124

Advances in Molecular Relaxation and Interaction Processes, 23 (1982) 69–73
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

THE CORRELATION OF MOLECULAR ROTATIONAL AND TRANSLATIONAL KINETIC ENERGY IN LIQUID CH_2Cl_2 AND $CHCl_3$ *

M.W. EVANS and M. FERRARIO
Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed, SY23 1NE, Wales.

(Received 1 February 1982)
* This work forms part of the E.M.L.G. Pilot Project.

ABSTRACT

A "molecular dynamics" computer simulation of liquid CH_2Cl_2 and $CHCl_3$ has revealed a time dependence of the simple kinetic energy correlation function $\langle v^2(0)J^2(t)\rangle/(\langle v^2(0)\rangle\langle J^2(0)\rangle)$ where $\underline{v}$ is the c. of m. linear velocity and $\underline{J}$ the molecular angular momentum. This is constant at unity for all t in conventional analytical theory, which is therefore in need of development. The variates $\underline{v}$ and $\underline{J}$ are not Gaussian during the approach to equilibrium.

INTRODUCTION

The computer simulation of molecular liquids (1,2) may be used to reveal aspects of molecular dynamics which are hidden from conventional theoretical and experimental analysis. In this letter we report the use of computer simulation in liquid CH_2Cl_2 and $CHCl_3$ to reveal an important new property of liquid state transient behaviour involving the interaction between rotational and translational momentum. The variates are assumed to be uncoupled in classical theory, such as that of rotational Brownian motion. Consequently some simple correlation functions vanish or remain constant for all t. In a molecular dynamics computer simulation with site-site (atom-atom) potentials we can see clearly how this assumption breaks down, thus pointing out the need for further fundamental analytical work.

METHOD, RESULTS AND DISCUSSION

The equations of motion for 108 molecules of CH_2Cl_2 or $CHCl_3$ were solved

0378-4487/82/0000–0000/$02.75

using thoroughly tested algorithm TETRA of the SERC CCP5 group, originally written by Singer and co-workers (3). This was modified to include among other things, charge-charge interaction. The intermolecular potential energy was represented by a site-site Lennard-Jones form with the parameters σ and ε/k of table 1.

TABLE 1

Intermolecular pair potential for CH_2Cl_2 and $CHCl_3$*

Molecule		σ/Å	ε/k /K	q_H	q_C	q_{Cl}
CH_2Cl_2	H-H	2.75	13.4			
	Cl-Cl	3.35	175.0	0.098|e|	0.098|e|	-0.109|e|
	C-C	3.20	51.0			
$CHCl_3$	H-H	2.75	13.4		0.056|e|	-0.063|e|
	Cl-Cl	3.50	175.0	0.131|e|		
	C-C	3.20	51.0			

* Cross-terms evaluated by $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$; $\left(\frac{\varepsilon}{k}\right)_{AB} = \left[\left(\frac{\varepsilon}{k}\right)_A \left(\frac{\varepsilon}{k}\right)_B\right]^{\frac{1}{2}}$

Thermodynamic stability and efficacy were checked by computing the temperature, pressure, internal and total energy, and the specific heat at constant volume at three state points. These agreed satisfactorily with the available experimental data and will be reported fully elsewhere. Long range effects were accounted for with periodic boundary conditions but no Ewald summation was used.

A wide variety of static and dynamic properties were evaluated but relevant to our purpose are $\langle J^n(t) v^n(0)\rangle / (\langle J^n(0)\rangle\langle v^n(0)\rangle)$ with integral n. Here $\underline{J}$ is the molecular *angular* momentum in the lab. frame and $\underline{v}$ the centre of mass *linear* velocity.

In conventional theory (e.g. of rotational Brownian motion) these vanish for all *odd* n (because of parity reversal symmetry) and remain constant at unity for all *even* n (because $\underline{J}$ and $\underline{v}$ are assumed to be uncorrelated (Gaussian) variates). Fig. (1) from the simulation shows that for n = 2 this correlation function exists (i.e. has time dependence). This corroborates some earlier work of Bellemans et al. (5) carried out on model potentials such as rods and disks. (For n = 1 the computed correlation function vanishes for all t).

