

Generalized Einstein relations for rotational and translational diffusion of molecules including spin*

Lian-Pin Hwang and Jack H. Freed

Department of Chemistry, Cornell University, Ithaca, New York 14853
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In this work the validity of generalized Einstein relations, $D(\omega) = kT/I\beta(\omega)$, where $D(\omega)$ and $\beta(\omega)$ are frequency-dependent diffusion and damping coefficients, is examined from a general point of view. It is shown that generalized Smoluchowski (S) equations for both translational and rotational diffusion involving the $D(\omega)$, which are defined in terms of simple correlation functions of the fluctuating forces and torques, follow from the appropriate generalized Fokker-Planck (FP) expressions when the translational and angular momenta are taken as rapidly relaxing and a coarse graining in time is introduced. It is found useful in this context to distinguish between those forces and torques fluctuating at rates faster than the diffusive-type motions of the B particle versus those fluctuating more slowly. The appropriate FP equation for rotational diffusion is also derived. Generalized FP and S equations are also derived for the semiclassical case where the molecule(s) examined contains spin degrees of freedom. A proper application of the correspondence principle leads to certain terms referred to as "spin-force" or "spin-torque" terms which have the property of tending to restore the spins to their thermal equilibrium value, an important feature usually lacking in semiclassical treatments. Some simple examples of the generalized S equations are given in terms of memory function approximations of the random force and torque correlation functions. The resulting expressions are seen to bear a close formal similarity to typical expressions developed for simple jump models in either orientational or translational space. It is suggested that recent frequency-dependent experiments, including some previously interpreted in terms of simple jump models, may be amenable to analysis in terms of generalized Einstein and S equations.

I. INTRODUCTION

It is generally well recognized that small molecular particles in liquids should not be expected to obey simple diffusional equations of motion that are appropriate for large Brownian particles. There are, of course, many simple and complex models offered for their description.¹⁻⁴ There also exist fundamental statistical-mechanical theories of transport phenomena to deal with the problem, but these rapidly become unwieldy and gross simplifying assumptions are usually introduced at an early stage. In particular, we note the existence of several treatments based on modern methods which show how, in general, one may achieve a formally exact solution in the form of a Fokker-Planck equation but with a memory kernel or equivalently a frequency-dependent friction coefficient.⁵⁻⁷ The description of the latter is still an N -body problem, so simplifying stochastic assumptions are quickly introduced. More careful analyses have in the past typically centered on showing how, in the limit of a heavy solute particle, the well-known Fokker-Planck and Smoluchowski equations are achieved.⁵⁻⁸ When expansions in powers of the mass ratio of solute and solvent particles may not be invoked, one is typically satisfied with introducing a simple functional form for the frequency-dependent friction coefficient. The remaining problem then involves just the phase space of the solute particle. However, in many experiments, one is interested only in the distribution function for the position (or the orientation) of the solute particle, i. e., the linear (or angular) momentum is not directly observed. In general, however, the coupling of position or orientation to the relevant momenta may be significant so that their behavior is influenced by "inertial effects." Many authors have discussed models for such inertial ef-

fects,^{9,10} in terms of conventional Fokker-Planck expressions or some other simple models for the relevant momentum relaxation, and these have been of some success in analyzing experiments on small molecules in very nonviscous fluids. It appears, however, that for moderate-size molecules in aqueous or more viscous solvents, the typical inertial effects are unimportant, since the damping is strong enough. In conventional Brownian motion theory this means that $D/\beta \ll 1$, where β is the frictional coefficient and the diffusion coefficient D is given by the Einstein relation¹¹ as

$$D_T = kT/m\beta_T \quad (1.1)$$

for translational or

$$D_R = kT/I\beta_R \quad (1.2)$$

for rotational motion. However, even in the overdamped region, for particles of molecular size this may not necessarily be the appropriate limit. The translational or rotational diffusion still may require more complex description. In particular, one may postulate more complex models for β_R or β_T than the Stokes relations for Brownian particles.¹² More significantly, however, is the question whether Eqs. (1.1) and (1.2) are still valid. In fact, one may, by analogy with the fundamental concept of a frequency-dependent friction coefficient $\beta(\omega)$ (which includes the N -body dynamics) introduce frequency-dependent diffusion coefficients¹³:

$$D_T(\omega) = kT/m\beta_T(\omega), \quad (1.3)$$

and

$$D_R(\omega) = kT/I\beta_R(\omega), \quad (1.4)$$

which we shall call generalized Einstein relations. To the extent that this is valid, one would anticipate being

able to describe the molecular diffusion by a generalized Smoluchowski equation.

Our interest in this matter has been motivated by recent esr experiments,¹⁴⁻¹⁶ which appear to be rather sensitive to the frequency dependence of the spectral density generated by the molecular rotational reorientation. They are indicative of the breakdown of a simple Debye-like spectral density which is obtained when Eq. (1.2) is applicable. Thus, they are suggestive of the need for a more general relation, such as that of Eq. (1.4). In this context, we note that these esr experiments, as well as a wide variety of other experiments on both rotational and translational diffusion, have been analyzed in terms of Smoluchowski-type equations, i. e., diffusion of just the positional or orientational degrees of freedom. In many cases of reorientational relaxation, however, the idea of jump diffusion,²⁻⁴ in which the molecule reorients in steps of substantial angle, have been invoked to "explain" results of experiments utilizing different techniques (e. g., ir vs Raman or nmr vs dielectric relaxation) or results of a single experiment that is simultaneously sensitive to the relaxation of several spherical harmonics (e. g., slow-tumbling esr¹⁴⁻¹⁶). Jumps of finite length have also been invoked to describe results on translational diffusion of molecules.¹⁹ One may reasonably ask whether alternative (or more fundamental) explanations exist, perhaps in the context of generalized expressions like Eqs. (1.3) and (1.4).

It is our objective in this work to examine the question of the theoretical relevance and validity of Eqs. (1.3) and (1.4). We study this matter in the context of already well-developed theoretical methods. Thus, in Sec. II we outline the derivation of a generalized rotational Fokker-Planck (FP) equation along lines quite similar to the typical derivation of the translational case using a projection operator formalism.⁵ The combined generalized translational-rotational FP equation also follows from this derivation. Then in Sec. III the passage to generalized Smoluchowski equations is developed in terms of a coarse graining in time approach based upon a functional analysis approach.^{20,21} This analysis involves an expansion in the assumed weak coupling of orientation to angular momentum (or position to linear momentum), i. e., the momentum is taken as a rapidly relaxing variable compared to the orientation (or position).

Since many of the experiments that are expected to be relevant involve spin resonance, for which the coupling of spin and orientational (or translational) degrees of freedom can become very complex,¹⁴⁻¹⁹ we give in Sec. IV the derivations of generalized FP and Smoluchowski equations wherein the spin degrees of freedom are included explicitly. These expressions are of the semiclassical type, i. e., the spatial degrees of freedom of the molecules are treated classically, while the spins are quantum mechanical. There has been a fundamental difficulty with such expressions, often referred to as stochastic Liouville equations (in the case of conventional Markovian FP and Smoluchowski equations).²²⁻²⁴ That is, these expressions do not predict that the relax-

ation of the spins is to their thermal equilibrium value.²²⁻²⁴ Instead one usually introduces this as an ad hoc assumption in the high-temperature limit.²⁴ Recently it was shown how, for a particular physical situation (viz., relative diffusion of radical pairs with spin-dependent exchange interactions which can be much greater than kT), the Smoluchowski-type stochastic Liouville equation must be modified to correctly deal with this matter.²⁵ Another important objective of this work is to rigorously examine how semiclassical generalized FP and Smoluchowski equations including spin should be formulated to overcome this weakness. Our results will be seen to be a generalization of the model already noted.^{25b,26}

We give in Sec. V some examples of the generalized Smoluchowski equations using simple memory functions and we compare the results with typical jump-diffusion expressions. A summary and conclusions are given in Sec. VI.

II. GENERALIZED FOKKER-PLANCK EQUATIONS

A. Rotational diffusion

We consider a liquid containing N solvent molecules with moment of inertia components I_1, I_2, I_3 , in their principal axis coordinates and a solute particle (referred to as B particle) with moment of inertia components I_{1B}, I_{2B}, I_{3B} in its principal axis system. For simplicity here we first only consider the rotational part of the Hamiltonian for this classical system:

$$\mathcal{H} = \frac{L_{1B}^2}{2I_{1B}} + \frac{L_{2B}^2}{2I_{2B}} + \frac{L_{3B}^2}{2I_{3B}} + \sum_{i=1}^N \frac{1}{2} \left[\frac{L_{1i}^2}{I_1} + \frac{L_{2i}^2}{I_2} + \frac{L_{3i}^2}{I_3} \right] + \sum_{i=1}^N U(\mathbf{r}_B - \mathbf{r}_i, \Omega_B, \Omega_i) + \sum_{i < j}^N V(\mathbf{r}_i - \mathbf{r}_j, \Omega_i, \Omega_j), \quad (2.1)$$

where (L_1, L_2, L_3) are the components of angular momentum along the principal axes, $U(\mathbf{r}_B - \mathbf{r}_i, \Omega_B, \Omega_i)$ is the interaction potential between the solute particle and the i th solvent molecule when their orientations are specified by Euler angles Ω_B and Ω_i , respectively, relative to a fixed laboratory frame, and when their separation is given by $\mathbf{r}_B - \mathbf{r}_i$, and $V(\mathbf{r}_i - \mathbf{r}_j, \Omega_i, \Omega_j)$ is the similarly defined interaction potential between i th and j th solvent molecules.

