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Physica 111A (1982) 255–272 *North-Holland Publishing Co.*

DIELECTRIC RELAXATION AS A MULTIPLICATIVE STOCHASTIC PROCESS

I. GENERAL THEORY†

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Received 29 July 1981

A rigorous and general approach is developed to the relaxation of molecular dipoles on the microscopic scale, embodied in the orientational time-autocorrelation function. The usual difficulties of using the stochastic Liouville equation (SLE) are bypassed by replacing the cumulant expansion with a continued fraction. This reduces to that of Sack or Gross in the appropriate limit.

The autocorrelation function is formed from approximants of this continued fraction, which is ideally suited for numerical computation, and as a basis for the newly developed technique of semi-stochastic molecular dynamics simulation. The numerical solution automatically produces the spectral moments of interest to order of truncation, so that the number of unknowns is reduced to one at each and every stage of approximation. This concerns the rate of energy dissipation, denoted by β, a scalar, tensor or super-tensor according to the nature of the diffusion process under consideration.

The new continued fraction can be used to describe spatial rotational diffusion of the asymmetric top using the appropriate Fokker–Planck diffusion operator. It is a considerable improvement therefore on a model such as the planar itinerant librator, an approximant of the Mori continued fraction.

1. Introduction

Inertial effects in relaxation processes have been treated rigorously by Sack[1]), who produced a continued fraction expansion of the dielectric response function. The problem has also been considered by Gross[2]) on the basis of a generalised Liouville equation. He obtained the following expression for

† This work was supported in part by the U.S. National Institute of Health Grant No. GM 23942 and Contract No. EY-76-5-05-2690 between the Division of Biomedical and Environmental Research of the Department of Energy and Florida State University. MWE and MF acknowledge financial support from the S.R.C. Grant No. GR/A/8398.5.

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0378-4371/82/0000–0000/$02.75

the frequency response of the polarization:

$$p^*(\omega)/p_0 = 1 - \frac{i\omega}{\beta} \Big/ \left\{ \frac{i\omega}{\beta} + \beta \Big/ \left[1 + \frac{i\omega}{\beta} + 2\beta \Big/ \left(2 + \frac{i\omega}{\beta} + \cdots \right) \right] \right\}. \tag{1.1}$$

This means that although a single microscopic fluctuation mechanism is considered, a macroscopic description (of the far infra-red and dielectric spectrum) in terms of the usual relaxation concepts (Sack) would involve an infinity of discrete relaxation times, whose reciprocals form an arithmetic progression. The leading longest relaxation time (τ_0) is the original one of Debye.

The last decade has seen the evolution of zero-THz frequency dielectric spectroscopy[3-6]) to the point where it has become obvious that eq. (1.1) fails *qualitatively* to serve as a simple description of the observable spectral features in the far infra-red[7]) while seeming to work at lower frequencies. Many explanations have been proffered, based for example on the reduction of the Liouville equation by Mori to a continued fraction. Evans[8]) in 1976 showed that an approximant of Mori's continued fraction corresponded exactly in physical terms with the planar itinerant librator model of Coffey and Calderwood[9]). Subsequently this approximant/model has been examined for its ability to reproduce zero-THz spectra by Evans, Reid et al.[10]) in the liquid and related phases.

Both the phenomenological approximant and the model have several conceptual weaknesses, discussed elsewhere[10]), and in practical terms are hampered by the involvement of too many effectively unknown phenomenological quantities. Perhaps the most pervasive fault in both approaches has been the purely technical necessity of disposing of non-linearities such as those present in the (Euler) equations governing rotation of the asymmetric top in 3 dimensions. This means that itinerant libration was considered in the context of the asymmetric top diffusing with its permanent dipole constrained to two dimensions. This implies, of course, that the Mori approximant is also devoid of non-linearities in the behaviour of the total angular momentum vector $\boldsymbol{J}$ and of the dipole $\boldsymbol{\mu}$. The non-linearities are projected into the noise term of the Mori equation[11]).

Notwithstanding the greatly improved ability of these approximant models (and offshoots[12])) to match the complete zero-THz profile a fresh look at the problem is needed in order (a) to cut down the use of adjustable parameters to the absolute minimum; and (b) to consider rigorously the effect of non-linearities on rotational diffusion.

The technical reasons for the failure in the far infra-red of theories such as those of Sack and Gross, and lately of McConnell and co-workers[13]) is well known by now to be rooted in the nature of β in eq. (1.1). This has evolved

hand in hand with the theory of non-equilibrium statistical mechanics[14]) from a friction coefficient, invariant with time, to a correlation function of the random forces on a diffusing molecule. The new theories inject a sense of history into β which has become a memory function[15]). Yet the implied generalisation of Sack and Gross has not been accomplished, partly because of the difficulty of unravelling the memory function from the linear framework of the Mori continued fraction[16]). Mori's theory works in the context of additive stochastic processes, while those of Sack, Gross, McConnell et al. deal with multiplicative stochastic processes constrained by Markov's hypothesis on β; i.e. its statistical behaviour is taken as independent of past events. Of course at short times (or at f.i.r. frequencies) this conflicts diametrically with the self-evident fact that the "free rotation" of a molecule is governed exclusively by past events according to the fundamental laws of dynamics.

Independently, the non-equilibrium statistical mechanics (classical and quantum) of a very wide range of excitation/relaxation processes has been developing at an ever accelerating pace. The stochastic concepts have been extended to describe intramolecular phenomena such as radiationless decay and fluorescence of molecules excited by transient laser pulses. Lately Grigolini and co-workers have removed[17-28]) some of the conceptual difficulties of linear response theory and have shown also how to remove Markov's constraint by working with multidimensional vectors of dynamically independent variables in both quantum and classical regimes.

