Stochastic modeling of generalized Fokker–Planck equations. I [a)]

Arthur E. Stillman[b)] and Jack H. Freed

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853
(Received 22 June 1979; accepted 10 September 1979)

A relatively simple method is developed whereby the many-body features of a typical generalized Fokker–Planck equation (GFPE) for a diffusing molecule are first replaced by stochastic bath variables that are assumed to be Markovian. Then the combined molecular and bath variables are characterized as a multidimensional Markov process obeying a stochastic–Liouville equation, which is, in general, incomplete, because it ignores the back reaction of the molecule on the bath variables. In the final step, the equation is completed by subjecting it to the appropriate constraints required for detailed balance. In this form the augmented Fokker–Planck equation (AFPE) properly describes relaxation to thermal equilibrium, and, for the appropriate limiting conditions, it reduces to the classical Fokker–Planck equation. This procedure for stochastic modeling of GFPE is both an improvement on and a generalization of a method previously outlined by Hwang, Mason, Hwang, and Freed (HMHF). Detailed illustrations of AFPE's are presented for the simple case of a planar rotator subjected to fluctuating torques, and these models are extended to the case of three-dimensional rotational diffusion. Examples include fluctuating torque models related to that used by HMHF. It is shown that only if the fluctuating torque is independent of the orientation of the molecule (more precisely of any fluctuating equilibrium orientation of the molecule), does the model become equivalent to the usual generalized Langevin equation. Otherwise, more general nonlinear models are obtained, which, however, are easily handled by the present methods. Models related to the slowly relaxing local structure (SRLS) model of Polnaszek and Freed are also developed. They are shown to be a consequence of requiring relaxation to the instantaneous value of the fluctuating potential associated with the torque, whereas the fluctuating torque models are a consequence of requiring relaxation to a uniform orientational distribution. They differ further in that the SRLS models are "nonfrictional". For these reasons we characterize the fluctuating torques as being "collision-induced" and the SRLS as being "structure-induced".

I. INTRODUCTION

Recent studies in these laboratories on molecular dynamics in liquids by means of ESR[1–4] and NMR[5] have clearly indicated the important role of the fluctuating torques acting on the spin probes, especially in more viscous fluids. The existence of torque components which fluctuate on a time scale slower than that of angular momentum relaxation and of the order of or somewhat faster than the reorientational correlation time of the probe leads to a breakdown in the "white-noise" assumption of classical Brownian motion theory, which may be described (in a non-Markovian fashion) by a frequency-dependent friction coefficient.[1,6] Torque components characterized by even slower fluctuations were shown to yield a dynamical local ordering on the probe, which may be described by means of a slowly relaxing local structure (SRLS) model.[2,7] When these are cooperative long-range motions, such as for example (quasi-) critical fluctuations near critical points or second-order transition points, or director fluctuations in liquid crystals, then each such phenomenon may be treated as a multimode generalization of a SRLS mechanism, such that the projection of the cooperative motions at the site of the probe induces slowly fluctuating torques and/or forces upon the probe.[7,8] In general, the non-Brownian particle will experience a whole spectrum of fluctuating torques, which may in some sense be Fourier analyzed in terms of the rapidly and the more slowly varying torque modes. In the Brownian limit, wherein the probe becomes very large, then all such modes will necessarily be rapidly relaxing and the simple-classical form of Brownian motion theory should be recovered.

In the belief that these models have more general applicability beyond their usage in magnetic-resonance relaxation, we wish, in this work, to present a more unified discussion of their characteristic features and their validity.

The many-body aspects of the motion of a probe molecule in a liquid may, in principle, be dealt with through the use of such procedures as the generalized Fokker–Planck (GFP) approach such as employed by HF[6] for rotational reorientation. That is, one may write

$$\left[\frac{\partial}{\partial t} + i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot \nabla_{L_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{L_B}\right] f_B$$

$$= -\nabla_{L_B} \cdot \langle \mathbf{R}_B \rangle_\rho = \nabla_{L_B} \cdot \int_0^t d\tau\, \mathbf{G}_{RR}(t) \cdot \left[\frac{\omega_B}{kT} + \nabla_{L_B}\right] f_B \,, \tag{1.1}$$

where

$$\mathbf{G}_{RR}(t) \equiv \langle \mathbf{R}_B(0)\mathbf{R}_B(t) \rangle_B \,. \tag{1.1'}$$

In Eq. (1.1), $f_B = f_B(\omega_B, \Omega_B, t)$ is the distribution function of the B or probe particle in terms of its angular velocity ω_B, and the Euler angles Ω_B specifying the orientation of a co-ordinate frame fixed in the molecule and the laboratory co-ordinate frame; $\mathbf{J}_B$ is the rotational operator for the B particle, $\hat{\mathbf{L}}_B$ is its angular-momentum, $\hat{\mathbf{L}}_B \cdot \nabla_{L_B}$ is the precessional term, $\langle \mathbf{N}_B \rangle$ is the average torque acting on the B particle (with the averaging over

[a)]Supported by NSF Grants CHE 77-26996 and DMR 77-17510.
[b)]NSF Post Doctoral Fellow.

 0021-9606/80/010550-17$01.00

the equilibrium distribution of the bath molecules), while $\mathbf{R}_B$ is the fluctuating part of the torques (i.e., $\langle \mathbf{N}_B \rangle$ has been substracted out). Now $\langle \mathbf{R}_B \rangle_\rho$ is the instantaneous $\mathbf{R}_B(t)$ averaged over all the bath molecules with the complete distribution function at time t. It is usually rewritten in terms of the correlation operator $\mathbf{G}_{RR}(t)$ as shown in Eq. (1.1) by taking advantage of the fact that the equilibrium average $\langle \mathbf{R}_B \rangle$ is by definition zero, and then by using an appropriate choice of initial conditions. The operator $\mathbf{G}_{RR}(t)$ is still an operator on f_B (implied by the subscript B on the angular brackets), a fact that is often ignored,[9] as well as a "correlation function" of the random torques. From an analysis of the properties of $\mathbf{G}_{RR}(t)$, HF suggest that only the more rapidly relaxing components of the fluctuating torque be included in the $\mathbf{G}_{RR}(t)$, while the slowly relaxing components (e.g., SRLS) be included in a redefined $\langle \mathbf{N}_B(t) \rangle_\rho$ which now is a slowly varying function of time. More precisely, we let $\langle \mathbf{R}_B \rangle_\rho = \langle \mathbf{R}_B^F \rangle_\rho + \langle \mathbf{R}_B^S \rangle_\rho$ (the faster and slower parts, respectively) in Eq. (1.1) and now let $\langle \mathbf{N}_B \rangle \to \langle \mathbf{N}_B(t) \rangle_\rho \equiv \langle \mathbf{N}_B \rangle + \langle \mathbf{R}_B^S \rangle_\rho$, while $\mathbf{G}_{RR}(t) \to \langle \mathbf{R}_B^F(0) \mathbf{R}_B^F(t) \rangle_B$. This separation is, in principle, purely arbitrary, but may be justified in part in terms of the different physical implications of these torques. In any event the resultant problem associated with an $\langle \mathbf{N}_B(t) \rangle_\rho$ or a $\mathbf{G}_{RR}(t)$ is still a many-body problem, which we prefer to deal with by stochastic modeling. In particular, in this work we shall be concerned with the different features for modeling a $\langle N_B(t) \rangle_\rho$ (e.g., SRLS) versus a $\mathbf{G}_{RR}(t)$ (e.g., "fluctuating torques").

It has been possible, by simple stochastic modeling of Eq. (1.1), to obtain results which are consistent with some of our experiments,[1-5,8] but the generalization and underlying principles of such procedures is, perhaps, unclear. In this work we wish to present a general procedure for generating appropriate stochastic models, which was first suggested by HMHF[1] in a form they called the "augmented stochastic Liouville" (ASL) approach. But this earlier, very brief, treatment was limited in its scope and applicability. Its most serious defect, in terms of fundamental principles, was its failure to explicitly include the constraints of detailed balance into the formulation of the ASL, thus rendering it largely a "high-temperature-limit" theory except in special cases when needed corrections could be introduced in a largely *ad hoc* fashion. Furthermore, HMHF, in their preliminary effort, point out that while the simple model they used had some of the correct qualitative features to be consistent with their experimental results (and it was rendered consistent with detailed balance), there were physically unsound features in that (1) the fluctuating torques were assumed to be independent of the orientation of the B particle, and thus not quenched by the reorientational motion; and (2) the experimental results indicated that the fluctuating torques were slowly relaxing (i.e., $|V_0 \tau_V|^2 \gg 1$, where V_0 is the magnitude of the torque with relaxation time τ_V) but they only developed the formalism for fairly rapidly relaxing torques. Subsequently Polnaszek and Freed[2,7a] utilized the ASL approach in modeling SRLS and spin relaxation in liquid crystals. Their simplified treatment is limited by the assumptions that (1) the fluctuations in the order parameter and/or local director are small and (2) these fluctuations are slow compared with the reorientational correlation time, and (3) the back reaction of the reorientation of the B particle on the SRLS was neglected. Also, if the time scales do become comparable, there exists the basic question of whether the SRLS and fluctuating torque models become equivalent, or whether there are more subtle differences between the two physical models. A major objective of the present work is to resolve all these matters. That is, we develop a more general procedure for obtaining ASL models consistent with the constraints of detailed balance. This, then enables us to remove the limitations of the earlier work as well as to gain better insight into the nature of these models and to provide the means of generating more realistic models (which can include several torque modes), for careful comparison with experiment.

We are also motivated by recent interest[10] in stochastic molecular dynamics by means of trajectory calculations of generalized Langevin equations (GLE). While the methods of solution described in our work are those appropriate for ASL or augmented Fokker–Planck equations (AFPE), nevertheless this work is relevant to the methods of stochastic molecular dynamics in that the ASL equations (or AFPE) may be transformed to augmented Langevin equations (ALE) (cf. Appendix A), which are then directly amenable to the trajectory calculations. In fact, our approach appears to us to be even more convenient than the use of the GLE approach, because the ALE equations have time-independent coefficients rather than the "memory kernels" of the GLE, and also nonlinear couplings are easily included in the ALE; in fact, the fluctuating torque and SRLS models both involve nonlinear couplings. Lastly, we believe, it offers the appeal of a direct approach to the stochastic modeling such that the physical assumptions being made are quite transparent.

In Sec. II we illustrate our method for stochastic modeling by considering the simple example of a planar rotator experiencing fluctuating torques, and we obtain augmented Fokker–Planck equations, which reduce to the regular Fokker–Planck equations in the proper limits. Simple procedures for generating generalized Smoluchowski forms for the planar rotator models of Sec. II are given in Sec. III. Stochastic models for SRLS in the planar rotator case are discussed in Sec. IV, and they are contrasted with the models of Sec. II. The augmented Langevin equations associated with the models of the previous sections appear in Sec. V, where they are compared with the GLE approach. The analogous models for three-dimensional rotational diffusion are developed and discussed in Sec. VI. Further discussion appears in Sec. VII, while a summary and conclusions is given in Sec. VIII. The general method is outlined in Appendix A.

II. THE METHOD: THE PLANAR ROTATOR AND FLUCTUATING TORQUES

A. The planar rotator

We illustrate the methodology with the simple example of a planar rotator.[11,12] The equation of motion is for this case

$$I\frac{d}{dt}\dot{\gamma} = T(\gamma, \dot{\gamma}, t) , \tag{2.1}$$

where γ is the angle the rotator makes with the laboratory frame and $\dot{\gamma}$ is the corresponding angular velocity, while I is the moment of inertia and $T(\gamma, \dot{\gamma}, t)$ is the (random) torque on the rotator, which may be a function of γ and $\dot{\gamma}$.

In classical Brownian motion theory, one employs the Langevin equation, which is obtained from Eq. (2.1) by letting

$$T(\gamma, \dot{\gamma}, t) = I[-\beta\dot{\gamma} + R(t)] + N(\gamma) , \tag{2.2}$$

i.e., a separation of the fluctuating torques into the systematic or frictional part with friction coefficient β and the random part $R(t)$ with the further requirements that it be characterized as a Gaussian random process with white noise such that

$$\langle R(t)\rangle = 0 \tag{2.3a}$$

and

$$\langle R(t)R(t')\rangle = (kT/I)\beta\delta(t-t') . \tag{2.3b}$$

We have also included in Eq. (2.2) a time-independent or mean torque $N(\gamma)$. If the correlation function of the random torques, Eq. (2.3b) has a finite relaxation, then we may redefine this "fluctuation-dissipation" theorem to be

$$\hat{\beta}(\tau) = (I/kT)\langle R(t)R(t+\tau)\rangle , \tag{2.4}$$

and Eq. (2.2) becomes[13,14]

$$T(\gamma, \dot{\gamma}, t) = I\left(-\int_0^t \hat{\beta}(t-\tau)\dot{\gamma}(\tau)d\tau + R(t)\right) + N(\gamma) \tag{2.5}$$

with a time-dependent friction coefficient $\hat{\beta}(t-\tau)$.

B. Stochastic-Liouville approach

We do not wish in this work to make the arbitrary separation of Eq. (2.5), which is called a generalized Langevin equation (GLE).[13,14] It is only one of several possible ways of expressing one's physical intuition of the nature of the problem.[15] Instead we pass from the equation of motion Eq. (2.1) directly to the associated "Liouville equation," which is nothing more than an equation of continuity for the joint probability distribution in γ and $\dot{\gamma}$, given by $P(\gamma, \dot{\gamma}, t)$. That is,

$$\frac{\partial}{\partial t}P(\gamma, \dot{\gamma}, t) = \left(-\dot{\gamma}\frac{\partial}{\partial\gamma} - I^{-1}T(\gamma, \dot{\gamma}, t)\frac{\partial}{\partial\dot{\gamma}}\right)P(\gamma, \dot{\gamma}, t) . \tag{2.6}$$

We now let

$$T(\gamma, \dot{\gamma}, t) = T'(\gamma, \dot{\gamma}, \Xi(t)) + N(\gamma) \tag{2.7}$$

and assume that the fluctuating part of the torque, $T'(\gamma, \dot{\gamma}, \Xi(t))$, is a function of the random bath variables $\Xi(t)$ which obey some stochastic law. Thus Eq. (2.6) is appropriately a "stochastic Liouville equation."[16-19] We are free to choose the stochastic law in keeping with our physical intuition, although the most convenient type is that of a stationary Markov process. We may express the stationary Markov properties of the Ξ by the master equation

$$\frac{\partial}{\partial t}f(\Xi, t) = -\Gamma_\Xi f(\Xi, t) , \tag{2.8}$$

where Γ_Ξ is the appropriate time-dependent Markovian operator for the distribution function $f(\Xi, t)$. The process we have outlined may be called "stochastification" following van Kampen.[18]

Let us consider the relevant bath variables Ξ to be n dimensional. It then immediately follows that the collective set of variables $\gamma, \dot{\gamma}$, and Ξ are together an $n+2$ dimensional Markov process.[12,17-19] [The torque itself is by Eq. (2.7) no longer an independent variable.] The associated probability density $P(\gamma, \dot{\gamma}, \Xi, t)$ varies in time due to the "reversible drift" or dynamical terms, [e.g., the $\dot{\gamma}(\partial/\partial\gamma) + I^{-1}N(\gamma)(\partial/\partial\dot{\gamma})$ terms in Eq. (2.6)] as well as the "irreversible" term(s) introduced by Eq. (2.8). That is, Eqs. (2.6)-(2.8) together yield (cf. Refs. 12, 17-19)

$$\begin{aligned}\frac{\partial}{\partial t}P(\gamma, \dot{\gamma}, \Xi, t) &= \left(-\dot{\gamma}\frac{\partial}{\partial\gamma} - I^{-1}[N(\gamma) + T'(\gamma, \dot{\gamma}, \Xi, t)]\frac{\partial}{\partial\dot{\gamma}} - \Gamma_\Xi\right)P(\gamma, \dot{\gamma}, \Xi, t) \\ &\equiv -\Gamma(\gamma, \dot{\gamma}, \Xi)P(\gamma, \dot{\gamma}, \Xi, t) .\end{aligned} \tag{2.9}$$

We note that Eq. (2.9) is of the form of a Fokker-Planck equation. It is developed for the general case in Appendix A.