The Liouville equation is given by

$$i \frac{\partial \rho_{N+1}}{\partial t} = i [\mathcal{H}, \rho_{N+1}] \equiv \mathcal{L} \rho_{N+1}, \quad (2.2)$$

where ρ_{N+1} is the $N+1$ particle distribution function and the Liouville operator \mathcal{L} is separated into two parts:

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_B, \quad (2.3)$$

$$\mathcal{L}_0 = -i \left\{ \sum_{i=1}^N \left(\frac{\partial \mathcal{H}}{\partial P_{\theta_i}} \frac{\partial}{\partial \theta_i} + \frac{\partial \mathcal{H}}{\partial P_{\varphi_i}} \frac{\partial}{\partial \varphi_i} + \frac{\partial \mathcal{H}}{\partial P_{\psi_i}} \frac{\partial}{\partial \psi_i} \right) - \left(\frac{\partial \mathcal{H}}{\partial \theta_i} \frac{\partial}{\partial P_{\theta_i}} + \frac{\partial \mathcal{H}}{\partial \varphi_i} \frac{\partial}{\partial P_{\varphi_i}} + \frac{\partial \mathcal{H}}{\partial \psi_i} \frac{\partial}{\partial P_{\psi_i}} \right) \right\} \quad (2.4)$$

for the solvent particles and

$$\mathcal{L}_B = -i \left\{ \left(\frac{\partial \mathcal{H}}{\partial P_{\theta_B}} \frac{\partial}{\partial \theta_B} + \frac{\partial \mathcal{H}}{\partial P_{\varphi_B}} \frac{\partial}{\partial \varphi_B} + \frac{\partial \mathcal{H}}{\partial P_{\psi_B}} \frac{\partial}{\partial \psi_B} \right) - \left(\frac{\partial \mathcal{H}}{\partial \theta_B} \frac{\partial}{\partial P_{\theta_B}} + \frac{\partial \mathcal{H}}{\partial \varphi_B} \frac{\partial}{\partial P_{\varphi_B}} + \frac{\partial \mathcal{H}}{\partial \psi_B} \frac{\partial}{\partial P_{\psi_B}} \right) \right\} \quad (2.5)$$

for the B particle. Here $(\theta_i, \varphi_i, \psi_i)$ are the Euler angles Ω_i and $(P_{\theta_i}, P_{\varphi_i}, P_{\psi_i})$ are the associated conjugate momenta. Equations (2.4) and (2.5) may be rewritten in a form appropriate for angular momentum components in the principal axis system of the molecular inertia tensors as²⁷

$$\mathcal{L}_0 = -i \sum_{k=1}^N (i\omega_k \cdot \mathbf{J}_k + \mathbf{N}_k \cdot \nabla_{L_k} + \hat{L}_k \cdot \nabla_{L_k}) \quad (2.6)$$

and

$$\mathcal{L}_B = -i(i\omega_B \cdot \mathbf{J}_B + \mathbf{N}_B \cdot \nabla_{L_B} + \hat{L}_B \cdot \nabla_{L_B}), \quad (2.7)$$

where \mathbf{J}_B is the rotational operator for the B particle given by

$$\mathbf{J}_B \equiv -i\mathbf{r}_B \times \nabla_{\mathbf{r}_B}; \quad (2.8)$$

similarly

$$\mathbf{J}_k \equiv -i\mathbf{r}_k \times \nabla_{\mathbf{r}_k} \quad (2.9)$$

(These operators have properties like the quantum mechanical angular momentum operators. They are discussed in detail by Favro.²⁸) The \mathbf{N}_B and \mathbf{N}_k are the torques on the B particle and solvent particle, and are given by

$$\mathbf{N}_B = -i\mathbf{J}_B \sum_i U(\mathbf{r}_B - \mathbf{r}_i, \Omega_B, \Omega_i), \quad (2.10)$$

$$\mathbf{N}_k = -i\mathbf{J}_k U(\mathbf{r}_B - \mathbf{r}_k, \Omega_B, \Omega_k) - i\mathbf{J}_k \sum_{i \neq k} V(\mathbf{r}_i - \mathbf{r}_k, \Omega_i, \Omega_k). \quad (2.11)$$

Also ω_k is the angular velocity and \hat{L}_k is the precession term with components \hat{L}_{i_k} defined in the principal axis system of the inertia tensor by

$$\hat{L}_i = L_j L_k (I_k^{-1} - I_j^{-1}) \mathcal{E}_{ijh}, \quad (2.12)$$

where \mathcal{E}_{ijh} defines the cyclic permutations.

We now introduce a projection operator \hat{P} by the definition

$$\hat{P}\alpha \equiv \rho^f \int \prod_i d\Gamma_i \alpha, \quad (2.13)$$

where the integration is over the complete phase space Γ_i of all the solvent molecules, and ρ^f is defined by

$$\rho^f \equiv \frac{\exp \left\{ -\frac{1}{kT} \left[\mathcal{H} - \left(\frac{L_{1B}^2}{2I_{1B}} + \frac{L_{2B}^2}{2I_{2B}} + \frac{L_{3B}^2}{2I_{3B}} \right) \right] \right\}}{\int \prod_{i=1}^N d\Gamma_i \exp \left\{ -\frac{1}{kT} \left[\mathcal{H} - \left(\frac{L_{1B}^2}{2I_{1B}} + \frac{L_{2B}^2}{2I_{2B}} + \frac{L_{3B}^2}{2I_{3B}} \right) \right] \right\}}. \quad (2.14)$$

Thus ρ^f is the distribution function of the solvent molecules in the presence of the potential field of the B particle.

In particular when \hat{P} operates on ρ_{N+1} we have

$$\hat{P}\rho_{N+1} = \rho^f \int \prod_i d\Gamma_i \rho_{N+1} \equiv \rho^f f_B(\Omega_B, \mathbf{L}_B, t), \quad (2.15)$$

where $f_B(\Omega_B, \mathbf{L}_B, t)$ is the one-particle distribution function of the B particle.

We now introduce the boundary conditions on either ρ_{N+1} or f_B that they vanish (as do all their derivatives), in the limit that any of the angular momentum variables approach $\pm\infty$. It then may be shown from those boundary conditions as well as Eqs. (2.6) and (2.15) that

$$\hat{P}(\mathcal{L}_0 \rho_{N+1}) = 0. \quad (2.16)$$

The projection operator is now applied to the Liouville equation (2.2), and with the help of Eq. (2.16) we obtain

$$\rho^f i(\partial/\partial t) f_B = \hat{P}\mathcal{L}_B(1 - \hat{P})\rho_{N+1} + \hat{P}\mathcal{L}_B \hat{P}\rho_{N+1}. \quad (2.17)$$

Now, since \hat{P} commutes with any operator just dependent upon the B particle variables, we may show

$$\hat{P}\omega_B \cdot \mathbf{J}_B \rho_{N+1} = \rho^f \omega_B \cdot \mathbf{J}_B f_B \quad (2.18)$$

so

$$\hat{P}\omega_B \cdot \mathbf{J}_B \hat{P}\rho_{N+1} = \rho^f \omega_B \cdot \mathbf{J}_B f_B \quad (2.19)$$

and

$$\hat{P}\omega_B \cdot \mathbf{J}_B(1 - \hat{P})\rho_{N+1} = 0, \quad (2.20)$$

which result from the idempotency of \hat{P} .

Similarly we obtain

$$\hat{P}\hat{L}_B \cdot \nabla_{L_B} \hat{P}\rho_{N+1} = \rho^f \mathbf{L}_B \cdot \nabla_{L_B} f_B \quad (2.21)$$

and

$$\hat{P}\hat{L}_B \cdot \nabla_{L_B}(1 - \hat{P})\rho_{N+1} = 0. \quad (2.22)$$

Thus from Eqs. (2.17), (2.7), and (2.19)–(2.22), we obtain

$$\begin{aligned} & (\partial/\partial t + i\omega_B \cdot \mathbf{J}_B + \hat{L}_B \cdot \nabla_{L_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{L_B}) f_B \\ & = -(\rho^f)^{-1} \hat{P}\mathbf{N}_B \cdot \nabla_{L_B}(1 - \hat{P})\rho_{N+1}, \end{aligned} \quad (2.23)$$

where

$$\langle \mathbf{N}_B \rangle \equiv \int \prod_{i=1}^N d\Gamma_i \mathbf{N}_B \rho^f \quad (2.24)$$

is the average torque acting on the B particle. We now add to the rhs of Eq. (2.23) a net zero term,

$$\begin{aligned} & \nabla_{L_B} \cdot \int \prod_i d\Gamma_i \langle \mathbf{N}_B \rangle (1 - \hat{P})\rho_{N+1} \\ & = \nabla_{L_B} \cdot \left(\langle \mathbf{N}_B \rangle \int \prod_i d\Gamma_i \rho_{N+1} - \langle \mathbf{N}_B \rangle \int \prod_i d\Gamma_i \rho^f f_B \right) = 0, \end{aligned} \quad (2.25)$$

so that

$$\begin{aligned} & -(\rho^f)^{-1} \hat{P}\mathbf{N}_B \cdot \nabla_{L_B}(1 - \hat{P})\rho_{N+1} + \nabla_{L_B} \cdot \int \prod_i d\Gamma_i \langle \mathbf{N}_B \rangle (1 - \hat{P})\rho_{N+1} \\ & = - \int \prod_i d\Gamma_i \langle \mathbf{N}_B - \langle \mathbf{N}_B \rangle \rangle \cdot \nabla_{L_B}(1 - \hat{P})\rho_{N+1}. \end{aligned} \quad (2.26)$$

We now assume that the initial condition of $\rho_{N+1}(t)$ is given by⁵

$$\rho_{N+1}(0) = \rho^f f_B(0). \quad (2.27)$$

This enables us to simplify Eq. (2.26) (cf. Appendix A)

and we obtain the generalized rotational FP equation

$$\left[\frac{\partial}{\partial t} + i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot \nabla_{\mathbf{L}_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{\mathbf{L}_B} \right] f_B = \nabla_{\mathbf{L}_B} \cdot \int_0^t d\tau \mathbf{G}(t-\tau) \cdot \left[\frac{\omega_B}{kT} + \nabla_{\mathbf{L}_B} \right] f_B(\tau), \quad (2.28)$$

where $\mathbf{G}(t-\tau)$ is the operator equivalent of the correlation function for the fluctuating or random torques on the B particle, and is defined by

$$\mathbf{G}(t) \equiv \int \prod_i^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{R}_B \rho^i = \langle \mathbf{R}_B \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{R}_B \rangle, \quad (2.29)$$

with

$$\mathbf{R}_B \equiv \mathbf{N}_B - \langle \mathbf{N}_B \rangle. \quad (2.30)$$

B. Translational diffusion

It follows from Resibois discussion⁵ of the translational case (and references cited therein) that the generalized translational FP equation is given by

$$\left[\partial/\partial t + \mathbf{v}_B \cdot \nabla_{\mathbf{r}_B} + \langle \mathbf{F}_B \rangle \cdot \nabla_{\mathbf{p}_B} \right] f_B^T = \nabla_{\mathbf{p}_B} \cdot \int_0^t d\tau \mathbf{G}_T(t-\tau) \cdot \left[\frac{\mathbf{v}_B}{kT} + \nabla_{\mathbf{p}_B} \right] f_B^T, \quad (2.31)$$

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_B \cdot \nabla_{\mathbf{r}_B} + \langle \mathbf{F}_B \rangle \cdot \nabla_{\mathbf{p}_B} + i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot \nabla_{\mathbf{L}_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{\mathbf{L}_B} \right] f_B^{TR} = \nabla_{\mathbf{p}_B} \cdot \int_0^t d\tau \mathbf{G}_{T,T}(t-\tau) \cdot \left[\frac{\mathbf{v}_B}{kT} + \nabla_{\mathbf{p}_B} \right] f_B^{TR} + \nabla_{\mathbf{L}_B} \cdot \int_0^t d\tau \mathbf{G}_{R,R}(t-\tau) \cdot \left[\frac{\omega_B}{kT} + \nabla_{\mathbf{L}_B} \right] f_B^{TR} + \nabla_{\mathbf{p}_B} \cdot \int_0^t d\tau \mathbf{G}_{T,R}(t-\tau) \cdot \left[\frac{\omega_B}{kT} + \nabla_{\mathbf{L}_B} \right] f_B^{TR} + \nabla_{\mathbf{L}_B} \cdot \int_0^t d\tau \mathbf{G}_{R,T}(t-\tau) \cdot \left[\frac{\mathbf{v}_B}{kT} + \nabla_{\mathbf{p}_B} \right] f_B^{TR}, \quad (2.35)$$

where

$$\mathbf{G}_{T,R}(t) \equiv \langle \mathbf{T}_B \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{R}_B \rangle, \quad (2.36)$$

$$\mathbf{G}_{R,T}(t) \equiv \langle \mathbf{R}_B \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{T}_B \rangle \quad (2.37)$$

and only when these cross-correlation operators are negligible is it possible to separate out uncoupled distribution functions for f_B^T and f_B^R , where in Eqs. (2.36) and (2.37) \mathcal{L} is the sum of the Liouville operators for the pure rotational and translational cases, and the averaging is over the combined phase space variables.