The main aim of this paper is to describe a new approach to the evaluation of the spectrum of the variable $\boldsymbol{\mu}$, for example an electric or magnetic dipole moment. The relaxation of $\boldsymbol{\mu}$ is described by:

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \mathrm{i}L_S\boldsymbol{\mu} + \boldsymbol{\Omega}(t) \times \boldsymbol{\mu}, \tag{1.2}$$

where the Liouvillian L_S is concerned with the variable of interest ($\boldsymbol{\mu}$) and $\boldsymbol{\Omega}$, for example a molecular angular velocity or a Larmor frequency, is in turn driven by a Liouvillian L_B as follows:

$$\frac{\mathrm{d}\boldsymbol{\Omega}}{\mathrm{d}t} = \mathrm{i}L_B\boldsymbol{\Omega}. \tag{1.3}$$

Eqs. (1.2) and (1.3) form a multiplicative stochastic system developed by Kubo[14]), who neglects the contribution to the time evolution of $\boldsymbol{\Omega}$ due to the interaction between L_S and L_B. As described in refs. 17 to 28 it has been possible to rewrite the exact motion eq. (1.3) as an additive stochastic, but multidimensional, equation similar in structure to a matrix Langevin equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{A} = \boldsymbol{\Gamma}\mathbf{A} + \boldsymbol{F}, \tag{1.4}$$

where $\mathbf{A}$ is the column vector

$$\mathbf{A} = \begin{pmatrix} f_0 \\ f_1 \\ \vdots \\ f_n \end{pmatrix} \tag{1.5}$$

consisting of the dynamical variables $f_0, f_1, \ldots, f_n (\boldsymbol{\Omega} = f_0)$. The dynamics of f_0 reduce to those of $\boldsymbol{\Omega}$ when $f_1 = \cdots = f_n = 0$, i.e. when $n = 0$ any non-Markov behaviour in $\boldsymbol{\Omega}$ is disregarded.

One of the major benefits[17-28]) of replacing eq. (1.3) with (1.4), and consequently of Mori's equation[8]) with (1.4), is that it enables us to construct easily the Fokker–Planck equation for $\boldsymbol{\Omega}$. We shall denote this by

$$\frac{\mathrm{d}}{\mathrm{d}t} P(\mathbf{A}, \mathbf{A}_0 \,|\, t, 0) = D_{\mathbf{A}} P(\mathbf{A}, \mathbf{A}_0 \,|\, t, 0), \tag{1.6}$$

where $D_{\mathbf{A}}$ is the diffusion operator and P a conditional probability.

Eqs. (1.2) and (1.3) represent the theory[14,25,29]) of the stochastic Liouville equation (SLE), whose major feature consists of replacing the Liouvillian L_B with the diffusion operator of the stochastic variable $\boldsymbol{\Omega}$. If use is made of suitable left-eigenstates[5,14]) eq. (1.3) may be rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{\Omega} = D_{\boldsymbol{\Omega}}\boldsymbol{\Omega} \tag{1.7}$$

($D_{\boldsymbol{\Omega}}$ denotes the usual Markoffian diffusion operator), where $\boldsymbol{\Omega}$ is now regarded as an operator in the space spanned by the eigenstates of $D_{\boldsymbol{\Omega}}$. In ref. 19 it was demonstrated that SLE theory may be generalised to non-Markov $\boldsymbol{\Omega}$ by replacing eq. (1.7) with

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\boldsymbol{\Omega}} = D_{\mathbf{A}}\hat{\boldsymbol{\Omega}}. \tag{1.8}$$

Eq. (1.2) may then be written as

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \hat{\mathscr{L}}_0\boldsymbol{\mu} \tag{1.9}$$

where

$$\begin{aligned}\hat{\mathscr{L}}_0 &= \mathrm{i}L_S + \mathscr{L}_1 + D_{\mathbf{A}} \\ &\equiv \mathrm{i}L_S + \hat{\boldsymbol{\Omega}}\times + D_{\mathbf{A}}.\end{aligned} \tag{1.10}$$

It is important to note that $\hat{\mathcal{L}}_0$ is a dynamical operator *which is neither hermitian nor antihermitian.*

Eq. (1.10) expresses the generalised SLE in operator form[19]). In ref. 19 it was used to deal with a column vector with a single element only. From a purely computational point of view the mathematical approach of ref. 19 rapidly becomes intractable as elements are added to the column vector of interest (i.e. as $\boldsymbol{\mu}$, for example, becomes multidimensional or non-Markovian). This is because the problem is dealt with by building up the diffusion equation for the process involving both $\boldsymbol{\mu}$ and $\boldsymbol{\Omega}$. This makes the numerical diagonalisation of the diffusion operator a costly business in terms of time and storage.

Nee and Zwanzig[30]) have studied the problem[31]) of calculating the autocorrelation function of the variable $\boldsymbol{\mu}$ of eq. (1.2) when $L_S = 0$. They found that the correlation function may be described by the following non-Markov equation:

$$\frac{\partial}{\partial t}\langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}(t)\rangle = -2\int_0^t \mathrm{d}s \boldsymbol{D}(t-s)\langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}(s)\rangle, \tag{1.11}$$

where $\boldsymbol{D}(t)$ is obtained from the inverse Laplace transform of the tensor:

$$\boldsymbol{D}(\omega) = \mathscr{L}\langle \boldsymbol{\Omega}\boldsymbol{\Omega}(t)\rangle \tag{1.12}$$

in an isotropic sample of dielectric.

In section 2 we generalise the equations used by Nee and Zwanzig (NZ) en route to developing a solution to (1.10) suitable for application on a computer. This reduces to NZ when $\boldsymbol{\mu}$ is Markovian. The new solution contains matrices which can be diagonalised in a way depending only on the size of $\boldsymbol{A}$ without the added difficulty of degrees of freedom resulting from the inclusion of $\boldsymbol{\Omega}$ in the set of stochastic variables.

