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Evaluation of Mori Theory with a Molecular Dynamics Simulation

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A Mori three variable approximation (on the basis of Nee-Zwanzig formalism) is used in an attempt to describe analytically the results of a molecular dynamics simulation of 108 triatomic molecules of C_{2v} symmetry interacting via a three centre Lennard-Jones atom-atom potential. The simulation results expose the limitations of the analytical theory in that the latter is able to describe only the general features of the simulation.

Introduction

One of the most useful ways of fitting spectroscopic data from static frequencies up to the THz has been to truncate the Mori continued fraction expansion for the orientational auto-correlation function [1] $\langle \mathbf{u}(t)\cdot\mathbf{u}(o)\rangle$, where $\mathbf{u}=\mu/|\mu|$. Here μ is the dipole vector. If this is done at the level of the second memory function [2], $\phi_1(t)$, with:

$$\phi_1(t)=\phi_1(0)\exp(-\gamma t) \tag{1}$$

the resulting expression for the complex permittivity may be used to reproduce the characteristic shift in peak frequency of the power absorption coefficient, and thereby interpret this in terms of a mean square torque. A more stringent test of the effect of the truncation (Eq. (1)) may be carried out by using the data from a molecular dynamics simulation [3] of the various correlation functions, mean square torque and mean square angular momentum involved in (1). The only independent phenomenological parameter left is then γ. In this communication we use the simulation of a C_{2v} triatomic (asymmetric top) with no polar properties to estimate (1) directly through its ability or otherwise to reproduce the following simulated autocorrelation functions:

(1) The orientational autocorrelation function $\langle \mathbf{e}_A(t)\cdot\mathbf{e}_A(0)\rangle$ where $\mathbf{e}_A$ is the unit vector along the axis of I_A the smallest principal moment of inertia.
(2) The rotational velocity autocorrelation function $\langle \dot{\mathbf{e}}_A(t)\cdot\dot{\mathbf{e}}_A(0)\rangle$.
(3) The angular momentum auto-correlation function $\langle J(t)\cdot J(0)\rangle$.
(4) The torque a.c.f. $\langle \mathbf{T}_q(t)\cdot\mathbf{T}_q(0)\rangle$.
All vectors are defined in the laboratory frame of reference.
(5) The simulated mean square torque $\langle \mathbf{T}_q(0)\cdot\mathbf{T}_q(0)\rangle$ and angular momentum $\langle \mathbf{J}(0)\cdot\mathbf{J}(0)\rangle$.
The computer liquid is non-polar so that the problem does not arise of dealing with the dynamic internal field. However, we remark that (1) forms the basis of the theory of Lobo et al. [4], who incorporate inertial and memory effects into the dielectric friction treatment of Nee and Zwanzig [5]. It has also been used by Kivelson and Madden [6] for macro-micro correlation.
The paper is developed as follows. In Sect. 1 we review briefly the meaning of (1) and the relations implied analytically between the various autocorrelation functions of interest. In Sect. 2 the simulation is described in detail. Finally we discuss the results and suggest ways of improving the analytical modelling.

Section 1

The meaning of (1) may be clarified as follows, by considering, (Nee and Zwanzig [5]), spherically isotropic Brownian motion via the diffusion equation for

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the probability density function if:

$$\frac{\partial f}{\partial t}(\mathbf{u};t)=\int_0^t ds\,\hat{\phi}(t-s)(\mathbf{u}\times\nabla_u)^2 f(\mathbf{u};s) \tag{2}$$

where $\hat{\phi}$ is the memory kernel, related to the frequency dependent friction coefficient $\zeta(\omega)$ by:

$$\frac{k\tau}{\zeta(\omega)}=\int_0^\infty dt\,\phi(t)\exp(i\omega t)=\phi(\omega). \tag{3}$$

The operator $(\mathbf{u}\times\nabla_u)^2$ is the angular part of the Laplacian, i.e.:

$$(\mathbf{u}\times\nabla)^2 f=\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\left(\frac{\partial f}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2} \tag{4}$$

in spherical polar coordinates (θ,ϕ).
Integrating (3) by parts over all orientations gives the equation of motion for the average dipole moment $(\mu=|\mu|\,\mathbf{u})$.