These fundamental results imply the following courses for further work.

i) In considering an analytical theory of, for example, far infra-red/dielectric

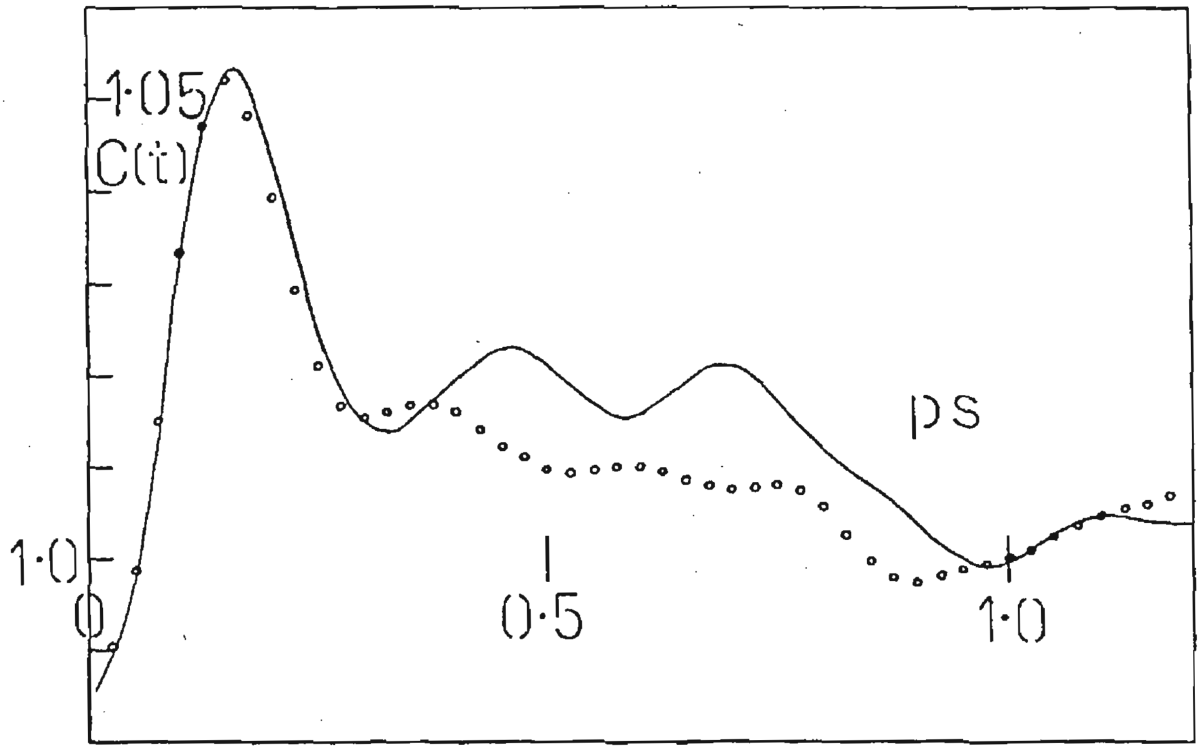

Fig. 1 (a) —— $<v^2(0)J^2(t)>/(<v^2(0)><J^2(0)>)$

$<v^2(t)J^2(0)>/(<v^2(0)><J^2(0)>)$ = C(t)

for liquid CH_2Cl_2 at 177 K (0.2 K above the freezing point) at 1bar. Note these two functions are identical from time reversal symmetry, and any difference represents the level of statistical noise in the computer simulation.