In a forthcoming paper we shall apply the new theory to zero-THz results using a fast FORTRAN algorithm capable of calculating to any order the spectral moments of $\langle \boldsymbol{\mu}\boldsymbol{\mu}(0)\rangle$ (as defined by Gordon[32]) from successive approximants of a continued fraction which is a generalisation of that of Sack or Gross. We note that the latter leave all spectral moments undefined. The theory of section 2 is in fact effective in building up a general algorithm for many fields of excitation/relaxation, including that of semi-stochastic computer simulation[33]) of molecular dynamics.

2. General theory

In section 1 we defined the problem of evaluating the spectrum of a variable μ governed by eq. (1.9). Mori[11]) develops the solution through a continued fraction which is valid *only when the dynamical operator $\mathscr{L}_0$ is antihermitian.* In appendix A we show that Mori's solution can be generalised to involve the use of non-hermitian Liouvillians. This seemingly trivial extension has wide reaching practical implications which include:

i) the development of a zero-THz theory with none of the disadvantages of section 1;

ii) the development of a rapidly convergent continued fraction for use in semi-stochastic simulations.

Define the ket or state $|f_0\rangle$ as (the state $|p_0(\Omega)\rangle$ is the equilibrium eigenstate of D_A, i.e., $D_A|p_0\rangle = 0$ and $\langle\tilde{p}_0|$ is its left conjugate):

$$|f_0\rangle = \mu|p_0(\Omega)\rangle. \tag{2.1}$$

If we write eq. (A.47) for $k = 0$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_0\rangle = -\int_0^t |f_0(s)\rangle\Delta_1\Phi_1(t-s)\,\mathrm{d}s + |f_1(t)\rangle. \tag{2.2}$$

As shown in appendix A this is obtained with a suitable definition of scalar products. If the state $|f_0\rangle$ is to be given by eq. (2.1) it is convenient to define the scalar product as follows. Take the observables α and β as

$$\alpha = \varphi(\gamma)f(A), \tag{2.3}$$

$$\beta = \psi(\gamma)q(A), \tag{2.3'}$$

where γ is the physical space of the variable μ. Then the scalar product is

$$\langle\beta \mid \alpha\rangle = \left\{\int \mathrm{d}\gamma\psi^*(\gamma)\cdot\varphi(\gamma)w_0(\gamma)\right\}\langle\tilde{p}_0|q^*(A)f(A)|p_0\rangle, \tag{2.4}$$

where $w_0(\gamma)$ is the equilibrium distribution.

Eq. (2.2) is an important result whose physical meaning is as follows. It is possible to replace a multiplicative stochastic process[34]) with an additive one provided that we introduce a memory kernel. In other words, a non-additive stochastic process is equivalent to a non-Markovian one. Similar results have been indicated by Mori and Fujisaka[35]) and by Hynes[36]).

The major advantage of the theory in appendix A is embodied in the continued fraction, eq. (A.44), which is the key to fast computation of the spectrum of variables satisfying eq. (1.2). This result is as easily applicable to EPR spectroscopy[29]) as it is to dielectric relaxation, and is directly compar-

able to perturbation theories such as that of ref. 29. This will be the subject of a future numerical paper.

The application of the generalised SLE to relaxation involving rotational Brownian motion consists therefore of replacing eq. (1.2) with (2.2).

In order to emphasise the generality of this procedure we point out the physical conditions required to obtain from eq. (2.2) the results by Nee and Zwanzig[30]). Firstly we have to assume that part of the total hamiltonian is zero, $L_S = 0$. This is always the case for dielectric relaxation.

Because

$$D_A|p_0(A)\rangle = 0, \tag{2.5}$$

then by using eq. (A.8) we can write

$$\begin{aligned} |f_n\rangle &= (1-P)(iL_1 + D_A)|f_0\rangle \\ &= (1-P)\, iL_1|f_0). \end{aligned} \tag{2.6}$$

We also have

$$\langle p_0(A)|\Omega|p_0(A)\rangle = 0. \tag{2.6'}$$

This is because the physical meaning of this matrix element is the average value of the molecular angular velocity at equilibrium.

We can write the memory kernel of eq. (2.2) as follows:

$$\begin{aligned} \Delta_1\Phi_1(t) &= -\langle\tilde{f}_0|f_0\rangle^{-1}\langle\tilde{f}_1|f_1\rangle\langle\tilde{f}_1|f_1\rangle^{-1} \\ &\quad \times \langle\tilde{f}_0|\, i\mathscr{L}_1(1-P)\exp\{(1-P)\mathscr{L}_0 t\}\mathscr{L}_0|f_0\rangle \\ &= -\langle f_0|f_0\rangle^{-1}\langle f_0|\mathscr{L}_0(1-P)\exp\{(1-P)\mathscr{L}_0 t\}\mathscr{L}_1|f_0\rangle. \end{aligned} \tag{2.7}$$

To obtain the result of NZ we must assume

$$e^{(1-P)\mathscr{L}_0 t} = e^{D_A t} \tag{2.8}$$

and using eq. (2.6)

$$\Delta_1\Phi_1(t) = -\langle f_0|f_0\rangle^{-1}\langle f_0|\Omega \times \Omega(t) \times \mu|p_0(\Omega)\rangle). \tag{2.9}$$

In an isotropic specimen

$$\langle\mu\mu\rangle = \mathbf{I}\langle\mu^2\rangle, \tag{2.10}$$

where $\mathbf{I}$ is the identity matrix and $\langle\cdots\rangle$ denote an average evaluated as follows:

$$\langle\mu_i\mu_j\rangle = \int d\gamma\mu_i(\gamma)\mu_i(\gamma). \tag{2.11}$$

If we apply the definition of scalar product given in eq. (2.4), we obtain

$$\langle f_0|f_0\rangle = \mathbf{I}\langle\mu_i^2\rangle.$$

By applying again the definition of eq. (2.4) and the isotropic assumption we have

$$\langle f_0|\boldsymbol{\Omega}\times\boldsymbol{\Omega}(t)\times\boldsymbol{\mu}|p_0(\boldsymbol{\Omega})\rangle_{xx}$$
$$=\langle p_0|\int d\gamma\mu_x(\gamma)[\Omega_y(\Omega_x(t)\mu_y-\Omega_y(t)\mu_x)$$
$$-\Omega_z(\Omega_z(t)\mu_x-\Omega_x(t)\mu_z)]|p_0\rangle$$
$$=-2\langle\mu_i^2\rangle\langle\Omega\Omega(t)\rangle. \tag{2.12}$$

In order to obtain this result we have assumed that the rotator is a spherical top. Consequently:

$$\Delta_1\Phi_1(t)=2\langle\Omega\Omega(t)\rangle, \tag{2.13}$$

which is the result of Nee and Zwanzig.

