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CUMULANT EXPANSION OF THE ORIENTATIONAL AUTO-CORRELATION FUNCTION

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ABSTRACT

A general method is developed to relate the orientational and angular momentum auto-correlation functions of a vector embedded in the rotating asymmetric top. It is shown that a previous attempt along these lines by Nee and Zwanzig contains an error which is rectified in this paper. The reduction to the free rotor limit is discussed carefully. The continuity equation, whose solution is a time-ordered exponential does not produce an orientational a.c.f. valid at the free rotor limit. This is because in this limit the kinematic relation between orientation and angular velocity is no longer a multiplicative stochastic process.

INTRODUCTION

In any consideration of molecular dynamics in the liquid state the relation between the orientational autocorrelation function (a.c.f.) and the angular velocity a.c.f. is one of the most fundamental problems. The orientation is exemplified with respect to a dipole embedded in a polar molecule. A special case is that of the spherical top with an embedded axial vector $\underline{u}(t)$ where the unsolved problems associated with asymmetric top rotation are side-stepped. McConnell et al.[1-4] have recently illustrated how even this problem can become tremendously intricate when considering the direct integration of the general kinematic relation $\dot{\underline{u}} = \underline{\omega} \times \underline{u}$, where $\underline{u}$ is a unit vector (e.g. along the dipole moment direction) and $\underline{\omega}$ the angular velocity. The problem has also been approached by Nee and Zwanzig in their paper on dielectric friction. This is a simpler approach than that of McConnell et al., [2] but unfortunately contains a fundamental error which we seek to correct in this paper. We discuss the difficulties remaining even after this correction has been made; difficulties which must be surmounted if progress is to be made analytically in this field.

THEORY: DIPOLE RELAXATION AS A MULTIPLICATIVE STOCHASTIC PROCESS

Consider the motion of the asymmetric top in which is embedded a unit vector $\underline{u}$.

Denote the resultant angular velocity vector by $\underline{\omega}$. The kinematic relation:

$$\dot{\underline{u}}(t) = \underline{\omega}(t) \times \underline{u}(t) \equiv \underline{A}(t)\underline{u}(t) \qquad (1)$$

is of course an example of a multiplicative stochastic process if the angular velocity $\underline{\omega}$ is subject to stochastic (Brownian) motion describable by a statistical formalism such as the integro-differential

$$\frac{d}{dt}\underline{\omega}(t) = -\int_0^t \underline{\beta}(t-s)\underline{\omega}(s) + \underline{f}(t) \qquad (2)$$

This is Hamilton's equation modified by application of projection operators [6]. Here $\underline{f}(t)$ is the stochastic projected torque and $\underline{\beta}(t)$ the memory matrix.

This is a familiar equation, first derived by Mori [7] for any physical variable $\underline{A}(t)$. When applied to rotational motion extra care is needed as it is a linear equation while the fundamental Euler equation contains a non-linear term when written in the frame defined by the principal axes of the body. As a result the Gaussian assumption for the stochastic projected torque $\underline{f}(t)$ is a rough approximation as non-linearities are projected into the noise.

Eqn. (2) together with the expansion of the second fluctuation-dissipation theorem for the stochastic torque $\underline{f}(t)$

$$\langle \underline{f}(t)\underline{f}^T(s)\rangle = \underline{\beta}(t-s)\langle \underline{\omega}(o)\underline{\omega}^T(o)\rangle \qquad (3)$$

lead to the following result for the autocorrelation matrix $\langle \underline{\omega}(t)\underline{\omega}^T(o)\rangle$ which is defined in terms of its Laplace transform

$$\underline{\phi}(z) = \mathcal{L}_a(\langle \underline{\omega}(t)\underline{\omega}^T(o)\rangle\langle \underline{\omega}(o)\underline{\omega}^T(o)\rangle^{-1}) = \frac{1}{z\underline{1} + \hat{\underline{\beta}}(z)} \qquad (4)$$

where $\mathcal{L}_a$ is the Laplace transform operator and $\hat{\underline{\beta}}(z) = \mathcal{L}_a(\underline{\beta}(t))$.

The motion of the dipole is stochastically modulated by the angular velocity and eq. (1) has the formal solution

$$\underline{u}(t) = \overleftarrow{\exp}\left[\int_0^t \underline{A}(s)ds\right]\underline{u}(o) \qquad (5)$$

The time ordered exponentials are defined by their series expansions, in which the order of intergrands is crucial

$$\overleftarrow{\exp}\left[\int_0^t \underline{M}(s)ds\right] \equiv \underline{1} + \sum_{n=1}^{\infty}\int_0^t dt_1\int_0^{t_1} dt_2\int_0^{t_2} dt_3 \times \ldots\ldots\ldots$$

$$\ldots \times \int_0^{t_{n-1}} dt_n \underline{M}(t_1)\underline{M}(t_2)\underline{M}(t_3) \ldots\ldots \underline{M}(t_n) \qquad (5.1)$$

$$\overrightarrow{\exp}\left[\int_0^t \underline{M}(s)ds\right] \equiv \underline{1} + \sum_{n=1}^{\infty}\int_0^t dt_1\int_0^{t_1} dt_2 \ldots\ldots\int_0^{t_{n-2}} dt_{n-1}\int_0^{t_{n-1}} dt_n$$

$$\times\, \underline{M}(t_n)\underline{M}(t_{n-1})\ldots\ldots\underline{M}(t_2)\underline{M}(t_1) \qquad (5.2)$$

The antisymmetric matrix $\underline{A}(t)$ defined in eqn. (1) may be written explicitly as

$$\underline{A}_{ik}(t) = \underline{\varepsilon}_{ijk}\omega_j(t) = \begin{bmatrix} o & -\omega_3(t) & \omega_2(t) \\ \omega_3(t) & o & -\omega_1(t) \\ -\omega_2(t) & \omega_1(t) & o \end{bmatrix} \qquad (6)$$

where $\underline{\varepsilon}_{ijk}$ is the Ricci tensor. A time ordered exponential $\overleftarrow{\exp}$ is needed as the matrix $\underline{A}(t)$ does not commute with itself if taken at different times.

This is always a major problem when considering the formal solution, eqn. (5) as it will not allow us to write a finite comulant expansion of the average of the exponential in eqn. (5), even in the case where the process $\underline{\omega}(t)$ is assumed to be Gaussian. This is at the root of the difficulty of constructing $<\underline{u}(t).\underline{u}(o)>$ analytically from $<\underline{\omega}(t).\underline{\omega}(o)>$ in all but the simplest of cases.