$$\frac{\partial}{\partial t}\langle\mu;t\rangle=-2\int_0^t ds\,\phi(t-s)\langle\mu;s\rangle \tag{5}$$

Multiply through by $\mu(0)$ and average over an isotropic distribution of orientations, then:

$$\frac{\partial}{dt}\langle\mu(t)\cdot\mu(0)\rangle=-2\int_0^t ds\,\phi(t-s)\langle\mu(s)\cdot\mu(0)\rangle \tag{6}$$

$$\phi(\omega)=\mathcal{L}_a\langle\Omega(t)\,\Omega(0)\rangle \tag{7}$$

is the memory function of $\langle\mu(t)\cdot\mu(0)\rangle$ and the Ω symbol denotes an angular velocity component. The scalar product in (7) means therefore that the angular momentum is isotropically distributed in the laboratory frame of reference so that we are considering dynamically the motion of spherical top with embedded dipole. The rigorous treatment of asymmetric top motion would involve a tensorial form for the angular momentum function analogous to $\phi(\omega)$.
The meaning of (1) is now clear if we take a Mori continued fraction expansion for the memory function in the Laplace domain:

$$\tilde{\phi}(p)=\phi_0(0)/(p+\phi_1(0)/(p+\ldots)\ldots) \tag{8}$$

approximated with (1), so that:

$$\tilde{\phi}(p)=\phi_0(0)(p+\gamma)/(p(p+\gamma)+\phi_1(0))$$

is the Laplace transform of the angular velocity correlation function $\langle\Omega(t)\,\Omega(0)\rangle$. We have:

$$\phi_0(0)=\langle\Omega(0)\,\Omega(0)\rangle$$

the mean square angular velocity. – Using (6) the normalised dipole a.c.f. takes the well-known form:

$$\mathcal{L}_a\langle\mu(t)\cdot\mu(0)\rangle$$
$$=\langle\mu(0)\cdot\mu(0)\rangle/(p+\phi_0(0)/(p+\phi_1(0)/(p+\gamma))). \tag{9}$$

The spectra and time-domain functionals of (8) and (9) are known and documented. It is possible to use the theorems:

$$\langle\dot{\mu}(t)\cdot\dot{\mu}(0)\rangle=-\frac{d^2}{dt^2}\langle\mu(t)\cdot\mu(0)\rangle \tag{10}$$

and

$$\langle\dot{\Omega}(t)\dot{\Omega}(0)\rangle=-\frac{d^2}{dt^2}\langle\Omega(t)\,\Omega(0)\rangle \tag{11}$$

to arrive at the rotational velocity and torque autocorrelation functions respectively. We have in addition the following general relations:

$$\phi_1(0)=\langle\ddot{\mathbf{u}}(0)\cdot\ddot{\mathbf{u}}(0)\rangle/\langle\dot{\mathbf{u}}(0)\cdot\ddot{\mathbf{u}}(0)\rangle$$
$$-\langle\dot{\mathbf{u}}(0)\cdot\dot{\mathbf{u}}(0)\rangle/\langle\mathbf{u}(0)\cdot\mathbf{u}(0)\rangle \tag{12}$$

$$\phi_0(0)=\langle\dot{\mathbf{u}}\rangle\cdot\dot{\mathbf{u}}(0)\rangle/\langle\mathbf{u}(0)\cdot\mathbf{u}(0)\rangle$$
$$=\langle\Omega(0)\,\Omega(0)\rangle \tag{13}$$

