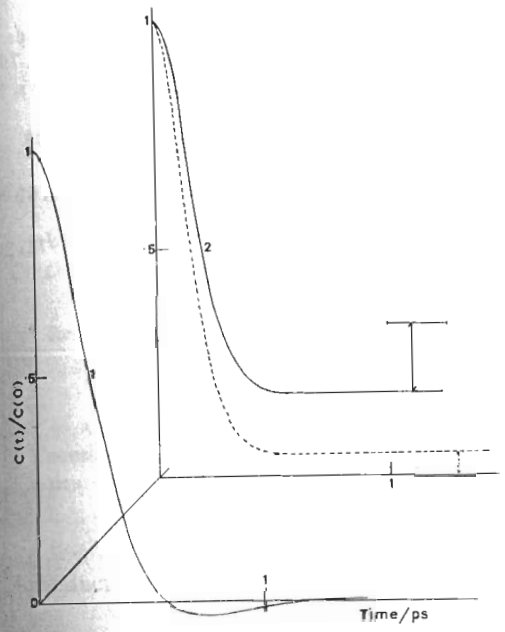

Fig. 5. (1) Best fit to the simulated velocity autocorrelation function. (2) $\langle v_x^2(t)v_x^2(0)\rangle/\langle v_x^2(0)v_x^2(0)\rangle$ with the non-gaussian parameter $\epsilon_4 = 1.55$, ---: $\langle v_x^4(t)v_x^4(0)\rangle/\langle v_x^4(0)v_x^4(0)\rangle$. Differences from gaussian behaviour shown by arrows.

where v is the change of the velocity in the lapse of time Δt. We assume that the first moment of the stochastic force vanishes; then any moment $\mu^n(v)$ except the first, which is

$$\mu^1(\omega) = -\beta v,$$

depends on the stochastic force through the general formula:

$$\mu^n(v) = (1/\Delta t) \times \int_0^{\Delta t} dt_1 \int_0^{\Delta t} dt_2 \ldots \int_0^{\Delta t} dt_n \langle f(t_1) \ldots f(t_n)\rangle, \quad n \geqslant 2.$$

In the gaussian case $\mu^n(v) = 0$, for $n \geqslant 3$. In order to avoid gaussianicity we can reasonably assume that

$$\langle f(t_1) \ldots f(t_n)\rangle = n!\,\epsilon_n \Delta^n \delta(t_1 - t_2)\delta(t_2 - t_3) \ldots \delta(t_{n-1} - t_n) + (\text{gaussian contribution}),$$

where $\Delta = (\langle v^2\rangle)^{1/2}$, which means that the stochastic force is not a gaussian process, but it is still a purely random one. As a consequence, directly from eq. (6) we obtain the result that the correction to the Fokker–Planck equation reads

$$\Gamma_1 = \beta(\epsilon_3 \Delta^3 \partial^3/\partial v^3 + \epsilon_4 \Delta^4 \partial^4/\partial v^4 + \ldots).$$

The parameters ϵ_3, ϵ_4, ... have to be taken as being small perturbation parameters in such a way as to modify the result, provided by the usual Fokker–Planck equation. It is clear that gaussianicity is destroyed by the presence of Γ_1. A non-Markov, non-gaussian differential equation of the general form

$$\frac{\partial P}{\partial t} = \omega\left(\frac{\partial W}{\partial v} - \frac{\partial v}{\partial W}\right)P + \beta\left(\frac{\partial}{\partial W} + \Delta^2 \frac{\partial^2}{\partial W^2} + \epsilon_3 \Delta^3 \frac{\partial^3}{\partial W^3} + \epsilon_4 \Delta^4 \frac{\partial^4}{\partial W^4} + \ldots\right)P$$

can be built up to take account of memory and inertial effects which dominate the simulated coefficients at short times [9]. By expanding the solution P on the set of Hermite polynomials $\mathrm{He}_n(v/\Delta)\,\mathrm{He}_m(W/\Delta)$ times $\exp[-(v^2 + W^2)/2\Delta^2]$ we can reduce the problem to the numerical diagonalization of the matrix expression of the diffusion operator in the above equation.

By varying ϵ_3 and ϵ_4 we have evaluated

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

and have obtained the results of fig. 5, in qualitative agreement with the simulation, i.e. a negative deviation from the long-time limit. A full account of the numerical solution of equations similar to this is given by Risken and Vollmer [10]. An account of our specific method is published elsewhere [3].

Further work on this subject will be concerned with similar analytical evaluation for the rotational and roto-translational motions. However, the analysis in this case is severely complicated, as usual, by the dynamical properties of the rotating asymmetric top. The route to be taken involves a generalisation of Favro's elegant gaussian–markovian operator methods [6].

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