The a.c.f. $<\underline{u}(t)\underline{u}^T(o)>$ may be obtained from eqn. (5) by first multiplying by $\underline{u}^T(o)$ and then averaging. Two different types of averaging are needed, one on the stochastic process $\underline{\omega}(t)$, the other on the initial equilibrium distribution for $\underline{u}(o)$. Following Fox [8], we indicate the first with < ....> and the other with the brackets [....]. The result is

$$<\left[\underline{u}(t)\underline{u}^T(o)\right]> = <\overleftarrow{\exp}\left\{\int_o^t \underline{A}(s)ds\right\}>\left[\underline{u}(o)\underline{u}^T(o)\right] \tag{7}$$

The moments of the matrix $\underline{A}(t)$ are defined in terms of the ones of the angular velocity as:

$$<\underline{A}_{ik}(t)> = \underline{\varepsilon}_{ijk}<\omega_j(t)> = \underline{o} \tag{8.1}$$

$$\text{and } <\underline{A}_{ik}(t)\underline{A}_{ln}(s)> = \underline{\varepsilon}_{ijk}\underline{\varepsilon}_{lmn}<\omega_j(t)\omega_m(s)> \tag{8.2}$$

assuming that $\underline{\omega}(t)$ is a Gaussian process with zero mean. We limit ourselves to the calculation of the second and fourth cumulants, see appendix, as a complete calculation, from first principles, has already been given by Ford, Lewis and McConnell[3], using graphical methods for the simplest cases of Brownian motion of a spherical top and for the case where rotation is constrained to a plane.

$$\begin{aligned}\text{Now as } (<\underline{A}(s_1)\underline{A}(s_2)>)_{in} &= \underline{\varepsilon}_{ijk}\underline{\varepsilon}_{lmn}<\omega_j(s_1)\omega_n(s_2)> \\ &= <\omega_n(s_1)\omega_i(s_2)> - <\omega_m(s_1)\omega_n(s_2)>\delta_{in}\end{aligned} \tag{9}$$

then in this approximation eqn. (7) becomes

$$\begin{aligned}<\left[\underline{u}(t)\underline{u}^T(o)\right]>\left[\underline{u}(o)\underline{u}^T(o)\right]^{-1} &= \overleftarrow{\exp}\left\{\int_o^t ds_1\int_o^{s_1} ds_2 <\underline{A}(s_1)\underline{A}(s_2)>\right\} \\ &= \overleftarrow{\exp}\left\{\int_o^t ds_1\int_o^{s_1} ds_2 \quad <\underline{\omega}(s_1)\underline{\omega}^T(s_2)>^T \right. \\ &\qquad \left. - \underline{1}\,\mathrm{Tr}\left[<\underline{\omega}(s_1)\underline{\omega}^T(s_2)>\right]\right\}\end{aligned} \tag{10}$$

with $\underline{1}$ as the identity matrix and Tr[ ] meaning the trace. This approximation is exact in the following cases. The first is when the autocorrelation function $\underline{\Phi}(t)$ is very short lived i.e. can be expressed by a Dirac delta function. This corresponds to disregarding memory and inertial effects in the dipole diffusion process. The other case is that of when the rotational motion of the dipole is constrained to a plane so that the process becomes one dimensional and the gaussian assumption results in only one cumulant, the second, different from zero. Ford, Lewis, McConnell and Scaife [1-4] have discussed this problem and have shown the difference between the case of planar diffusion and that of three dimensional diffusion of a spherical top when the relaxation of the angular velocity is Markhovian, i.e. exponential with decay time $1/\beta$. These differences appear in the terms of order equal or greater than the fourth (in the adimensional parameter $(1/\beta^2)(kT/I)^{\frac{1}{2}}$ of the time expansion of the orientational autocorrelation function).

The errors in the paper by Nee and Zwanzig [5] can be explained as follows. Starting again from eqn. (1) Nee and Zwanzig used a different approach, using the continuity theorem (conservation of matter), which leads to the diffusion equation for the probability density for the dipole variables only

$$\frac{\partial}{\partial t} f(\underline{u},t) = - \underline{\omega}(s) x \underline{u} . \frac{\partial}{\partial \underline{u}} f(\underline{u},t) \qquad (11)$$

whose formal solution is

$$f(\underline{u},t) = \overleftarrow{\exp} \left[- \int_0^t ds\, \underline{\omega}(s) . (\underline{u} \times \underline{\nabla}_u) \right] f(\underline{u},o) \qquad (12)$$

Now they assume $\underline{\omega}(t)$ to be a Gaussian process with zero mean, and averaging over it they get

$$\bar{f}(\underline{u},t) = \overleftarrow{\exp} \left[- \int_0^t ds_1 \int_0^{s_1} ds_2 \; (\underline{u} \times \underline{\nabla}_u)^T \langle \underline{\omega}(s_1) \underline{\omega}^T(s_2) \rangle \right.$$

$$\left. \times \; (\underline{u} \times \underline{\nabla}_u) \right] \bar{f}(\underline{u},o) \qquad (13)$$

In view of the considerations we have already set out eqn. (13) is not correct in general because higher order cumulants do not vanish (Non commutativity of the operators $\underline{\omega}(t) . \underline{u} \times \underline{\nabla}_u$ at different times).

The irretrievable error comes in the differentation of their equivalent of eqn. (13). The correct results in general are

$$\frac{d}{dt} \overleftarrow{\exp} \left[\int_0^t \underline{M}(s) ds \right] = \underline{M}(t) \overleftarrow{\exp} \left[\int_0^t \underline{M}(s) ds \right]$$

$$\frac{d}{dt} \overrightarrow{\exp} \left[\int_0^t \underline{M}(s) ds \right] = \overrightarrow{\exp} \left[\int_0^t \underline{M}(s) ds \right] \underline{M}(t) \qquad (14)$$

and in our particular case

$$\frac{d}{dt} \bar{f}(\underline{u},t) = (\underline{u} \times \underline{\nabla}_u)^T \int_0^t ds \langle \underline{\omega}(t) \underline{\omega}^T(s) \rangle (\underline{u} \times \underline{\nabla}_u) \; \bar{f} \; (\underline{u},t) \qquad (15)$$

The incorrect Nee /Zwanzig result is

$$\frac{\partial}{\partial t} \bar{f}(\underline{u},t) = (\underline{u} \times \underline{\nabla}_u)^T \int_0^t ds \langle \underline{\omega}(t) \underline{\omega}^T(s) \rangle (\underline{u} \times \underline{\nabla}_u) \; \bar{f} \; (\underline{u},s) \qquad (15')$$

The consequences of this error are discussed below.