III. GENERALIZED SMOLUCHOWSKI EQUATIONS

A. Rotational diffusion

We now wish to simplify the generalized FP equation (2.28) by obtaining a distribution function for just the orientational space of the B particle, i. e., let

$$P(\Omega, t) \equiv \int d^3L_B f_B(t). \quad (3.1)$$

In general, $P(\Omega, t)$ will be a function of the initial values of both Ω_B and \mathbf{L}_B . However, we wish to consider the analog to the Smoluchowski equation in which \mathbf{L}_B is a fast variable; that is, angular momentum relaxes much faster than orientational variables, which relax on a much slower time scale τ_θ . Thus we wish to introduce

where \mathbf{v}_B and \mathbf{p}_B are the velocity and momentum of the B particle, while $\langle \mathbf{F}_B \rangle$ is the average force on the B particle (which is normally zero unless there are finite walls or external forces) and

$$\mathbf{G}_T(t) \equiv \langle \mathbf{T}_B \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{T}_B \rangle \quad (2.32)$$

with

$$\mathbf{T}_B = \mathbf{F}_B - \langle \mathbf{F}_B \rangle \quad (2.33)$$

and

$$\mathbf{F}_B = -\nabla_{\mathbf{r}_B} \sum_i U(\mathbf{r}_B - \mathbf{r}_i, \Omega_B, \Omega_i) \quad (2.34)$$

with \mathcal{L} in Eq. (2.32) the appropriate Liouville operator for translational motion⁵ analogous to the rotational form of Eqs. (2.3), (2.6), and (2.7) and the averaging is over the linear phase space variables.

C. Combined translational-rotational diffusion

More generally, the combined distribution function for the B particle in terms of both its translational and rotational phase space is found by these type of arguments to be given by

a coarse graining in time approximation such that the distribution function is averaged over times $t_c \gg \tau_J$ but still small compared to τ_θ . Such coarse graining also means we will not be interested in frequencies $\omega \gtrsim \omega_c \equiv t_c^{-1}$.

Since orientational relaxation occurs via its coupling to the angular momentum in Eq. (2.28), the possibility of choosing a t_c such that $\tau_\theta \gg t_c \gg \tau_J$ means that the coupling is weak. This is, of course, analogous to a "motional narrowing" approximation. Since the random torques cause the system to go to equilibrium, then in the coarse graining picture they guarantee that the angular momentum of the B particle is at equilibrium (see below). Then we wish to treat the systematic terms $i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot \nabla_{\mathbf{L}_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{\mathbf{L}_B}$, which couple the orientational degrees of freedom to \mathbf{L}_B , as perturbations (e. g., $\langle \mathbf{N}_B \rangle$ should not be too large) so we shall label them by μ and rewrite Eq. (2.28) as

$$\left[\partial/\partial t + \mu \hat{\mathbf{L}}_B \cdot \nabla_{\mathbf{L}_B} + \mu i\omega_B \cdot \mathbf{J}_B + \mu \langle \mathbf{N}_B \rangle \cdot \nabla_{\mathbf{L}_B} \right] f_B(t) = \nabla_{\mathbf{L}_B} \cdot \int_0^t d\tau \mathbf{G}(t-\tau) \cdot \left[\frac{\omega_B}{kT} + \nabla_{\mathbf{L}_B} \right] f_B(\tau). \quad (3.2)$$

[That the precessional term couples Ω to \mathbf{L}_B may be seen by transforming the above expressions to the lab frame].²⁷ Then, in terms of a perturbational approach, we could expand $f_B(t)$ in powers of the parameter μ :

$$f_B(t) \equiv f(t) = f_0(t) + \mu f_1(t) + \dots + \mu^n f_n(t) + \dots \quad (3.3)$$

Similarly, the operator correlation function could be expanded as

$$\mathbf{G} = \mathbf{G}_0 + \mu \mathbf{G}_1 + \dots + \mu^n \mathbf{G}_n + \dots \quad (3.4)$$

However, an expansion like Eq. (3.3) is generally very slowly convergent in t , and we are seeking an expression valid for $t \gg \tau_j$. We therefore introduce at this point the coarse graining in time approximation by means of a method based upon functional analysis which is similar to the Bogoliubov method^{20,21} introduced in the study of the Boltzmann equation. Thus for given

$$f(t) = f(\Omega, \mathbf{L}, t), \quad (3.5)$$

we assume that $f(t)$, smoothed over times $\sim t_c$ (such that the angular momentum appears to be at equilibrium), has its time dependence determined mainly by the time dependence of the orientational degrees of freedom, i. e., $P(\Omega, t)$. More precisely we let $f(t)$ be a functional of $P(\Omega, t)$ such that

$$f(\Omega, \mathbf{L}, t) = f(\Omega, \mathbf{L} | P(\Omega, t)) \quad (3.6)$$

Now, in place of Eq. (3.3), we introduce the expansion

$$f(\Omega, \mathbf{L} | P(\Omega, t)) = \sum_{n=0}^{\infty} \mu^n f_n(\Omega, \mathbf{L} | P(\Omega, t)) \quad (3.7)$$

The important difference between Eqs. (3.7) and (3.3) is that the $f_n(\Omega, \mathbf{L} | P(\Omega, t))$ are still functions of the perturbation parameter μ via their functional dependence upon $P(\Omega, t)$, which itself depends upon μ . It is this functional assumption which readily leads to coarse graining.²¹ Furthermore, we replace the time derivative $(\partial/\partial t)f_B(t)$ in Eq. (3.2) by the functional derivative²⁹

$$\frac{\partial f(\Omega, \mathbf{L} | P(\Omega, t))}{\partial t} = \int_{\Omega'} \frac{\delta f(\Omega, \mathbf{L} | P(\Omega, t))}{\delta P(\Omega', t)} \frac{\partial P(\Omega', t)}{\partial t} d\Omega' \quad (3.8)$$

We can obtain an expression for $(\partial/\partial t)P(\Omega, t)$ by integrating Eq. (3.2) over \mathbf{L} as in Eq. (3.1). Note that in all such integrations we shall assume that as $L \rightarrow \infty$, $f_B(t)$ and all its derivatives vanish with the convergence more rapid than L^{-1} in order that $f_B(t)$ be a well-defined distribution function. Also we require $\mathbf{G}(t)$ be finite as $L \rightarrow \infty$. Thus, when the integration is performed, and these boundary conditions are employed, Eq. (3.2) becomes:

$$\begin{aligned} \frac{\partial}{\partial t} P(\Omega, t) &= -i\mu \mathbf{J} \cdot \int d^3 L \omega f(t) \\ &\cong -i\mathbf{J} \cdot \sum_{n=0}^{\infty} \int d^3 L \omega \mu^{n+1} f_n(\Omega, \mathbf{L} | P(\Omega, t)), \end{aligned} \quad (3.9)$$

where we have dropped the subscript B , since the meaning is clear. We then may rewrite Eq. (3.8) as

$$\begin{aligned} \frac{\partial f(\Omega, \mathbf{L} | P(\Omega, t))}{\partial t} &= \sum_{n=1}^{\infty} \sum_{m=0}^{n-1} \mu^n \int_{\Omega'} \frac{\delta f_{n-m-1}(\Omega, \mathbf{L} | P(\Omega, t))}{\delta P(\Omega', t)} \\ &\quad \times \left[i\mathbf{J} \cdot \int d^3 L \omega f_m(\Omega, \mathbf{L} | P(\Omega, t)) d\Omega' \right]. \end{aligned} \quad (3.10)$$

The expansion of $G(t)$ such as by Eq. (3.4) is further discussed in Appendix B, where it is shown that it is

useful to separate torque components into those which are fluctuating more rapidly or comparable to the reorientation rate of the B particle and those which fluctuate more slowly. The latter are more appropriately included into a redefined average torque $\langle \mathbf{N}_B \rangle$, which is then still time dependent but on a slower time scale.

Now Eqs. (3.7), (3.10), and (3.4) may be substituted into Eq. (3.2), and terms of the same explicit dependence upon μ^n are collected. One then obtains for μ^0 terms

$$\nabla_L \cdot \int_0^t d\tau \mathbf{G}_0(t-\tau) \cdot \left(\frac{\omega}{kT} + \nabla_L \right) f_0(\Omega, \mathbf{L} | P(\Omega, \tau)) = 0, \quad (3.11)$$

while for μ^n ,

$$\begin{aligned} \sum_{m=0}^{n-1} \int_{\Omega'} \frac{\delta f_{n-m-1}(\Omega, \mathbf{L} | P(\Omega, t))}{\delta P(\Omega', t)} \left[-i\mathbf{J} \cdot \int d^3 L \omega f_m(\Omega, \mathbf{L} | P(\Omega', t)) d\Omega' \right] \\ + [i\omega \cdot \mathbf{J} + \hat{\mathbf{L}} \cdot \nabla_L + \langle \mathbf{N} \rangle \cdot \nabla_L] f_{n-1}(\Omega, \mathbf{L} | P(\Omega', t)) \\ = \nabla_L \cdot \int_0^t d\tau \sum_{m=0}^n \left\{ \mathbf{G}_m(t-\tau) \cdot \left[\frac{\omega}{kT} + \nabla_L \right] f_{n-m}(\tau) \right\}. \end{aligned} \quad (3.12)$$

Note that since the $f_n(\Omega, \mathbf{L} | P(\Omega, t))$ functionals still depend upon μ , the collection of terms according to Eqs. (3.11)–(3.12) is not mandatory, but rather is performed to obtain reasonably convergent solutions.^{20,21} One could anticipate some difficulties for higher-order expansions, but we shall only consider the lowest order $n=0$ and 1 terms.