Let us now for the sake of clarity choose a particular form for Γ_Ξ. We choose it so as to be consistent with the usual properties assumed for the fluctuating torques in Brownian motion theory [e.g., Eqs. (2.1)-(2.5)]. That is, let us assume for simplicity that

$$T' = I\,V f(\gamma)\sqrt{\frac{kT}{I}} , \tag{2.9'}$$

such that its amplitude $V(t)$ is characterized by a stationary and Gaussian random process with zero mean; then together with its Markovian property we have an Ornstein-Uhlenbeck process,[20] for which we can immediately write

$$\Gamma_\Xi = \Gamma_V = -\tau_V^{-1}\left(\frac{\partial}{\partial V}V + V_0^2\frac{\partial^2}{\partial V^2}\right) , \tag{2.10}$$

where V_0 is the root mean square torque amplitude and τ_V^{-1} is the damping coefficient for $V(t)$. The equilibrium distribution associated with Eq. (2.10) is[20]

$$P_0(V) = (2\pi V_0^2)^{-1/2}\exp(-V^2/2V_0^2) . \tag{2.11}$$

The angular function $f(\gamma)$ is taken to have a simple periodic form. Finally, we are neglecting any dependence of $T'(t)$ upon $\dot{\gamma}$ as would be characteristic of simple torques derivable from potentials,[6] despite its apparent contradiction of Eqs. (2.2) and (2.5) above. We return to this point later.

The fundamental assumption needed to obtain Eq. (2.9) is that the reaction of the rotator on the bath may be ignored.[12,17] This is a fundamental flaw of the method as emphasized by Kubo,[17] since it does not guarantee relaxation to thermal equilibrium, i.e., it violates detailed balance. In particular, $\dot{\gamma}$ will not relax to its Boltzmann distribution at temperature T, but to infinite

temperature. In order to correct this problem we must recognize that the back reaction of the rotator on the bath (via the fluctuating torques) must necessarily modify the dynamics of the problem, either by affecting the reversible drift terms and/or the irreversible Markovian operator $\Gamma_{\mathbf{z}}$ in Eq. (2.9). There are no other choices. Thus, we regard Eq. (2.9) as incomplete, and we inquire into the general constraints which a complete expression like Eq. (2.9) must fulfill if it is to obey detailed balance.

C. Detailed balance and the augmented Fokker-Planck equation

Haken[21] has expressed the consequences of detailed balance upon Fokker–Planck equations in a form that is particularly useful for our present applications. We illustrate for the specific forms of Eqs. (2.9) and (2.10). (The more general forms are given in Appendix A.)

We first specify (based upon physical insight) the equilibrium distribution as

$$P_0(\gamma, \dot{\gamma}, V) = N \exp[-\Phi(\gamma, \dot{\gamma}, V)] , \tag{2.12}$$

where N is the normalization constant and Φ is a "generalized thermodynamic potential." Then we consider the variables $\gamma, \dot{\gamma}, V$ as a three-dimensional vector $\mathbf{q}$ such that it has components $q_1 = \gamma$, $q_2 = \dot{\gamma}$, and $q_3 = V$. Then the three necessary and sufficient conditions for detailed balance are

(1) All diffusion coefficients, K_{ik} [i.e., twice the coefficients of second derivative(s) in Eq. (2.9) with (2.10)] are symmetric. Here subscripts i and k range from 1 to 3, so that K_{ik} represents a second rank tensor in the three-dimensional space of variables q_1, q_2, q_3. This condition is trivially obeyed in Eq. (2.10) where $K_{33} = 2\tau_V^{-1} V_0^2$ plays the role of the coefficient of diffusion of variable V.

(2) The irreversible drift coefficients D_i [i.e., the coefficients of the first derivative(s) in Eq. (2.10) associated with the irreversible "diffusive" process] obey

$$D_i - \frac{1}{2}\sum_k \frac{\partial K_{ik}}{\partial q_k} = -\frac{1}{2}\sum_k K_{ik}\frac{\partial \Phi}{\partial q_k} . \tag{2.13}$$

For $i = 1$ or 2 all terms vanish and Eq. (2.13) is trivially satisfied. For $i = 3$ we have

$$-\tau_V^{-1} V = -\tau_V^{-1} V_0^2 \frac{\partial \Phi}{\partial V} \tag{2.13'}$$

since $D_3 = -\tau_V^{-1} V$.

If, following Eq. (2.11), we write

$$P_0(\gamma, \dot{\gamma}, V) = N \exp[-\hat{\Phi}(\gamma, \dot{\gamma}) - V^2/2V_0^2] , \tag{2.12'}$$

where $\hat{\Phi}(\gamma, \dot{\gamma})$ is independent of V, then it immediately follows that Eq. (2.13') is obeyed.

(3) The reversible drift coefficients J_i [i.e., the coefficients of the first derivatives in Eq. (2.9)] obey, using Eq. (2.9'),

$$\sum_i \left(\frac{\partial J_i}{\partial q_i} - J_i \frac{\partial \Phi}{\partial q_i}\right) \equiv \sum_i \Psi_i = 0 . \tag{2.14}$$

Here $J_1 = \dot{\gamma}$, $J_2 = I^{-1}N(\gamma) + Vf(\gamma)\sqrt{kT/I}$, and $J_3 = 0$.

To test Eq. (2.14) we must assume a particular form of $\hat{\Phi}(\gamma, \dot{\gamma})$ which appears in Eq. (2.13'). In particular, we would expect $\dot{\gamma}$ to be characterized by a simple Boltzmann velocity distribution at equilibrium and γ by the corresponding Boltzmann distribution in the potential field $U(\gamma)$ which is related to the torque by

$$N(\gamma) = -\frac{d}{d\gamma} U_N(\gamma) . \tag{2.15a}$$

Also,

$$T'(\gamma, t) = -\frac{d}{d\gamma} U'(\gamma) = -IV \frac{d}{d\gamma} g(\gamma) \sqrt{\frac{kT}{I}} , \tag{2.15b}$$

where $f(\gamma) = -(d/d\gamma)g(\gamma)$. That is, we have

$$\hat{\Phi}(\gamma, \dot{\gamma}) = I\dot{\gamma}^2/2kT + U_N(\gamma)/kT . \tag{2.16}$$

When we now consider each set of terms Ψ_i for $i = 1$, 2, and 3 in Eq. (2.14) separately, we find that $\Psi_1 = \dot{\gamma}N(\gamma)/kT$, $\Psi_2 = -\dot{\gamma}N(\gamma)/kT - \dot{\gamma}Vf(\gamma)\sqrt{I/kT}$, and $\Psi_3 = 0$, so that $\Psi_1 + \Psi_2 + \Psi_3 = -\dot{\gamma}Vf(\gamma)\sqrt{I/kT}$. Thus Eq. (2.14) is not obeyed! It is clear that one or more of the J_i must be modified in order that detailed balance be satisfied. Since we note that it is the stochastic properties of V which are to be modeled, and in particular we are looking for the correction to Eqs. (2.9) [with Eqs. (2.10) and (2.11)] due to the reaction of the rotator on the bath variable V, it seems most reasonable to correct Eq. (2.9) to be in accord with Eq. (2.14) by allowing $J_3 \neq 0$. Thus we have

$$\frac{\partial}{\partial V} J_3 - \frac{V}{V_0^2} J_3 = \sqrt{\frac{I}{kT}} Vf(\gamma)\dot{\gamma} .$$

This expression is most simply satisfied by letting $J_3 = -\sqrt{(I/kT)}V_0^2 f(\gamma)\dot{\gamma}$ (so that it is independent of the variable V). Thus, Eqs. (2.9)–(2.11) become with this correction the augmented Fokker–Planck equation (AFPE):

$$\partial P(\gamma, \dot{\gamma}, V)/\partial t = -\Gamma(\gamma, \dot{\gamma}, V) P(\gamma, \dot{\gamma}, V) , \tag{2.17a}$$

where

$$\Gamma(\gamma, \dot{\gamma}, V) = \dot{\gamma}\frac{\partial}{\partial \gamma} + I^{-1}N(\gamma)\frac{\partial}{\partial \dot{\gamma}} + \sqrt{\frac{kT}{I}} Vf(\gamma)\frac{\partial}{\partial \dot{\gamma}} - V_0^2\sqrt{\frac{I}{kT}} f(\gamma)\dot{\gamma}\frac{\partial}{\partial V} - \tau_V^{-1}\left(\frac{\partial}{\partial V} V + V_0^2 \frac{\partial^2}{\partial V^2}\right) . \tag{2.17b}$$

It may readily be verified that Eq. (2.12') with Eq. (2.16) is a stationary solution to Eq. (2.17).

D. The Fokker-Planck limit

The final requirement we place upon the AFPE, Eq. (2.17), is that it reduce to the correct FP equation in γ and $\dot{\gamma}$ in the limit of very rapidly relaxing torques. [In fact, it was this requirement that was sufficient for HMHF to infer an AFPE similar to, but somewhat simpler than, Eq. (2.17) (see below) without explicitly invoking detailed balance.] To show that it does, it is first convenient to convert $\Gamma(\gamma, \dot{\gamma}, V)$ to symmetric form by the similarity transformation[22,23]:

$$\tilde{\Gamma}(\gamma, \dot{\gamma}, V) \equiv P_0^{1/2} \Gamma(\gamma, \dot{\gamma}, V) P_0^{1/2} , \tag{2.18}$$

with $P_0(\gamma,\dot\gamma, V)$ given by Eq. (2.13) with Eq. (2.16).

We obtain

$$\tilde\Gamma(\gamma,\dot\gamma,\dot\gamma,V)=\dot\gamma\frac{\partial}{\partial\gamma}+I^{-1}N(\gamma)\frac{\partial}{\partial\dot\gamma}+\sqrt{\frac{kT}{I}}Vf(\gamma)\frac{\partial}{\partial\dot\gamma}-V_0^2\sqrt{\frac{I}{kT}}f(\gamma)\dot\gamma\frac{\partial}{\partial V}-\tau_V^{-1}\left(V_0^2\frac{\partial^2}{\partial V^2}-\frac{V^2}{4V_0^2}+\frac{1}{2}\right). \tag{2.19}$$

We now convert Eq. (2.19) to simpler form by first introducing dimensionless variables: $\dot\gamma^*\equiv\alpha\dot\gamma$, $V^*\equiv\alpha V$, $V_0^*\equiv\alpha V_0$, $v^*\equiv V^*/\sqrt{2V_0^*}$, $N^*\equiv\alpha^2I^{-1}N$; $\tau_V^*\equiv\alpha^{-1}\tau_V$ with $\alpha\equiv\sqrt{I/2kT}$ and then introducing the notation

$$\mathfrak{N}_\pm\equiv\left(\dot\gamma^*\mp\frac{\partial}{\partial\dot\gamma^*}\right), \tag{2.20a}$$

$$\mathfrak{M}_\pm\equiv\left(v^*\mp\frac{\partial}{\partial v^*}\right), \tag{2.20b}$$

so that Eq. (2.19) becomes

$$\alpha\tilde\Gamma(\gamma,\dot\gamma,\dot\gamma,V)=\tfrac{1}{2}(\mathfrak{N}_++\mathfrak{N}_-)\frac{\partial}{\partial\gamma}+\tfrac{1}{2}N^*(\gamma)(\mathfrak{N}_--\mathfrak{N}_+)+\tfrac{1}{2}V_0^*f(\gamma)(\mathfrak{N}_-\mathfrak{M}_+-\mathfrak{N}_+\mathfrak{M}_-)+\tfrac{1}{2}\tau_V^{*-1}\mathfrak{M}_+\mathfrak{M}_-\ . \tag{2.21}$$

The convenience of this notation becomes apparent when we introduce[1,11a] the Hermite functions (i.e., eigenfunctions of the one-dimensional quantum-mechanical harmonic oscillator) as

$$|n\rangle\equiv h_n(\dot\gamma^*)=[\pi^{1/2}2^nn!]^{-1/2}\exp\left(-\frac{\dot\gamma^{*2}}{2}\right)H_n(\dot\gamma^*)\ , \tag{2.22a}$$

$$|m\rangle\equiv h_m(v^*)=[\pi^{1/2}2^nn!]^{-1/2}\exp\left(-\frac{v^{*2}}{2}\right)H_m(v^*), \tag{2.22b}$$

where $H_n(\dot\gamma^*)$ and $H_m(v^*)$ are the Hermite polynomials, and we recognize that

$$\mathfrak{N}_+|n\rangle=\sqrt{2(n+1)}\,|n+1\rangle\ , \tag{2.23a}$$

$$\mathfrak{N}_-|n\rangle=\sqrt{2n}\,|n-1\rangle \tag{2.23b}$$

are the raising and lowering operatures on $|n\rangle$ with similar expressions for $\mathfrak{M}_\pm|m\rangle$.