Eqn. (15) may be reduced to a familiar form defining the time dependent diffusion tensor $\underline{D}(t)$.

$$\underline{D}(t) = \int_0^t \langle \underline{\omega}(t) \underline{\omega}^T(s) \rangle ds = \int_0^t \langle \underline{\omega}(t-s) \underline{\omega}^T(o) \rangle ds = \int_0^t \langle \underline{\omega}(\tau) \underline{\omega}^T(o) \rangle d\tau \qquad (16)$$

producing

$$\frac{\partial}{\partial t} \bar{f}(\underline{u},t) = (\underline{u} \times \underline{\nabla}_u)^T \; \underline{D}(t) (\underline{u} \times \underline{\nabla}_u) \; \bar{f}(\underline{u},t) \qquad (15'')$$

When the angular velocity correlation function is very short lived we have from (16) that the diffusion tensor is no longer time dependent and that all cumulants but the second vanish. As a result eqn. (15') fortuitously reduces to the Favro equation [9] for rotational diffusion, Eqn. (15) also, of course reduces to Favro's equation in this limit. Inertial and memory effects are neglected in this limit and the diffusion tensor is defined in terms of the inertia $\underline{I}$ and friction $\underline{\beta}$ as

$$\underline{D} = kT\,/(\underline{\beta}\underline{I}) \tag{17}$$

The dipole autocorrelation matrix can be recovered from eqn. (15") by using

$$<\left[\underline{u}(t)\underline{u}^T(o)\right]> = \iint d\underline{u}(t)\,d\underline{u}_o\,\underline{u}(t)\underline{u}_o^T\;P_{eq}\;(\underline{u}_o)\;\times\;\bar{f}(\underline{u},t) \tag{18}$$

where $\bar{f}(\underline{u},t)$ is the solution of eqn. (15") with the initial condition $\underline{u}(t = o) = \underline{u}_o$. $P_{eq}(\underline{u}_o)$ is the equilibrium distribution of $\underline{u}_o$.

Inserting (18) in both sides of eqn. (15") and integrating by parts we finally obtain:

$$\frac{\partial}{\partial t} <\left[\underline{u}(t)\underline{u}^T(o)\right]> \;=\left[\underline{D}^T(t) - \underline{1}\;Tr\left[\underline{D}(t)\right]\right]\;\times <\left[\underline{u}(t)\underline{u}^T(o)\right]>$$

$$\equiv -\underline{M}(t)\;<\left[\underline{u}(t)\underline{u}^T(o)\right]> \tag{19}$$

whose solution is:

$$<\left[\underline{u}(t)\underline{u}^T(o)\right]> = \overleftarrow{\exp}\left[-\int_o^t \underline{M}(s)ds\right]\left[\underline{u}(o)\underline{u}^T(o)\right] \tag{20}$$

Eqn. (20) is exactly equal to equation (10), since they are both constructed with the same approximation. Eqn. (15"), the basis of eqn. (20), contains however more information than eqn. (10) about the dynamics of the diffusion of the dipole orientation vector $\underline{u}(t)$. This is illustrated for the spherical top below, where we derive the second rank orientational a.c.f. $\frac{1}{2} <3\left[\underline{u}(t).\underline{u}(o)\right]^2 - 1>$. Note that eqn. (20) cannot be obtained from the erroneous equation (15').

In the general case (diffusion in three dimensional space of the spherical or symmetric top, or totally anisotropic diffusion) $\underline{M}(t_1)$ and $\underline{M}(t_2)$ do not commute when $t_1 \neq t_2$. In the above approximation of disregarding cumulants of order higher than the two, however, we have the form:

$$T_r< \underline{u}(t)\underline{u}(o)^T> = <\underline{u}(t).\underline{u}(o)> = T_r\left[\exp\;(\;-\int_o^t \underline{M}(s)ds)<\underline{u}(o)\underline{u}^T(o)>\right]$$

$$\tfrac{1}{3}\left[\exp(\int_o^t M_{11}(s)ds) + \exp\;(\int_o^t M_{22}(s)ds) + \exp(\int_o^t M_{33}(s)ds)\right] \tag{21}$$

where we have used

$$<\underline{u}(o)\underline{u}^T(o)> = \frac{1}{3}\,\underline{1}$$

i.e. $f(\underline{u},t)$ = const. is the equilibrium solution of eqn (15"). Note that eqn. (21) is applicable to asymmetric top diffusion and accounts for memory and inertial effects in a way dependent on how these are evaluated for $\underline{M}$ itself via the angular velocity correlation matrix.

GENERALISED HUBBARD RELATION

For isotropic diffusion, eqn. (15″) reduces to

$$\frac{\partial}{\partial t} f(\underline{u},t) = \underline{D}(t)(\underline{u} \times \underline{\nabla}_u)^2 f(\underline{u},t) \tag{22}$$

After some algebra it can be shown that eqn. (22) implies

$$\frac{\partial}{\partial t} \langle P_1(\cos\theta(t))\rangle = -2D(t) \langle P_1(\cos\theta(t))\rangle \tag{23}$$

$$\frac{\partial}{\partial t} \langle P_2(\cos\theta(t))\rangle = -6D(t) \langle P_2(\cos\theta(t))\rangle \tag{24}$$

in standard notation.

This means

$$\langle \underline{u}(t).\underline{u}(o)\rangle = \exp\left[-2\int_o^t D(s)ds\right] \tag{25}$$

$$\tfrac{1}{2}\langle 3\left[\underline{u}(t).\underline{u}(o)\right]^2 - 1\rangle = \exp\left[-6\int_o^t D(s)ds\right] \tag{26}$$

the "Hubbard relations". It is possible to obtain these from eqn. (20) but not from eqn. (10).