By equipartition:

$$\phi_0(0)=\frac{2kT}{I} \tag{14}$$

where I is the moment of inertia and k the Boltzmann constant, and by a consideration of equilibrium statistical mechanics:

$$\langle\ddot{\mathbf{u}}(0)\cdot\ddot{\mathbf{u}}(0)\rangle=\frac{10}{4}\left(\frac{2kT}{I}\right)^2+\frac{\langle T_q^2\rangle}{I^2} \tag{15}$$

where $\langle T_q^2\rangle$ is the equilibrium mean square torque. The centripetal acceleration is

$$\frac{10}{4}\left(\frac{2kT}{I}\right)^2.$$

Therefore, finally:

$$\phi_1(0)=\frac{3kT}{I}+\frac{\langle T_q^2\rangle}{2kTI}. \tag{16}$$

It is clear that the continued fraction (Eqs. (9) and (8)) must be extended far enough to define $\phi_1(0)$ if the analytical theory is to be useful enough to extract the mean square torque from spectroscopic data. Since all further $\phi_n(0)$ also involve $\langle T_q^2\rangle$ (16), (9) and (8) constitute a first approximation only to the value estimated by simulation. The approximation represented by (1) is not exactly consistent with an exponentially decaying torque autocorrelation function, as stated in Lobo et al., since analytically:

$$\langle\dot{\Omega}(t)\,\dot{\Omega}(0)\rangle=\frac{1}{2}\left[(x-\gamma)^2\left(1+\frac{\gamma}{2x}\right)\exp(x-\gamma)t\right.$$
$$\left.+(\gamma+x)^2\left(1-\frac{\gamma}{2x}\right)\exp-(\gamma+x)t\right]$$

or:

$$\langle\dot{\Omega}(t)\dot{\Omega}(0)\rangle=\exp(-\gamma t)\left[\left(\frac{3\gamma x}{2}+\frac{\gamma^3}{2x}\right)\sin xt-x^2\cos xt\right]$$

according as to whether

$$x^2=(\phi_1(0)-\gamma^2/4)$$

is respectively greater or less than zero.
The only free variable is the decay frequency γ of the second memory function, all other quantities may be simulated independently.

Section 2

An algorithm originally due to P. Schofield and developed by Renaud and Singer [7] was used to simulate the molecular dynamics of 108 triatomic molecules interacting with atom-atom potentials of the Lennard-Jones type, with parameters $\sigma=3.0\times10^{-10}$ m, $\varepsilon/k=173.5$ K. The equations of motion were integrated with a two-step predictor-corrector Gear algorithm with periodic boundary conditions and long-range potential cut-off. Labelling the molecule by ABC the dimensions follow as $AB=BC=1\times10^{-10}$ m, $M_A=M_B=M_C=2.5\times10^{-25}$ kgm, $\leqq ABC=60°$.
The molecules were initially deployed on a convenient lattice which melted (Fig. 1) over the first 2,000 or 3,000 steps of the simulations. The temperature of the run was set at 220 K and allowed to fluctuate over the range ±25 K. Temperatures were scaled as necessary. One time step in the simulation $=0.01$ ps. The molar volume of the sample was 1×10^{-4} m^3. After rejecting the first 2,000 time steps over which the total energy is not in equilibrium, the next 3,000 were stored at 0.03 ps intervals on magnetic tape for statistical analysis. Correlation functions were calculated (Figs. 2–4) using these data for $\mathbf{e}_A$ and J, T_q and $\dot{\mathbf{e}}_A=J\times\mathbf{e}_A$. The fluctuations of the squared angular momentum and squared torque over 3.0 ps are illus-