We now consider Eq. (3.11). Since $\mathbf{G}_0(t-\tau)$ and t are both arbitrary and $\mu=0$, we may satisfy Eq. (3.11) with

$$(\omega/kT + \nabla_L) f_0(\Omega, \mathbf{L} | P(\Omega, t)) = 0, \quad (3.13)$$

with solution

$$f_0(\Omega, \mathbf{L} | P(\Omega, t)) \propto \prod_i (2\pi I_i kT)^{-1/2} \exp(-L_i^2/2I_i kT). \quad (3.14)$$

The proportionality constant is then chosen in accordance with the functional dependence of f_0 , so we have

$$f_0(\Omega, \mathbf{L} | P(\Omega, t)) = P(\Omega, t) \prod_i (2\pi I_i kT)^{-1/2} \exp(-L_i^2/2I_i kT). \quad (3.14')$$

We now consider Eq. (3.12) for $n=1$. There is clearly only one term from the summation in the first term on the lhs, but utilizing Eq. (3.14) [or (3.14')] it is seen to vanish, since ω is an odd function of \mathbf{L} . There are two terms from the summation on the rhs of Eq. (3.12), but the term in f_0 vanishes by Eq. (3.13). Thus we have for $n=1$

$$\begin{aligned} (i\omega \cdot \mathbf{J} + \hat{\mathbf{L}} \cdot \nabla_L + \langle \mathbf{N} \rangle \cdot \nabla_L) f_0(\Omega, \mathbf{L} | P(\Omega, t)) \\ = \nabla_L \cdot \int_0^t d\tau \mathbf{G}_0(t-\tau) \cdot \left(\frac{\omega}{kT} + \nabla_L \right) f_1(\Omega, \mathbf{L} | P(\Omega, t)). \end{aligned} \quad (3.15)$$

The equation is now premultiplied by \mathbf{L} and integrated over angular momentum space to yield

$$\begin{aligned} (i\mathbf{J} - \langle \mathbf{N} \rangle/kT) P(\Omega, t) &= (kT)^{-1} \int (d^3 L) \mathbf{L} \nabla_L \\ &\quad \cdot \int_0^t d\tau \mathbf{G}_0(t-\tau) \cdot (\omega/kT + \nabla_L) f_1(\Omega, \mathbf{L} | P(\Omega, t)), \end{aligned} \quad (3.16)$$

where the precessional term may be shown to vanish by

first operating with ∇_L on f_0 given by Eq. (3.14') and then summing the components of the scalar product. The rhs of Eq. (3.16) may be simplified as shown in Appendix B (see also Appendix C). One then may write

$$(i\mathbf{J} - \langle \mathbf{N} \rangle / kT)P(\Omega, t) = (kT)^{-1} \int (d^3L) L \nabla_L \cdot \int_0^t d\tau \mathbf{K}(t - \tau) \cdot (\omega / kT + \nabla_L) f_1(\Omega, L | P(\Omega, t)), \quad (3.17)$$

where

$$\mathbf{K}(t) \equiv \prod_{i=1}^N \int d\Gamma_i \mathbf{R}_B [\exp(-i\mathcal{L}_0 t)] \mathbf{R}_B \rho^f \quad (3.18)$$

is the modified correlation function. It is clear from the form of Eq. (3.18) and the definitions of the various terms [cf. Eqs. (2.6) and (2.30)] that $\mathbf{K}(t)$ is a function of only Ω_B and t . Once that is recognized, and the rhs of Eq. (3.17) is integrated by parts, and the usual boundary conditions invoked, then one gets

$$\left(i\mathbf{J} - \frac{\langle \mathbf{N} \rangle}{kT}\right)P(\Omega, t) = -(kT)^{-2} \int_0^t d\tau \mathbf{K}(t - \tau) \cdot \langle \omega(t) \rangle_L^{(1)}, \quad (3.19)$$

where

$$\langle \omega(t) \rangle_L^{(1)} \equiv \int d^3L \omega f_1(\Omega, L | P(\Omega, t)). \quad (3.20)$$

This result may be Laplace transformed to yield

$$(i\mathbf{J} - \langle \mathbf{N} \rangle / kT)P(\Omega, s) = -[\mathbf{K}[s] / (kT)^2] \cdot \langle \omega(s) \rangle_L^{(1)}. \quad (3.21)$$

Now we note that to lowest order in μ the Laplace transform of Eq. (3.9) becomes (where $\mu - 1$)

$$sP(\Omega, s) - P(\Omega, t=0) = -i\mathbf{J} \cdot \langle \omega(s) \rangle_L^{(1)} \mu \\ = i\mathbf{J} \cdot (kT)^2 \mathbf{K}[s]^{-1} \cdot (i\mathbf{J} - \langle \mathbf{N} \rangle / kT)P(\Omega, s), \quad (3.22)$$

where the second equality follows from Eq. (3.21).

Since $\mathbf{K}[s]$ is the Fourier-Laplace transform (i.e., $s = -i\omega$) of the random torque acting on the molecule, then we may invoke the fluctuation-dissipation theorem to relate it to a friction coefficient (in units of sec^{-1}) as

$$\mathbf{K}[s] \equiv I kT \beta[s], \quad (3.23)$$

where $I = \frac{1}{3}(I_1 + I_2 + I_3)$ and then we may define a generalized Einstein relation

$$\mathbf{D}_R[s] \equiv kT / I \beta[s]. \quad (3.24)$$

Then Eq. (3.22) becomes

$$\{s - i\mathbf{J} \cdot \mathbf{D}_R[s] \cdot (i\mathbf{J} - \langle \mathbf{N} \rangle / kT)\} P(\Omega, s) = P(\Omega, t=0). \quad (3.25)$$

The Laplace inversion yields

$$\frac{\partial P(\Omega, t)}{\partial t} = \int_0^t d\tau i\mathbf{J} \cdot \mathbf{D}_R(t - \tau) \cdot \left[i\mathbf{J} - \frac{\langle \mathbf{N} \rangle}{kT}\right] P(\Omega, \tau), \quad (3.26)$$

which is seen to be a generalized Smoluchowski equation. It yields the classical Smoluchowski equation when \mathbf{D}_R may be taken as time independent. Specific examples of this limit are discussed in Sec. V.

B. Combined translational-rotational diffusion

The combined generalized Smoluchowski equation for the B particle in terms of its position and orientation may be obtained from Eq. (2.35) in a manner similar to

the derivation of Eq. (3.26). Define a distribution function of the B particle in orientational and position space, i.e.,

$$P(\mathbf{r}, \Omega, t) = \int d^3L_B \int d^3P_B f_B^{TR}(t). \quad (3.27)$$

When the inertial effect is unimportant, we may treat the systematic terms $\mathbf{v}_B \cdot \nabla_{\mathbf{r}_B} + \langle \mathbf{F}_B \rangle \cdot \nabla_{\mathbf{P}_B} + i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot \nabla_{L_B} + \langle \mathbf{N}_B \rangle \cdot \nabla_{L_B}$, which couple the orientation-position coordinates to L_B and P_B , as perturbations, and impose the same boundary condition on linear momentum space as on angular momentum space discussed previously. After some straightforward calculations, we obtain

$$\frac{\partial P(\mathbf{r}, \Omega, t)}{\partial t} = \int_0^t d\tau (\nabla_{\mathbf{r}}, i\mathbf{J}) \cdot \mathcal{D}(t - \tau) \cdot \left(\nabla_{\mathbf{r}} - \langle \mathbf{F}_B \rangle / kT \right) P(\mathbf{r}, \Omega, t), \quad (3.28)$$

where the Laplace transform of $\mathcal{D}(t)$ is defined by

$$\mathcal{D}[s] \equiv (kT)^2 \mathcal{K}^{-1}[s] \quad (3.29)$$

and $\mathcal{K}(t)$ is a matrix defined by

$$\mathcal{K}(t) = \begin{pmatrix} \mathbf{K}_{TT}(t) & \mathbf{K}_{TR}(t) \\ \mathbf{K}_{RT}(t) & \mathbf{K}_{RR}(t) \end{pmatrix}, \quad (3.30)$$

with

$$\mathbf{K}_{AB}(t) = \prod_{i=1}^N \int d\Gamma_i \mathbf{A}[\exp(-i\mathcal{L}_0 t)] \mathbf{B} \rho^f \quad (3.31)$$

for

$$\mathbf{A}, \mathbf{B} = \mathbf{R} \text{ or } \mathbf{T},$$

where Γ_i refers to the 12-dimensional linear and angular phase space of the i th solvent particle. It can easily be shown from the Hermitian property of the Liouville operator that $\mathbf{K}_{AB} = \mathbf{K}_{BA}^\dagger$. Then $\mathcal{D}(t)$ has the same Hermitian property that the time-independent diffusion tensor does.²⁷

C. Relative translational diffusion

In the study of molecular translational diffusion, one is often interested in the relative translational diffusion of two particles.^{19,25} The two particle FP equation has been derived in the Brownian limit by Mazo.⁶ In order that one may expect a generalized Smoluchowski equation to be meaningful for this case we take these two particles to have similar sizes and masses. This enables the momenta of both particles to reach equilibrium in the same time scale. We further require that the average force between the two particles (see below) is slowly varying in space. We also neglect coupling to rotational motion for simplicity. Then, the generalized Smoluchowski equation for the translational motions of two particles A and B may be derived by the same procedure discussed in this section from the generalized two B -particle FP equation given in Mazo's work.⁶ After some simple calculations we obtain

$$\frac{\partial P(\mathbf{r}_A, \mathbf{r}_B, t)}{\partial t} = \sum_{i,j=A,B} \int_0^t d\tau \nabla_i \cdot \mathbf{D}_{i,j}(t - \tau)$$

$$\cdot \left(\nabla_j - \frac{\langle \mathbf{F}_j \rangle}{kT} \right) P(\mathbf{r}_A, \mathbf{r}_B, \tau) d\tau, \quad (3.32)$$

which is of similar form to the typical results in the Brownian limit (e.g., Ref. 8), except that now the time-dependent \mathbf{D}_{ij} are included. The \mathbf{D}_{ij} may be defined as

$$\begin{pmatrix} \mathbf{D}_{AA}[s] & \mathbf{D}_{AB}[s] \\ \mathbf{D}_{AB}[s]^\dagger & \mathbf{D}_{BB}[s] \end{pmatrix} \equiv (kT)^2 \begin{pmatrix} \mathbf{K}_{AA}[s] & \mathbf{K}_{AB}[s] \\ \mathbf{K}_{AB}[s]^\dagger & \mathbf{K}_{BB}[s] \end{pmatrix}^{-1}, \quad (3.33)$$

where

$$\mathbf{K}_{m,n}(t) = \prod_{i=1}^N \int d\Gamma_i \mathbf{T}_m [\exp(-i\mathcal{L}_0 t)] \mathbf{T}_n \rho^f \quad (3.34)$$

and $m, n = A$ or B .