In the specific case of classical rotational diffusion in the isotropic limit we have:

$$\langle \underline{\omega}(t).\underline{\omega}(o)\rangle = \langle \underline{\omega}(o).\underline{\omega}(o)\rangle \exp(-\beta t)$$

$$D(s) = \frac{1}{3}\int_o^s e^{-\beta t}\langle\omega^2(o)\rangle dt \tag{27}$$

so that

$$\langle \underline{u}(t).\underline{u}(o)\rangle = \exp\left[-\frac{2kT}{I}\left(t + \frac{e^{-\beta t}}{\beta} - \frac{1}{\beta}\right)\right] \tag{28}$$

where we have used $\langle\omega^2(o)\rangle = 3kT/I$. Note that we obtain the same result from eqn. (21). This is identical with the result quoted by Wyllie [10] for Brownian motion on a spherical surface. This result cannot be obtained from eqn. (15′). Furthermore Eq. (28) coincides with the result given by Ford et al [3] in considering the motion of the disk, apart from the factor two which is due to our use of three dimension space, and it is correct for the spherical top only for a second-order truncated expansion in $(kT/I)^{\frac{1}{2}}\, 1/_{\beta}$.

DISCUSSION

As a consequence of the incorrect structure of the eqn. labelled by us eqn. (15′) the derivation based on eqn. (49) of Nee and Zwanzig is also incorrect. In particular their eqn. (53) should be discarded as well as their eqn. (57). In addition the derivation based on their eqn. (63) for two-dimensional rotational diffusion is also incorrect, i.e. their eqns (63) to (71) should be discarded.

PROBLEMS REMAINING

We note that any attempt to describe the orientational autocorrelation function in terms of a single time ordered exponential does not result (using stochastic considerations) in correct free rotor behaviour (appendix (A) and cannot reproduce any negative region in the orientational autocorrelation function. This is a fundamental problem because the free rotor orientational a.c.f. for linear molecular symmetry, for example, is the hypergeometric Kummer integral, with a large negative lobe at intermediate times.

The only way of dealing with this problem is to use a multiparticle Fokker-Planck equation as per G. T. Evans [11] , for example, or alternatively to develop the so called extended diffusion models following Gordon [12], McClung [13] , Cukier [14], and others. It is well known that the original m and J diffusion models do not define properly the mean square torque, and consequently do not work at all in the far infra-red region, where the characteristic shift in the peak absorption frequency is not matched. Cukier, however, has discussed some improvements, and related the extended diffusion formalism to the Mori continued fraction.

Another alternative is to apply the projection operator method direct to the orientational a.c.f., following Quentrec and Bezot [15] and Evans et al [16] . This does not easily allow us to relate the orientational and angular velocity a.c.f.'s.

It is clear that eqn. (11) is not valid in the region where the molecular dynamics reduce to a series of binary collisions rather than continuous potential perturbation, as is the case in the dense liquid state.

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APPENDIX A

THE FREE ROTOR LIMIT

In the case where the friction vanishes, $\underline{\omega}(t)$ is no longer a stochastic process. Eqn.(1) can now be exactly solved for each particle. It becomes:

$$\dot{\underline{u}}^{(i)}(t) = \underline{\omega}^{(i)} x \underline{u}^{(i)}(t), (i = 1, \ldots, N) \equiv \underline{A}^{(i)} \underline{u}^{(i)}(t) \qquad (A1)$$

where N is the total number of molecules in the liquid. The solution for each particle i is:

$$\underline{u}^{(i)}(t) = \exp\left[\underline{A}^{(i)} t\right] \underline{u}^{(i)}(o) \qquad (A2)$$

The correlation function of interest is

$$\langle P_1(\cos \theta(t))\rangle = \sum_{i=1}^{N} (\underline{u}^{(i)}(t) . \underline{u}^{(i)}(o)) = \frac{1}{N} \sum_{i=1}^{N} (\underline{u}^{(i)}(o)^T)(\exp\left[\underline{A}^{(i)} t\right] \underline{u}^{(i)}(o))$$

where $\cos(\theta)(t) = \underline{u}(t) . \underline{u}(o)$ (A3)

To caluclate explicitly the matrix exponential we look for its eigenvalues, i.e. we transform it to a coordinate set where the matrix $\underline{A}^{(i)}$ is diagonal.

The secular equation related to the matrix $\underline{A}$ is

$$\lambda^3 + \lambda(\omega_1^2 + \omega_2^2 + \omega_3^2) = 0 \qquad (A4)$$

whose roots are

$$\lambda_1^{(i)}(o) = o; \quad \lambda_2^{(i)} = i\sqrt{(\omega_1^{(i)2} + \omega_2^{(i)2} + \omega_3^{(i)2})} = i\omega^{(i)}$$

$$\lambda_3^{(i)} = - i\sqrt{(\omega_1^{(i)2} + \omega_2^{(i)2} + \omega_3^{(i)2})} = - i\omega^{(i)} \qquad (A5)$$

where $\omega^{(i)2} = \omega^{(i)} . \omega^{(i)}$

Let $\underline{A}^{(i)}$ be the diagonal matrix whose non-zero elements are the eigen-values λ_1, λ_2, λ_3. It is related to the matrix $\underline{A}^{(i)}$ by

$$\underline{C}^{(i)}\underline{A}^{(i)}\underline{C}^{(i)T} = \vec{\underline{A}}^{(i)} \qquad (A6)$$

where $C^{(i)}$ is the orthogonal matrix which defines the transformation. The transformed vector $\underline{\tilde{u}}^{(i)}(t)$ is given by

$$\underline{\tilde{u}}^{(i)}(t) = \underline{C}\underline{u}^{(i)}(t) \qquad (A7)$$

We can use eqns. (A6) and (A3) to obtain

$$<P_1(\cos\theta(t))> = \sum_{i=1}^{N} (\underline{u}^{(i)}(o))^T (\underline{C}^{(i)T}\underline{C}^{(i)} \exp(\underline{A}^{(i)}t) \underline{C}^{(i)T}\underline{C}^{(i)}\underline{u}^{(i)}(o))$$

$$= \frac{1}{N} \sum_{i=1}^{N} (\underline{\tilde{u}}^{(i)}(o))^T (\exp\left[\underline{\tilde{A}}^{(i)}t\right] \underline{\tilde{u}}^{(i)}(o)) \qquad (A8)$$

The advantage of eqn. (A8) is that now we know the elements of the matrix defined by the exponentials, in fact

$$\exp\left[\underline{\tilde{A}}^{(i)}t\right] = \begin{bmatrix} \exp(\lambda_1^{(i)}t) & o & o \\ o & \exp(\lambda_2^{(i)}t) & o \\ o & o & \exp(\lambda_3^{(i)}t) \end{bmatrix} \qquad (A9)$$

We will now replace the sum by the integral over the probability density. The averaging is carried out first over the initial conditions of the dipole orientation $\underline{u}^{(i)}(o)$ and then over the angular velocity distribution function, $P(\underline{\omega})$, which we assume to be a Boltzmann type.