The limit of rapidly relaxing torques corresponds to

$$(V_0^*\tau_V^*)^2\ll1\ , \tag{2.24}$$

for which simple perturbation theory may be used in Eq. (2.21) for the drift term in V_0^* compared to the diffusion term in τ_V^{*-1}. To perform this, we define the "reduced" diffusion equation

$$\frac{\partial P(\gamma,\dot\gamma,t)}{\partial t}\equiv\langle m=0|\frac{\partial P(\gamma,\dot\gamma,V,t)}{\partial t}|m=0\rangle=-\langle0|\Gamma(\gamma,\dot\gamma,V)P(\dot\gamma,\dot\gamma,V,t)|0\rangle\ , \tag{2.25}$$

which is the average over the equilibrium distribution in the fluctuating torque, V, since

$$|0\rangle\equiv|m=0\rangle=\langle m=0|=H_0(v^*)=[P_0(V)]^{1/2} \tag{2.26}$$

[cf. Eq. (2.11)]. It is more convenient to Laplace transform Eq. (2.25) and perform the perturbation theory by means of a resolvent expansion[12,24] or more rigorously by a total time ordered cumulant (TTOC) expansion.[24] That is, we let

$$\tilde P(\gamma,\dot\gamma,s)\equiv\langle0|\tilde P(\gamma,\dot\gamma,V,s)|0\rangle=\langle0|\frac{1}{s+\tilde\Gamma}|0\rangle P(\gamma,\dot\gamma,0)\ , \tag{2.27a}$$

where $P(\gamma,\dot\gamma,0)$ is an arbitrary initial value.[12] Then we may write for the resolvent expansion

$$\langle0|\frac{1}{s+\tilde\Gamma}|0\rangle=\langle0|\frac{1}{s+\tilde\Gamma_0+\tilde\Gamma_V+\tilde\Gamma_1}|0\rangle=\sum_{n=0}^{\infty}\langle0|\left(\frac{-1}{s+\tilde\Gamma_0+\tilde\Gamma_V}\tilde\Gamma_1\right)^n\frac{1}{s+\tilde\Gamma_0+\tilde\Gamma_V}|0\rangle\ , \tag{2.27b}$$

where

$$\alpha\tilde\Gamma_0=\tfrac{1}{2}(\mathfrak{N}_++\mathfrak{N}_-)\frac{\partial}{\partial\gamma}+\tfrac{1}{2}N^*(\gamma)(\mathfrak{N}_--\mathfrak{N}_+)\ , \tag{2.28a}$$

$$\alpha\tilde\Gamma_V=\tfrac{1}{2}\tau_V^{*-1}\mathfrak{M}_+\mathfrak{M}_-\ , \tag{2.28b}$$

and

$$\alpha\tilde\Gamma_1=\tfrac{1}{2}V_0^*f(\gamma)(\mathfrak{N}_-\mathfrak{M}_+-\mathfrak{N}_+\mathfrak{M}_-)\ . \tag{2.28c}$$

Even in the limit $\tau_V^{*-1}\to\infty$, there is a lowest order contribution in $V^*\tau_V^{*-1}$ coming from each term in the infinite series expansion of Eq. (2.27). While it is not difficult to sum this series, we instead introduce the TTOC expansion for which it is no longer necessary. That is we replace Eq. (2.27) by[24]

$$\tilde P(\gamma,\dot\gamma,s)=\frac{1}{s+\tilde\Gamma_0-\mathcal{S}(s)}P(\gamma,\dot\gamma,t=0)\equiv\frac{1}{s+\tilde\Gamma(\gamma,\dot\gamma,s)}P(\gamma,\dot\gamma,0)\ , \tag{2.29a}$$

where

$$\mathcal{S}(s)=\sum_{w=0}^{\infty}(-1)^{w+1}\langle0|\tilde\Gamma_1\left[\frac{1}{s+\tilde\Gamma_0+\tilde\Gamma_V}(1-|0\rangle\langle0|)\tilde\Gamma_1\right]^w|0\rangle=\sum_{l=1}^{\infty}\sum_{m_1,m_2,\cdots m_l=1}^{\infty}{}'\langle0|\tilde\Gamma_1|m_1\rangle\langle m_1|\frac{1}{s+\tilde\Gamma_0+E_{m_1}}\tilde\Gamma_1|m_2\rangle\cdots\langle m_n|\frac{1}{s+\tilde\Gamma_0+E_{m_1}}\tilde\Gamma_1|0\rangle \tag{2.29b}$$

and

$$\tilde\Gamma_V|m\rangle=E_m|m\rangle=m\tau_V^{-1}|m\rangle\ . \tag{2.30}$$

The prime on the second summation on the rhs of Eq. (2.29b) restricts the summations over the set of $|m\rangle$ to exclude the equilibrium ket $|m\rangle=|0\rangle$. Thus, to lowest order in $\tilde\Gamma_1$ (i.e., second order) we obtain

$$\mathcal{S}(s)=-\tfrac{1}{2}V_0^2f^2(\gamma)\mathfrak{N}_+\left[\frac{1}{s+\tilde\Gamma_0+\tau_V^{-1}}\right]\mathfrak{N}_-\xrightarrow{\tau_V^{-1}\to\infty}-V_0^2f^2(\gamma)\tau_V\mathfrak{N}_+\mathfrak{N}_-/2\ . \tag{2.31}$$

The simple Brownian motion limit is $-\beta\mathfrak{N}_+\mathfrak{N}_-/2$. This is easily recovered if $f^2(\gamma)=1$ ignoring any orientation dependence of the torques and letting $\beta\equiv V_0^2\tau_V$. These results for $f^2(\gamma)=1$ are essentially equivalent to the form given by HMHF, although they explicitly consider matrix elements in the complete space spanned by the basis $|r\rangle|m\rangle|n\rangle$, where $|r\rangle\equiv(1/\sqrt{2\pi})\,e^{ir\gamma}$. If, however, we were to adopt a simple γ-dependent form for $f(\gamma)$, e.g.,

$f(\gamma)=\sin 2\gamma=(1/2i)(e^{2i\gamma}+e^{-2i\gamma})$, then $f^2(\gamma)=-[\frac{1}{4}(e^{4i\gamma}+e^{-4i\gamma})+\frac{1}{2}]$, and this does not rigorously reduce to the simple Brownian limit.

This problem may be removed by letting $f(\gamma)=f(\gamma-\varphi)$, where φ is another stochastic variable characterizing the torque. This leads to a physically sounder model, e.g., for $f(\gamma)=\sin 2\gamma$ the torque goes to zero whenever $\gamma=0$; but for $f(\gamma)=\sin 2(\gamma-\varphi)$ with φ randomly fluctuating over the range 0 to 2π, then the torque on the rotator becomes truly random. If we assume an isotropic diffusion in φ, then we may replace Eq. (2.17b) by the four-dimensional Markov process:

$$\Gamma(\gamma,\dot\gamma,V,\varphi)=\dot\gamma\frac{\partial}{\partial\gamma}+I^{-1}N(\gamma)\frac{\partial}{\partial\gamma}+\sqrt{\frac{kT}{I}}Vf(\gamma-\varphi)\frac{\partial}{\partial\dot\gamma}-V_0^2\sqrt{\frac{I}{kT}}f(\gamma-\varphi)\dot\gamma\frac{\partial}{\partial V}-\tau_V^{-1}\left(V_0^2\frac{\partial^2}{\partial V^2}+\frac{\partial}{\partial V}V\right)-\tau_\varphi^{-1}\frac{\partial^2}{\partial\varphi^2}\,. \tag{2.32}$$

It is easy to show that Eq. (2.32) obeys the conditions for detailed balance that are outlined above. Furthermore, by redefining Eq. (2.25) to involve an average over the equilibrium distribution in $Vf(\gamma-\varphi)$, i.e., $|m=0\rangle|p=0\rangle$, where $|p\rangle=(1/\sqrt{2\pi})\,e^{ip\varphi}$, and carrying out the approach of Eqs. (2.27)–(2.31), we obtain instead of Eq. (2.31) for $f(\gamma)=\sin r(\gamma-\varphi)$ with $r\neq 0$ the result

$$\mathcal{G}(s)=-\tfrac{1}{2}V_0^2(\tau_V^{-1}+r^2\tau_\varphi^{-1})^{-1}\mathfrak{N}_+\mathfrak{N}_-/2 \tag{2.33}$$

in the limit that $\tau_V^{-1},\ \tau_\varphi^{-1}\to\infty$ so that

$$\beta\equiv\tfrac{1}{2}V_0^2(\tau_V^{-1}+r^2\tau_\varphi^{-1})^{-1}\,, \tag{2.34}$$

which is again consistent with a classical Brownian motion result.

E. Other examples

1. Diffusion in φ only

There is still another variation which can yield a reasonable model for the one-dimensional rotator. One may let V be constant, while only φ is the Markov variable [so Eq. (2.11) is replaced by $\Gamma_\varphi=-\tau_\varphi^{-1}(\partial^2/\partial\varphi^2)$]. It would then not be sensible to allow $J_3\neq 0$ in Eq. (2.14). Instead, we let $J_4\neq 0$, i.e., a reversible drift term related to the fluctuations in φ. One has from Eq. (2.14) that $[\Phi=\hat\Phi(\gamma,\dot\gamma)]$

$$\frac{\partial J_4}{\partial\varphi}=\sqrt{\frac{I}{kT}}Vf(\gamma-\varphi)\dot\gamma=-\frac{\partial J_4}{\partial\gamma}\,. \tag{2.35a}$$

This immediately yields upon integration

$$J_4=\sqrt{\frac{I}{kT}}Vg(\gamma-\varphi)\dot\gamma=[U_T'(\gamma-\varphi)/kT]\dot\gamma\,, \tag{2.35b}$$

so that Eq. (2.17b) would become

$$\Gamma(\gamma,\dot\gamma,\varphi)=\dot\gamma\frac{\partial}{\partial\gamma}+I^{-1}N(\gamma)\frac{\partial}{\partial\dot\gamma}+\sqrt{\frac{kT}{I}}Vf(\gamma-\varphi)\frac{\partial}{\partial\dot\gamma}+\dot\gamma\sqrt{\frac{I}{kT}}V\frac{\partial}{\partial\varphi}[\,g(\gamma-\varphi)\sim]-\tau_\varphi^{-1}\frac{\partial^2}{\partial\varphi^2}\,. \tag{2.36}$$

In this form we require that $f(\gamma-\varphi)$ and $g(\gamma-\varphi)$ are expandable in Fourier series, such that there is no component that is constant [i.e., independent of $(\gamma-\varphi)$]. Any constant component of $U_T'(\gamma-\varphi)$ is thus incorporated into $U_N(\gamma)$. It is easy to verify that Eq. (2.36) obeys the conditions for detailed balance with respect to $\Phi=\hat\Phi$ as given by Eq. (2.16). We now show that in the limit that $\tau_\varphi^{-1}\to\infty$, the classical Brownian motion result is obtained. To do this we let $g(\gamma-\varphi)=(1/r)\cos r(\gamma-\varphi)$, so that $f(\gamma-\varphi)=\sin r(\gamma-\varphi)$. We now symmetrize Eq. (2.33) by means of Eqs. (2.18) and (2.16) for Φ to obtain

$$\tilde\Gamma(\gamma,\dot\gamma,\varphi)=\dot\gamma\frac{\partial}{\partial\gamma}+I^{-1}N(\gamma)\frac{\partial}{\partial\dot\gamma}+\frac{V}{\sqrt{2}}\left[f(\gamma-\varphi)\frac{\partial}{\partial\dot\gamma^*}+\left\{2g(\gamma-\varphi)\frac{\partial}{\partial\varphi}+f(\gamma-\varphi)\right\}\dot\gamma^*\right]-\tau_\varphi^{-1}\frac{\partial^2}{\partial\varphi^2}\,. \tag{2.37}$$

We then consider the matrix element of the terms in V:

$$\frac{V}{\sqrt{2}}\langle p'|f(\gamma-\varphi)\frac{\partial}{\partial\dot\gamma}+\dot\gamma^*\left(\frac{\partial}{\partial\varphi}[\,g(\gamma-\varphi)\sim]+g(\gamma-\varphi)\frac{\partial}{\partial\varphi}\right)|p\rangle$$
$$=-\frac{i}{2\sqrt{2}}V\left[e^{ir\gamma}\left(\frac{\partial}{\partial\dot\gamma^*}+\frac{r-2p}{r}\dot\gamma^*\right)\delta_{p',p-r}-e^{-ir\gamma}\left(\frac{\partial}{\partial\dot\gamma^*}+\frac{r+2p}{r}\dot\gamma^*\right)\delta_{p',p+r}\right], \tag{2.38}$$

which for $p=0$ becomes

$$-\frac{i}{2\sqrt{2}}V\mathfrak{N}_-[e^{ir\gamma}\delta_{p',-r}-e^{-ir\gamma}\delta_{p',r}]_{p=0} \tag{2.39a}$$

and for $p'=0$ becomes

$$+\frac{i}{2\sqrt{2}}V\mathfrak{N}_+[e^{ir\gamma}\delta_{p,r}-e^{-ir\gamma}\delta_{p,-r}]_{p'=0}\,. \tag{2.39b}$$

Then the analogue of Eq. (2.31) becomes

$$\mathcal{G}(s)=-\tfrac{1}{4}V^2\mathfrak{N}_+\left[\frac{1}{s+\tilde\Gamma_0+r^2\tau_\varphi^{-1}}\right]\mathfrak{N}_-\xrightarrow[\tau_\varphi^{-1}\to\infty]{}-\beta\mathfrak{N}_+\mathfrak{N}_-/2\,, \tag{2.40}$$

with

$$\beta\equiv V^2\tau_\varphi/2r^2\,, \tag{2.40'}$$

which is again the simple Brownian Fokker–Planck limit but with a redefined β.

Thus we see there are several relatively simple forms for an AFPE for the planar rotator which obey detailed balance and also reduce to the classical FP equation in the proper limit.

2. Jump models

Our previous examples have all been for cases in which the Markov operator, Eq. (2.8), is that of a simple Fokker–Planck operator [e.g., Eq. (2.10)]. It is readily possible to generalize the method to cases where the Fokker–Planck operator includes higher derivatives as pointed out in Appendix A. Perhaps more interesting are stationary Markov operators in integral form, such as those which arise from master equation or Boltzmann equation approaches.[25] While it is in general possible to convert such integral forms to higher order differential forms by a Kramers–Moyal expansion,[25] it is rather easy in some cases to deal directly with the time-inde-

pendent transition or jump probabilities to guarantee that they obey detailed balance. This is especially true for the present examples where Γ_V and Γ_φ were not modified by the back reaction of the rotator. Various jump models have been employed in orientation space,[26,27] as well as in angular momentum space.[11a,11b,28,29] By simple analogies to the "forms" of those expressions we may, for example, write

$$\tilde{\Gamma}_V|m\rangle = \tau_V^{-1}(1-\delta_{m,0}) \tag{2.41}$$

to replace Eq. (2.10) for the "extended diffusion" case in which collisions at the rate τ_V^{-1} completely randomize V [cf. Eq. (14) of Ref. 10 for the analogous model for $\dot{\gamma}$]. For jump models in the variable φ, we can replace the operator $\Gamma_\varphi = -\tau_\varphi^{-1}(\partial^2/\partial\varphi^2)$ by

$$\Gamma_\varphi|p\rangle = \tau_\varphi^{-1}p^2[1+(\tau_j/\tau_\varphi)p^2]^{-1}|p\rangle\ , \tag{2.42}$$

where τ_j is the mean time between jumps and (τ_j/τ_φ) is proportional to the size of the mean jump angle.[26,27] In the limit $\tau_j/\tau_\varphi \to 0$ (i.e., jumps of infinitesimal angle) we recover our previous results for simple diffusion in φ.

The main point is that our method for generating the AFPE has yielded the additional reversible drift terms needed for detailed balance, and we are rather free to modify the stationary-Markov operators Γ_V and Γ_φ consistent with the Gaussian equilibrium distribution in $\dot{\gamma}$.