Eq. (2.8) is an approximation which can only be valid when $\mathscr{L}_1$ is small compared with D_A. In other words, the result by NZ is correct only as μ tends to the limit of Markovian behaviour. Any continued fraction based on (1.11), such as that of Quentrec and Bezot[37]), is not realistic in any other limit, as has been pointed out by Evans et al.[3–5]), who have tested out the continued fraction expansion of eq. (1.11) with zero-THz spectroscopy. This is fully in agreement with a recent paper by Ferrario and Evans[26]) who used a less efficient cumulant-based theory (appendix B). The neglect of cumulants of higher order than the second is incorrect (appendix B) when the stochastic variable $\boldsymbol{\Omega}$ is multidimensional.

The theory of appendix A and this section is unaffected by any inaccuracy of this kind and can be regarded as a general and rigorous approach to the problem of dielectric relaxation as considered originally by Sack or Gross. In particular we can avoid the use of cumulant expansion when attempting to relate $\langle\boldsymbol{\Omega}(t)\boldsymbol{\Omega}(0)\rangle$ and $\langle\boldsymbol{\mu}(t)\boldsymbol{\mu}(0)\rangle$, for 3-D diffusion a hideously complicated problem. We would also like to stress the fact that in principle we have no need even to assume that the stochastic variable $\boldsymbol{\Omega}$ is Gaussian (a prerequisite of cumulant methods[26]) when we have available the relevant Fokker–Planck equation.

In a subsequent paper we shall evaluate $\langle\boldsymbol{\mu}(t)\boldsymbol{\mu}(0)\rangle$ and $\langle\boldsymbol{\Omega}\boldsymbol{\Omega}(t)\rangle$ numerically as indicated in this section. To indicate the nature of the specific calculation we provide here explicit expressions for $\boldsymbol{\lambda}_0$, $\boldsymbol{\Delta}_1^2$ and $\boldsymbol{\lambda}_1$ as defined by eqs. (A.36) and (A.41), from which:

$$\boldsymbol{\lambda}_0=0, \tag{2.14}$$

$$\boldsymbol{\Delta}_1^2=\begin{pmatrix}\langle\bar{p}_0|\Omega_y^2|p_0\rangle+\langle\bar{p}_0|\Omega_z^2|p_0\rangle, & -\langle\bar{p}_0|\hat{\Omega}_y\hat{\Omega}_x|p_0\rangle, & -\langle\bar{p}_0|\hat{\Omega}_z\hat{\Omega}_x|p_0\rangle\\ -\langle\bar{p}_0|\hat{\Omega}_x\hat{\Omega}_y|p_0\rangle, & \langle\bar{p}_0|\Omega_z^2|p_0\rangle+\langle\bar{p}_0|\Omega_x^2|p_0\rangle, & -\langle\bar{p}_0|\hat{\Omega}_z\hat{\Omega}_y|p_0\rangle\\ -\langle\bar{p}_0|\hat{\Omega}_x\hat{\Omega}_z|p_0\rangle, & -\langle\bar{p}_0|\hat{\Omega}_y\hat{\Omega}_z|p_0\rangle, & \langle\bar{p}_0|\Omega_x^2|p_0\rangle+\langle\bar{p}_0|\Omega_y^2|p_0\rangle\end{pmatrix} \tag{2.15}$$

$$\boldsymbol{\lambda}_1 = (\boldsymbol{\Delta}_1^2)^{-1} \begin{pmatrix} \sum_i \langle \bar{p}_0|\hat{\Omega}_y|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_y|p_0\rangle & -\sum_i \langle \bar{p}_0|\hat{\Omega}_y|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_x|p_0\rangle & -\sum_i \langle \bar{p}_0|\hat{\Omega}_z|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_x|p_0\rangle \\ +\sum_i \langle \bar{p}_0|\hat{\Omega}_z|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_z|p_0\rangle & & \\ -\sum_i \langle \bar{p}_0|\hat{\Omega}_x|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_y|p_0\rangle & \sum_i \langle \bar{p}_0|\hat{\Omega}_z|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_z|p_0\rangle & -\sum_i \langle \bar{p}_0|\hat{\Omega}_z|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_y|p_0\rangle \\ & +\sum_i \langle \bar{p}_0|\hat{\Omega}_x|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_x|p_0\rangle & \\ -\sum_i \langle \bar{p}_0|\hat{\Omega}_x|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_z|p_0\rangle & -\sum_i \langle \bar{p}_0|\hat{\Omega}_y|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_z|p_0\rangle & \sum_i \langle \bar{p}_0|\hat{\Omega}_z|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_x|p_0\rangle \\ & & +\sum_i \langle \bar{p}_0|\hat{\Omega}_y|p_i\rangle E_i \langle \bar{p}_i|\hat{\Omega}_y|p_0\rangle \end{pmatrix} \tag{2.16}$$

where the E_i's and the $|p_i\rangle$'s are the eigenvalues and the eigenvectors respectively of the diffusion operator D_A defined by

$$D_A|p_i\rangle = E_i|p_i\rangle. \tag{2.17}$$

The order of magnitude of the matrix $\boldsymbol{\Delta}_1^2$ is that of the mean square molecular angular velocity. The matrix $\boldsymbol{\lambda}_1$ has the same order of magnitude as the rate of energy dissipation of the molecule. When $|\boldsymbol{\Delta}_1| < |\boldsymbol{\lambda}_1|$ the truncation results from assuming $\boldsymbol{\Delta}_2^2 = 0$. This is a "medium memory" case. When the memory is small, $|\boldsymbol{\Delta}_1| \ll |\boldsymbol{\lambda}_1|$ is equivalent to the Markov limit. A strong dynamical memory (such as in the free rotor limit) will require the evaluations of several subsequent contributions, a straightforward numerical procedure, which automatically gives up the spectral moments $\boldsymbol{\Delta}_1^2, \boldsymbol{\Delta}_2^2, \ldots, \boldsymbol{\Delta}_n^2$, i.e. provides sum rules to order n.