In the most general case

$$P(\underline{\omega}) = Z \exp\left[-\frac{1}{2kT}(I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2)\right] \qquad (A10)$$

where Z is the normalisation constant given by

$$\frac{1}{Z} = \iiint_{\infty}^{\infty} d^3\omega\, P(\underline{\omega}) = \left(\frac{(I_1 I_2 I_3)^{\frac{1}{2}}}{(2\pi kT)^{3/2}}\right)^{-1} \qquad (A11)$$

Eqn. (A8) may be written as:

$$<P_1(\cos\theta(t))> = \int d^3\omega P(\underline{\omega}) \left[(\underline{\tilde{u}}(o))^T (\exp\{\underline{\tilde{A}}\, t\})\underline{\tilde{u}}(o))\right] \qquad (A12)$$

the brackets $\left[........\right]$ meaning the average on the initial equilibrium condition. For an isotropic fluid we can assume without lack of generality that at equilibrium the orientations of the single molecule are isotropically distributed, so for any orientation of the laboratory fixed frame we have for each cartesian component k

$$\left[\tilde{u}_k(o)\tilde{u}_k(o)\right] = 1/3 \qquad (A13)$$

as $\underline{\tilde{u}}^{(i)}(o).\underline{\tilde{u}}^{(i)}(o) = 1$, i.e. the length of the dipole is fixed. Using these considerations eqn. (A12) reduces to

$$<P_1(\cos\theta(t))> = \frac{1}{3}\int d^3\omega\, P(\underline{\omega})\, \mathrm{Tr}\left[\exp(\underline{\tilde{A}}t)\right]$$

$$= \frac{1}{3}\int d^3\omega\, P(\underline{\omega}) \left[1 + \exp(i\omega t) + \exp(-i\omega t)\right] \qquad (A14)$$

The integral in eqn. (A14) is very easy to compute in the case where the spherical top is considered. We have:

$$<P_1 (\cos \theta(t))> = \frac{1}{3} \int_0^\infty d\omega \left[4\pi\omega^2 Z \exp(\frac{-I\omega^2}{2kT}) \left[1 + \exp(i\omega t) + \exp(-i\omega t)\right]\right.$$

$$= \frac{1}{3} + \frac{2}{3} (1 - \frac{kTt^2}{I}) \exp (\frac{- kTt^2}{2I}) \qquad \text{(A15)}$$

We have used the fact that:

$$4\pi \int_{-\infty}^{\infty} d\omega \left[\omega^2 Z \exp(\frac{-I\omega^2}{2kT}) \exp (\pm i\omega t)\right] = - \frac{d^2}{dt^2} (2\pi \mathcal{F}_a^{-1} \left[4\pi Z \exp (\frac{-I\omega^2}{2kT}) \right] \qquad \text{(A16)}$$

and that the inverse Fourier transform, indicated $\mathcal{F}_a^{-1}$, of the gaussian in (A16) is:

$$2\pi \mathcal{F}_a^{-1} \left[(\frac{2\pi kT}{I})^{-1/2} \exp(\frac{-I\omega^2}{2kT}) \right] = \exp(\frac{-kTt^2}{2I}) \qquad \text{(A17)}$$

If we try to use eqn. (2) directly in the limit of no friction, $\beta = o$, we obtain:

$$<P_1 (\cos \theta(t))> = \exp(\frac{-kTt^2}{2I}) \qquad \text{(A18)}$$

which is not correct because $\omega(t)$ is no longer a stochastic process and our considerations are no longer to the point.
Note that for this reason the free rotor limit considered as such by McConnell et al, eqn. (A18), is not meaningful in the case of three dimensional rotational diffusion. The correct result for the spherical top is eqn. (A15).

The same calculation may be repeated for the symmetric top with $I_1 = I_2 \neq I_3$. The integral becomes

$$<\underline{u}(t).\underline{u}(o)> = \frac{1}{3}\iiint d^3\omega \frac{(I_1^2 I_3)^{\frac{1}{2}}}{(2\pi kT)^{3/2}} \exp\left[- \frac{\omega^2}{2kT} (I_1 + (I_3 - I_1) \frac{\omega_3^2}{\omega^2})\right]$$

$$\times \left(1 + 2 \cos (t\omega)\right)$$

$$= \frac{1}{3} + \frac{4\pi}{3} (\frac{I_3}{I_1})^{\frac{1}{2}} \int_{-1}^{1} d \cos \theta \int_0^\infty d\omega (2\pi kT/I_1)^{-\frac{3}{2}} \qquad \text{(A19)}$$

$$\times \omega^2 \exp\left(- \frac{\omega^2}{2KT/I_1} (1 - a \cos^2\theta)\right)\cos\omega t$$

where $a = (I_1 - I_3)/I_1$.

First we integrate over d $\cos\theta$

$$<\underline{u}(t).\underline{u}(o)> = \frac{1}{3} + \frac{4\pi}{3} (\frac{I_3}{I_1})^{\frac{1}{2}} \int_0^\infty d\omega\, \omega^2 (2\pi kT/I_1)^{-\frac{3}{2}} \exp \frac{\omega^2}{2kT/I_1} \qquad \text{(A20)}$$

$$\times \cos (t\omega) \int_{-1}^{1} dx \exp\left(\frac{I_1\omega}{2kT} ax^2\right)$$

By observing that the integrand in is an even function of x we reduce the interval of integration to the positive regions $o \leq x \leq 1$.

$$\langle \underline{u}(t).\underline{u}(o)\rangle = \frac{1}{3} + \frac{4\pi}{3}\left(\frac{I_3}{I_1}\right)^{\frac{1}{2}} (2\pi kT/I_1)^{-1}$$

$$\times \int_0^\infty d\omega \cos(t\omega) \exp\left(-\frac{\omega^2}{2kT/I_1}\right) (-a)^{\frac{1}{2}} \operatorname{erf}\left(\omega\left(-\frac{I_1 a}{2kT}\right)^{\frac{1}{2}}\right) \tag{A21}$$

where we put

$$\operatorname{erf}\left(y = \left(-\frac{I_1 a}{2kT}\right)^{\frac{1}{2}}\right) = \frac{2}{\sqrt{\pi}} \int_0^{y = \omega\left(-\frac{I_1 a}{2kT}\right)^{\frac{1}{2}}} e^{-x^2}\, dx \tag{A22}$$

It is to be noted that a could be both greater and less than zero. In the former case the argument of the erf function is complex and a complex factor appears also in the integral (A21) from the term $(-a)^{\frac{1}{2}}$, but the whole expression remains a real function.