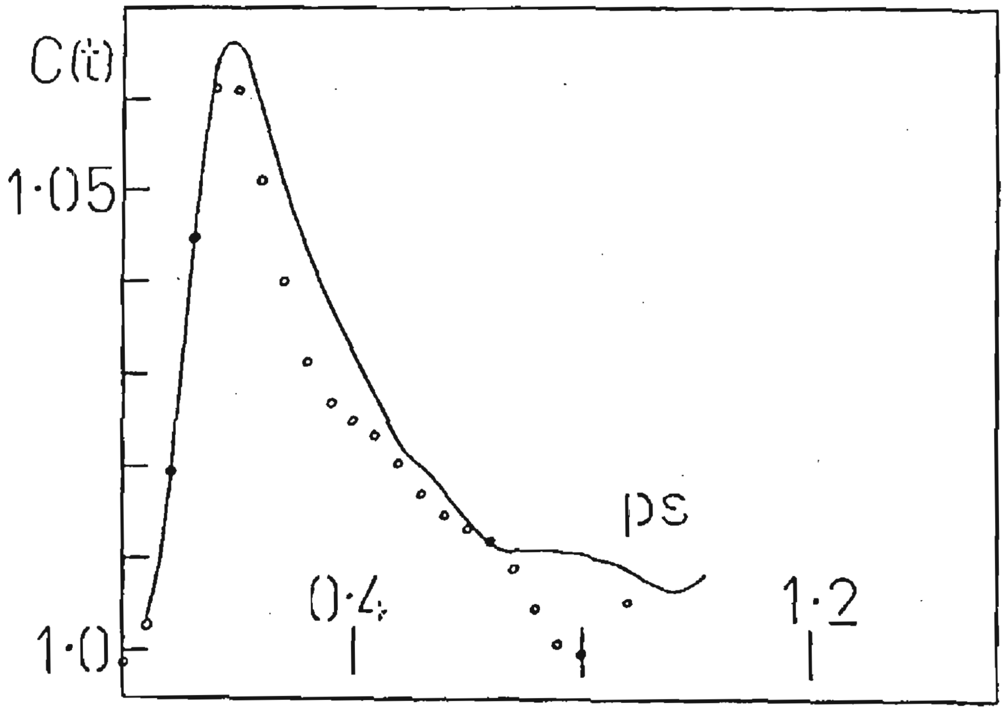

Fig. 1 (b) As for (a), $CHCl_3$ at 293 K, 1bar.