III. GENERALIZED SMOLUCHOWSKI FORMS FOR THE PLANAR ROTATOR

We now consider another limit which is of interest in the experimental studies of Freed and co-workers.[1-5,8] This is the limit for which inertial terms are unimportant (e.g., a coarse graining in time). We first consider the Markov operator Eq. (2.32) in its symmetrized form [cf. Eq. (2.21)]:

$$\begin{aligned}\alpha\tilde{\Gamma}(\gamma,\dot{\gamma},V,\varphi) = {}& \tfrac{1}{2}(\mathfrak{R}_+ + \mathfrak{R}_-)\frac{\partial}{\partial\gamma} + \tfrac{1}{2}N^*(\gamma)(\mathfrak{R}_- - \mathfrak{R}_+) \\ & + \tfrac{1}{2}V_0^* f(\gamma-\varphi)(\mathfrak{R}_-\mathfrak{M}_+ - \mathfrak{R}_+\mathfrak{M}_-) + \tfrac{1}{2}\tau_V^{*-1}\mathfrak{M}_+\mathfrak{M}_- \\ & - \tau_\varphi^{*-1}\frac{\partial^2}{\partial\varphi^2} + \alpha\frac{\beta'}{2}\mathfrak{R}_+\mathfrak{R}_-\ ,\end{aligned} \tag{3.1}$$

where we have added a simple frictional term in β', which we assume arises from some fast torque mode, the averaging over which has already been performed in accordance with the previous section. We now wish to perform perturbation theory with respect to the terms off diagonal in the basis of Eq. (2.22a). For this purpose, we can develop a scheme analogous to that of Eqs. (2.25)–(2.30) where we replace $|m\rangle \to |n\rangle$ and redefine

$$\alpha\tilde{\Gamma}_0 \equiv \tfrac{1}{2}\tau_V^{*-1}\mathfrak{M}_+\mathfrak{M}_- - \tau_\varphi^{*-1}\frac{\partial^2}{\partial\varphi^2}\ , \tag{3.2a}$$

$$\begin{aligned}\alpha\tilde{\Gamma}_1 \equiv {}& \tfrac{1}{2}(\mathfrak{R}_+ + \mathfrak{R}_-)\frac{\partial}{\partial\gamma} + \tfrac{1}{2}N^*(\gamma)(\mathfrak{R}_- - \mathfrak{R}_+) \\ & + \tfrac{1}{2}V_0^* f(\gamma-\varphi)(\mathfrak{R}_-\mathfrak{M}_+ - \mathfrak{R}_+\mathfrak{M}_-)\end{aligned} \tag{3.2b}$$

and replace $\alpha\tilde{\Gamma}_V$ by

$$\alpha\tilde{\Gamma}_{\dot{\gamma}} \equiv \frac{\alpha}{2}\beta'\mathfrak{R}_+\mathfrak{R}_-\ . \tag{3.2c}$$

We then obtain

$$\begin{aligned}\tilde{P}(\gamma,V,\varphi,s) &\equiv \langle n=0|\tilde{P}(\gamma,\dot{\gamma},V,\varphi,s)|n=0\rangle \\ &= \frac{1}{s+\tilde{\Gamma}_0 - \mathcal{G}(s)}P(\gamma,V,\varphi,t=0) \\ &\equiv \frac{1}{s+\tilde{\Gamma}(\gamma,V,\varphi,s)}P(\gamma,V,\varphi,0)\ ,\end{aligned} \tag{3.3}$$

where

$$\mathcal{G}(s) = \sum_{n=1}^{\infty}\langle 0|\tilde{\Gamma}_1|n\rangle\langle n|\frac{1}{s+\tilde{\Gamma}_0+E_n}\Gamma_1|0\rangle + \text{H.O.T.} \tag{3.4a}$$

and

$$\tilde{\Gamma}_{\dot{\gamma}}|n\rangle = n\beta'|n\rangle \equiv E_n|n\rangle\ . \tag{3.4b}$$

For simplicity we consider the two cases (1) $\tilde{\Gamma}_0 = 0$ and $V_0 = 0$ corresponding to an ordinary FP equation, and (2) $N(\gamma) = 0$.

(1) Here

$$\mathcal{G}(s) = \frac{R'}{1+s/\beta'}\left(\frac{\partial^2}{\partial\gamma^2} - \frac{\partial N}{\partial\gamma}\frac{1}{2kT} - \frac{N^2}{(2kT)^2}\right) + \text{H.O.T.}\ ,$$

where

$$R' = kT/I\beta'\ , \tag{3.5}$$

which for $s/\beta' \ll 1$ yields the ordinary Smoluchowski equation for this model, just as one expects. The neglect of higher-order terms merely requires $|\tilde{\Gamma}_1|/\beta' \ll 1$.

(2) Here

$$\begin{aligned}\mathcal{G}(s) = R'\beta'\Big(& (s+\tilde{\Gamma}_0+\beta')^{-1}\frac{\partial^2}{\partial\gamma^2} - V_0^*\frac{\partial}{\partial\gamma}(s+\tilde{\Gamma}_0+\beta')^{-1} \\ & \times f(\gamma-\varphi)\mathfrak{M}_- + V_0^* f(\gamma-\varphi)\mathfrak{M}_+(s+\tilde{\Gamma}_0+\beta')^{-1}\frac{\partial}{\partial\gamma} \\ & - V_0^{*2}f(\gamma-\varphi)\mathfrak{M}_+(s+\tilde{\Gamma}_0+\beta')^{-1}f(\gamma-\varphi)\mathfrak{M}_-\Big) + \text{H.O.T.}\end{aligned} \tag{3.6}$$

[Note that in Eq. (3.6) the two terms in V_0^* are transposes of each other as required for $\tilde{\Gamma}(\gamma,V,\varphi,s)$ to be symmetrized.] This is a more complex form; the condition for neglecting the higher order terms here is $|\tilde{\Gamma}_1|/|\tilde{\Gamma}_0+\beta'| \ll 1$. This condition is satisfied in a simple fashion if $V_0 \ll \beta'$. Let us suppose that $\beta' \to \infty$, so that

$$\begin{aligned}\lim_{\beta'\to\infty}\mathcal{G}(s) = {} & R'\frac{\partial^2}{\partial\gamma^2} - \sqrt{\frac{kT}{2I}}\frac{V_0}{\beta'}\left(\frac{\partial}{\partial\gamma}f(\gamma-\varphi)\mathfrak{M}_- - f(\gamma-\varphi)\mathfrak{M}_+\frac{\partial}{\partial\gamma}\right) \\ & - \frac{V_0^2}{2\beta'}[f(\gamma-\varphi)]^2\mathfrak{M}_+\mathfrak{M}_-\end{aligned} \tag{3.7a}$$

and

$$\tilde{\Gamma}(\gamma,V,\varphi) \cong \tilde{\Gamma}_0 - \lim_{\beta'\to\infty}\mathcal{G}(s)\ . \tag{3.7b}$$

We now assume that

$$\sqrt{\frac{kT}{I}}\frac{V_0}{\beta'} \ll \hat{\tau}_V^{-1} \quad \text{with } \hat{\tau}_V^{-1} \equiv \tau_V^{-1} + V_0^2/\beta'\ ,$$

which is satisfied if $\sqrt{kT/I} \ll V_0$, so it is possible to use second-order TTOC perturbation theory to determine

$$\tilde{P}(\gamma, s) \equiv \langle m=0; p=0 | \tilde{P}(\gamma, V, \varphi, s) | m=0; p=0 \rangle$$

$$= \frac{1}{s + \tilde{\Gamma}(\gamma, s)} P(\gamma, t=0) \ . \tag{3.8}$$

We assume, for simplicity, that $f(\gamma - \varphi) = 1$. Then we may perform the perturbation theory by letting

$$\tilde{\Gamma}_0 = -R' \frac{\partial^2}{\partial \gamma^2} \ , \tag{3.9a}$$

$$\tilde{\Gamma}_1 = -\frac{1}{\beta'} \sqrt{\frac{kT}{2I}} V_0 \left(\mathfrak{M}_+ \frac{\partial}{\partial \gamma} - \frac{\partial}{\partial \gamma} \mathfrak{M}_- \right) \ , \tag{3.9b}$$

$$\tilde{\Gamma}_{V,\varphi} = \frac{\hat{\tau}_V^{-1}}{2} \mathfrak{M}_+ \mathfrak{M}_- \ , \tag{3.9c}$$

so that

$$\mathcal{S}(s) = \frac{R' V_0^2}{\beta'} \frac{\partial}{\partial \gamma} (s + \tilde{\Gamma}_0 + \hat{\tau}_V^{-1})^{-1} \frac{\partial}{\partial \gamma}$$

$$\xrightarrow{\hat{\tau}_V^{-1} \gg s, R'} \frac{R' V_0^2 \hat{\tau}_V}{\beta'} \frac{\partial^2}{\partial \gamma^2} \tag{3.10a}$$

and

$$\tilde{\Gamma}(\gamma, s) = \tilde{\Gamma}_0 - \mathcal{S}(s) \rightarrow -R' \left(1 + \frac{V_0^2 \hat{\tau}_V}{\beta'} \right) \frac{\partial^2}{\partial \gamma^2} \ . \tag{3.10b}$$

In order that the second term in Eq. (3.10b) be comparable to the first term, we require

$$(V_0^2/\beta') \hat{\tau}_V \sim 1 \ ,$$

which is possible if $V_0^2 \tau_V \gtrsim \beta'$. This clearly violates our initial premise that all of the fast torque modes have been incorporated into β'. Thus for $\sqrt{kT/I} \ll V_0 \ll \beta'$, $\tau_V^{-1}, S \ll \beta'$ and $f(\gamma - \varphi) = 1$ the second case is also seen to reduce to an ordinary Smoluchowski equation and no breakdown of Hubbard–Einstein relation between R and β (i.e., $R = kT/I\beta$) is expected. Yet the (noninertial) breakdown of Hubbard–Einstein relations is actually quite common in magnetic resonance experiments.[30] In terms of our stochastic modeling it appears that the restriction that $f(\gamma - \varphi) = 1$ must be lifted and/or some of the perturbative limiting inequalities are not being met.[31] An alternative explanation for this breakdown could lie in SRLS models, which are discussed in the next section.

IV. MODELS OF SLOWLY RELAXING LOCAL STRUCTURE (SRLS)

We now wish to consider a variation of the model in which the fluctuating torque is characterized by a constant magnitude V while only φ is the Markov variable [cf. Sec. II, Eq. (2.36)]. In that model, relaxation was taken as tending to the uniform distribution in the angle φ [cf. Eq. (2.16)]. Instead, we now require that relaxation is toward the instantaneous value of the potential energy [cf. Eq. (2.15b)] $U_T'(\gamma - \varphi)$ so that the "thermodynamic potential" becomes

$$\Phi(\gamma, \dot{\gamma}, \varphi) = I\dot{\gamma}^2/2kT + U_T'(\gamma - \varphi)/kT \ . \tag{4.1}$$

[We are letting $N(\gamma) = 0$ for simplicity.] We are again led to Eq. (2.9) with Eq. (2.9') as our incomplete AFPE, where

$$\Gamma_{\mathfrak{M}} = \Gamma_\varphi = -\tau_\varphi^{-1} \frac{\partial^2}{\partial \varphi^2} \tag{4.2}$$

as in the earlier case. However, with Φ given by Eq. (4.1), Eq. (2.14) is satisfied, i.e., the reversible drift coefficients are "complete," but Eq. (2.13) is not fulfilled, so the irreversible drift coefficients are incomplete. In particular, Eq. (2.13) becomes ($q_4 = \varphi$)

$$D_4 = -\tfrac{1}{2} K_{44} (\partial \Phi / \partial \varphi) = -\tau_\varphi^{-1} T'(\gamma - \varphi)/kT \ . \tag{4.3}$$

Thus D_4 cannot be zero, and Eq. (4.2) must be modified according to Eq. (4.3). The complete AFPE thus is

$$\Gamma(\gamma, \dot{\gamma}, \varphi) = \dot{\gamma} \frac{\partial}{\partial \gamma} + I^{-1} T'(\gamma - \varphi) \frac{\partial}{\partial \dot{\gamma}}$$

$$- \tau_\varphi^{-1} \left(\frac{\partial^2}{\partial \varphi^2} + \frac{\partial}{\partial \varphi} \frac{T'(\gamma - \varphi)}{kT} \right) \ , \tag{4.4}$$

and we can rewrite the torque $T'(\gamma - \varphi)$ according to Eq. (2.15b). Equation (4.4) may be symmetrized to

$$\tilde{\Gamma}(\gamma, \dot{\gamma}, \varphi) = \dot{\gamma} \frac{\partial}{\partial \gamma} + I^{-1} T'(\gamma - \varphi) \frac{\partial}{\partial \dot{\gamma}}$$

$$- \tau_\varphi^{-1} \left[\frac{\partial^2}{\partial \varphi^2} + \frac{1}{2kT} \left(\frac{\partial T'(\gamma - \varphi)}{\partial \varphi} \right) - \frac{[T'(\gamma - \varphi)]^2}{(2kT)^2} \right] \ , \tag{4.5}$$

or alternatively in operator notation when we add the effects of a rapidly relaxing torque mode providing damping coefficient β', we have

$$\alpha \tilde{\Gamma}(\gamma, \dot{\gamma}, \varphi) = \tfrac{1}{2} (\mathfrak{M}_+ + \mathfrak{M}_-) \frac{\partial}{\partial \gamma} + \tfrac{1}{2} T^*(\gamma - \varphi)(\mathfrak{M}_+ - \mathfrak{M}_-) - \tau_\varphi^{*-1}$$

$$\times \left(\frac{\partial^2}{\partial \varphi^2} + \frac{\partial T^*(\gamma - \varphi)}{\partial \varphi} - [T^*(\gamma - \varphi)]^2 \right) + \frac{\alpha \beta'}{2} \mathfrak{M}_+ \mathfrak{M}_- \ , \tag{4.6}$$

where $T^*(\gamma - \varphi) \equiv \alpha^2 T'(\gamma - \varphi)/I$.

Suppose we now consider the limit $|T^*(\gamma - \varphi)| \tau_\varphi^* \ll 1$ so that perturbation theory may be used to average over the equilibrium distribution in φ. We see, however, from the terms in τ_φ^{*-1} in Eq. (4.6) [as well as from Eq. (4.1)], that the equilibrium distribution in φ depends upon the value of γ. We defer analysis of this limit, but consider the Smoluchowski limit when $|T^*(\gamma - \varphi)|/\alpha\beta' \ll 1$. Our usual analysis gives, as $\beta' \rightarrow \infty$, the result

$$\tilde{\Gamma}(\gamma - \varphi) = -R' \left[\frac{\partial^2}{\partial \gamma^2} - \frac{1}{2kT} \left(\frac{\partial}{\partial \gamma} T'(\gamma - \varphi) \right) - \frac{[T'(\gamma - \varphi)]^2}{(2kT)^2} \right]$$

$$- \tau_\varphi^{-1} \left[\frac{\partial^2}{\partial \varphi^2} + \frac{1}{2kT} \left(\frac{\partial}{\partial \varphi} T'(\gamma - \varphi) \right) - \frac{[T'(\gamma - \varphi)]^2}{(2kT)^2} \right] \ . \tag{4.7}$$

We may compare Eq. (4.7) with the result of Eq. (3.7) by rewriting $T'(\gamma - \varphi) = I\bar{V} f(\gamma) \sqrt{kT/I}$ according to Eq. (2.15b). We see that there are very marked differences. In Eq. (4.7) we get a simple sum of two ordinary Smoluchowski equations, one for the rotator reorienting with diffusion coefficient R' relative to the orienting potential $U'(\gamma - \varphi)$, and the other for the torque (or local "director") reorienting with diffusion coefficient $R_\varphi \equiv \tau_\varphi^{-1}$ also trying to minimize the potential $U'(\gamma - \varphi)$.

More generally, the systematic or reversible back-reaction term of the rotator on the torque in the model

of Eq. (2.21) or Eq. (3.1) or Eq. (2.36) leads to a frictional contribution, while in the present case the irreversible drift term in Eq. (4.6) merely supplies an instantaneous restoring potential to the rotator, and it does not supply a frictional term. This is most easily seen by considering the limit in Eq. (4.5) of $\tau_\varphi^{-1} \to \infty$ and very large $|T'|$. (Alternatively one may examine the ALE of Sec. V.) This means that the torque rapidly reorients to minimize the potential $U'(\gamma - \varphi)$ at the *instantaneous value* of γ, so the torque itself must rapidly go to zero. For example, let $U'(\gamma - \varphi) \propto g(\gamma - \varphi) = (1/r)\cos r(\gamma - \varphi)$ so $T'(\gamma - \varphi) \propto f(\gamma - \varphi) = \sin r(\gamma - \varphi)$, then the torque acts to bring $\varphi = \gamma$ for which $f(\gamma - \varphi) = 0$. On the other hand, the model of Eq. (2.36) has the property that the torque relaxes to a uniform distribution in φ, while the reversible or "back-reaction" term of the rotator acting on the torque does not go to zero. A more quantitative analysis of the behavior of Eq. (4.5) [or (4.6)] in this limit of very fast torque relaxation may be developed by a "Born-Oppenheimer"-type of approximation analogous to that given previously,[7a] wherein the probability distribution for φ is first solved for fixed γ (and $\dot\gamma$) {i.e., one solves for the eigenstates of $\Gamma_\gamma(\varphi) = \tau_\varphi^{-1}[\partial^2/\partial\varphi^2 + (\partial/\partial\varphi)(T'/kT)]$}, and then the distribution in γ (and $\dot\gamma$) is solved in the "effective potential" for each eigenstate of $\Gamma_\gamma(\varphi)$. [The actual application in Ref. 7(a) corresponds to the reverse case of $\tau_\varphi^{-1} \to 0$ and a rapidly relaxing rotator.]