The integral in eqn. (A21) is not easy to evaluate but as Morita [17] noticed its form is useful in the case when a Fourier transform is needed. In fact as erf(y) is an odd function of y the whole integrand is even in ω and the properties

$$\int_0^\infty dx \int_0^\infty d\nu\, g(x) \cos xt \cos \nu t\, dx dt = \pi\, g(\nu) \tag{A23}$$

can be easily used to get the spectrum.

In the case of the asymmetric top the integral is far more complicated

$$\langle \underline{u}(t).\underline{u}(o)\rangle = \frac{1}{3} + \frac{1}{3}\iiint d^3\omega\, P(\omega)\, \left(2 \cos\omega t\right)$$

$$= \frac{1}{3} + 2\int_0^\infty d\omega\, \omega^2 \int_{-1}^{1} d \cos\theta \int_0^{2\pi} d\phi\, \frac{(I_1 I_2 I_3)^{\frac{1}{2}}}{(2\pi KT)^{3/2}}$$

$$\times \exp\left(\frac{\omega^2}{2kT/I_1}\left[1 + \frac{(I_2 - I_1)}{I_1} \sin^2\phi \sin^2\theta + \frac{(I_3 - I_1)}{I_1} \cos^2\theta\right]\right) \tag{A24}$$

$$\times \cos(t\omega)$$

APPENDIX B

THE CONTRIBUTION OF THE FOURTH CUMULANT

In the cumulant expansion of the averaged exponential in eqn. (7) the cumulants of order higher than the second do not vanish, even when $\underline{\omega}(t)$ is Gaussian, because of time ordering. In this appendix we confine ourselves to the development of the fourth cumulant for the general angular velocity a.c.f., assuming only that $\underline{\omega}(t)$ is gaussian. This generalises the work of McConnell et al.

The fourth time-ordered cumulant may be expressed in terms of the moments of the process $\underline{A}(t)$ as

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle \underline{A}(t_1)\underline{A}(t_2)\underline{A}(t_3)\underline{A}(t_4)\rangle_c$$

$$= \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle \underline{A}(t_1)\underline{A}(t_2)\underline{A}(t_3)\underline{A}(t_4)\rangle$$

$$- \langle \underline{A}(t_1)\underline{A}(t_2)\rangle \langle \underline{A}(t_3)\underline{A}(t_4)\rangle - \langle \underline{A}(t_1)\underline{A}(t_3)\rangle\langle \underline{A}(t_2)\underline{A}(t_4)\rangle$$

$$- \langle \underline{A}(t_1)\underline{A}(t_4)\rangle\langle \underline{A}(t_2)\underline{A}(t_3)\rangle \tag{B1}$$

This simplifies if we assume a gaussian process with zero mean, giving

$$\int_0^t dt_1 \;\ldots\ldots\; \int_0^{t_3} dt_4 \left\langle A_{il}(t_1) A_{lm}(t_2) A_{mn}(t_3) A_{nj}(t_4) \right\rangle_c$$

$$= \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \Big[\langle A_{il}(t_1) A_{mn}(t_3)\rangle \langle A_{lm}(t_2) A_{nj}(t_4)\rangle$$

$$- \langle A_{il}(t_1) A_{lm}(t_3)\rangle \langle A_{mn}(t_2) A_{nj}(t_4)\rangle$$

$$+ \langle A_{il}(t_1) A_{nj}(t_4)\rangle \langle A_{lm}(t_2) A_{mn}(t_3)\rangle$$

$$- \langle A_{il}(t_1) A_{lm}(t_4)\rangle \langle A_{mn}(t_2) A_{nj}(t_4)\rangle \Big] \qquad \text{(B2)}$$

Using eqn (B2) we can express this result in terms of the moments of the stochastic process $\underset{\sim}{\omega}(t)$. We show explicitly how this may be done for the first term on the right hand side of eqn. (B2). We have

$$\langle A_{il}(t_1) A_{mn}(t_3)\rangle \langle A_{lm}(t_2) A_{nj}(t_4)\rangle$$

$$= \langle \varepsilon_{is_1l}\,\omega_{s_1}(t_1)\,\varepsilon_{ms_3n}\,\omega_{s_3}(t_3)\rangle$$

$$\times \langle \varepsilon_{ls_2m}\,\omega_{s_2}(t_2)\; \varepsilon_{ns_4j}\,\omega_{s_4}(t_4)\rangle$$

$$= \varepsilon_{is_1l}\; \varepsilon_{ms_3n}\; \varepsilon_{ls_2m}\; \varepsilon_{ns_4j}\; \langle \omega_{s_1}(t_1)\,\omega_{s_3}(t_3)\rangle$$

$$\times \langle \omega_{s_2}(t_2)\,\omega_{s_4}(t_4)\rangle$$

$$= (\delta_{is_2}\;\delta_{ms_1} - \delta_{im}\;\delta_{s_1s_2})\;(\delta_{ms_4}\delta_{js_3} - \delta_{mj}\;\delta_{s_3s_4})$$

$$\times \langle \omega_{s_1}(t_1)\,\omega_{s_3}(t_3)\rangle \langle \omega_{s_2}(t_2)\,\omega_{s_4}(t_4)\rangle$$

$$= \Big[\langle \omega_m(t_1)\;\omega_j(t_3)\rangle \langle \omega_i(t_2)\,\omega_m(t_4)\rangle$$

$$- \langle \omega_j(t_1)\,\omega_k(t_3)\rangle \langle \omega_i(t_2)\,\omega_k(t_4)\rangle$$

$$+ \langle \omega_k(t_1)\,\omega_n(t_3)\rangle \langle \omega_k(t_2)\,\omega_n(t_4)\rangle\,\delta_{ij}$$

$$- \langle \omega_k(t_1)\,\omega_j(t_3)\rangle \langle \omega_k(t_2)\,\omega_i(t_4)\rangle \Big] \qquad \text{(B3)}$$