Since the averaging in $\langle \mathbf{F}_j \rangle$ and \mathbf{D}_{ij} is over the phase space of all particles excluding particles A and B , and the medium is presumably isotropic (no external field, no boundary effect), one may conclude that \mathbf{D}_{ij} , $\langle \mathbf{F}_j \rangle$, and $P(\mathbf{r}_A, \mathbf{r}_B, t)$ depend only on the relative coordinate $\mathbf{r} = \mathbf{r}_A - \mathbf{r}_B$. Then Eq. (3.32) may be transformed to the new coordinates, and only the terms with relative coordinates retained. We obtain

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = \int_0^t d\tau \nabla_{\mathbf{r}} \cdot \mathbf{D}(t-\tau) \cdot \left(\nabla_{\mathbf{r}} - \frac{\mathbf{F}(\mathbf{r})}{kT} \right) P(\mathbf{r}, \tau), \quad (3.35)$$

where

$$\mathbf{D}(t) \equiv \mathbf{D}_{AA}(t) + \mathbf{D}_{BB}(t) - [\mathbf{D}_{AB}(t) + \mathbf{D}_{AB}^\dagger(t)] \quad (3.36)$$

and

$$\mathbf{F}(\mathbf{r}) = \langle \mathbf{F}_A \rangle = - \langle \mathbf{F}_B \rangle. \quad (3.37)$$

Also the Laplace transform of Eq. (3.35) is

$$\{s - \nabla_{\mathbf{r}} \cdot \mathbf{D}(s) \cdot [\nabla_{\mathbf{r}} - \mathbf{F}(\mathbf{r})/kT]\} P(\mathbf{r}, s) = P(\mathbf{r}, t=0). \quad (3.38)$$

IV. GENERALIZED FOKKER-PLANCK AND SMOLUCHOWSKI EQUATIONS INCLUDING SPIN

When the molecule (or B particle) contains spin degrees of freedom, then we modify the definition of the total Hamiltonian as

$$\mathcal{H} \rightarrow \mathcal{H} + \mathcal{H}_s(\Omega_B) \quad (4.1)$$

and the Liouville operator as

$$\mathcal{L}_B \rightarrow \mathcal{L}_B + \hbar^{-1} \mathcal{H}_s(\Omega_B)^x - \frac{1}{2} [\mathbf{J}_B \mathcal{H}_s(\Omega_B)^*] \cdot \nabla_{L_B}, \quad (4.2)$$

$$\mathcal{L} \rightarrow \mathcal{L} + \hbar^{-1} \mathcal{H}_s(\Omega_B)^x - \frac{1}{2} [\mathbf{J}_B \mathcal{H}_s(\Omega_B)^*] \cdot \nabla_{L_B} \equiv \mathcal{L}_t + \hbar^{-1} \mathcal{H}_s(\Omega_B)^x, \quad (4.3)$$

where $\hbar^{-1} \mathcal{H}_s(\Omega_B)^x \equiv \mathcal{L}_s$ is the quantum-mechanical spin super-operator where the superscript x implies taking the commutator (i.e., $A^x B \equiv [A, B]$). It is both a quantum mechanical spin function as well as a classical function of Ω_B . \mathcal{L}_B and \mathcal{L} are defined as before in Eq. (2.3). The new term $\frac{1}{2} [\mathbf{J}_B \mathcal{H}_s(\Omega_B)^*] \cdot \nabla_{L_B}$ arises from applying the Poisson bracket to the semiclassical term $\mathcal{H}_s(\Omega)$, i.e., one considers $[\mathcal{H}_s(\Omega_B), \rho_{N+1}]_{L_B, \Omega_B}$ [cf. Eqs. (2.2) and (2.5)]. The superscript $+$ on this term denotes taking the anticommutator (i.e., $A^+ B \equiv AB + BA$), which is necessary in order to guarantee the Hermitian property of ρ_{N+1} , i.e., $\rho_{N+1} = \rho_{N+1}^\dagger$. Here ρ_{N+1} is a spin density operator as well as a classical distribution function.²²⁻²⁴

The analysis proceeds as given in Sec. II till Eq. (2.23). One must add two terms $i\mathcal{H}_s^x(\Omega_B)f_B(t)$ and $-i[\mathbf{J}_B \mathcal{H}_s(\Omega_B)^*] \cdot \nabla_{L_B} f_B(t)$ to the lhs of Eq. (2.23), but the analysis of the rhs as discussed in Appendix A is somewhat modified. Equation (A2) becomes

$$i \frac{\partial}{\partial t} (1 - \hat{P}) \rho_{N+1} = (1 - \hat{P})(\mathcal{L}_t + \mathcal{L}_s)(1 - \hat{P}) \rho_{N+1} + (1 - \hat{P})(\mathcal{L}_t + \mathcal{L}_s) \hat{P} \rho_{N+1}. \quad (4.4)$$

We now multiply Eq. (4.4) by $\exp[i(1 - \hat{P})\mathcal{L}_t t' + \mathcal{L}_s t']$ and integrate from 0 to t . We then consider the lhs and rhs of Eq. (4.4) separately. Thus:

$$\begin{aligned} \text{lhs} &= i \{ \exp[i(1 - \hat{P})\mathcal{L}_t t + i\mathcal{L}_s t] \} (1 - \hat{P}) \rho_{N+1}(t) \\ &+ \int_0^t \{ \exp[i(1 - \hat{P})\mathcal{L}_t t' + i\mathcal{L}_s t'] \} [(1 - \hat{P})\mathcal{L}_t + \mathcal{L}_s] \\ &\times (1 - \hat{P}) \rho_{N+1}(t') dt', \end{aligned} \quad (4.5)$$

where we have used the fact that

$$(1 - \hat{P}) \rho_{N+1}(0) = 0, \quad (4.6)$$

which follows from the initial condition, Eq. (2.27).

Now for the rhs we have

$$\begin{aligned} \text{rhs} &= \int_0^t dt' \{ \exp[i(1 - \hat{P})\mathcal{L}_t t' + i\mathcal{L}_s t'] \} \\ &\times \{ (1 - \hat{P})(\mathcal{L}_t + \mathcal{L}_s)(1 - \hat{P}) \rho_{N+1}(t') \\ &+ (1 - \hat{P})(\mathcal{L}_t + \mathcal{L}_s) \hat{P} \rho_{N+1}(t') \} \\ &= \int_0^t dt' \{ \exp[i(1 - \hat{P})\mathcal{L}_t t' + i\mathcal{L}_s t'] \} \\ &\times \{ [(1 - \hat{P})\mathcal{L}_t + \mathcal{L}_s](1 - \hat{P}) \rho_{N+1}(t') \\ &+ (1 - \hat{P})(\mathcal{L}_t + \mathcal{L}_s) \rho^f f_B(t') \}, \end{aligned} \quad (4.7)$$

where the second equality follows from

$$\hat{P} \mathcal{L}_s (1 - \hat{P}) \rho_{N+1}(t') = \mathcal{L}_s \hat{P} (1 - \hat{P}) \rho_{N+1}(t') = 0. \quad (4.8)$$

Then Eq. (4.4) becomes

$$\begin{aligned} (1 - \hat{P}) \rho_{N+1}(t) &= -i \int_0^t \{ \exp[-i(1 - \hat{P})\mathcal{L}_t(t-t') - i\mathcal{L}_s(t-t')] \} \\ &\times (1 - \hat{P}) \mathcal{L}_t \rho^f f_B(t') dt' \end{aligned} \quad (4.9)$$

when use is made of

$$(1 - \hat{P}) \mathcal{L}_s \rho^f f_B(t') = \mathcal{L}_s (1 - \hat{P}) \rho^f f_B(t') = 0. \quad (4.10)$$

Equation (4.9) is the required generalization of Eq. (A3). We may now apply Eq. (A6) to obtain [cf. Eqs. (A1) and (A7)]

$$\begin{aligned} \nabla_{L_B} \cdot \int \prod_i^N d\Gamma_i \mathbf{R}_B (1 - \hat{P}) \rho_{N+1} \\ = - \nabla_{L_B} \cdot \int_0^t d\tau \mathbf{G}^s(t-\tau) \cdot \left[\frac{\omega_B}{kT} + \nabla_{L_B} \right] f_B(\tau), \end{aligned} \quad (4.11)$$

where

$$\mathbf{G}^s(t) = \int \prod_i^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1 - \hat{P})\mathcal{L}_t t - i\mathcal{L}_s t] \} \mathbf{R}_B \rho^f \quad (4.12)$$

is the spin-dependent operator correlation function for the random torques. We then obtain a generalized spin-dependent FP (or generalized stochastic Liouville equa-

tion)

$$\begin{aligned} & [\partial/\partial t + i\omega_B \cdot \mathbf{J}_B + \hat{\mathbf{L}}_B \cdot (\nabla_{L_B}) + \langle \mathbf{N}_B \rangle \cdot \nabla_{L_B} - \frac{1}{2} i[\mathbf{J}_B \mathcal{H}_s(\Omega_B)^*] \\ & \cdot \nabla_{L_B} + i\mathcal{H}_s(\Omega_B)^*/\hbar] f_B(t) = \nabla_{L_B} \cdot \int_0^t d\tau \mathbf{G}^s(t-\tau) \\ & \cdot \left[\frac{\omega_B}{kT} + \nabla_{L_B} \right] f_B(\tau). \end{aligned} \quad (4.13)$$

We now consider the passage to a generalized spin-dependent Smoluchowski equation. The procedure is nearly the same as the derivation given for Eqs. (3.25) and (3.26) except we include $\frac{1}{2} i[\mathbf{J}_B \mathcal{H}_s(\Omega_B)^*] \cdot \nabla_{L_B}$ as one of the perturbation terms. One merely notes the following simple changes. First Eq. (3.9) becomes

$$\begin{aligned} & [\partial/\partial t + i\mathcal{L}_s] P(\Omega, t) = -i\mathbf{J} \cdot \int d^3L \omega f_B(t) \\ & = -i\mathbf{J} \cdot \sum_{n=0}^{\infty} \int d^3L \omega \mu^{n+1} f_n(\Omega, \mathbf{L} | P(\Omega, t)), \end{aligned} \quad (4.14)$$

with $P(\Omega, t)$ a spin density operator as well as a distribution function in Ω_B . Secondly Eq. (3.8) becomes

$$\begin{aligned} & \frac{\partial f(\Omega, \mathbf{L} | P(\Omega, t))}{\partial t} + i\mathcal{L}_s f(\Omega, \mathbf{L} | P(\Omega, t)) \\ & = \int_{\Omega'} \frac{\delta f(\Omega, \mathbf{L} | P(\Omega, t))}{\delta P(\Omega', t)} \left\{ \frac{\partial P(\Omega', t)}{\partial t} + i\mathcal{L}_s P(\Omega', t) \right\} d\Omega'. \end{aligned} \quad (4.15)$$

One can then carry out the same procedure as in the derivation of Eq. (3.19) which now becomes

$$\left(i\mathbf{J} - \frac{\langle \mathbf{N}_B \rangle}{kT} + \frac{i[\mathbf{J} \mathcal{H}_s(\Omega)^*]}{2kT} \right) P(\Omega, s) = \frac{-\mathbf{K}[s + i\mathcal{L}_s]}{(kT)^2} \cdot \langle \omega(s) \rangle_L^{(1)}. \quad (4.16)$$

Then the equivalent of Eq. (3.22) becomes

$$\begin{aligned} & sP(\Omega, s) - P(\Omega, t=0) = i\mathbf{J} \cdot (kT)^2 (\mathbf{K}[s + i\mathcal{L}_s])^{-1} \\ & \cdot (i\mathbf{J} - \langle \mathbf{N} \rangle) P(\Omega, s), \end{aligned} \quad (4.17)$$

where

$$\mathbf{K}[s + i\mathcal{L}_s] \equiv \int dt e^{-st} \sum_{i=1}^N \int d\Gamma_i \mathbf{R}_B \{ \exp[-i(\mathcal{L}_0 + \mathcal{L}_s)t] \} \mathbf{R}_B \rho^f \quad (4.18)$$

$$= \int dt e^{-st} \prod_{i=1}^N \int d\Gamma_i \mathbf{R}_B \{ \exp(-i\mathcal{L}_0 t) \} \mathbf{R}_B \rho^f \exp(-\mathcal{L}_s^* t / \hbar), \quad (4.19)$$

where the second equality follows because the only non-spin variable in $\mathcal{H}_s^*(\Omega_B)$ is Ω_B and, in general, $\mathcal{H}_s^*(\Omega_B)$ is a simple function of Ω_B (i.e., not an operator on Ω_B). Thus $\mathcal{H}_s^*(\Omega_B)$ commutes with \mathcal{L}_0 , which is not an operator on B variables, and it commutes with \mathbf{R}_B and ρ^f , which are also just simple functions of Ω_B [cf. Eqs. (2.10) and (2.14)].