We now consider more specifically the physical implications of Eq. (4.7) itself. In the limit $\tau_\varphi^{-1} \gg R'$, the torque itself relaxes rapidly, so the rotator no longer feels the torque as it reorients; i.e., by comparing terms we see that

$$\tilde\Gamma(\gamma, \varphi) \xrightarrow{\tau_\varphi^{-1}/R' \to \infty} -R'\frac{\partial^2}{\partial\gamma^2} - \tau_\varphi^{-1} \times \left[\frac{\partial^2}{\partial\varphi^2} + \frac{1}{2kT}\left(\frac{\partial}{\partial\varphi}T'(\gamma - \varphi)\right) - \frac{[T'(\gamma - \varphi)]^2}{(2kT)^2}\right]. \quad (4.8a)$$

This would correspond to the limit of a Brownian rotator, for which the "local structure" rapidly adjusts to any motion of the Brownian particle, which is simply governed by its diffusion coefficient R'. In the other limit we get

$$\tilde\Gamma(\gamma - \varphi) \xrightarrow{\tau_\varphi^{-1}/R' \to 0} -R'\left[\frac{\partial^2}{\partial\gamma^2} + \frac{1}{2kT}\left(\frac{\partial}{\partial\varphi}T'(\gamma - \varphi)\right) - \frac{[T'(\gamma - \varphi)]^2}{(2kT)^2}\right] - \tau_\varphi^{-1}\frac{\partial^2}{\partial\varphi^2}. \quad (4.8b)$$

In this limit the rotator relaxes much faster than the "local structure." Thus it must relax in the potential resulting from the instantaneous local structure, which itself relaxes on a much slower time scale. Equation (4.8b) is, in fact, the slowly relaxing local structure model of Polnaszek and Freed[2,4,7a] (more precisely, a one-dimensional version of it) which was originally developed by ignoring any back reaction on the local structure such as appears in Eq. (4.7). We now have shown that this is indeed a sound approach in the physically interesting limit $R'\tau_\varphi \gg 1$.

One may also develop a SRLS model in which both the magnitude and orientation of the potential due to the local structure are fluctuating. We still require Eq. (4.1) to hold; then we find for the AFPE that generalizes Eq. (4.4)

$$\Gamma(\gamma, \dot\gamma, V, \varphi) = \Gamma(\gamma, \dot\gamma, \varphi) - \tau_V^{-1}V_0^2\left(\sqrt{\frac{I}{kT}}\,g(\gamma - \varphi)\frac{\partial}{\partial V} + \frac{\partial^2}{\partial V^2}\right), \quad (4.9)$$

where $\Gamma(\gamma, \dot\gamma, \varphi)$ is given by Eq. (4.4), and we may absorb coefficients by letting $2K_V \equiv \tau_V^{-1}V_0^2$, since V_0 no longer has any special significance. The diffusion in V is seen to be more complex, since it is now dependent upon $g(\gamma - \varphi)$. But this form does not constrain fluctuations in V very much when $g(\gamma - \varphi)$ is small. It may perhaps be worthwhile to include the constraint that V fluctuate about zero with a Gaussian distribution independent of $g(\gamma - \varphi)$. Thus, if we replace Eq. (4.1) by

$$\Phi(\gamma, \dot\gamma, \varphi) = I\dot\gamma^2/2kT + U_T'(\gamma - \varphi)/kT + V^2/2V_0^2. \quad (4.10)$$

Equation (4.10) is modified by the addition of the term $-\tau_V^{-1}(\partial/\partial V)V$ on the right. Except for the somewhat unusual form of Φ in Eq. (4.10), the physical features of the model seem reasonable.

Just as was done in Sec. II E for fluctuating torque models, we can introduce jumps in the local structure, except that in the present case they must be weighted as required for detailed balance according to Eq. (4.1) (cf. Ref. 22 for analogous models in orientation space). We anticipate that the Ivanov-type jump models[26,27] can be developed more soundly in terms of such models of a "jumping local structure."

V. AUGMENTED LANGEVIN EQUATIONS (ALE)

Once we have obtained the AFPE, it is then possible to relate it back to the associated Langevin equations,[21] which we refer to as augmented Langevin equations (ALE). They can provide some additional insight into the physical nature of the models. Thus, following the outline of Appendix A we have

(1) Rotator with fluctuations in V and φ [cf. Eq. (2.32)]. For this case we obtain

$$\frac{d}{dt}\begin{pmatrix}\gamma\\ \dot\gamma\\ V\\ \varphi\end{pmatrix} = \begin{pmatrix}\dot\gamma\\ Vf(\gamma - \varphi)\sqrt{kT/I} + I^{-1}N(\gamma)\\ -V_0^2 f(\gamma - \varphi)\sqrt{I/kT}\,\dot\gamma - \tau_V^{-1}V\\ 0\end{pmatrix} + \begin{pmatrix}0\\ 0\\ V_0\sqrt{\tau_V^{-1}}\,\xi_V(t)\\ \sqrt{\tau_\varphi^{-1}}\,\xi_\varphi(t)\end{pmatrix}, \quad (5.1)$$

where $\xi_V(t)$ and $\xi_\varphi(t)$ are independent Gaussian random functions such that

$$\langle\xi_i(t)\rangle = 0 \quad i = V \text{ or } \varphi, \quad (5.2a)$$

$$\langle\xi_i(t + \tau)\xi_j(t)\rangle = \delta_{ij}\delta(\tau) \quad i, j = V \text{ and/or } \varphi. \quad (5.2b)$$

Thus the $\xi_i(t)$ have units of $\sqrt{\text{time}^{-1}}$. The ALE for γ is trivial as usual; that for $\dot\gamma$ is simply in terms of the torques, as it should be [cf. Eq. (2.1)], while that for V has a simple damping term in $\tau_V^{-1}V$ (resulting from relaxation to a Gaussian distribution in V) as well as a

term resulting from a coupling to $\dot{\gamma}$, i.e., the reaction of the rotator on the bath. These ALE automatically obey fluctuation–dissipation by virtue of Eqs. (5.2). This is to be expected, since fluctuation dissipation is derivable from the condition of detailed balance. Thus we see that all aspects of this model are physically quite reasonable from the point of view of the ALE as well as the AFPE. [Note that, had we modified either J_1 or J_2 in Eq. (2.14) to "complete" the AFPE, then physically unreasonable ALE would have been obtained.]

(2) Rotator with fluctuations only in φ [cf. Eq. (2.36)]:

$$\frac{d}{dt}\begin{pmatrix}\gamma\\ \dot{\gamma}\\ \varphi\end{pmatrix}=\begin{pmatrix}\dot{\gamma}\\ \sqrt{kT/I}\,Vf(\gamma-\varphi)\\ \sqrt{I/kT}\,Vg(\gamma-\varphi)\dot{\gamma}\end{pmatrix}+\begin{pmatrix}0\\ 0\\ \sqrt{\tau}_{\varphi}^{-1}\xi_{\varphi}(t)\end{pmatrix}, \tag{5.3}$$

with $\xi_{\varphi}(t)$ again obeying Eqs. (5.2). The new term in the ALE for φ represents the back reaction of the rotator on the bath which is necessary for a frictional effect.

(3) Rotator with relaxing structure [cf. Eq. (4.4)]. We obtain

$$\frac{d}{dt}\begin{pmatrix}\gamma\\ \dot{\gamma}\\ \varphi\end{pmatrix}=\begin{pmatrix}\dot{\gamma}\\ \sqrt{kT/I}\,Vf(\gamma-\varphi)\\ -\sqrt{I/kT}\,Vf(\gamma-\varphi)\tau_{\varphi}^{-1}\end{pmatrix}+\begin{pmatrix}0\\ 0\\ \sqrt{\tau}_{\varphi}^{-1}\xi_{\varphi}(t)\end{pmatrix}. \tag{5.4}$$

Here the new term in the ALE for φ does not couple its motion back to $\dot{\gamma}$, as needed for frictional effects. Instead, there is only the damping term associated with relaxation of φ to the nonuniform distribution, $U'(\gamma-\varphi)$ [which is analogous to the $\tau_V^{-1}V$ term in Eq. (5.1)].

We now wish to show that it is possible to obtain a GLE [cf. Eq. (2.1) with Eq. (2.5)] from the ALE only for the first example [Eq. (5.1)] and provided that $f(\gamma-\varphi)=1$. To demonstrate this we note that from Eq. (5.1)

$$\varphi(t)=\sqrt{\tau}_{\varphi}^{-1}\int_0^t\xi_{\varphi}(\tau)d\tau \tag{5.5}$$

and

$$V(t)=V(0)\,e^{-t/\tau_V}-V_0^2\sqrt{\frac{I}{kT}}\int_0^t e^{-(t-\tau)/\tau_V}f[\gamma(\tau)-\varphi(\tau)]\times\dot{\gamma}(\tau)d\tau+\sqrt{\tau}_V^{-1}\int_0^t e^{-(t-\tau)/\tau_V}\xi_V(\tau)d\tau\,, \tag{5.6}$$

so that

$$\frac{d}{dt}\dot{\gamma}=I^{-1}N(\gamma)-V_0^2\int_0^t e^{-(t-\tau)/\tau_V}f[\gamma(t)-\varphi(t)]\times f[\gamma(\tau)-\varphi(\tau)]\dot{\gamma}(\tau)d\tau+\mathcal{R}(t)\,, \tag{5.7}$$

where

$$\mathcal{R}(t)\equiv\sqrt{\frac{kT}{I}}V(0)f[\gamma(t)-\varphi(t)]\,e^{-t/\tau_V}+\sqrt{\frac{kT}{I}}\sqrt{\tau}_V^{-1}\int_0^t e^{-(t-\tau)/\tau_V}\xi_V(\tau)d\tau\,. \tag{5.8}$$

We note that only if $f(\gamma-\varphi)=1$ can the second term of Eq. (5.7) be written in the GLE form[13,14]

$$-\int_0^t K(t-\tau)\dot{\gamma}(\tau)d\tau\,,$$

where $K(t-\tau)$ is a memory kernel. Then if $\mathcal{R}(t)$ is associated with a random torque, Eq. (5.7) is seen to reduce to the GLE,

$$\frac{d}{dt}\dot{\gamma}=I^{-1}N(\gamma)-\int_0^t K(t-\tau)\dot{\gamma}(\tau)d\tau+\mathcal{R}(t)\,, \tag{5.9}$$

where

$$K(t-\tau)=V_0^2\,e^{-(t-\tau)/\tau_V}\,. \tag{5.10}$$

The exponential form for this memory kernel is a consequence of the Ornstein–Uhlenbeck process assumed for $V(t)$. Other stochastic models will yield other forms for the memory kernel. Thus the GLE is seen to reduce to a special case of the ALE. Clearly, by arguments analogous to those presented above, neither Eqs. (5.3) nor (5.4) will reduce to GLE's. This emphasizes the generality of the present approach, and it provides new insight into the nature of the departure from simple Brownian theory which is described by GLE's.

VI. THREE-DIMENSIONAL ROTATIONAL DIFFUSION: AFPE

We now wish to generalize our approach to three-dimensional rotational diffusion. Here we write the stochastic-Liouville equation for a spherical top [i.e., we are neglecting the precessional term for simplicity, cf. Eq. (1.1)],

$$\frac{\partial P(\Omega,\boldsymbol{\omega},\mathbf{V}(t),t)}{\partial t}=-\Gamma[\Omega,\boldsymbol{\omega},V(t)]P(\Omega,\boldsymbol{\omega},V(t),t)\,,$$

$$\Gamma[\Omega,\boldsymbol{\omega},V(t)]=i\boldsymbol{\omega}\cdot\mathbf{J}+\sqrt{\frac{kT}{I}}\mathbf{V}(t)\cdot\nabla_{\omega}+I^{-1}\mathbf{N}(\Omega)\circ\nabla_{\omega}\,, \tag{6.1}$$

where Ω represents the Euler angles between the top and a lab frame, $\boldsymbol{\omega}$ is the angular momentum, $\mathbf{T}'(t)\equiv I^{-1}\sqrt{kT/I}\,\mathbf{V}(t)$ is the fluctuating torque, $\mathbf{J}$ is the rotational operator for the spherical top, and ∇_{ω} is the gradient operator on the angular velocity. We assume a simple Uhlenbeck–Ornstein process for $\mathbf{V}(t)$:

$$\Gamma_{\mathbf{V}}=-\tau_V^{-1}(\nabla_V\cdot\mathbf{V}+V_0^2\nabla_V^2)\,, \tag{6.2}$$

where ∇_V is the gradient operator on $\mathbf{V}$. Equation (6.2) is consistent with relaxation of $\mathbf{V}$ to the equilibrium distribution:

$$P_0(\mathbf{V})\propto\exp(-|\mathbf{V}|^2/2V_0^2)\,. \tag{6.2'}$$

We shall require that our AFPE relax to

$$P_0(\Omega,\boldsymbol{\omega},\mathbf{V})\propto\exp[-U_N(\Omega)/kT-I|\boldsymbol{\omega}|^2/2kT-|\mathbf{V}|^2/2V_0^2]\,, \tag{6.2''}$$

where $\mathbf{N}(\Omega)=-i\mathbf{J}U_N(\Omega)$. Then, by analogy to Sec. II [in particular, Eq. (2.14)] we obtain for our AFPE

$$\frac{\partial P(\Omega,\boldsymbol{\omega},\mathbf{V},t)}{\partial t}=-\Gamma(\Omega,\boldsymbol{\omega},\mathbf{V})P(\Omega,\boldsymbol{\omega},\mathbf{V},t)\,, \tag{6.3a}$$

$$\Gamma(\Omega,\boldsymbol{\omega},\mathbf{V})=i\boldsymbol{\omega}\cdot\mathbf{J}+\sqrt{\frac{kT}{I}}\mathbf{V}\cdot\nabla_{\omega}-V_0^2\sqrt{\frac{I}{kT}}\boldsymbol{\omega}\cdot\nabla_V+I^{-1}\mathbf{N}(\Omega)\cdot\nabla_{\omega}-\tau_V^{-1}(\nabla_V\circ\mathbf{V}+V_0^2\nabla_V^2)\,. \tag{6.3b}$$

It may readily be verified that Eq. (6.3) relaxes to $P_0(\Omega, \omega, \mathbf{V})$ given by Eq. (6.2''). We now transform to dimensionless variables,

$$\mathbf{v}^* \equiv \mathbf{V}/\sqrt{2}V_0 , \tag{6.4a}$$

$$\omega^* \equiv \omega\sqrt{I/2kT} , \tag{6.4b}$$

and then define operators $\mathfrak{R}_\pm$, $\mathfrak{M}_\pm$ by

$$\mathfrak{R}_\pm = \omega^* \mp \nabla_{\omega^*} , \tag{6.5a}$$

$$\mathfrak{M}_\pm = \mathbf{v}^* \mp \nabla_{v^*} . \tag{6.5b}$$

We also "symmetrize" $\Gamma(\Omega, \omega, \mathbf{V})$ by analogy to Eq. (2.18) to obtain

$$\alpha\tilde{\Gamma}(\Omega, \omega, \mathbf{V}) = \tfrac{1}{2}(\mathfrak{R}_+ + \mathfrak{R}_-)\cdot\mathbf{J} + \tfrac{1}{2}\mathbf{N}^*(\Omega)(\mathfrak{R}_- - \mathfrak{R}_+) + \tfrac{1}{2}V_0^*(\mathfrak{M}_+\cdot\mathfrak{R}_- - \mathfrak{M}_-\cdot\mathfrak{R}_+) + \tfrac{1}{2}\tau_V^{*-1}\mathfrak{M}_+\cdot\mathfrak{M}_- \tag{6.6}$$

[cf. Eq. (2.21) and related definition]. The natural basis for representing $\mathbf{V}$ is

$$|j_1 k_1 p_1\rangle \equiv Y_{j_1 p_1}(\theta_v, \varphi_v) R_{k_1 j_1}(v) , \tag{6.7}$$

where the $Y_{j_1 p_1}(\theta_v, \varphi_v)$ are the spherical harmonics in the angles θ_v and φ_v referring to the orientation of $\mathbf{V}$ relative to the lab frame, and[10,29]

$$|jk\rangle \equiv R_{k,j}(v) = N_{jk}\, e^{-v^2/2} v^j L_k^{(j+1/2)}(v^2) , \tag{6.8}$$

where $N_{jk} = [2\pi^{3/2} k!/(j+\tfrac{1}{2}+k)!\,]^{1/2}$ and $v \equiv |\mathbf{V}^*|$, and the $L_k^{(j+1/2)}(v^2)$ are the associated Laguerre polynomials.