The total expression is recovered in the same manner and is

$$\langle A_{il}(t_1) A_{lm}(t_2) A_{mn}(t_3) A_{nj}(t_4)\rangle_c$$

$$= \langle \omega_m(t_1)\omega_j(t_3)\rangle \langle \omega_i(t_2)\omega_m(t_4)\rangle - \langle \omega_j(t_1)\omega_k(t_3)\rangle \langle \omega_i(t_2)\omega_k(t_4)\rangle$$

$$+ \langle \omega_k(t_1)\omega_n(t_3)\rangle \langle \omega_k(t_2)\omega_n(t_4)\rangle \delta_{ij} - \langle \omega_k(t_1)\omega_j(t_3)\rangle \langle \omega_k(t_2)\omega_i(t_4)\rangle$$

$$+ \langle \omega_j(t_1)\omega_i(t_3)\rangle \langle \omega_k(t_2)\omega_k(t_4)\rangle - \langle \omega_m(t_1)\omega_i(t_3)\rangle \langle \omega_j(t_2)\omega_m(t_4)\rangle$$

$$+ \langle \omega_k(t_1)\omega_k(t_3)\rangle \langle \omega_j(t_2)\omega_i(t_4)\rangle - \langle \omega_k(t_1)\omega_k(t_3)\rangle \langle \omega_n(t_2)\omega_n(t_4)\rangle\;\delta_{ij}$$

$$+ \langle \omega_m(t_1)\omega_m(t_4)\rangle \langle \omega_i(t_2)\omega_j(t_3)\rangle - \langle \omega_j(t_1)\omega_k(t_4)\rangle \langle \omega_i(t_2)\omega_k(t_3)\rangle$$

$$+\langle\omega_k(t_1)\omega_n(t_4)\rangle\langle\omega_k(t_2)\omega_n(t_3)\rangle\delta_{ij} - \langle\omega_k(t_1)\omega_i(t_4)\rangle\langle\omega_k(t_2)\omega_j(t_3)\rangle$$
$$+ \langle\omega_j(t_1)\omega_i(t_4)\rangle\langle\omega_k(t_2)\omega_k(t_3)\rangle - \langle\omega_m(t_1)\omega_i(t_4)\rangle\langle\omega_j(t_2)\omega_m(t_3)\rangle$$
$$+ \langle\omega_k(t_1)\omega_k(t_4)\rangle\langle\omega_j(t_2)\omega_i(t_3)\rangle - \langle\omega_k(t_1)\omega_k(t_4)\rangle\langle\omega_n(t_2)\omega_n(t_3)\rangle\delta_{ij} \quad \text{(B4)}$$

Eqn. (B4) is to be integrated on the four ordered times t_1, t_2, t_3, t_4.

We note that there are two different kinds of terms which can be represented by the two general forms

$$\int_o^t dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \int_o^{t_3} dt_4 \langle\omega_{n_1}(t_1)\omega_{n_3}(t_3)\rangle\langle\omega_{n_2}(t)\omega_{n_4}(t_4)\rangle \quad \text{(B5)}$$

and

$$\int_o^t dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \int_o^{t_3} dt_4 \ \langle\omega_{n_1}(t_1)\omega_{n_4}(t_4)\rangle\langle\omega_{n_2}(t_2)\omega_{n_3}(t_3)\rangle \quad \text{(B6)}$$

At this point we take advantage of the continued fraction of Mori [7] to write

$$\langle\omega_{n_1}(t_1)\omega_{n_2}(t_2)\rangle \equiv \phi_{n_1 n_2}(t_1 - t_2); \quad t_1 > t_2 \quad \text{(B7)}$$

as a sum of complex eponentials, in the manner of Quentrec and Bezot [15] i.e.

$$\phi_{n_1 n_2}(t) = \sum_p \beta_p^{(n_1 n_2)} \exp\left[- \alpha_p^{(n_1 n_2)} t\right] \quad \text{(B8)}$$

where both $\beta_p^{(n_1 n_2)}$ and $\alpha_p^{(n_1 n_2)}$ are complex numbers. In general $p \to \infty$
The fact that the matrix $\underline{\phi}(t)$ has real coefficients implies that these coefficients occur together in the sum with their complex conjugates.

Eqn. (B5) may be written as

$$\int_o^t dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \int_o^{t_4} dt_4 \ \phi_{n_1 n_3}(t_1 - t_3)\phi_{n_2 n_4}(t_2 - t_4)$$

$$= \int_o^t dt_1 \ \ldots . \int_o^{t_3} dt_4 \sum_p \sum_q \beta_p^{(n_1 n_3)} \ \beta_q^{(n_2 n_4)}$$

$$\times \exp\left[- \alpha_p^{(n_1 n_3)}(t_1 - t_3) - \alpha_q^{(n_2 n_4)}(t_2 - t_4)\right]$$

$$= \int_o^t dt_1 \ \ldots .. \int_o^{t_2} \sum_p \sum_q \beta_p^{(n_1 n_3)} \ \beta_q^{(n_2 n_4)} \exp\left[- \alpha_p^{(n_1 n_3)}(t_1 - t_2)\right.$$
$$\left.- (\alpha_p^{(n_1 n_3)} + \alpha_q^{(n_2 n_4)}) \ (t_2 - t_3) - \alpha_q^{(n_2 n_4)}(t_3 - t_4)\right]$$

$$= \sum_p \sum_q \beta_p^{(n_1 n_3)} \ \beta_q^{(n_2 n_4)} \ 1 * \exp\left[-\alpha_p^{(n_1 n_3)} t\right]$$
$$*\exp\left[- (\alpha_p^{(n_1 n_3)} + \alpha_q^{(n_2 n_4)})t\right] * \exp\left[-\alpha_q^{(n_2 n_4)} t\right] * 1 \quad \text{(B9)}$$

where the * means the convolution integral.