We then find that the equivalents of Eqs. (3.25) and (3.26) are

$$\begin{aligned} & \left\{ s + i\mathcal{L}_s - i\mathbf{J} \cdot \mathbf{D}_R[s + i\mathcal{L}_s] \cdot \left[i\mathbf{J} - \frac{\langle \mathbf{N} \rangle}{kT} + \frac{i[\mathbf{J} \mathcal{H}_s(\Omega)^*]}{2kT} \right] \right\} P(\Omega, s) \\ & = P(\Omega, t=0) \end{aligned} \quad (4.20)$$

and

$$\begin{aligned} & \frac{\partial P(\Omega, t)}{\partial t} = -i\mathcal{L}_s P(\Omega, t) + \int_0^t d\tau i\mathbf{J} \cdot \mathbf{D}_R(t-\tau) \{ \exp[-i\mathcal{L}_s(t-\tau)] \} \\ & \cdot \left[i\mathbf{J} - \frac{\langle \mathbf{N} \rangle}{kT} + \frac{i[\mathbf{J} \mathcal{H}_s(\Omega)^*]}{2kT} \right] P(\Omega, \tau), \end{aligned} \quad (4.21)$$

which is the generalized rotational spin-dependent Smoluchowski equation. Note that in these equations

$$\mathbf{D}_R[s + i\mathcal{L}_s] \equiv \frac{(kT)^2}{\mathbf{K}[s + i\mathcal{L}_s]} = \frac{(kT)}{I\beta[s + i\mathcal{L}_s]}, \quad (4.22)$$

showing that to lowest order in μ the effect of backflow from the spin system on the lattice dynamics may be neglected. When this lowest order approximation is not valid, one has to return to Eq. (4.13) instead of Eq. (4.21) to allow for the disturbance of the angular momentum due to the "spin-torque" ($i\mathbf{J}\mathcal{H}_s^*$).

We now note that a completely analogous discussion of the translational case will result in the generalized translational spin-dependent Smoluchowski equation such that in Eq. (3.38) one merely replaces s by $s + i\mathcal{L}_s$ and also adds the spin force term $\nabla_r \mathcal{H}_s(r)^*/2kT$. The combined generalized spin-dependent translational and rotational Smoluchowski equation is achieved in the same way.

We now note that the first term on the rhs of Eq. (4.21) gives the dynamical motion of the spin degrees of freedom (i.e., it is an imaginary term giving the quantum-mechanical oscillations) while the second term has a real part which gives the relaxation to equilibrium. We therefore consider this second term in the limit as $t \rightarrow \infty$, such that $P(\Omega, t)$ achieves its equilibrium value $P_{eq}(\Omega)$. Since $\mathbf{D}_R(t-\tau)$ and τ are arbitrary, we have that $P_{eq}(\Omega)$ obeys (cf. Ref. 28 for the classical Brownian case)

$$\left[i\mathbf{J} - \frac{\langle \mathbf{N} \rangle}{kT} + \frac{i[\mathbf{J} \mathcal{H}_s(\Omega)^*]}{2kT} \right] P_{eq}(\Omega) = 0. \quad (4.23)$$

Thus the spin-torque term has the same role as that of a classical torque such that $P_{eq}(\Omega)$ will be a spin-dependent distribution function. The general solution to Eq. (4.23) is quite complex so we shall, here, only consider a high temperature approximation: $\mathcal{H}_s(\Omega)/kT \ll 1$, and we let $\langle \mathbf{N} \rangle = 0$ for simplicity. Then it is easy to show that the high-temperature expansion of the canonical distribution in \mathcal{H}_s , i.e.,

$$P_{eq}(\Omega) \cong 1 - \mathcal{H}_s/kT + \frac{1}{2} (\mathcal{H}_s/kT)^2 \quad (4.24)$$

will satisfy Eq. (4.23) to second order in \mathcal{H}_s . However, in general, the full canonical distribution,

$$P_{eq}(\Omega) = \sum_n \frac{(-1)^n}{n!} \left(\frac{\mathcal{H}_s}{kT} \right)^n, \quad (4.25)$$

does not satisfy Eq. (4.23) with $\langle \mathbf{N} \rangle = 0$, since in general $[\mathbf{J} \mathcal{H}_s, \mathcal{H}_s] \neq 0$. This might be indicative of the fact that at lower temperatures, the lattice is not to be expected to behave as a constant temperature bath. When, however, $[\mathbf{J} \mathcal{H}_s, \mathcal{H}_s] = 0$, then Eq. (4.25) will satisfy Eq. (4.23). This is, for example, like the relative translational case treated elsewhere^{25b} such that two identical electron spins \mathbf{S}_1 and \mathbf{S}_2 interact via an exchange interaction $J(\mathbf{r})$. However, in such cases, the system is nonergodic, e.g., the "exchange force" $\nabla_r J(\mathbf{r}) \mathbf{S}_1 \cdot \mathbf{S}_2^z /$

$2kT$ cannot interconvert singlet and triplet states, so it cannot relax an initial condition of say pure triplets, but it will distribute them in \mathbf{r} space according to a Boltzmann distribution in the triplet exchange energy. It is necessary, for ergodicity, that $[J\mathcal{H}_s, \mathcal{H}_s] \neq 0$, so the spin-torque or spin-force induces transitions between the eigenstates of \mathcal{H}_s . In many cases (Refs. 14–18, 23, 24) one has $\mathcal{H}_s = \mathcal{H}_s^0 + \mathcal{H}_s^f(\Omega)$, where $\mathcal{H}_s^f(\Omega)$ is a small orientation-dependent perturbation and $[\mathcal{H}_s^0, \mathcal{H}_s^f(\Omega)] \neq 0$ as well as $[\mathcal{H}_s^0, J\mathcal{H}_s^f(\Omega)] \neq 0$. In these cases then, the spin force can mix spin states; however, it should be noted that the spin force does not include the dominant \mathcal{H}_s^0 term in any way. The presence of \mathcal{H}_s^0 in an equation like (4.24) is to be inferred from the condition $i\mathcal{H}_s^x P_{\text{eq}}(\Omega) = 0$ required in Eq. (4.21) to achieve $\partial P_{\text{eq}}(\Omega)/\partial t = 0$ (when explicit time-dependent terms are not present in \mathcal{H}_s).

We note, finally, that a similar discussion would apply to the term $\frac{1}{2}[J_B \mathcal{H}_s(\Omega_B)^*] \cdot \nabla_{L_B}$ in Eq. (4.13) such that $f_B(\text{eq})$ will be spin dependent.

V. EXAMPLES

We now wish to illustrate the use of the previously derived generalized Smoluchowski equations with some simple examples. We shall adopt here the approach of replacing (e.g.) the modified torque correlation function, Eq. (3.18), by some simple memory function rather than deal with the remaining complex N -body problem (cf. Refs. 30 and 31 for typical memory function approaches).

A. Rotational diffusion

In particular, let us take the case of $\langle N_B \rangle = 0$, and consider an axially symmetric B particle, such that the generalized spherical harmonics (or Wigner rotation matrices) $\mathcal{D}_{KM}^L(\Omega) \sqrt{(2L+1)/8\pi^2}$ are the well-known eigenfunctions of the Brownian diffusion operator.^{23,24,28} Then from Eq. (3.25) and the known properties of $\mathbf{J} \cdot \mathbf{D} \cdot \mathbf{J}$,²⁸ we have for the conditional probability function, or Green's function, subject to the initial condition

$$P(t=0) = \delta(\Omega - \Omega_0) = \sum_{L,K,M} \left(\frac{2L+1}{8\pi^2} \right) \mathcal{D}_{KM}^{L*}(\Omega_0) \mathcal{D}_{KM}^L(\Omega), \quad (5.1)$$

the result

$$P(\Omega_0 | \Omega, s) = \frac{\sum_{L,K,M} \left(\frac{2L+1}{8\pi^2} \right) \mathcal{D}_{KM}^{L*}(\Omega_0) \mathcal{D}_{KM}^L(\Omega)}{s + L(L+1)D_{R,\perp}(s) + K^2(D_{R,\parallel}(s) - D_{R,\perp}(s))}, \quad (5.2)$$

where

$$D_{R,\parallel}[s] = (kT)^2 / K_{\parallel}[s], \quad (5.3a)$$

$$D_{R,\perp}[s] = (kT)^2 / K_{\perp}[s], \quad (5.3b)$$

and we have taken

$$K_{\parallel}(t) = \prod_{i=1}^N \int d\Gamma_i(\mathbf{R}_B)_z [\exp(-i\mathcal{L}_0 t)] (\mathbf{R}_B)_z \rho^f, \quad (5.4a)$$

$$K_{\perp}(t) = \prod_{i=1}^N \int d\Gamma_i(\mathbf{R}_B)_j [\exp(-i\mathcal{L}_0 t)] (\mathbf{R}_B)_j \rho^f, \quad j = x \text{ or } y \quad (5.4b)$$

which is a statement that the tensor $\mathbf{K}(t)$ may be diagonalized in the principal coordinate system (x, y, z) of the

B particle, and we have assumed that any time-dependent fluctuations of the principal axis system of $\mathbf{K}(t)$ may be neglected. This simplifying assumption that the random torques exerted on the body are related only to the symmetry of the body is a familiar one in rotational Brownian motion.²⁸ (Of course, for anisotropic liquids, the symmetry may be taken relative to the external laboratory frame.^{16,32})

It will immediately be seen that Eq. (5.2) is equivalent to the standard result for simple rotational Brownian motion, except for the important feature of a frequency dependent $\mathbf{D}[s]$. We now illustrate this frequency dependence with simple memory functions. First we consider exponential memory functions

$$K_{\alpha}(t) \equiv (I_{\alpha} kT) V_{\alpha}^2 \exp(-t/\tau_{M,\alpha}), \quad \alpha = \parallel \text{ or } \perp \quad (5.5)$$

which yield

$$D_{R,\alpha}(s) = D_{R,\alpha}^0 (1 + s\tau_{M,\alpha}), \quad \alpha = \parallel \text{ or } \perp \quad (5.6)$$

where

$$D_{R,\alpha}^0 = kT / I_{\alpha} V_{\alpha}^2 \tau_{M,\alpha} \equiv kT / I_{\alpha} \beta_{\alpha}^0 \quad (5.6')$$

is the zero-frequency limit of the rotational diffusion coefficient and β_{α}^0 is the corresponding limit of the friction coefficient. The simple result of Eq. (5.6) is a direct consequence of the simple exponential memory function. If, instead, we use a Gaussian memory function,

$$K_{\alpha}(t) \equiv (I_{\alpha} kT) V_{\alpha}^2 \pi^{-1/2} \exp[-(t/2\tau_{G,\alpha})^2], \quad (5.7)$$

then

$$\beta_{\alpha}(\omega) = \beta_{\alpha}^0 \{ \exp[-(\omega\tau_{G,\alpha})^2] \} [1 + i\text{erf}(-i\omega\tau_{G,\alpha})], \quad (5.8)$$

with

$$\beta_{\alpha}^0 = V_{\alpha}^2 \tau_{G,\alpha} \quad (5.8')$$

and $s = -i\omega$.