Finally we would like to emphasise the relation between the generalised continued fraction, eq. (A.44) and that of Kubo, Gross or Sack. Kubo[14] showed that in the monodimensional case when D_A can be replaced by the Fokker–Planck operator,

$$D_\Omega = \beta \frac{\partial}{\partial \Omega}\left(\Delta^2 \frac{\partial}{\partial \Omega} + \Omega\right), \tag{2.18}$$

we have the well-known result

$$\langle \mu\mu(t)\rangle / \langle \mu^2\rangle = \exp\left[-\frac{\Delta^2}{\beta^2}\left(e^{-\beta t} - 1 + \beta t\right)\right], \tag{2.19}$$

providing the bandshape

$$I(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty \exp\left[-\frac{\Delta^2}{\beta^2}(e^{-\beta t} - 1 + \beta t) - i\omega t\right] dt. \tag{2.20}$$

Kubo shows that this can be replaced by the continued fraction

$$I(\omega) = \frac{1}{\pi} \cfrac{1}{i\omega + \Delta^2 + \cfrac{\beta + 2\Delta^2}{i\omega + 2\beta + \cdots}} \tag{2.21}$$

In appendix C we show that in this, the simplest case of isotropic rotational diffusion, or when any of the matrices $\boldsymbol{\lambda}_i$ and $\boldsymbol{\Delta}_i^2$ are diagonal, eq. (A.44) reduces to eq. (2.21), which is Sack's eq. (4.11).

As far as the state of the art in this field is concerned the most significant recent reference is to the work of McConnell et al.[13a]), who re-derived eq. (2.21) for planar rotational diffusion. Subsequently Ford et al.[13b]) extended the calculation for the asymmetric top to a higher order of approximation. Without a higher dimensionality (or memory) the latter theories are not suitable for experimental application[4]).

Acknowledgement

S.R.C. is thanked for financial support.

Appendix A

We shall generalise the continued fraction expansion of Mori to the general case where the equation of motion

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{A} = \mathscr{L}_0 \boldsymbol{A} \tag{A.1}$$

involves a dynamical operator $\mathscr{L}_0$ which is neither hermitian nor anti-hermitian.

We shall use a quantum-like formalism where the scalar product between two observables $\boldsymbol{B}$ and $\boldsymbol{C}$ is denoted by $\langle \boldsymbol{B} \mid \boldsymbol{C} \rangle$. The "state" $|\boldsymbol{C}\rangle$ is the usual hermitian conjugate of the operator $\boldsymbol{C}$.

We shall build up a chain of "states", the first of which is

$$|f_0\rangle = |\boldsymbol{A}\rangle. \tag{A.2}$$

According to the quantum-like formalism introduced above we can write the starter projection operator P_0 as follows:

$$\boldsymbol{P}_0 = |f_0\rangle\langle f_0 \mid f_0\rangle^{-1}\langle f_0|. \tag{A.3}$$

We can then write

$$|f_0(t)\rangle = P_0|f_0(t)\rangle + (1-P_0)|f_0(t)\rangle$$
$$= |f_0\rangle\Phi_0(t) + |f_0'(t)\rangle, \tag{A.4}$$

where

$$\Phi_0(t) = \langle f_0 \mid f_0\rangle^{-1}\langle f_0 \mid f_0(t)\rangle \tag{A.5}$$

and

$$|f_0'(t)\rangle = (1-P_0)|f_0(t)\rangle \tag{A.6}$$

By using the following definitions:

$$\mathscr{L}_1 = (1-P_0)\mathscr{L}_0 \tag{A.7}$$

$$|f_1\rangle = \mathscr{L}_1|f_0\rangle \tag{A.8}$$

and from eqs. (A.1), (A.4) and (A.6) we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_0'(t)\rangle = \mathscr{L}_1|f_0'(t)\rangle + |f_1(t)\rangle\Phi_0(t). \tag{A.9}$$

It is convenient to define

$$|f_1(t)\rangle = \exp\{\mathscr{L}_1 t\}\mathscr{L}_1|f_0\rangle = \mathscr{L}_1\exp\{\mathscr{L}_1 t\}|f_0\rangle. \tag{A.10}$$

From eq. (A.9) we obtain

$$|f_0'(t)\rangle = \int_0^t |f_1(t-s)\rangle\Phi_0(s)\,\mathrm{d}s. \tag{A.11}$$

Eq. (A.4) may therefore be written as

$$|f_0(t)\rangle = |f_0\rangle\Phi_0(t) + \int_0^t |f_1(t-s)\rangle\Phi_0(s)\,\mathrm{d}s. \tag{A.12}$$

In order to extend this result to kth generator state we define

$$|f_k\rangle = \mathscr{L}_k|f_{k-1}\rangle, \tag{A.13}$$

$$|f_k(t)\rangle = \exp\{\mathscr{L}_k t\}\mathscr{L}_k|f_{k-1}\rangle, \tag{A.14}$$

where

$$\mathscr{L}_k = (1-P_{k-1})\mathscr{L}_{k-1}. \tag{A.15}$$

From eqs. (A.13) and (A.15) we obtain

$$|f_k\rangle = (1-P_{k-1})(1-P_{k-2})\cdots(1-P_0)\mathscr{L}_0|f_{k-1}\rangle. \tag{A.16}$$