We may also write for a basis for ω

$$|j_2 k_2 p_2\rangle \equiv Y_{j_2 p_2}(\theta_\omega, \varphi_\omega) R_{k_2 j_2}(\omega) \tag{6.9}$$

with $R_{k_2 j_2}(\omega)$ defined as in Eq. (6.8) and $\omega \equiv |\boldsymbol{\omega}^*|$.

Instead of the simple product representation $|j_1 k_1 p_1\rangle \times |j_2 k_2 p_2\rangle = |j_1 p_1 j_2 p_2\rangle$ the coupled representation $|\gamma j_1 j_2 JM\rangle$ proves to be useful. Here γ contains the quantum numbers k_1 and k_2, J results from the vector coupling of j_1 to j_2, and $M = p_1 + p_2$.

In order that Eq. (6.6) be a reasonable model, it must reduce to the Fokker–Planck equation for $V_0^2\tau_V^2 \ll 1$, i.e.,

$$\Gamma(\Omega, \omega) = i\omega\cdot\mathbf{J} + I^{-1}\mathbf{N}(\Omega)\cdot\nabla_\omega - \beta\nabla_\omega\cdot\left(\omega + \frac{kT}{I}\nabla_\omega\right) , \tag{6.10a}$$

or in symmetrized and operator form,

$$\alpha\tilde{\Gamma}(\Omega, \omega) = \tfrac{1}{2}(\mathfrak{R}_+ + \mathfrak{R}_-)\cdot\mathbf{J} + \tfrac{1}{2}\mathbf{N}^*(\Omega)\cdot(\mathfrak{R}_- - \mathfrak{R}_+) + \frac{\alpha\beta}{2}\mathfrak{R}_+\cdot\mathfrak{R}_- . \tag{6.10b}$$

It is shown in Appendix A that

$$\tau_V^{-1}\mathfrak{M}_+\cdot\mathfrak{M}_-|\gamma j_1 j_2 JM\rangle = \tau_V^{-1}(j_1 + 2k_1)|\gamma j_1 j_2 JM\rangle . \tag{6.11}$$

To second order [cf. Eqs. (2.29), (2.31) in the limit $\tau_V^{-1} \to \infty$] we then have a contribution to $\tilde{\Gamma}$ from averaging over the equilibrium state for $\mathbf{V}$ (i.e., $j_1 = 0$, $p_1 = 0$) of

$$-\frac{V_0^2}{4}\tau_V \sum_{''}\langle\gamma' 0 j_2 JM|\mathfrak{M}_+\cdot\mathfrak{R}_- - \mathfrak{M}_-\cdot\mathfrak{R}_+|\gamma'' 1 j_2'' J'' M''\rangle\langle\gamma'' 1 j_2'' J'' M''|\mathfrak{M}_+\cdot\mathfrak{R}_- - \mathfrak{M}_-\cdot\mathfrak{R}_+|\gamma'' 0 j_2 JM\rangle$$

$$= -\frac{V_0^2}{4}\tau_V \sum_{''}\langle\gamma' 0 j_2 j_2 p_2|\mathfrak{M}_-\cdot\mathfrak{R}_+|\gamma'' 1 j_2'' j_2 p_2\rangle\langle\gamma'' 1 j_2'' j_2 p_2|\mathfrak{M}_+\cdot\mathfrak{R}_-|\gamma 0 j_2 j_2 p_2\rangle , \tag{6.12}$$

where we made use of the raising and lowering properties of $\mathfrak{M}_\pm$ outlined in Appendices B and C and the summation is over all of the double-primed indices. By use of Edmonds[32] [Eqs. (7.1.6) and 5.4.1)], Eq. (6.12) reduces to (cf. Appendix B)

$$\frac{3V_0^2\tau_V}{2}(2j_2+1)^{-1}\sum_{''}(-1)^{j_2'+j_2''}\langle\gamma' j_2'\|\mathfrak{R}_+\|\gamma'' j_2''\rangle\langle\gamma'' j_2''\|\mathfrak{R}_-\|\gamma j_2\rangle . \tag{6.13}$$

But by analogy to Appendix B [cf. Eqs. (B1), (B5), and (B6)]

$$\frac{\beta}{2}\langle\gamma' j_1 j_2 JM|\mathfrak{R}_+\cdot\mathfrak{R}_-|\gamma j_1 j_2 JM\rangle = \frac{\beta}{2}(2j_2+1)^{-1}\sum_{''}(-1)^{j_2'+j_2''}\langle\gamma' j_2'\|\mathfrak{R}_+\|\gamma'' j_2''\rangle\langle\gamma'' j_2''\|\mathfrak{R}_-\|\gamma j_2\rangle . \tag{6.14}$$

Thus if we let

$$\beta \equiv 3V_0^2\tau_V , \tag{6.15}$$

we see that the correct FP limiting result is obtained.[33]

We note that Eq. (6.3) is written for a fluctuating torque $\mathbf{T}'$ that is independent of Ω. More generally, we can write $\mathbf{T}'(\Omega - \Psi) = I^{-1}\sqrt{kT/I}\,\mathbf{V}(\Omega - \Psi)$, where

$$\mathbf{T}'(\Omega - \Psi) = -i\mathbf{J}U(\Omega - \Psi) , \tag{6.16}$$

such that the potential $U(\Omega - \Psi)$ is a minimum when $\Omega = \Psi$. We can think of the Euler angles Ψ as defining a fluctuating set of axes (relative to the lab frame) which have the property of a fluctuating "director." In general, we may expand the potential $U(\Omega - \Psi)$ in generalized spherical harmonics[2,7a]:

$$U(\Omega - \Psi) = \sum_{L,K,M} u_{KM}^L \mathfrak{D}_{KM}^L(\Omega - \Psi) = \sum_{L,K,M,N} u_{KM}^L \mathfrak{D}_{KN}^L(\Omega)\mathfrak{D}_{NM}^L(-\Psi) . \tag{6.17}$$

We are then free to choose each coefficient u_{KM}^L as a stochastic variable (the generalization of the planar rotator model in which V is fluctuating, e.g., by an Uhlenbeck–Ornstein process), although one usually truncates the expansion with only one or at most a few L values. We must regard the Euler angles Ψ as stochastic variables, which fluctuate isotropically (for a fluctuating torque model) or else with respect to a Boltzmann distribution in the instantaneous value of the orienting potential (for a SRLS model).

The case of fluctuations in Ψ with the u^L_{KM} remaining constant leads to the Markov operator [cf. Eq. (2.35b) and $\mathcal{J}_z = -i(\partial/\partial\varphi)$; $\Phi = \hat{\Phi}(\Omega, \omega)$]

$$\Gamma(\Omega, \omega, \Psi) = i\omega \circ \mathbf{J} + I^{-1}\mathbf{N}(\Omega) \cdot \nabla_\omega + I^{-1}\mathbf{T}'(\Omega - \Psi) \cdot \nabla_\omega + \frac{i\omega}{kT} \cdot \mathcal{J}[U(\Omega - \Psi) \sim] + \Gamma_\Psi , \quad (6.18)$$

and where the diffusion in isotropic space of Ψ may be represented quite generally by the Markov operator

$$\Gamma_\Psi = \mathcal{J} \cdot \mathbf{R}_\Psi \cdot \mathcal{J} , \quad (6.19)$$

where $\mathcal{J}$ is the rotational operator, analogous to J, but operating on the set of Euler angles Ψ, and $\mathbf{R}_\Psi$ is the diffusion tensor of the director. The rotational diffusion expressed by Eq. (6.19) may be handled by well-known procedures.[12] Equation (6.18) represents the generalization of Eq. (2.36) for the planar rotator to three dimentions. Since the fluctuating torque given by Eqs. (6.16) and (6.17) is now a function of Euler angles Ω and Ψ, the coupling term to ω in Eq. (6.18) is more complex to analyze than that of the previous example, so we plan to discuss it elsewhere. The more general model, in which the u^L_{KM} may fluctuate is, of course, even more complex. The results Eq. (6.3) or Eq. (6.18) may be regarded as stochastic models for Eq. (1.1) in terms of fluctuating torque models.

We may now generalize the SRLS model to three dimensions. Thus, we may write for the Smoluchowski form [cf. Eqs. (4.3) and (4.7); $\Phi = U(\Omega - \Psi)/kT$]

$$\bar{\Gamma}(\Omega, \Psi) = \mathbf{J} \cdot \mathbf{R}_\Omega \cdot \mathbf{J} + \frac{\mathbf{J} \circ \mathbf{R}_\Omega \cdot (JU(\Omega - \Psi))}{2kT} + \frac{\mathbf{T}' \cdot \mathbf{R}_\Omega \cdot \mathbf{T}'}{(2kT)^2} + \mathcal{J} \cdot \mathbf{R}_\Psi \cdot \mathcal{J} + \frac{\mathcal{J} \circ \mathbf{R}_\Psi \cdot (\mathcal{J}U(\Omega - \Psi))}{2kT} + \frac{\mathbf{T}' \circ \mathbf{R}_\Psi \cdot \mathbf{T}'}{(2kT)^2} , \quad (6.20)$$

where the orientation of the probe is again specified by Euler angles Ω, while Ψ represents the Euler angles of the director due to the SRLS. Here $\mathbf{R}_\Omega$ is the rotational diffusion tensor of the probe molecule. Note that we may define a "torque" acting on the director by

$$\mathbf{T}_D(\Omega - \Psi) \equiv -i\mathcal{J}U(\Omega - \Psi) = iJU(\Omega - \Psi) = -\mathbf{T}(\Omega - \Psi) , \quad (6.21)$$

i.e., it is equal and opposite in sense to the torque acting on the probe molecule.

Equation (6.20) is the generalization of Eq. (4.7) to three dimensions. It also differs from the form used previously[2,7] in that the director diffuses under a potential of mean torque, which is dependent on the orientation of the molecule. Again, for $\mathbf{R}_\Omega \gg \mathbf{R}_\Psi$, the last two terms in Eq. (6.20) may be neglected (compared to the second and third terms), justifying the earlier approach.[2,7] Thus Eq. (6.20) may be regarded as a stochastic model for Eq. (1.1) (after integrating out the variable ω) in terms of a SRLS model. (One could, of course, combine the models of SRLS and fluctuating torques as well as include many other modes, but that clearly increases the complexity of the modeling, without introducing any new principles.)

VII. FURTHER COMMENTS

A. Increasing the bath variables

In our development we have assumed that the torque is a function of bath variables (such as V and φ) which are characterized by Markov processes. One could generalize our procedures by, for example, including the various time derivatives of these bath variables and then allow the collection of, say, V, $\dot{V} = \partial V/\partial t$, etc., to constitute a multidimensional Markov process. Suppose we were to let $\dot{V}$ obey an Ornstein–Uhlenbeck process. Then by application of Eq. (A3) there would result a new reversible drift term proportional to $\dot{V}(\partial/\partial V)$. The conditions required for detailed balance [cf. Eqs. (A11)] may then be applied to generate the AFPE. In this manner more sophisticated models could be developed, provided there is sufficient physical insight and/or experimental details to warrant them.

An expanded dynamical basis set has also been utilized by Kivelson and Keyes[34] in their Mori[13b] treatment of rotational reorientation. We find differences in our results, however, even before the set of dynamical variables has been augmented. This is readily illustrated by the classical Brownian example of the inertial planar rotator. The AFPE is simply the classical Fokker–Planck equation for this case [cf. Eqs. (2.29)–(2.31)] so that the autocorrelation function[12]

$$g(t) = \langle e^{i\gamma(t)}\, e^{-i\gamma(0)} \rangle = e^{-1/4S(t)} , \quad (7.1)$$

where

$$S(t) = (\beta/4R)(\beta t - 1 + e^{-\beta t})^{-1} . \quad (7.2)$$

Equation (7.1) may be expanded in terms of an infinite sum of exponentials.[12] In contrast, the Kivelson–Keyes approach yields a sum of two exponentials for this case. The two-variable theories do differ in that the dynamical variables for the Kivelson–Keyes approach are $Q(t) = e^{i\gamma(t)}$ and $\dot{Q}(t)$ rather than $\gamma(t)$ and $\dot{\gamma}(t)$. Kivelson and Keyes find that each new dynamical variable yields another exponential term to their calculation of $g(t)$. Thus, they would require an infinite number of variables (i.e., various projections of time derivatives of Q) in order to obtain an infinite number of exponential terms and hence a spectrum with infinite moments. In this sense we may regard their approach as a "low order" theory. The difficulty may be removed by using the natural dynamical variables (e.g., γ and $\dot{\gamma}$) in a simple linear Mori theory, and then by generating the AFPE from the resulting ALE using standard methods such as outlined in Appendix A.[35] This approach would still be equivalent to a GLE approach, and as discussed in Sec. V, is just a special case of the present method. Additional comments on this comparison have been made by HMHF.[1]

B. Spin-dependent AFPE

We now wish to comment on applications to magnetic resonance. In general, the AFPE should be generalized to explicitly include the spin degrees of freedom of the spin bearing molecule. That is, Eq. (1.1) for the GFPE may be reformulated including these spin degrees of freedom as HF have shown.[6] Thus, Eq. (1.1) becomes

$$[\partial/\partial t + i\boldsymbol{\omega}_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot \nabla_{L_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{L_B} - \tfrac{1}{2} i[\mathbf{J}_B \mathcal{H}_s(\Omega_B)^+] \cdot \nabla_{L_B} + i\mathcal{H}_s(\Omega_B)^x/\hbar] f_B(t) = \nabla_{L_B} \cdot \int_0^t \mathbf{G}^s_{RR}(t-\tau) \cdot \left(\frac{\boldsymbol{\omega}_B}{kT} + \nabla_{L_B}\right) f_B(\tau) = -\nabla_{L_B} \cdot \langle \mathbf{R}_B \rangle_\rho \,, \tag{7.3}$$

where $\mathcal{H}_s(\Omega_B)$ is the spin Hamiltonian which contains terms in Ω_B, and the superscripts x and $+$ imply commutator and anticommutator operations on the term(s) to the right. Thus, $f_B(t)$ is a classical distribution function in the molecular and bath variables [analogous to $P(t)$ in this work], but it is also a spin-density matrix in spin space.[6] Thus $i\mathcal{H}_s(\Omega_B^x)/\hbar$ on the left is the usual quantum-mechanical drift term, while the term $\frac{1}{2} i J_B \mathcal{H}_s(\Omega_B)^+$ is seen to play the role of a "spin torque," i.e., the reaction of the spins on the molecular degrees of freedom due to the orientation-dependent spin energy. The correlation operator $G^s_{RR}(t)$ also becomes spin dependent.