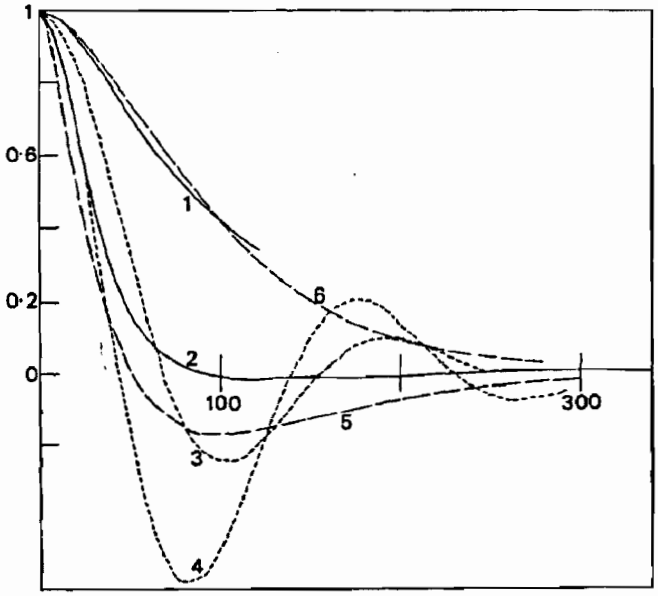

Fig. 2. Simulated and analytical autocorrelation functions at 220 K. These are normalised at the origin. (1) Simulated orientational autocorrelation function $\langle\mathbf{e}_A(t)\cdot\mathbf{e}_A(0)\rangle$. Here $\mathbf{e}_A$ is the unit vector along the axis of the least principal moment of inertia. (2) Simulated rotational velocity a.c.f. $\langle\dot{\mathbf{e}}(t)\cdot\dot{\mathbf{e}}(0)\rangle$. ----(6) Least mean squares best fit of the orientational a.c.f. of Mori three variable theory. ----(5) the angular momentum a.c.f. calculated from the best fit (6). (3) Calculated torque a.c.f. using $\phi_1(0)/\phi_0(0)$ from the best fit (6). (4) Calculated torque a.c.f. using $\phi_1(0)/\phi_0(0)=1.57$. *Ordinate* $C(t)$; *Abscissa* time steps

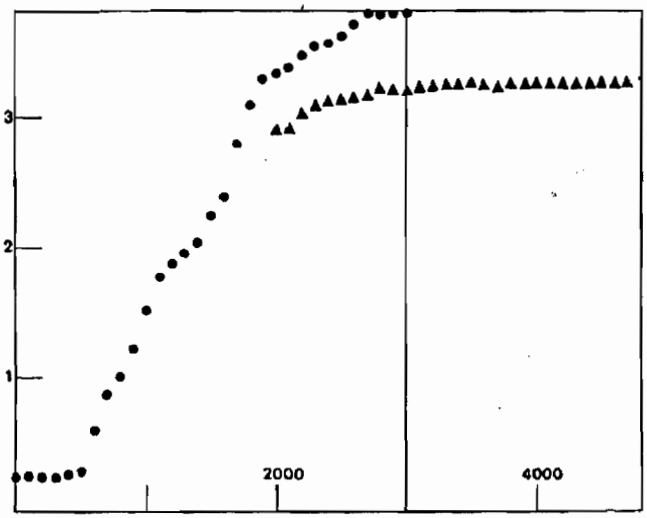

Fig. 1. Melting of the initial lattice in a computer simulation of 108 L-J triatomics. ●220 K, ▲100 K. *Ordinate* total energy (in reduced units), *Abscissa* time steps 1 time step $=10^{-2}$ ps

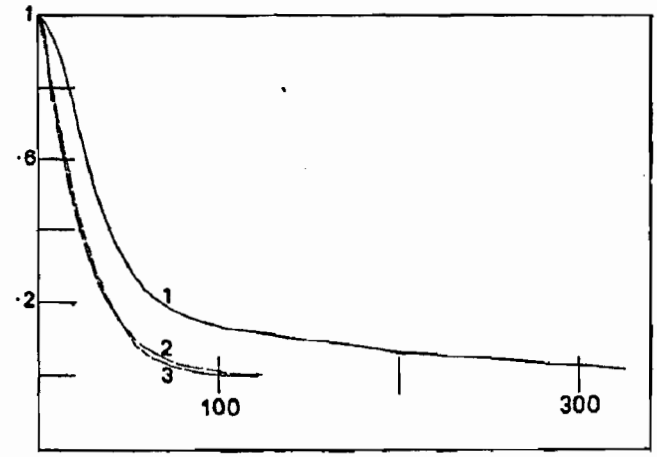

Fig. 3. Simulated (1) and analytical ((2), (3)) autocorrelation functions (2) $\phi_1(0)/\phi_0(0)=1.57$, (3) calculated from a least mean squares best fit. *Ordinate:* $C(t)$; *Abscissa:* time steps