The inversion of Eq. (5.8) to obtain $D_{R,\alpha}(\omega)$ is clearly more complex in the present case. One has

$$\text{Re} D_{R,\alpha}(\omega) = D_{R,\alpha}^0 \{ \exp(\omega\tau_{G,\alpha})^2 / [1 + A_{\alpha}(\omega)]^2 \}, \quad (5.9a)$$

$$\text{Im} D_{R,\alpha}(\omega) = A_{\alpha}(\omega) \text{Re} D_{R,\alpha}(\omega), \quad (5.9b)$$

with

$$A_{\alpha}(\omega) = i\text{erf}(-i\omega\tau_{G,\alpha}). \quad (5.9c)$$

Many experiments monitor the orientational spectral densities $j_{L,K}(\omega)$ given by

$$\begin{aligned} j_{L,K}(\omega) &\equiv \text{Re} \int_0^{\infty} e^{i\omega t} \langle \mathcal{D}_{KM}^{L*}(\Omega_t) \mathcal{D}_{KM}^L(\Omega_0) \rangle dt \\ &= \text{Re} \{ -i\omega + L(L+1)D_{R,\perp}(\omega) + K^2(D_{R,\parallel}(\omega) - D_{R,\perp}(\omega)) \}, \end{aligned} \quad (5.10)$$

where the second equality follows from application of Eq. (5.2). When the exponential memory function Eq. (5.6) is used, then we have

$$\begin{aligned} j_{L,K}(\omega) &= \text{Re} \{ -i\omega [1 + L(L+1)D_{R,\perp}^0 \tau_{M,\perp} + K^2(D_{R,\parallel}^0 \tau_{M,\parallel} \\ &\quad - D_{R,\perp}^0 \tau_{M,\perp})] + [L(L+1)D_{R,\perp}^0 + K^2(D_{R,\parallel}^0 - D_{R,\perp}^0)]^{-1} \}. \end{aligned} \quad (5.11)$$

The zero-frequency spectral density is again seen to be

formally equivalent to the Brownian motion result, but the frequency dependence is different with the exception of the limit $D_{R,\alpha}^0 \tau_{M,\alpha} \rightarrow 0$, i. e., rapidly fluctuating torques.³³

We now consider the Gaussian memory function, Eq. (5.7), but for spherical symmetry such that $D_{R,1} = D_{R,11} = D_R$ for ease in presentation. Then

$$j_L = \tau_L \left\{ e^{(\omega\tau_G)^2 / [1 + A(\omega)^2]} + \tau_L^2 \omega^2 e^{-(\omega\tau_G)^2} [1 + A(\omega)]^2 \right. \\ \left. \times \left[1 + \frac{\tau_L A(\omega) e^{(\omega\tau_G)^2} (\omega\tau_G)^{-1}}{1 + A(\omega)^2} \right] \right\}^{-1}, \quad (5.12)$$

with $\tau_L = [L(L+1)D_R^0]^{-1}$. In the limit $\omega\tau_G \ll 1$, this simplifies to

$$j_L(\omega) \xrightarrow{\omega\tau_G \ll 1} \tau_L \left[1 + \omega^2 \tau_L^2 \left(1 + \frac{\tau_G}{\tau_L} \frac{2}{\sqrt{\pi}} \right)^2 \right]^{-1}, \quad (5.13)$$

which is identical to the result from Eq. (6.11) for spherical symmetry when we let $\tau_G(2/\sqrt{\pi}) \rightarrow \tau_M$. It appears, therefore, that for $\omega\tau_M \ll 1$, the results for $j_L(\omega)$ are not very sensitive to the precise details of the memory function used, although as $\omega\tau_M \gtrsim 1$, the sensitivity to the model becomes much greater.

We note also that the imaginary part of the Fourier-Laplace transform in Eq. (6.10) can also be observed in spectra as a dynamic frequency shift.¹⁵⁻¹⁷

The results of a variety of experiments that measure j_L have been interpreted in terms of jump diffusion models, where the molecule reorients in finite steps. For a particular model of isotropic reorientation introduced by Egelstaff,⁴ the Ivanov³ theory may be expressed as

$$j_L(\omega) = \text{Re}[-i\omega(1 + \tau_j/\tau_L) + \tau_L^{-1}]^{-1} [1 + \tau_j/\tau_L]. \quad (5.14)$$

This corresponds to a model in which $W(\delta)$, the distribution function for diffusive steps by angle δ , is given by

$$W(\delta) = A \sin(\frac{1}{2}\delta) \exp(-\delta/\theta), \quad (5.15)$$

where A is a normalization constant and $\theta < \pi$. Also, τ_j is the mean time between jumps. It is seen that Eq. (5.14) is quite similar to Eq. (5.11) for spherically symmetric diffusion [cf. also Eq. (5.13)]. Thus frequency-dependent experimental results which are interpreted in terms of jump diffusion may actually be reflecting a frequency dependent $D_R(s)$.

The application of the spin-dependent generalized Smoluchowski equation (4.21) is considerably more complex and is discussed in detail elsewhere,^{15,16,34} but we note here that the frequency dependence due to $\mathbf{D}_R[s + i\mathcal{L}_s]$ is of crucial importance and it can have significant effects on the predicted spin resonance spectra.

B. Relative translational diffusion

We may similarly obtain for the Green's function solution to Eq. (3.38) [with $F(\mathbf{r})=0$]

$$P(\mathbf{r}_0 | \mathbf{r}, s) = \frac{1}{8\pi^3} \int d^3\rho e^{-i\rho \cdot (\mathbf{r}-\mathbf{r}_0)} [s + \rho^2 D(s)]^{-1}, \quad (5.16)$$

where we have neglected the dependence of $D(\mathbf{r}, t)$ on

intermolecular separation $r = |\mathbf{r}|$. [We are already neglecting rotation-translation coupling in Eq. (3.38).] Again, this result is equivalent to the usual Brownian-motion result² except that it contains the frequency-dependent diffusion coefficient. For the case of an exponential memory function [cf. Eqs. (5.5) and (5.6)] we have

$$P(\mathbf{r}_0 | \mathbf{r}, s) = \frac{1}{8\pi^3} \int d^3\rho e^{-i\rho \cdot (\mathbf{r}-\mathbf{r}_0)} [s(1 + \rho^2 D^0 \tau_M) + \rho^2 D^0]^{-1}, \quad (5.17)$$

when we assume that all the $K_{m,n}(t)$ in Eq. (3.33) have the same memory function. We wish again to note that this result is similar to, but not the same as, the well-known result for a simple-jump diffusion model²:

$$P(\mathbf{r}_0 | \mathbf{r}, s) = \frac{1}{8\pi^3} \int d^3\rho e^{-i\rho \cdot (\mathbf{r}-\mathbf{r}_0)} [1 + \rho^2 D^0 \tau_j] \\ \times [s(1 + \rho^2 D^0 \tau_j) + \rho^2 D^0]^{-1} \quad (5.18)$$

corresponding to an exponential distribution

$$A(\Delta r) = [4\pi D^0 \tau_j \Delta r]^{-1} \exp[-\Delta r / (D^0 \tau_j)^{1/2}], \quad (5.19)$$

where $A(\Delta r)$ is the probability of a jump of magnitude Δr in a single step, while τ_j is again the mean time between jumps. Thus, frequency-dependent experimental results interpreted in terms of translational jump diffusion may also be amenable to explanation in terms of a frequency-dependent $D(s)$.

We note, in passing, that Eqs. (5.16)–(5.18) are conditional probability distributions defined in the space $0 \leq |\mathbf{r}| < \infty$. Normally, however, for relative diffusion there is a distance of closest approach d such that $d \leq |\mathbf{r}| < \infty$. In these cases, Eqs. (5.16)–(5.18) must be appropriately modified.³⁴ However, Eq. (3.38) can automatically satisfy the boundary condition at d with an appropriately chosen $F(\mathbf{r}) \neq 0$ [e. g., $F(r) = \infty$ for $r \leq d$].

VI. SUMMARY AND CONCLUSIONS

We have shown in this work how general considerations allow us to obtain generalized Einstein relations such as Eqs. (1.3) and (1.4). The frequency-dependent diffusion coefficients so defined are features of generalized (time-dependent) Smoluchowski equations. These equations are seen to follow from typical generalized FP equations provided it may be assumed that the translational and/or angular momenta are rapidly relaxing variables. However, it is likely required that the fluctuating forces or torques be dominated by fluctuations in surroundings as distinct from the motion of the B particle. The resulting generalized Smoluchowski equations have the interesting property that the fluctuating force (or torque) correlation functions, in terms of which the frequency-dependent $\beta(\omega)$ and $D(\omega)$ are defined, appear simply as averages over the lattice at equilibrium, largely unperturbed by the back reaction of the B particle. This is not true for the original generalized FP equations, wherein one has operator correlation functions in the space of the B -particle variables. We have not, in this work, attempted a comparison of the faster relaxing momentum variables relative to the positional or orientational relaxation. Such an analysis would probably require distinguishing between

any fluctuating force and torque components that are fast enough to cause momentum relaxation from those which are slower but not too slow to contribute to $D(\omega)$, and this could be expected to lead to deviations of the $\beta(\omega)$ governing momentum relaxation from Eqs. (1.3) and (1.4).

While the generalized FP equations for translational motion have been derived previously, we have obtained here the result for rotational motion in terms of well-defined rotational variables and operators.

We have also derived generalized FP and Smoluchowski equations including spin for the B particle. The resulting expressions are semiclassical, i. e., classical in ordinary phase space but quantum mechanical in spin. These are of the type referred to as stochastic Liouville equations which have been previously developed in terms of time independent classical Markov descriptions of the lattice variables. The present generalization thus allows for non-Markovian descriptions of the lattice. It is also shown how a proper application of the correspondence principle in passing from quantum mechanical commutators to classical Poisson brackets for the phase-space variables leads naturally to a new term referred to as a "spin-force" or "spin-torque" term representing the back reaction of the spins on the lattice. This term has the property of tending to restore the spins to their proper thermal equilibrium value, an important feature usually lacking in semiclassical treatments. Some of the properties of the spin dependent FP and Smoluchowski equations are discussed in this context.