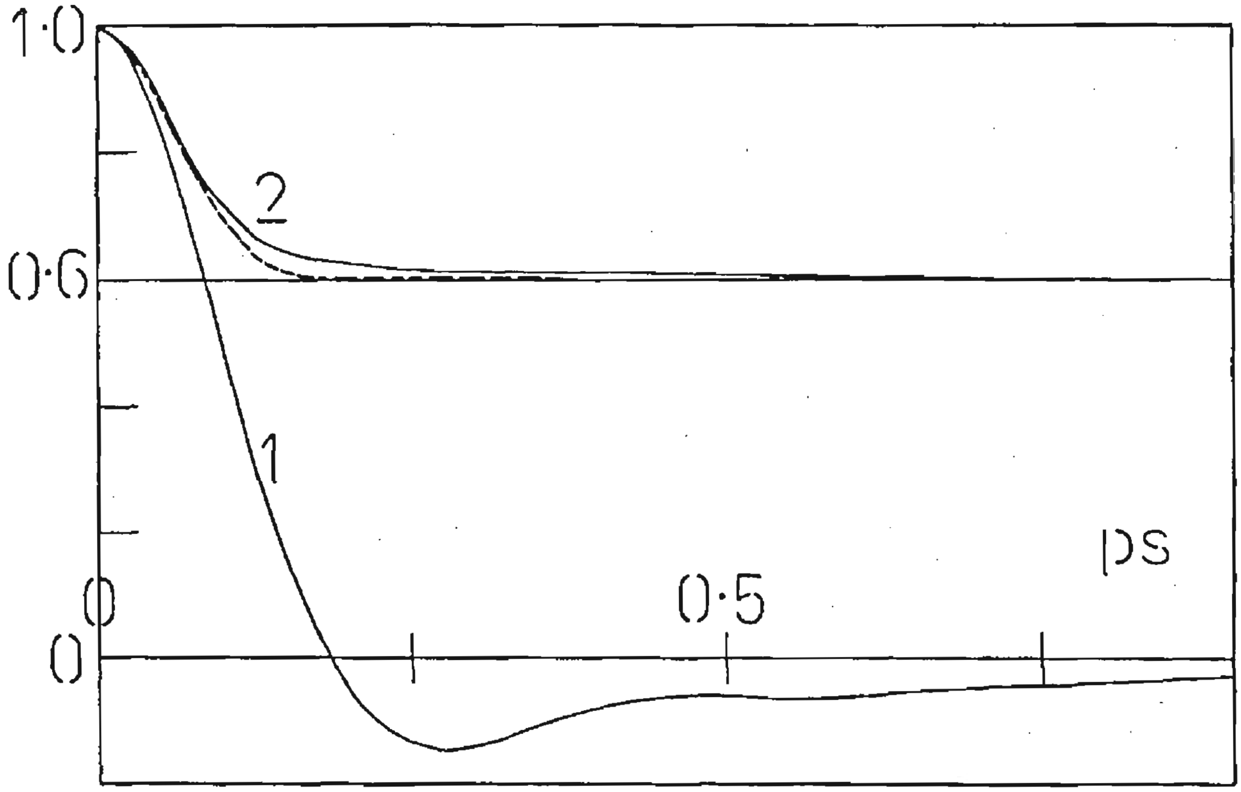

Fig. 2 (a) Non-Gaussian behaviour of linear velocity, $\underline{v}$ for CH_2Cl_2 at 177 K, 1bar.

(1) – $C_{\underline{v}}(t) = <\underline{v}(t).\underline{v}(0)>/<v^2(0)>$ (2) – $C_{v2}(t) = <\underline{v}(t).\underline{v}(t).\underline{v}(0).\underline{v}(0)>/<v^4(0)>$

– – – – The Gaussian result (8): $C_{v2}(t) = \frac{3}{5}\left(1 + \frac{2}{3} C_v^2(t)\right)$