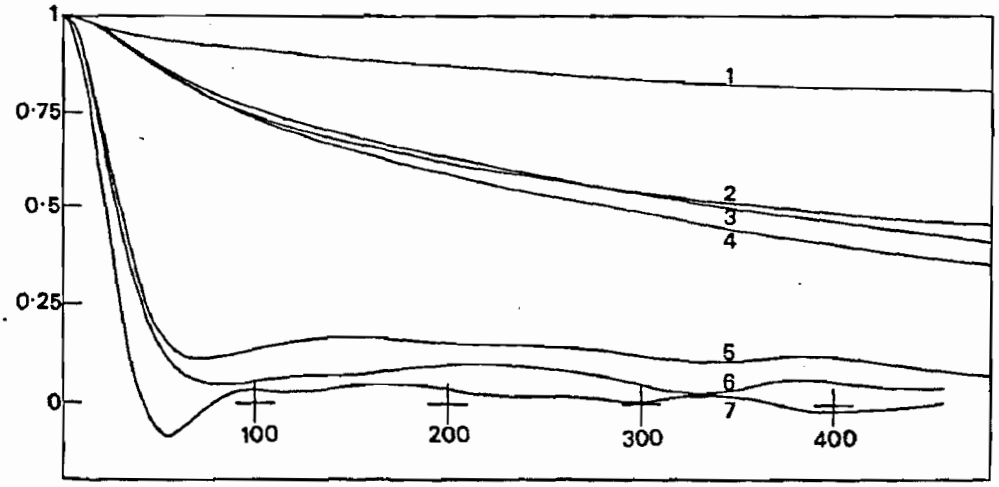

Fig. 4. Simulated autocorrelation functions at 100 K. (1) r_{cm}, centre of mass; (2) e_C; (3) e_B; (4) e_A; (5) J; (6) $\dot{e}_A$; (7) V. Here the e vectors are those along the principal axes of inertia, J is the angular momentum, and V the linear velocity

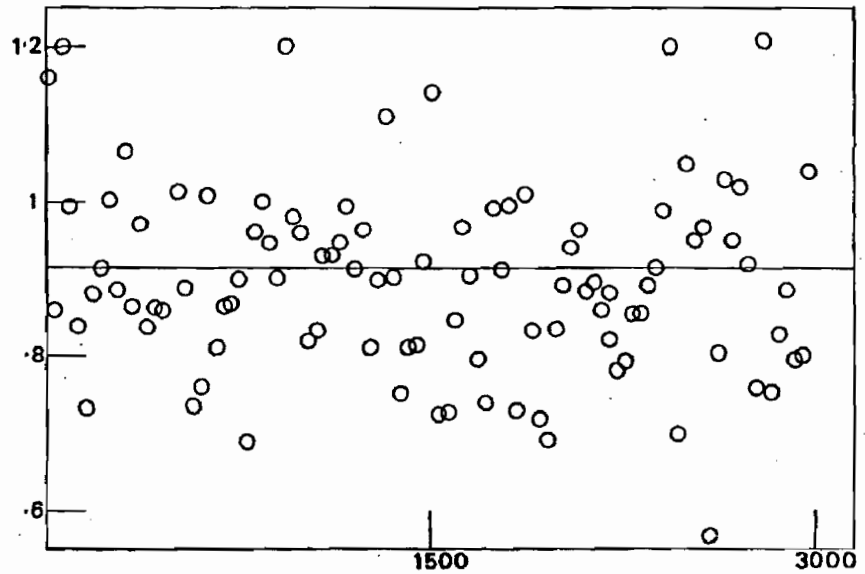

Fig. 5. Simulated mean square torque over 3,000 time steps, the horizontal bar denotes the mean level. *Ordinate:* Mean square torque in reduced units. *Abscissa:* Time steps