We have not, in this work, attempted to demonstrate from any microscopic theory the range of experimental relevance of introducing a frequency-dependent $D(\omega)$ in place of the usual $D(\omega=0)$ except that we note that the usual Brownian motion results are obtained in the limit of rapidly fluctuating forces and torques. We prefer instead to offer the general expressions to be used in analyzing actual experiments, of a frequency-dependent nature, to see whether real evidence may be obtained for their importance. Recent results in our laboratory have been encouraging on this score. For purposes of having convenient results for such comparisons, we have approximated the force and torque correlation functions by simple memory functions. One interesting feature of these results is that they lead to frequency-dependent forms which are quite similar (but not identical) to those predicted from simple jump-type models. This suggests the possibility that analyses of (frequency-dependent) experiments previously interpreted in terms of jump models may be amenable to interpretation by a frequency-dependent $D(\omega)$.

APPENDIX A: THE RANDOM TORQUE OPERATOR CORRELATION FUNCTION

We wish here to simplify the form of Eq. (2.26), which we rewrite as

$$\int \prod_i^N d\Gamma_i \mathbf{R}_B \cdot \nabla_{L_B} (1 - \hat{P}) \rho_{N+1} = \nabla_{L_B} \cdot \int \prod_i^N d\Gamma_i \mathbf{R}_B (1 - \hat{P}) \rho_{N+1}, \quad (\text{A1})$$

where $\mathbf{R}_B = \mathbf{N}_B - \langle \mathbf{N}_B \rangle$, and we have used the independence

of \mathbf{R}_B on L_B . We now apply the operator $(1 - \hat{P})$ to Eq. (2.2) to obtain

$$i \frac{\partial}{\partial t} (1 - \hat{P}) \rho_{N+1} = (1 - \hat{P}) (\mathcal{L}_0 + \mathcal{L}_B) (1 - \hat{P}) \rho_{N+1} + (1 - \hat{P}) (\mathcal{L}_0 + \mathcal{L}_B) \rho^f f_B. \quad (\text{A2})$$

We now assume that the initial state of the system is given by Eq. (2.27). Then the formal solution to Eq. (A2) becomes

$$(1 - \hat{P}) \rho_{N+1}(t) = -i \int_0^t \{ \exp[-i(1 - \hat{P})(\mathcal{L}_0 + \mathcal{L}_B)(t - \tau)] \} \times (1 - \hat{P}) \mathcal{L}_0 \rho^f f_B(\tau) d\tau. \quad (\text{A3})$$

Now note that

$$(1 - \hat{P}) \mathcal{L}_0 \rho^f f_B(t) = (1 - \hat{P}) \mathcal{L}_B \rho^f f_B(t), \quad (\text{A4})$$

which follows from $\mathcal{L}_0 \rho^f = 0$. Then we may use the definition, Eq. (2.14) of ρ^f , to show that

$$\omega_B \cdot \mathbf{J}_B \rho^f = (\omega_B/kT) \langle \mathbf{N}_B \rangle \rho^f. \quad (\text{A5})$$

This enables us to rewrite Eq. (A4) as

$$(1 - \hat{P}) \mathcal{L}_0 \rho^f f_B(t) = \mathbf{R}_B \cdot (\omega_B/kT) \rho^f f_B(t) + \mathbf{R}_B \cdot \rho^f \cdot \nabla_{L_B} f_B(t) \quad (\text{A6})$$

When Eqs. (A3), (A4) and (A6) are substituted into Eq. (A1) we obtain:

$$-\nabla_{L_B} \cdot \int_0^t d\tau \mathbf{G}(t - \tau) \cdot \left[\frac{\omega_B}{kT} + \nabla_{L_B} \right] f_B(\tau) \quad (\text{A7})$$

[cf. Eq. (2.28)] with $\mathbf{G}(t)$ given by Eq. (2.29).

APPENDIX B: EXPANDING THE OPERATOR CORRELATION FUNCTION FOR THE TORQUES

The operator correlation function for the random torques is given by Eq. (2.29),

$$\mathbf{G}(t) = \int \prod_i^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1 - \hat{P})\mathcal{L}t] \} \mathbf{R}_B \rho^f. \quad (\text{B1})$$

It appears on the rhs of Eq. (3.2) as

$$\nabla_L \cdot \int_0^t d\tau \mathbf{G}(t - \tau) \cdot [\omega/kT + \nabla_L] f(\tau). \quad (\text{B2})$$

We now wish to study its expansion in powers of the coupling parameter μ . We may rewrite the definition of \mathcal{L} [cf. Eqs. (2.3), (2.6), and (2.7)] as

$$\mathcal{L} = \mathcal{L}_c - \mu i (\omega \cdot \mathbf{J} + \hat{\mathbf{L}} \cdot \nabla_L + \langle \mathbf{N}_B \rangle \cdot \nabla_L), \quad (\text{B3a})$$

where

$$\mathcal{L}_c \equiv \mathcal{L}_0 - i (\mathbf{N}_B - \langle \mathbf{N}_B \rangle) \cdot \nabla_L = \mathcal{L}_0 - i \mathbf{R}_B \cdot \nabla_L \quad (\text{B3b})$$

and is independent of μ . Then we may expand $\mathbf{G}(t)$ as

$$\mathbf{G}(t) = \mathbf{G}_0(t) + \text{linear and higher order terms in } \mu, \quad (\text{B4})$$

where

$$\mathbf{G}_0(t) \equiv \int \prod_i^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1 - \hat{P})\mathcal{L}_c t] \} \mathbf{R}_B \rho^f. \quad (\text{B5})$$

Since \mathcal{L}_c only neglects the systematic terms for the B particle, it is clear that $\mathbf{G}_0(t)$ has the same random

properties as $\mathbf{G}(t)$ itself. The latter are discussed in Appendix C. The validity of the expansion equation (B4) is seen to depend on whether the correlation function of the random torque $\mathbf{G}(t)$ is well approximated by random fluctuations induced by the solvent as compared to any (possibly systematic) effects from the B particle itself trying to minimize an instantaneous non-zero \mathbf{R}_B by reorienting. I. e., a sufficient condition should be that the memory in $\mathbf{G}(t)$ due to fluctuations from the surroundings be short (or at most comparable) to the time required for the B particle to minimize \mathbf{R}_B by reorienting.³⁵ Any fluctuating torque components which are *slowly* relaxing in this sense are best handled by inclusion in a redefined $\langle \mathbf{N}_B(t) \rangle$, and the resulting (generalized) Smoluchowski equation solved with this time dependence explicitly included.

The first order term μ on the rhs of Eq. (3.2) [cf. Eq. (B2)] is thus given by

$$\nabla_L \cdot \int_0^t d\tau \int \prod_{i=1}^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1-\hat{P})\mathcal{L}_c(t-\tau)] \} \mathbf{R}_B \rho^f \cdot \left(\frac{\omega}{kT} + \nabla_L \right) f_1(\Omega, \mathbf{L} | P(\Omega, t)) \quad (\text{B6})$$

We now multiply Eq. (B6) by \mathbf{L} and then integrate over \mathbf{L} to obtain

$$\int d^3L \mathbf{L} \nabla_L \cdot \int_0^t d\tau \int \prod_{i=1}^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1-\hat{P})\mathcal{L}_c(t-\tau)] \} \times \mathbf{R}_B \rho^f \left(\frac{\omega}{kT} + \nabla_L \right) f_1(\Omega, \mathbf{L} | P(\Omega, t)) \quad (\text{B7})$$

Note now that

$$\exp[-i(1-\hat{P})\mathcal{L}_c(t-\tau)] \equiv \exp[-i(1-\hat{P})[\mathcal{L}_0 - i(\mathbf{N} - \langle \mathbf{N} \rangle) \cdot \nabla_L](t-\tau)] = \exp[-i(1-\hat{P})\mathcal{L}_0(t-\tau)] + \int_0^{t-\tau} dt' \{ \exp[-i(1-\hat{P})\mathcal{L}_0(t-\tau-t')] \} \times (1-P)(-i)^2 (\mathbf{N} - \langle \mathbf{N} \rangle) \cdot \nabla_L \exp[-i(1-\hat{P})\mathcal{L}_c t'] \quad (\text{B8})$$

We now substitute Eq. (B8) into Eq. (B7) and then recognize that when the integration over L is performed in Eq. (B7), the contribution from the second term on the rhs of Eq. (B8) drops out due to the boundary conditions satisfied by $f_1(\Omega, \mathbf{L} | P(\Omega, t))$. Then Eq. (B7) becomes

$$\int d^3L \mathbf{L} \nabla_L \cdot \int_0^t d\tau \int \prod_{i=1}^N d\Gamma_i \mathbf{R}_B \{ \exp[-i(1-\hat{P})\mathcal{L}_0(t-\tau)] \} \times \mathbf{R}_B \rho^f \cdot \left(\frac{\omega}{kT} + \nabla_L \right) f_1(\Omega, \mathbf{L} | P(\Omega, t)) \quad (\text{B9})$$

Note that the exponential operator in Eq. (B9) is more simply written as $\exp[-i\mathcal{L}_0(t-\tau)]$ by Eq. (2.16). This result appears in Eq. (3.17).

APPENDIX C: TIME EVOLUTION OF THE AVERAGED FLUCTUATING TORQUE

The random torque operator $\mathbf{R}_B(t)$ is defined as

$$\mathbf{R}_B(t) \equiv \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{R}_B \quad (\text{C1})$$

where $\mathbf{R}_B = \mathbf{N}_B - \langle \mathbf{N}_B \rangle$ and it appears in the definition of

$\mathbf{G}(t)$ [cf. Eq. (B1)]. Its averaged value is defined by

$$\langle \mathbf{R}_B(t) \rangle \equiv \int \prod_{i=1}^N d\Gamma_i \{ \exp[-i(1-\hat{P})\mathcal{L}t] \} \mathbf{R}_B \rho^f \quad (\text{C2})$$

Clearly $\langle \mathbf{R}_B(t=0) \rangle = 0$. We wish now to prove that $\langle \mathbf{R}_B(t) \rangle = 0$ for all t . Thus we consider the time derivative of $\langle \mathbf{R}_B(t) \rangle$:

$$\begin{aligned} \langle \dot{\mathbf{R}}_B(t) \rangle &\equiv \prod_j \int d\Gamma_j \dot{\mathbf{R}}_B(t) \rho^f \\ &= \prod_j \int d\Gamma_j (-i) \mathcal{L} \mathbf{R}_B(t) \rho^f \\ &\quad + \prod_j \int d\Gamma_j \rho^f \left[\prod_k \int d\Gamma_k (i) \mathcal{L} \mathbf{R}_B(t) \rho^f \right] = 0 \quad (\text{C3}) \end{aligned}$$

Thus $\langle \mathbf{R}_B(t) \rangle$ must be constant in time, and since $\langle \mathbf{R}_B(0) \rangle = 0$, then $\langle \mathbf{R}_B(t) \rangle = 0$.

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