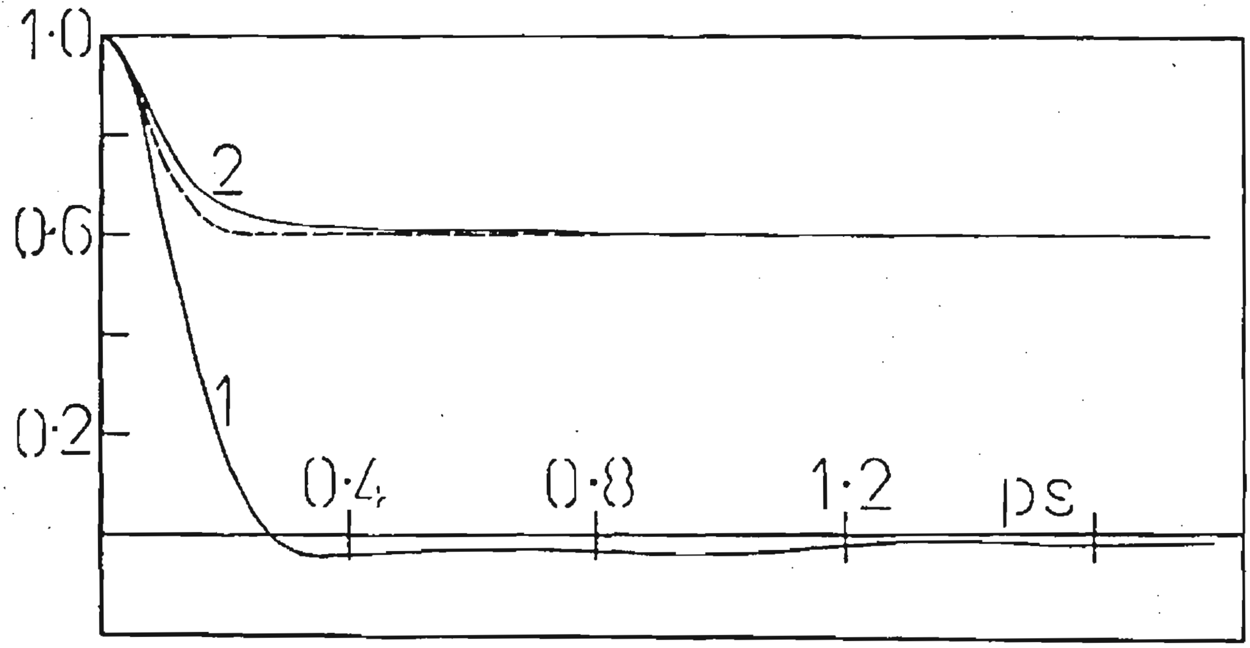

Fig. 2 (b) As for (a), $CHCl_3$, at 293 K, 1bar.

spectroscopy it is essential to take note of the parallel information from computer simulation and construct a joint conditional probability density function (1) of v and J which has analytical properties matching those computed above for odd and even n. This is by no means a trivial problem, but is, at the same time, fundamental to further progress.

ii) Our computer results (e.g. Fig. 2) show also that both $<v^2(t)v^2(0)>/<v^4(0)>$ and $<J^2(t)J^2(0)>/<J^4(0)>$ are transiently non-Gaussian in statistical nature. This corroborates earlier indications of other, differently structured algorithms (7-11). The analytical description of this result must involve the use of, for example, Brownian motion theory with a superimposed potential barrier (such as that in a Kramers equation (12)). The simulation results for J cannot be explained on the simple basis that the Euler equations are transiently non-Gaussian even for free asymmetric top rotation (13). The non-Gaussian nature of v cannot be explained at all without the consideration of molecular interaction and potential walls which are non-linear in the restoring force. We are pursuing this question with the generalised Mori theory of Grigolini et al. (14).

ACKNOWLEDGEMENTS

The Italian CNR is thanked for a European Fellowship to MF and the UK SERC for support for MWE.

REFERENCES

1 M.W. Evans, G.J. Evans, W.T. Coffey and P. Grigolini, Molecular Dynamics and Theory of Broad Band Spectroscopy, Wiley/Interscience, N.Y., in press, 1982 (ca. 800 pp.).

2 M.W. Evans and M. Ferrario, Chem. Phys., Munich, in press.

3 K. Singer and D. Fincham, CCP5 algorithm, SERC, Daresbury Lab., U.K.

4 R. del Re, J. Chem. Soc., 36 (1958) 161.

5 A. Bellemans and J.-P. Ryckaert, personal communication.

6 M.W. Evans, Acc. Chem. Res., 14 (1981) 253.

7 A. Rahman, Phys. Rev., 136 (1964) 405.

8 B.J. Berne and G.D. Harp, Adv. Chem. Phys., 17 (1970) 63.

9 M.W. Evans, W.T. Coffey and G.J. Evans, Adv. Mol. Rel. Int. Proc., 20 (1981) 11.

10 M.W. Evans, M. Ferrario and P. Grigolini, Z. Phys., (B) 41 (1981) 165.

11 U. Balucani, V. Tognetti, R. Vallauri, P. Grigolini and M.P. Lombardo, Phys. Letters, submitted.

12 M.W. Evans, M. Ferrario and W.T. Coffey, Adv. Mol. Rel. Int. Proc., 20 (1981) 1.

13 M. Ferrario, checked with stochastic computer simulation, to be published.

14 P. Grigolini and P. Marin, Paper presented at EUCMOS 15, J. Mol. Structure, in press, E.M.L.G. session, Univ. of East Anglia, 1981.