The form of Eq. (7.3) compared to Eq. (1.1), as well as the result of HF that, at least for high temperatures, the form of $G^s_{RR}(t)$ implies relaxation to the instantaneous spin-dependent potential energy given by $\mathcal{H}_s(\Omega)/kT$, suggests that we write our spin-dependent AFPE with $\mathcal{H}^+_s(\Omega)$ treated in a manner analogous to a potential. Thus, for example, a spin-dependent form of Eq. (2.36) becomes

$$\Gamma_s(\gamma, \dot{\gamma}, \varphi) = \Gamma(\gamma, \dot{\gamma}, \varphi) + i\mathcal{H}_s(\gamma)^x/\hbar - \frac{1}{2}\left(\frac{\partial}{\partial \gamma}\mathcal{H}_s(\gamma)^+/kT\right)\frac{\partial}{\partial \dot{\gamma}} \,, \tag{7.4}$$

where $\Gamma(\gamma, \dot{\gamma}, \varphi)$ is given by Eq. (2.36), while $i\mathcal{H}_s(\gamma)^x/\hbar$ is the spin drift term which depends upon γ; the third term is the drift term due to the spin torque. That is, we now write

$$\Phi = I\dot{\gamma}^2/2kT + U_N(\gamma)/kT + \mathcal{H}_s(\gamma)/kT \,. \tag{7.5}$$

The extension to three dimensions is straightforward. Equation (7.4) and related forms can then be handled by standard methods for dealing with spin-dependent stochastic-Liouville equations.[1,6,11a,22,36]

VIII. SUMMARY AND CONCLUSIONS

We have shown how, by relatively simple procedures, one may achieve useful stochastic models for molecular dynamics in condensed phases, which are generalizations of the classical Fokker–Planck equations for Brownian particles. Our method is first based on the procedure of "stochastification," by which a stochastic Liouville equation (SLE) is first written for the distribution function of all the relevant (coupled) dynamical variables, at least some of which are random functions of time due to dynamical interactions with the "bath." The relevant bath variables are then assumed to obey, in general, a multidimensional Markov process for which a Fokker–Planck form may be written. The augmented SLE or incomplete AFPE is then written for the composite process.

The next step is to "complete" the AFPE by subjecting the incomplete form to all the constraints of detailed balance. These constraints usually require the addition of new reversible and/or irreversible drift terms to the incomplete AFPE representing the back reaction of the dynamical variables on the stochastic bath variables. The nature of these terms is seen to be strongly dependent upon the choice (based upon physical considerations) of the equilibrium distribution function associated with the conditions of detailed balance. The final choice of the new drift terms will typically involve some additional physical insights, although for the cases studied in this work they proved to be rather obvious. Further physical insight into the complete AFPE may be achieved by studying the associated ALE.

This procedure represents an improvement and a generalization of a procedure to generate complete SLE (or AFP equations) suggested by HMHF. Instead of examining the set of constraints due to detailed balance (as given by Haken), they required that the complete AFPE have the property that it reduce to the well-known classical FP equation of the Brownian particle when the proper limits are taken. We have shown in this work that the AFPE generated by the present procedures do indeed reduce to the classical FP equation when the proper limits are taken.

We have presented detailed illustrations of the method for the case of a planar rotator subjected to a fluctuating torque. The fluctuating torque could be described in terms of fluctuations in its magnitude and/or fluctuations in the equilibrium orientation of the rotator. In all cases the AFPE was shown to reduce to a FP equation when the torque fluctuations are very rapid. In another limit where inertial effects are small, it was shown how to obtain the "augmented" Smoluchowski form. These forms are related to the simple "fluctuating torque" model used by Freed and co-workers[1–4] to analyze electron–spin relaxation experiments.

These models are characterized by detailed balance with respect to a uniform distribution for the equilibrium orientation of the rotator. When this is replaced by detailed balance with respect to the instantaneous value of the orientation-dependent potential, then a "local structure" model is obtained, which is significantly different from the fluctuating torque models in that it does *not* lead to frictional effects (i.e., the torques do not depend upon the angular velocity of the rotator). The Smoluchowski form of this model was shown to be closely related to the three-dimensional SRLS model of Polnaszek and Freed,[2] which has been used in the interpretation of magnetic resonance relaxation experiments in ordered fluids.[2–5,7,8a] The present analysis included the back-reaction effects omitted in the earlier work, but it showed that for a *slowly* relaxing local structure, such corrections may indeed be ignored.

The fact that the fluctuating torque model is associated with a uniform equilibrium distribution function, while the SRLS model is associated with a nonuniform (instantaneous) distribution function, tempts us to distinguish them physically by referring to the former model as due to "collision-induced" torques and the latter as arising from "structure-induced" torques. It is the collision-induced torque model that we may relate to a GLE.

The generalization of these models to yield three-di-

mentional rotational AFPE was also presented, and methods of analysis based upon the symmetry of the full rotation group (e.g., Wigner-Eckart theorem) were outlined. The general conclusions about the planar rotator models were found to carry over to the three-dimensional cases.

The methods employed in the present work should be considered as guidelines for reasonable model building. Stochastic assumptions are currently an unfortunate aspect of even the most sophisticated Brownian motion theory. Whether these assumptions are incorporated into forms for memory functions and random forces or else into requirements for detailed balance and the correct perturbative limit is quite arbitrary. We believe that the method we have outlined and illustrated is a particularly useful one for the stochastic modeling of molecular dynamics in the analysis of experiments. It permits a straightforward translation of physical constraints and insights into an AFPE as well as ALE, which may then be solved by standard methods. In future work we plan to further develop and extend the models discussed here.

APPENDIX A: GENERAL METHOD OF CONSTRUCTING THE AFPE

Consider a set of independent dynamical variables $\mathbf{\Delta}$ whose equation of motion may be written in the form

$$\frac{d}{dt}\mathbf{\Delta} = \mathbf{F}(\mathbf{\Delta}; \mathbf{\Xi}(t), \boldsymbol{\lambda}) , \tag{A1}$$

where $\mathbf{\Xi}(t)$ denotes a set of independent stochastic (bath) variables and $\boldsymbol{\lambda}$ denotes a set of externally determined parameters such as temperature. In general, $\mathbf{F}(\mathbf{\Delta}; \mathbf{\Xi}, \boldsymbol{\lambda})$ may be a nonlinear function of the variables. The stochastic process for $\mathbf{\Xi}$ is assumed to be stationary and Markovian with an associated master equation

$$\frac{\partial}{\partial t} P(\mathbf{\Xi}, t; \boldsymbol{\lambda}) = -\Gamma_{\mathbf{\Xi}} P(\mathbf{\Xi}, t; \boldsymbol{\lambda}) . \tag{A2}$$

The ASLE may then be written as[18,19]

$$\frac{\partial}{\partial t} P(\mathbf{\Delta}, \mathbf{\Xi}, t; \boldsymbol{\lambda}) = -[\nabla_{\mathbf{\Delta}} \cdot \mathbf{F}(\mathbf{\Delta}; \mathbf{\Xi}, \lambda) + \Gamma_{\mathbf{\Xi}}] P(\mathbf{\Delta}, \mathbf{\Xi}, t; \boldsymbol{\lambda}) . \tag{A3}$$

Here $\nabla_{\mathbf{\Delta}}$ represents the divergence over the space spanned by $\mathbf{\Delta}$. It should be emphasized that Eq. (A3) is incomplete in that the back-reaction effects of $\mathbf{\Delta}$ on the diffusion of $\mathbf{\Xi}$ do not appear in Eq. (A2). Thus the stationary solution of Eq. (A3) will, in general, yield the correct Boltzmann distribution only in the limit of infinite temperature. Equivalently, we may say that the joint probability density of $\mathbf{\Delta}$ and $\mathbf{\Xi}$ as defined by Eq. (A3) does not relax to thermal equilibrium. In order to obtain the physically correct stationary solution, additional terms which have been neglected in Eq. (A3) need to be found. We note that the ASLE will relax to thermal equilibrium if we require that it obey the principle of detailed balance. We therefore seek additional terms to Eq. (A3) subject to the constraint that detailed balance be obeyed.

It is convenient to incorporate $\mathbf{\Delta}$ and $\mathbf{\Xi}$ into a new set of augmented dynamical variables $\mathbf{q}$. The condition required in order that detailed balance be obeyed is then[21]

$$\omega(\mathbf{q}', \mathbf{q}; \boldsymbol{\lambda}) P_0(\mathbf{q}; \boldsymbol{\lambda}) = \omega(\tilde{\mathbf{q}}, \tilde{\mathbf{q}}'; \boldsymbol{\lambda}) P_0(\tilde{\mathbf{q}}'; \boldsymbol{\lambda}) , \tag{A4}$$

where the tilde denotes a time-reversal transformation, P_0 is the stationary solution, and $\omega(\mathbf{q}', \mathbf{q}; \boldsymbol{\lambda})$ is the transition probability per second from $\mathbf{q}$ to $\mathbf{q}'$ defined in terms of the conditional probability by

$$\omega(\mathbf{q}', \mathbf{q}; \boldsymbol{\lambda}) = [(\partial/\partial\tau) P(\mathbf{q}' | \mathbf{q}; \tau; \boldsymbol{\lambda})]_{\tau=0} . \tag{A5}$$

In terms of $\mathbf{q}$, the ASLE may be written as

$$\frac{\partial}{\partial t} P(\mathbf{q}, t; \boldsymbol{\lambda}) = -\Gamma(\mathbf{q}) P(\mathbf{q}, t; \boldsymbol{\lambda}) . \tag{A6}$$

Haken[21] shows that Eq. (A4) leads to the *operator* identity

$$\Gamma(\mathbf{q}'; \boldsymbol{\lambda}) P_0(\mathbf{q}'; \boldsymbol{\lambda}) = P_0(\mathbf{q}'; \boldsymbol{\lambda}) \Gamma^{+}(\mathbf{q}'; \boldsymbol{\lambda}) , \tag{A7}$$

where Γ^{+} is the operator adjoint to Γ. If $\Gamma_{\mathbf{\Xi}}$ contains only first and second derivative terms, then $\Gamma(\mathbf{q})$ is of the form

$$-\Gamma(\mathbf{q}) = -\sum_i (\partial/\partial q_i) \cdot K_i(\mathbf{q}, \boldsymbol{\lambda}) + \frac{1}{2}\sum_{i,k} (\partial^2/\partial q_i \partial q_k) K_{ik}(\mathbf{q}, \boldsymbol{\lambda}) , \tag{A8}$$

where the K_i and K_{ik} are drift and diffusion coefficients, respectively, and except for their time independence are otherwise quite general (functions of $\mathbf{q}$ and $\boldsymbol{\lambda}$). $\Gamma_{\mathbf{\Xi}}$ may, in general, contain higher order derivative terms (or be an integral operator). This will complicate the analysis below without adding any fundamentally new features.

It is convenient to define irreversible drift coefficients by[21]

$$D_i(\mathbf{q}, \boldsymbol{\lambda}) \equiv \tfrac{1}{2}[K_i(\mathbf{q}, \boldsymbol{\lambda}) + \epsilon_i K_i(\tilde{\mathbf{q}}, \tilde{\boldsymbol{\lambda}})] \tag{A9a}$$

and reversible drift coefficients as

$$J_i(\mathbf{q}, \boldsymbol{\lambda}) \equiv \tfrac{1}{2}[K_i(\mathbf{q}, \boldsymbol{\lambda}) - \epsilon_i K_i(\mathbf{q}, \boldsymbol{\lambda})] , \tag{A9b}$$

where

$$\tilde{\mathbf{q}} = \{\epsilon_1 q_1, \epsilon_2 q_2, \ldots, \epsilon_n q_n\} , \tag{A10}$$

and $\epsilon_i = \pm 1$ depending on whether q_i changes sign upon time reversal. The necessary and sufficient conditions for detailed balance in terms of K_{ik}, D_i, and J_i follow from Eq. (A7) applied to Eq. (A8). They are given by Haken as

$$K_{ik}(\mathbf{q}, \boldsymbol{\lambda}) = \epsilon_i \epsilon_k K_{ik}(\tilde{\mathbf{q}}, \tilde{\boldsymbol{\lambda}}) , \tag{A11a}$$

$$D_i - \frac{1}{2}\sum_k \frac{\partial K_{ik}}{\partial q_k} = -\frac{1}{2}\sum_k K_{ik} \frac{\partial \Phi}{\partial q_k} , \tag{A11b}$$

and

$$\sum_i \left(\frac{\partial J_i}{\partial q_i} - J_i \frac{\partial \Phi}{\partial q_i}\right) = 0 , \tag{A11c}$$

where $\Phi(\mathbf{q}, \boldsymbol{\lambda})$ is the generalized thermodynamic potential defined by the stationary solution of Eq. (A6):

$$P_0(\mathbf{q}; \boldsymbol{\lambda}) = N \exp(-\Phi) , \tag{A12}$$

with N a normalization constant [e.g., Eq. (2.12)]. The AFPE is obtained by adding (or modifying) J_i and/or D_i terms to Eq. (A8) so that Eqs. (A11) are all fulfilled subject to a particular form for $\Phi(\mathbf{q}, \boldsymbol{\lambda})$ which must be determined by physical considerations. Since by Eq.

(A11c) the choice of additional J_i are not unique, physical considerations are also required here. In this manner, the back-reaction effects of Δ on Ξ are implicitly included in $\Gamma(\mathbf{q})$, and relaxation to thermal equilibrium is ensured. [When the Fokker–Planck equation (A8) has higher derivatives of the q_i, then Eq. (A7) may be applied to generate the new conditions which generalize Eqs. (A11).]