It is convenient to define a left-state to be associated with the right-state $|f_k\rangle$ in the following way:

$$\langle\tilde{f}_k| = \langle\tilde{f}_{k-1}|\mathscr{L}_0(1-P_0)\cdots(1-P_{k-2})(1-P_{k-1}) \tag{A.17}$$

and

$$\langle\tilde{f}_0| = \langle f_0|. \tag{A.17'}$$

The 'projection operator' P_k can then be written as

$$P_k = |f_k\rangle\langle\tilde{f}_k|f_k\rangle^{-1}\langle\tilde{f}_k|, \tag{A.18}$$

which, of course, satisfies the indempotence property

$$P_k^2 = P_k. \tag{A.19}$$

When $\mathscr{L}_0$ is not hermitian, however, the hermitian property of the projection operators is also lost. In the following we shall have to avoid the use of this property. We shall only use eq. (A.19) and

$$P_kP_{k'} = P_{k'}P_k. \tag{A.20}$$

The validity of eq. (A.20), in turn, depends on the fact that, by construction, the vectors $|\tilde{f}_k\rangle$ are orthogonal to the vectors $|f_{k'}\rangle$ eq. (A.16) according to the formula

$$\langle\tilde{f}_k|f_{k'}\rangle = 0, \quad \text{for} \quad k \neq k'. \tag{A.21}$$

By repeating the approach which led us to eq. (A.12) at k'th-order we obtain

$$|f_k(t)\rangle = |f_k\rangle\Phi_k(t) + \int_0^t |f_{k+1}(t-s)\rangle\Phi_k(s)\,\mathrm{d}s, \tag{A.22}$$

where

$$\Phi_k(t) = \langle\tilde{f}_k \mid f_k\rangle^{-1}\langle\tilde{f}_k \mid f_k(t)\rangle. \tag{A.22}$$

We focus our attention now on the following equation of motion:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\tilde{f}_0(t)| = \langle\tilde{f}_0(t)|\mathscr{L}_0. \tag{A.23}$$

Its solution is given by

$$\langle\tilde{f}_0(t)| = \langle\tilde{f}_0|\,\mathrm{e}^{\mathscr{L}_0t} = \langle f_0|\,\mathrm{e}^{\mathscr{L}_0t}. \tag{A.24}$$

The vector $\langle\tilde{f}_0(t)|$ is *not* the usual dual vector associated with $|f_0(t)\rangle$, i.e. is *not*

$$\langle f_0(t)| = \langle f_0|\exp\{\mathscr{L}_0^\dagger t\}. \tag{A.25}$$

Therefore, in the hermitian case of ref. 8 we have

$$\langle\tilde{f}_0(t)| = \langle f_0(-t)|. \tag{A.26}$$

If we define

$$\langle \tilde{f}_k(t)| = \langle \tilde{f}_{k-1}|\tilde{\mathscr{L}}_k \exp\{\tilde{\mathscr{L}}_k t\}, \tag{A.27}$$

where

$$\tilde{\mathscr{L}}_k = \tilde{\mathscr{L}}_{k-1}(1 - P_{k-1}) \tag{A.28}$$

and

$$\tilde{\mathscr{L}}_0 = \mathscr{L}_0, \tag{A.28'}$$

we can obtain the left equation corresponding to eqn. (A.12):

$$\langle \tilde{f}_0(t)| = \tilde{\boldsymbol{\Phi}}_k(t)\langle \tilde{f}_k| + \int_0^t \tilde{\boldsymbol{\Phi}}_k(s)\langle \tilde{f}_{k+1}(t-s)|\, ds, \tag{A.29}$$

where

$$\tilde{\boldsymbol{\Phi}}(s) = \langle \tilde{f}_k(t)|f_k\rangle\langle \tilde{f}_k|f_k\rangle^{-1}. \tag{A.30}$$

Eqs. (A.19) and (A.20) give

$$\tilde{\boldsymbol{\Phi}}_k(t)\langle \tilde{f}_k \mid f_k\rangle = \langle \tilde{f}_k \mid f_k\rangle \boldsymbol{\Phi}_k(t), \tag{A.31}$$

or

$$\langle \tilde{f}_k \mid f_k\rangle^{-1}\tilde{\boldsymbol{\Phi}}_k(t) = \boldsymbol{\Phi}_k(t)\langle \tilde{f}_k \mid f_k\rangle^{-1} \tag{A.31'}$$

and

$$\langle \tilde{f}_k| \exp\{\mathscr{L}_k t\}|f_{k+1}\rangle = \langle \tilde{f}_k|\, e^{\tilde{\mathscr{L}}_k t}|f_{k+1}\rangle = \langle \tilde{f}_k(t)|f_{k+1}\rangle. \tag{A.32}$$

For example, by expanding in series the exponential operator:

$$\begin{aligned}
&\langle \tilde{f}_k| \exp\{\mathscr{L}_k t\}|f_{k+1}\rangle = \langle \tilde{f}_{k-1}|\mathscr{L}_0(1-P_0)\cdots(1-P_{k-1}) \\
&\times \exp\{(1-P_{k-1})\cdots(1-P_0)\mathscr{L}_0 t\}(1-P_k)\cdots(1-P_0)\mathscr{L}_0|f_k\rangle \\
&= \sum_{l=0}^{\infty} \frac{t^l}{l!}\langle \tilde{f}_{k-1}|\mathscr{L}_0(1-P_0)\cdots(1-P_{k-1})_{l \text{ times}} \\
&\times \overbrace{[(1-P_{k-1})\cdots(1-P_0)\mathscr{L}_0(1-P_{k-1})\cdots(1-P_0)\mathscr{L}_0(1-P_{k-1})\cdots(1-P_0)\mathscr{L}_0]} \\
&\times (1-P_k)\cdots(1-P_0)\mathscr{L}_0|f_k\rangle \\
&= \sum_{l=0}^{\infty} \frac{t^l}{l!}\langle \tilde{f}_{k-1}|\mathscr{L}_0(1-P_0)\cdots(1-P_{k-1}) \\
&\times \overbrace{[\mathscr{L}_0(1-P_0)\cdots(1-P_{k-1})\mathscr{L}_0\cdots(1-P_0)\cdots(1-P_{k-1})\mathscr{L}_0]}^{l \text{ times}} \\
&\times (1-P_0)(1-P_1)\cdots(1-P_{k-1})(1-P_k)(1-P_{k-1})\cdots(1-P_0)\mathscr{L}_k|f_k\rangle \\
&= \langle \tilde{f}_{k-1}|\mathscr{L}_0(1-P_0)\cdots(1-P_{k-1}) \\
&\times \exp\{\tilde{\mathscr{L}}_k t\}(1-P_k)(1-P_{k-1})\cdots(1-P_0)\mathscr{L}_0|f_k\rangle \\
&= \langle \tilde{f}_k|\, e^{\tilde{\mathscr{L}}_k t}|f_{k+1}\rangle.
\end{aligned} \tag{A.33}$$

From eq. (A.14) we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_k(t)\rangle = \mathscr{L}_k|f_k(t)\rangle = \exp\{\mathscr{L}_k t\}\mathscr{L}_k|f_k\rangle. \tag{A.34}$$

By using eq. (A.13), and the property $1 = P_k + (1 - P_k)$, eq. (A.34), in turn, can be written as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_k(t)\rangle = \exp\{\mathscr{L}_k t\}|f_k\rangle\lambda_k + \exp\{\mathscr{L}_k t\}|f_{k+1}\rangle, \tag{A.35}$$

where

$$\lambda_k = \langle\tilde{f}_k \mid f_k\rangle^{-1}\langle\tilde{f}_k|\mathscr{L}_k|f_k\rangle. \tag{A.36}$$

Eq. (A.35) can also be written in the following useful form:

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_k(t)\rangle = |f_k(t)\rangle\lambda_k + |f_k\rangle\langle\tilde{f}_k|f_k\rangle^{-1}\langle\tilde{f}_k|\exp\{\mathscr{L}_k t\}|f_{k+1}\rangle + (1 - P_k)\exp\{\mathscr{L}_k t\}|f_{k+1}\rangle. \tag{A.37}$$

Eq. (A.32) allows us to replace eq. (A.37) with

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_k(t)\rangle = |f_k(t)\rangle\lambda_k + |f_k\rangle\langle\tilde{f}_k|f_k\rangle^{-1}\langle\tilde{f}_k(t)|f_{k+1}\rangle + (1 - P_k)\exp\{\mathscr{L}_k t\}|f_{k+1}\rangle. \tag{A.38}$$

By inserting eq. (A.29) into eq. (A.38) we obtain

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}|f_k(t)\rangle &= |f_k(t)\rangle\lambda_k + |f_k\rangle\langle\tilde{f}_k \mid f_k\rangle^{-1}\int_0^t \tilde{\Phi}_k(s)\langle\tilde{f}_{k+1}(t-s)|f_{k+1}\rangle \\ &\quad + (1 - P_k)\exp\{\mathscr{L}_k t\}|f_{k+1}\rangle \\ &= |f_k(t)\rangle\lambda_k + \int_0^t |f_k\rangle\langle\tilde{f}_k \mid f_k\rangle^{-1}\tilde{\Phi}_k(s)\Phi_{k+1}(t-s) \\ &\quad \times\langle\tilde{f}_{k+1} \mid f_{k+1}\rangle\,\mathrm{d}s + (1 - P_k)\exp\{\mathscr{L}_k t\}|f_{k+1}\rangle\end{aligned} \tag{A.39}$$

and by using eq. (A.31)

$$\frac{\mathrm{d}}{\mathrm{d}t}|f_k(t)\rangle = |f_k(t)\rangle\lambda_k - |f_k\rangle\int_0^t \Phi_k(s)\Delta_{k+1}^2\Phi_{k+1}(t-s)\,\mathrm{d}s + (1 - P_k)\exp\{\mathscr{L}_k t\}|f_{k+1}\rangle, \tag{A.40}$$

where

$$\Delta_{k+1}^2 = -\langle\tilde{f}_k|f_k\rangle^{-1}\langle\tilde{f}_{k+1}|f_{k+1}\rangle. \tag{A.41}$$

By multiplying eq. (A.40) on the left by

$$\langle \tilde{f}_k \mid \tilde{f}_k \rangle^{-1} \langle \tilde{f}_k |,$$

we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t} \Phi_k(t) = \Phi_k(t)\lambda_k - \int_0^t \Phi_k(s)\Delta_{k+1}^2 \Phi_{k+1}(t-s)\,\mathrm{d}s, \tag{A.42}$$

which gives by Laplace transformation

$$\hat{\Phi}_k(z) = \Phi_k(0)(z - \lambda_k + \Delta_{k+1}^2 \hat{\Phi}_{k+1}(z))^{-1}. \tag{A.43}$$

The Laplace transform of the correlation matrix of the variable of interest, $\Phi_0(t)$, is thus given by

$$\hat{\Phi}_0(z) = \cfrac{1}{z - \lambda_0 + \Delta_1^2 \cfrac{1}{z - \lambda_1 + \Delta_2^2 \cfrac{1}{z - \lambda_2 + \Delta_3^2 \ddots \Delta_n^2 \cfrac{1}{z - \lambda_{n-1} + \Delta_n^2 \hat{\Phi}_n(z)}}}} \tag{A.44}$$

This result is more general than that of Mori because the parameters λ_i and Δ_i^2 are complex numbers with, in general, non-vanishing real *and* imaginary parts.