The expression (B9) has the advantage of being easily Laplace transformed into

$$\Psi(s) = \sum_p \sum_q \beta_p^{(n_1 n_2)} \beta_q^{(n_2 n_4)}$$

$$\times \left[s^2 (s + \alpha_p^{(n_1 n_3)})(s + \alpha_p^{(n_1 n_3)} + \alpha_q^{(n_2 n_4)})(s + \alpha_q^{(n_2 n_4)}) \right] \quad \text{(B10)}$$

In the same way we can get the Laplace transform of eqn. (B6) as

$$\Psi^1(s) = \sum_p \sum_q \beta_p^{(n_1 n_4)} \beta q^{(n_2 n_4)}) \left[s^2 (s + \alpha_p^{(n_1 n_4)})^2 \right.$$

$$\left. \times (s + \alpha_p^{(n_1 n_4)} + \alpha_q^{(n_2 n_3)}) \right]^{-1} \quad \text{(B11)}$$

Expressions like eqn (B10) and eqn (B11) can be easily back-transformed. In both cases the elemental terms may assume the three different aspects

$$s^2(s + a)(s + b)(s + c) = \frac{As + B}{s^2} + \frac{C}{s + a} + \frac{D}{s + b} \quad \text{(B12.1)}$$

$$+ E/(s + c)$$

or $$\left[s^2(s + a)^2(s + b)\right]^{-1} = \frac{As + B}{s^2} + \frac{Cs + D}{(s + a)^2} + \frac{E}{(s + b)} \quad \text{(B12.2)}$$

$$\left[s^2(s + a)^3\right]^{-1} = \frac{As + B}{s^2} + \frac{Cs^2 + Ds + E}{(s + a)^3} \quad \text{(B12.3)}$$

where the coefficients A,B,C,D,E, satisfy respectively the following equalities

$$(As + B)(s + a)(s + b)(s + c) + Cs^2(s + b)(s + c) + Ds^2(s + a)(s + c) + Es^2(s + a)(s + b) = 1 \quad \text{(B13.1)}$$

$$(As + B)(s + a)^2(s + b) + (Cs + D)(s + b)s^2 + s^2(s + a)^2E = 1 \quad \text{(B13.2)}$$

and

$$(As + b)(s + a)^3 + (Cs^2 + Ds + E)s^2 = 1$$

The elementary inverse Laplace transforms are

$$\mathcal{L}^{-1} \; (As + B)/s^2 = A + Bt;$$

$$\mathcal{L}^{-1} \; C/(s + a) = C\exp(-at); \quad \mathcal{L}^{-1} \frac{Cs + D}{(s + a)^2} = Ce^{-at} + (D - aC)te^{-at};$$

$$\mathcal{L}^{-1} \frac{Cs^2 + Ds + E}{(s + a)^3} = C\exp(-at) + (D - 2aC)t\exp(-at)$$

$$+ (E - aD - a^2C)\frac{t^2}{2} \exp(-at) \quad \text{(B14)}$$

and the problem is to solve these simultaneously.

The general expression (B4) is complicated and bulky but can be simplified a great deal by assuming $\phi_{n_1 n_2}(t)$ to be a diagonal matrix and even more so in the case of the spherical top where $\underline{\phi}(t)$ is expressible as $\underline{\phi}(t)\ \underline{1}$.

We are able to write in these cases

$$\left\langle A(t_1)A(t_2)A(t_3)A(t_4)\right\rangle_c = \underline{\phi}(t_1 - t_3)\left(- \underline{\phi}(t_2 - t_4) + \underline{1}\, \mathrm{Tr}\left[\phi(t_2\ t_4\ )\right]\right)$$

$$+ \underline{\phi}(t_2\ t_4)(-\underline{\phi}(t_1 - t_3) + \underline{1}\ \mathrm{Tr}\left[\underline{\phi}(t_1 - t_3\right])$$

$$+ 2\ \underline{\phi}(t_2 - t_3)(\underline{1}\ \mathrm{Tr}\left[\underline{\phi}(t_1 - t_4)\right] - \underline{\phi}(t_1 - t_4))$$

$$+ \underline{\phi}\ (t_1 - t_4)\ (\underline{1}\ \mathrm{Tr}\left[\underline{\phi}(t_2 - t_3)\right] - \underline{\phi}(t_2 - t_3))$$

$$+ 2\ (- \underline{1}\ \mathrm{Tr}\left[\ \underline{\phi}(t_1 - t_3)\right]\ \mathrm{Tr}\left[\ \underline{\phi}\ (t_2 - t_4)\right]$$

$$+ \mathrm{Tr}\left[\ \underline{\phi}(t_1 - t_3)\ \underline{\phi}(t_2 - t_4)\right]\ \underline{1} \qquad \text{(B15)}$$

for the non-spherical case, and for the spherical top

$$\left\langle A(t_1)A(t_2)A(t_3)A(t_4)\right\rangle_c$$

$$= 4\ \phi(t_1 - t_3)\ \phi(t_2 - t_4) + 6\phi(t_1 - t_4)\phi(t_2 - t_3)$$

$$- 6\ \phi(t_1 - t_3)\ \phi(t_2 - t_4) - 6\phi(t_1 - t_4)\phi(t_2 - t_3) \qquad \text{(B16)}$$

In the simple case considered by McConnell and coworkers we have

$$\underline{\phi}(t_1 - t_2) = \exp(-\beta(t_1 - t_2))\underline{1} \qquad \text{(B17)}$$

which when put in (B16) and integrated

$$- 2 \int_o^t dt_1\ \ldots\ldots \int_o^{t_3} t_4\ \exp(- \beta\left[t_1 - t_3 + t_2 - t_4\right])$$

$$= - 2\left[1 * e^{-\beta t} * e^{-2\beta t} * e^{-\beta t} * 1\right]$$

$$= - \frac{2}{\beta^4}\left[\frac{1}{2}\ \beta t - \frac{5}{4} + \beta t_e^{-\beta t} + e^{-\beta t} + \frac{1e^{-2\beta t}}{4}\right] \qquad \text{(B18)}$$

If we use this result to compute the $1/\beta^4$ term in the expansion of the autocorrelation function we have

$$\frac{1}{\beta^4}\ 2(e^{-\beta t} - 1 + \beta t)^2 - \frac{2}{\beta^4}(\frac{1}{2}\ \beta t - \frac{5}{4} + \beta t e^{-\beta t} + e^{-\beta t} + \frac{1}{4}\ e^{-2\beta t})$$

$$= \frac{1}{\beta^4}\ (2\beta^2 t^2 + \frac{9}{2} - 5\beta t - 6e^{-\beta t} + \frac{3e^{-2\beta t}}{2} + 2\beta t e^{-\beta t}) \qquad \text{(B19)}$$

which is exactly the result of McConnell and co-workers. We have used the fact that

$$e^{ax^2 + bx^4} = 1 + ax^2 + (a^2 + b)x^4 + O(x^6)$$

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