It is now possible to generate the ALE from the complete $\Gamma(\mathbf{q})$.[21] The ALE may be written for each dynamical variable q_I as

$$\dot{q}_I = k_I(\mathbf{q}, \boldsymbol{\lambda}) + \sum_{j=1}^{m} g_{Ij}(\mathbf{q}, \boldsymbol{\lambda})\xi_j(t) \ , \tag{A13}$$

where the $\xi_j(t)$ are independent Gaussian δ-correlated random functions with

$$\langle \xi_j(t) \rangle = 0 \tag{A14a}$$

and

$$\langle \xi_I(t+\tau)\xi_J(t) \rangle = \delta_{IJ}\delta(\tau) \ . \tag{A14b}$$

k_I and g_{Ij} are related to the drift and diffusion coefficients by

$$K_I(\mathbf{q}, \boldsymbol{\lambda}) = k_I(\mathbf{q}, \boldsymbol{\lambda}) + \frac{1}{2}\sum_{k,j} (\partial g_{Ij}/\partial q_k) g_{kj} \tag{A15}$$

and

$$K_{Ik}(\mathbf{q}, \boldsymbol{\lambda}) = \sum_j g_{Ij}(\mathbf{q}, \boldsymbol{\lambda}) g_{kj}(\mathbf{q}, \boldsymbol{\lambda}) \ . \tag{A16}$$

In general, the matrix $\mathbf{K} = (K_{Im})$ is symmetric. Usually $\mathbf{K}$ is also nonnegative definite. If $\mathbf{K}$ is nonnegative definite, then there exists a real symmetric nonnegative definite matrix $\mathbf{G} = (g_{Ik})$ such that $\mathbf{G}^2 = \mathbf{K}$. Then

$$\mathbf{G} = \mathbf{U}^{-1}[(K_i^0)^{1/2}\delta_{ij}]\mathbf{U} \ , \tag{A17}$$

where $(K_i^0)\delta_{ij}$ is the eigenvalue matrix of $\mathbf{K}$, and $\mathbf{U}$ is the corresponding eigenvector matrix. Then the $k_I(\mathbf{q}, \boldsymbol{\lambda})$ are obtained from Eq. (A15).

APPENDIX B: MATRIX ELEMENTS OF $\mathfrak{M}_+ \cdot \mathfrak{M}_-$

We wish to evaluate the matrix element of $\mathfrak{M}_+ \cdot \mathfrak{M}_-$ in the coupled representation [cf. Eq. (6.11)]:

$$\tfrac{1}{2}\tau_V^{-1}\langle \gamma' j_1' j_2' JM | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \gamma j_1 j_2 JM \rangle \ . \tag{B1}$$

The standard relation between the coupled and uncoupled representations is

$$|\gamma j_1 j_2 JM\rangle = (-1)^{j_1 - j_2 + M}(2J+1)^{1/2} \sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} |\gamma j_1 m_1 j_2 m_2\rangle \ , \tag{B2}$$

where the $3-j$ symbols have been used. Thus, Eq. (B1) becomes

$$\frac{\tau_V^{-1}}{2}(-1)^{j_1 + j_1' - j_2 - j_2' + M + M'}(2J+1) \sum_{m_1, m_1', m_2} \begin{pmatrix} j_1' & j_2 & J' \\ m_1' & m_2 & -M' \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} \langle \gamma' j_1' m_1' | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \gamma j_1 m_1 \rangle \delta_{j_2', j_2} \ . \tag{B3}$$

One has from Edmonds [Eq. (5.4.1)] that

$$\langle \gamma' j_1' m_1' | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \gamma j_1 m_1 \rangle = (-1)^{j_1' - m_1'} \begin{pmatrix} j_1' & 0 & j_1 \\ -m_1' & 0 & m_1 \end{pmatrix} \langle \gamma' j_1' | \, | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \, | \gamma j_1 \rangle \ , \tag{B4}$$

where the double bars denote the reduced matrix elements according to the Wigner–Eckart theorem.[32] It follows from Eq. (B4) and the properties of the $3-j$ symbols that only $m_1' = m_1$ terms contribute to Eq. (B3). Moreover, from the triangle properties of the $3-j$ symbols, Eq. (B4) vanishes unless $j_1' = j_1$. Equation (B1) is therefore equivalent to

$$\tfrac{1}{2}\tau_V^{-1}\langle \gamma' j_1 M | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \gamma j_1 M \rangle \delta_{j_1', j_1}\delta_{j_2', j_2}\delta_{J', J}\delta_{M', M} = \tfrac{1}{2}\tau_V^{-1}(2j_1+1)^{-1/2}\langle \gamma' j_1 | \, | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \, | \gamma j_1 \rangle \delta_{j_1', j_1}\delta_{j_2', j_2}\delta_{J', J}\delta_{M', M} \ , \tag{B5}$$

where we made further use of the properties of the $3-j$ symbols, including their orthogonality properties. From Edmonds [Eq. (7.1.1)], we have

$$\begin{aligned} \langle \gamma' j_1 | \, | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \, | \gamma j_1 \rangle &= (2j_1+1)^{-1/2} \sum_{\gamma'' j_1''} (-1)^{j_1'' + j_1} \langle \gamma' j_1 | \, | \mathfrak{M}_+ | \, | \gamma'' j_1'' \rangle \langle \gamma'' j_1'' | \, | \mathfrak{M}_- | \, | \gamma j_1 \rangle \\ &= (2j_1+1)^{-1/2} \sum_{\gamma'' j_1''} \frac{\langle \gamma' j_1 0 | \mathfrak{M}_+(0) | \gamma'' j_1'' 0 \rangle \langle \gamma'' j_1'' 0 | \mathfrak{M}_-(0) | \gamma j_1 0 \rangle}{\begin{pmatrix} j_1 & 1 & j_1'' \\ 0 & 0 & 0 \end{pmatrix}^2} \ , \end{aligned} \tag{B6}$$

where

$$\mathfrak{M}_\pm(0) = v_0 \mp \nabla_{v,0} \ . \tag{B7}$$

v_0 and $\nabla_{v,0}$ are the $m=0$, first rank irreducible tensor components of $\mathbf{v}^*$ and $\nabla_v *$, respectively. The only nonvanishing matrix elements of $\mathfrak{M}_\pm(0)$ are $(\gamma \to k_1, \ \gamma' \to k_1', \ R_{k_1, j_1} \to |j_1 k_1\rangle)$:

$$\langle \gamma', j_1+1, 0 | v_0 \mp \nabla_{v,0} | \gamma, j_1, 0\rangle = \frac{j_1+1}{[(2j_1+1)(2j_1+3)]^{1/2}} \langle j_1+1, k_1' | v \mp \left(\frac{\partial}{\partial v} - \frac{j_1}{v}\right) | j_1 k_1\rangle \tag{B8a}$$

(cf. Edmonds, p. 80 for the irreducible tensor components of ∇), and

$$\langle \gamma', j_1-1, 0 | v_0 \mp \nabla_0 | \gamma, j_1, 0\rangle = \frac{j_1}{[(2j_1-1)(2j_1+1)]^{1/2}} \langle j_1-1, k_1' | v \mp \left(\frac{\partial}{\partial v} + \frac{j_1+1}{v}\right) | j_1, k_1\rangle \ . \tag{B8b}$$

These matrix elements involve the ladder and flip-flop operators discussed in Appendix C. By use of relations in Appendix C we finally obtain

$$\tfrac{1}{2}\tau_V^{-1} \langle \gamma' j_1' j_2' J' M' | \mathfrak{M}_+ \cdot \mathfrak{M}_- | \gamma j_1 j_2 J M\rangle = \tau_V^{-1}(j_1+2k_1)\delta_{j_1',j_1}\delta_{j_2',j_2}\delta_{J',J}\delta_{M',M} \ . \tag{B9}$$

APPENDIX C: LADDER AND FLIP-FLOP OPERATORS FOR ASSOCIATED LAGUERRE FUNCTIONS

From the definition of the $R_{k,j}(v) = |jk\rangle$ [Eq. (6.8)] and the recurrence relations[37]

$$x\frac{d}{dx}L_n^{(\alpha)}(x) = nL_n^{(\alpha)}(x) - (\alpha+n)L_{n-1}^{(\alpha)}(x) \ , \tag{C1}$$

$$\frac{d}{dx}L_n^{(\alpha)}(x) = -L_{n-1}^{(\alpha+1)}(x) \ , \tag{C2}$$

$$L_n^{(\alpha)}(x) = L_{n-1}^{(\alpha)}(x) + L_n^{(\alpha-1)}(x) \ , \tag{C3}$$

and

$$(1+\alpha+n)L_n^{(\alpha)}(x) = (n+1)L_{n+1}^{(\alpha)}(x) + xL_n^{(\alpha+1)}(x) \ , \tag{C4}$$

it is straightforward to show that

$$\langle j'k' | v - \frac{\partial}{\partial v} + \frac{j}{v} | jk\rangle = 2\sqrt{j+k+\tfrac{3}{2}}\,\delta_{k',k}\delta_{j',j+1} \tag{C5}$$

and

$$\langle j'k' | v + \frac{\partial}{\partial v} + \frac{j+1}{v} | jk\rangle = 2\sqrt{j+k+\tfrac{1}{2}}\,\delta_{k',k}\delta_{j',j-1} \ . \tag{C6}$$

Equations (C5) and (C6) define the "raising" and "lowering" operators, respectively. Also,

$$\langle j'k' | v + \frac{\partial}{\partial v} - \frac{j}{v} | jk\rangle = -2\sqrt{k}\,\delta_{k',k-1}\delta_{j',j+1} \tag{C7}$$

and

$$\langle j'k' | v - \frac{\partial}{\partial v} - \frac{j+1}{v} | jk\rangle = -2\sqrt{k+1}\,\delta_{k',k+1}\delta_{j',j-1} \tag{C8}$$

are the "flip-flop" operators.

[1] J. S. Hwang, R. P. Mason, L.-P. Hwang, and J. H. Freed, J. Phys. Chem. **79**, 489 (1975). Referred to as HMHF.

[2] C. F. Polnaszek and J. H. Freed, J. Phys. Chem. **79**, 2283 (1975).

[3] J. S. Hwang, K. V. S. Rao, and J. H. Freed, J. Phys. Chem. **80**, 1490 (1976).

[4] W.-J. Lin and J. H. Freed, J. Phys. Chem. **83**, 379 (1979).

[5] H. A. Lopes Cardozo, J. Bulthuis, J. H. Freed, and W. M. M. J. Bovée, Chem. Phys. Lett. **60**, 335 (1979).

[6] L.-P. Hwang and J. H. Freed, J. Chem. Phys. **63**, 118 (1975) (and references therein). Referred to as HF.

[7] (a) J. H. Freed, J. Chem. Phys. **66**, 4183 (1977); (b) J. H. Freed (unpublished).

[8] K. V. S. Rao, J. S. Hwang, and J. H. Freed, Phys. Rev. Lett. **37**, 515 (1976).

[9] HF explicitly consider this operator property of $G_{RR}(t)$ in their analysis of a coarse-grained generalized Smoluchowski form of Eq. (1.1) valid for times $t \gg \tau_J$, the angular-momentum relaxation time. In that limit, and only when $\mathbf{R}_B(t)$ fluctuates more rapidly than the probe can respond inertially, can $\mathbf{G}_{RR}(t)$ be simplified to a correlation function of $\mathbf{R}_B(t)$ which is no longer an operator on the B particle.

The generalized Smoluchowski form of HF valid for $t \gg \tau_J$ (or alternatively for Fourier-transform variable $\omega \ll \tau_J^{-1}$), in which limit inertial effects are unimportant, has been unjustly criticized for ignoring some correction terms which, in fact are just inertial corrections that begin to be important only when the constraint $t \gg \tau_J$ (or $\omega \ll \tau_J^{-1}$) is removed.

The HF result, Eq. (1.1), is a special case of their more general result (cf. Ref. 6, Secs. II.C and III.B) for the combined distribution function for the B particle in terms of both its translational and rotational phase space, f_B^{TR}, and the averaging is over translational and rotational degrees of freedom of the bath particles. This does not appear to have been generally appreciated. Only when cross correlations between torques and forces in the form of the operator $\mathbf{G}_{RT}(t)$ and its transpose are neglected is Eq. (1.1) strictly valid. We neglect such cross correlations in the present work, although the method developed below can readily be applied when they are present.

[10] S. A. Adelman and J. D. Doll, Accts. Chem. Res. **10**, 378 (1977) and references cited therein.

[11] (a) G. V. Bruno and J. H. Freed, J. Phys. Chem. **78**, 935 (1974); (b) R. A. Sack, Proc. Phys. Soc. London **70**, 402, 414 (1957); (c) J. H. Freed, J. Chem. Phys. **56**, 1407 (1972); (d) M. Evans, Chem. Phys. Lett. **39**, 601 (1976).

[12] J. H. Freed, in *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Chap. VIII.

[13] (a) R. Kubo, Rep. Prog. Phys. **29**, Part I, 255 (1966); (b) H. Mori, Prog. Theor. Phys. **33**, 423 (1965).

[14] B. J. Berne and G. D. Harp, Adv. Chem. Phys. **17**, 63 (1970).

[15] See, for example, M. Tokuyama and H. Mori, Prog. Theor. Phys. **55**, 411 (1976).

[16] R. Kubo, J. Math. Phys. **4**, 174 (1963).

[17] R. Kubo, J. Phys. Soc. Jpn. **26**, Suppl. 1 (1969).

[18] N. G. van Kampen, Phys. Rept. **24C**, 171 (1976).

[19] U. Frisch, in *Probabilistic Methods in Applied Mathematics*, edited by A. T. Bharucha-Reid (Academic, New York, 1968); A. Brissaud and U. Frisch, J. Math. Phys. **15**, 524 (1974).

[20] (a) G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 823 (1930); (b) M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).

[21] H. Haken, Rev. Mod. Phys. **47**, 67 (1975).

[22] C. F. Polnaszek, G. V. Bruno, and J. H. Freed, J. Chem. Phys. **58**, 3185 (1973).

[23] The transformation $\tilde{\Gamma} = P_0^{-1/2}\Gamma P_0^{1/2}$ will generally render $\tilde{\Gamma}$ symmetric or else possessing antisymmetric blocks, provided that $\Gamma P_0 \equiv 0$. If $\tilde{\Gamma}$ is not symmetric, it still may be readily symmetrized using methods discussed by G. V. Bruno, Ph. D.

thesis, Cornell University, Ithaca, NY, 1973. In particular, antisymmetric blocks may be transformed to complex symmetric blocks by these methods.
[24]B. Yoon, J. M. Deutch, and J. H. Freed, J. Chem. Phys. **62,** 4687 (1975).
[25]I. Oppenheim, K. E. Shuler, and G. H. Weiss, *Stochastic Processes in Chemical Physics: The Master Equation* (MIT Press, Cambridge, 1977), and reprints included therein.
[26]K. A. Valiev and E. N. Ivanov, Sov. Phys.-Usp. **16,** 1 (1973).
[27]S. A. Goldman, G. V. Bruno, C. F. Polnaszek, and J. H. Freed, J. Chem. Phys. **56,** 716 (1972).
[28]R. G. Gordon, J. Chem. Phys. **44,** 1830 (1966).
[29]M. Fixman and K. Rider, J. Chem. Phys. **51,** 2425 (1969).
[30]See, for example, D. S. Leniart, H. D. Connor, and J. H. Freed, J. Chem. Phys. **63,** 165 (1975).
[31]A. E. Stillman and J. H. Freed (to be published); Preliminary calculations using Eq. (3.1) with $N(\gamma) = 0$ and $f(\gamma - \varphi) = 1$ indicate that $\sqrt{kT/I} \gtrsim V_0$ and/or $V_0\tau_V \geq 1$ lead to a breakdown in the Einstein–Hubbard relation in the direction opposite from that observed in experiments.[30]
[32]A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, NJ, 1960).
[33]Fixman and Rider[29] discuss the FP equation and its solution by related techniques.
[34]D. Kivelson and T. Keyes, J. Chem. Phys. **57,** 4599 (1972).
[35]M. Ferrario and P. Grigolini, Chem. Phys. Lett. **62,** 100 (1979).
[36]J. H. Freed, in *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Chap. XIV; J. H. Freed, G. V. Bruno, and C. F. Polnaszek, J. Phys. Chem. **75,** 3385 (1971).
[37]E. D. Rainville, *Special Functions* (Chelsea, New York, 1960).