We can easily find a generalised equation in motion for the variables $|f_1\rangle$. By taking the Laplace transform of eq. (A.22),

$$|\hat{f}_k(z)\rangle = |f_k\rangle \hat{\Phi}_k(z) + |\hat{f}_{k+1}(z)\rangle \hat{\Phi}_k(z), \tag{A.45}$$

and inserting in eq. (A.43), we get

$$|\hat{f}_k(z)\rangle = (|f_k\rangle + |\hat{f}_{k+1}(z)\rangle)(z - \lambda_k + \Delta_{k+1}^2 \hat{\Phi}_{k+1}(z))^{-1} \tag{A.46}$$

and

$$z|\hat{f}_n(z)\rangle - |f_k\rangle = |f_k(z)\rangle(\lambda_k - \Delta_k^2 \Phi_{k+1}(z)) + |\hat{f}_{k+1}(z)\rangle. \tag{A.46'}$$

Inverse Laplace transformation gives, finally,

$$\frac{\mathrm{d}}{\mathrm{d}t} |f_k(t)\rangle = |f_k(t)\rangle \lambda_k - \int_0^t |f_k(s)\rangle \varphi_k(t-s)\,\mathrm{d}s + |f_{k+1}(t)\rangle, \tag{A.47}$$

where

$$\varphi_k(s) = \Delta_k^2 \Phi_{k+1}(s).$$

Appendix B

Assuming $\Omega(t)$ to be a stochastic process, cumulants can be used to solve the kinetic relation

$$\dot{u}(t) = \Omega(t) \times u(t), \tag{B.1}$$

which defines $u(t)$, the dipole unit vector, as a multiplicative stochastic process. However, several difficulties arise mainly because of the vectorial nature of the rotational diffusion process.

Nee and Zwanzig[30]) assumed $\Omega(t)$ to be a Gaussian process and came to the erroneous conclusion that only the first two cumulants are non-vanishing.

First of all, even in the case of Markovian relaxation for $\Omega(t)$, the Gaussian assumption which this implies is very rough indeed becuase a non-linear term is present in the Euler–Langevin equation, even for the spherical top. It is not generally possible to reduce the analysis to only two cumulants as non-cummutativity occurs when dealing with the same matrix at different times[36]), and destroys the rules which lead to vanishing higher order cumulants in the monodimensional case. Only when the lifetime of the correlation $\langle \Omega(t)\Omega^{T}(0)\rangle$ is very short, and approximable by a delta function $\delta(t)$, are Nee and Zwanzig correct, but this is in any case Debye relaxation[38]).

Consequently, even when we are looking at spherical top molecules[13,34]), with moment of inertia I and relaxation time $1/\beta$ for the Markovian process $\Omega(t)$ the orientational correlation function is:

$$\langle u(t)u(0)\rangle = \exp\{\Phi(t)\}, \tag{B.2}$$

where $\Phi(t)$ is an *infinite series* of terms in the adimensional parameter $(kT/I\beta^2)$.

Although the nth cumulant contributes to only the term in $(kT/I\beta^2)^n$ and to the higher order ones, when β is small convergence is not achieved very quickly, and it is not even clear whether the cumulant series is convergent. In fact[26]) in the limiting case $\beta \to 0$ the cumulant approach fails to reproduce the correct free rotor limit which can be found from eq. (B.1) only by dropping the stochastic nature of the process $\Omega(t)$ so that eq. (B.1) becomes a purely kinematic description of each molecule in the ensemble.

Appendix C

When dealing with the problem of the stochastic oscillator we can assume

$$iL_{SM} = i\Omega. \tag{C.1}$$

The stochastic variable Ω is assumed to be driven by

$$D_\Omega = \beta \frac{\partial}{\partial \Omega}\left(\Delta^2 \frac{\partial}{\partial \Omega} + \Omega\right). \tag{C.2}$$

We can expand D_Ω on the basis set of its eigenstates:

$$p_n(\Omega) = [(2\pi)^{1/2} n!]^{-1/2} 2^{-n/2} H_n\left(\frac{\Omega}{\sqrt{2}\Delta}\right) \exp\left\{-\frac{\Omega^2}{2\Delta^2}\right\}. \tag{C.3}$$

If we define

$$|f_0\rangle = |A\rangle|p_0(\boldsymbol{\Omega})\rangle, \tag{C.4}$$

where A is the variable of interest with the fluctuating frequency $\boldsymbol{\Omega}$, we obtain

$$\begin{aligned} |f_1\rangle &= [1 - (|A\rangle\langle A|)(|p_0(\boldsymbol{\Omega})\rangle\langle p_0(\boldsymbol{\Omega})|)]\, \mathrm{i}(L_S + \boldsymbol{\Omega} - \mathrm{i}D_\Omega)|A\rangle|p_0(\boldsymbol{\Omega})\rangle \\ &= \mathrm{i}|A\rangle|p_1(\boldsymbol{\Omega})\rangle\langle p_1(\boldsymbol{\Omega})|\boldsymbol{\Omega}|p_0\rangle. \end{aligned} \tag{C.5}$$

The kth order generating state is

$$|f_k\rangle = \mathrm{i}^k|A\rangle|p_k(\boldsymbol{\Omega})\rangle\langle p_k|\boldsymbol{\Omega}|p_{k-1}\rangle \cdots \langle p_1|\boldsymbol{\Omega}|p_0\rangle.$$

It is then easy to show that

$$\lambda_k = \langle \tilde{f}_k \,|\, f_k\rangle^{-1}\langle \tilde{f}_k|L_k|f_k\rangle = \mathrm{i}\omega_0 - k\beta, \tag{C.6}$$

where ω_0 is the proper frequency of the variable $|A\rangle$ ($\langle A|\,\mathrm{i}L_S|A\rangle = \mathrm{i}\omega_0$).

Using suitable properties of hermite polynomials[39]) we obtain

$$\Delta_n^2 = -\langle \tilde{f}_n \,|\, f_n\rangle / \langle \tilde{f}_{n-1} \,|\, f_{n-1}\rangle = n\Delta^2. \tag{C.7}$$

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