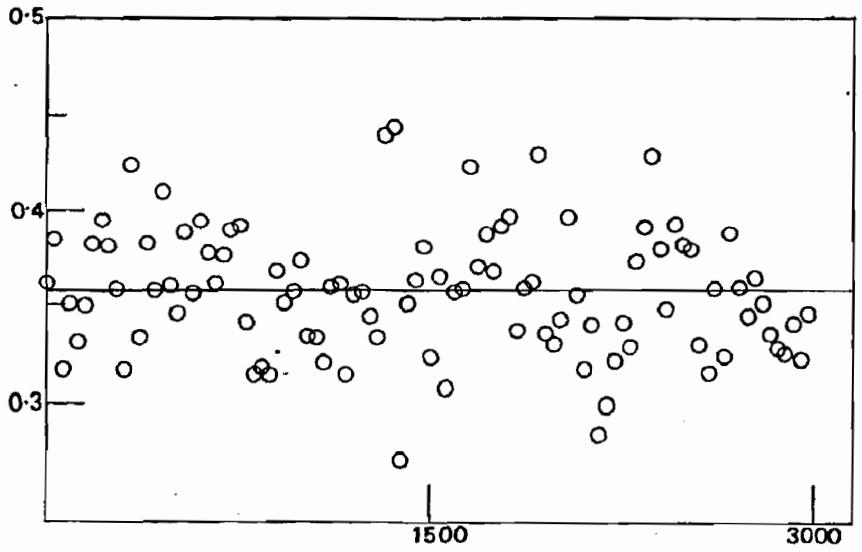

Fig. 6. Simulated mean square angular momentum over 3,000 time steps, as for Fig. 4. *Ordinate:* Mean square angular momentum in reduced units. *Abscissa:* Time steps

trated in Figs. 5 and 6. We have the mean values (in reduced units):

$$\langle \mathbf{J}(0)\cdot\mathbf{J}(0)\rangle = 2.8\times 10^{-19}$$

$$\langle \mathbf{T}_q(0)\cdot\mathbf{T}_q(0)\rangle = 9.1\times 10^{-5}$$

for the asymmetric top. Taking a "spherical-top equivalent" moment of inertia, after Lobo et al., then $\phi_1(0)/\phi_0(0)=1.6$.
By making a three-variable fit on the molecular dynamics data with $\gamma, \phi_0(0)$ and $\phi_1(0)$ as parameters we obtain the result; $\phi_1(0)/\phi_0(0)=67.75/3.2$ and the curves of Figs. 2 and 3.

Discussion

The three-variable interaction fit of Figs. 2 and 3 is such that the orientational a.c.f. is followed well, at least up to the midrange of its decay sequence but only the general features are reproduced for the related a.c.f.'s (rotational velocity, angular velocity and torque). In particular the characteristic negative tail of the rotational velocity a.c.f. is greatly exaggerated. The initial decay of the angular velocity a.c.f. is too sharp analytically. The torque a.c.f. is not, surprisingly, badly reproduced from the orientational a.c.f., the negative lobe being absent in the simulation. As a crude approximation the analysis is fairly useful. As a quantitative measure of its efficiency we can compare the ratio $\phi_1(0)/\phi_0(0)$ from the three variable fit and from the simulation. These are 21.5 and 1.6 respectively. It would clearly be advantageous to have available the rigorous formalism (a generalisation of that of Favro) for the asymmetric top so that the uncertainties caused by linearising the Euler equations (substituting spherical top geometry) can be eliminated. For the present we may conclude that the molecular dynamics method is easily capable of exposing the shortcomings of the three variable Mori model.
In order to improve the analytical treatment it would be advantageous to take into account the asymmetric top nature of the CH_2Cl_2 molecule and to generalise the Favro equation for the probability density function P:

$$\frac{\partial}{\partial t}P(\Omega,t) = -\mathbf{M}\cdot\mathbf{D}\cdot\mathbf{M}\,P(\Omega,t) \tag{17}$$

for rotational diffusion to include inertial and memory effects. Here $\mathbf{D}$ is the diffusion tensor and $\mathbf{M}$ is identical with the quantum mechanical angular momentum operator. In the case of the symmetric top the eigenstates of the diffusion operator $\Gamma=\mathbf{M}\cdot\mathbf{D}\cdot\mathbf{M}$ are provided by the Wigner rotation matrices $D^{(L)}_{MK}(\Omega)$ where $\Omega=(\alpha,\beta,\gamma)$, the set of Euler angles. The results for the asymmetric top may be obtained by a perturbation of those of the symmetric top. If we denote by $|\alpha\rangle$ the eigenstates of the diffusion operator in the case of the symmetric top, the general solution of (17) is:

$$|P(\Omega,t)\rangle = \sum_{\alpha\alpha'} C_{\alpha\alpha'}|\alpha\rangle\langle\alpha|\pi\rangle\langle\tilde{\pi}|\alpha'\rangle e^{-E\pi t}$$

where $|\pi\rangle$ and E_π are eigenstates and eigenvalues of Γ, respectively. The vector $C=(C_1, C_2, \ldots)$ denotes the initial condition of the physical system. The operator is endowed with an eigenvector whose eigenvalue vanishes, the other eigenvalues being represented by positive real numbers. If we look at the state $|A\rangle = (|\alpha_1\rangle, |\alpha_2\rangle, \ldots)$ *Eq.* (17) may be written in the matrix form:

$$\dot{\mathbf{A}} = \Gamma\cdot\mathbf{A}+\mathbf{f} \tag{18}$$

where the rapidly fluctuating force $\mathbf{f}$ can be replaced by its time average, which is vanishing. Inertial and memory effects may now be included by considering (18) as a Markov limit of:

$$\dot{\mathbf{A}} = \int_0^t \Phi(t,\tau)\,\mathbf{A}(\tau)\,d\tau+\mathbf{f}(t) \tag{19}$$

the structure of the "memory kernel" Φ being defined by the continued fraction expansion of its Laplace transform as demonstrated by Mori. By using the continued fraction (19) in turn may be replaced by the multi-Markovian form:

$$\frac{d}{dt}\mathbf{V}(t)+\mathbf{A}\cdot\mathbf{V}(t)+\mathbf{S}\cdot\mathbf{V}(t)=\mathbf{F}(t) \tag{20}$$

as demonstrated by Grigolini and co-workers. In (20) $\mathbf{A}$, $\mathbf{S}$ and $\mathbf{F}$ are, in general, supermatrices (whose elements are themselves matrices), and are defined fully elsewhere. The fluctuation-dissipation theorem corresponding to (20) is defined by:

$$\langle \mathbf{F}(t)\mathbf{F}(s)^T\rangle = 2\gamma S(t-s)$$

It is possible to use (20) to take care of inertial and memory effects by truncating at various levels the supermatrices. The rotational Mori theory will then be parameterised with three decay constants γ of the second memory tensor, together with the equilibrium average $\phi_1(0)$ and $\phi_0(0)$.
The main points of this paper may be summarised as follows.

(1) The simulation of rotational autocorrelation functions by molecular dynamics is a powerful method of exposing the shortcomings of early Mori approximants of the Liouville equation of motion. It may be possible to reproduce fairly accurately one of a set of autocorrelation functions but the others, as in Fig. 2, are not satisfactorily described. Also the computed and l.m.s. fitted ratios $\phi_1(0)/\phi_0(0)$ are not in agreement.

(2) In this respect the molecular dynamics simulation is more incisive than any spectroscopic technique used in isolation, and possibly more so than several in combination. However, the spectra have the advantage of dealing with the real world without first having to model the intermolecular potential.

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References

1. Evans, M.W., Evans, G.J., Davies, A.P.: Adv. Chem. Phys., in press
2. Evans, M.W., Evans, G.J.: J. Chem. Soc. Faraday Trans. 2 **72**, 1169 (1976)
3. Streett, W.B., Gubbins, K.E.: Ann. Rev. Phys. Chem. **28**, 373 (1977)
4. Lobo, R., Robinson, J.E., Rodriguez: J. Chem. Phys. **59**, 5992 (1973)
5. Nee, T.W., Zwanzig, R.: J. Chem. Phys. **52**, 6353 (1970)
6. Kivelson, D., Madden, P.: Mol. Phys. **30**, 1749 (1975)
7. Renaud, J., Singer, K.: Computer Phys. Commun., in press

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