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The short-time dynamics of molecular reorientation in liquids. I. The instantaneous generalized Langevin equation

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Up until relatively recently, experimental measurements of the rotational dynamics of small molecules in liquids were largely confined to seeing the effects of rotational diffusion. The molecular character of the process seemed of little relevance. However, newer measurements have begun to look in some detail at the microscopics behind molecular reorientation. We show in this paper that it is possible to understand the short-time dynamics of rotation in liquids at a molecular level by looking at the instantaneous normal modes of the remaining degrees of freedom. With the aid of some other, properly short-time, approximations, the reorientational dynamics can be cast into the form of an instantaneous generalized Langevin equation—one defined for each liquid configuration. One therefore obtains fully molecular expressions for the instantaneous rotational friction and fluctuating torque felt by a solute. The average friction so obtained seems to describe the basic nondiffusional aspects of rotation reasonably accurately and lends itself—as we illustrate in the companion paper—to more detailed investigations into the actual molecular mechanisms behind rotational relaxation. In the course of this work we also show that just as the autocorrelation function for the force on a rigid bond yields an accurate portrayal of the friction needed to study vibrational relaxation, quantitatively accurate results for the rotational friction can be provided by using molecular dynamics to compute the torque autocorrelation function for an orientationally rigid solute. © 2000 American Institute of Physics. [S0021-9606(00)50217-7]

I. INTRODUCTION

While molecules tend to have much the same vibrational and electronic character in liquids that they do in isolation, the same is clearly not the case for molecular rotation. The solvent displacements involved in rotating even the smallest molecules are simply too large to permit the kinds of free, high-angular momentum, rotations often seen in the gas phase. Worse still, the lack of intrinsic intramolecular forces controlling a molecule's rotation (as opposed to the situation with either vibrations or electronic structure) leaves rotational dynamics at the mercy of any random, spontaneous torques that might happen to be imposed by the surrounding solvent. So how should we be thinking about the nature of the reorientational motions that a molecule does undergo in a liquid? The subject is certainly a venerable one,¹ but the ability of newer generations of experiments to probe ever shorter time scales, and in particular, to begin to get at the genuinely molecular features of reorientational dynamics,²⁻⁶ make it worth our while to reconsider what theory has to say about the precise solute and solvent motions that come into play when molecules reorient in liquids.

There have, of course, been no shortage of experimental efforts in this arena, dating back to the earliest studies of solute relaxation dynamics.^{1,7,8} Nuclear magnetic resonance (NMR) studies of spin relaxation times,⁹ along with measurements of depolarized Raman¹⁰ and far-infrared and microwave¹¹ spectra have long been used to find reorientational correlation functions of the form

$$C_L(t) = \langle P_L[\cos \Theta(t)] \rangle, \quad (1.1)$$

with $\Theta(t)$ some angular displacement of the molecule over the time t and $P_L(x)$ the L th order Legendre polynomials (L being 1 or 2 depending on the particular experiment). The experiments invariably found these correlation functions to be exponentially decaying, indicative of the diffusive character of the dynamics at the observable time scales. With the advent of ultrafast fluorescence-anisotropy experiments, however, it became possible to measure the same $C_2(t)$ at a much finer time resolution.^{2,3,12-18} The fact that there was more to the dynamics than simple diffusion^{2,3,13,16} and the realization that even the diffusion reflects a considerable level of molecular detail^{2,17-20} eventually began to be appreciated.

Contributions have begun to appear, as well, from some rather different kinds of experiments nicely attuned to the details of rotational dynamics in liquids. Pulsed terahertz techniques now allow the rotational spectra of molecules in liquids to be measured reasonably directly⁴⁻⁶ and optical Kerr effect (OKE) methods (in the form of optically heterodyne-detected Raman-induced-Kerr-effect, OHD-RIKES, studies) are starting to go beyond the earliest applications to neat liquids and being applied specifically to the dynamics of solutes.²¹⁻²⁴ In addition, there has been a particular interest in the intriguing cases of H_2 dissolved in water^{25,26} and HCN dissolved in liquid He,²⁷ situations in which the quantal character of the rotational dynamics merits special attention.

From the theoretical side, most of what we know about rotational dynamics in dense liquids starts with the information provided by molecular dynamics simulations,²⁸⁻³¹

which, in addition to computing the orientational correlation function, Eq. (1.1), typically focus on the angular velocity autocorrelation function

$$C_{\omega\omega}(t) = \langle \vec{\omega}(t) \cdot \vec{\omega}(0) \rangle / \langle \vec{\omega}(0) \cdot \vec{\omega}(0) \rangle. \quad (1.2)$$

The models used to interpret these results, however, span a rather wide range of conceptual possibilities, tracing the historical evolution of our understanding of liquids. Gordon's extended diffusion models,³² though originally couched in gas-phase terms, were soon shown to be equivalent to an independent-binary-collision perspective on rotational behavior.³³ Formal kinetic theories were then proposed building on this same kind of hard-collision viewpoint.³⁴ The kinetic theories needed significant augmentation to account for correlated recollisions though, so solvent-cage models, which stress the librational character of molecular reorientation, have frequently been suggested as plausible, if not as microscopically well-defined, alternatives.^{35–37}

Actually, a somewhat broader perspective tends to form the basis of most of the ongoing discussion of rotational dynamics. The idea has its roots in the notion of rotational Brownian motion,^{38–41} which describes the dynamics through a rotational Langevin equation in which the solvent's role is to create a *rotational friction*. Indeed, many of the current issues in rotational dynamics can be phrased in terms of the origin and magnitude of such a friction: whether the friction is, in fact, anomalous around a solute in supercritical solvents,^{42–44} whether hydrogen-bonding solvents lead to a specific solute–solvent complex with concomitant effects on the rotational friction,^{2,45,46} and whether the concept of dielectric friction^{47–52} (taking into account, if so desired, realistic molecular charge distributions^{19,20}) provides a useful picture of the rotation of polar solutes in polar solvents.²

Of all of these issues, perhaps the most crucial from the point of view of this paper is the central theme of how molecular one needs to get in order to understand rotational friction. Traditionally, hydrodynamic predictions^{38,53–57} have proven reasonably reliable in accounting for the basic trends and magnitudes of the rotational friction, especially when supplemented by corrections for finite solute size⁵⁸ and for the free volume between the solute and the solvent molecules.⁵⁹ But the deficiencies of such continuum models are becoming increasingly clear. The observation of nonexponential decays for reorientational correlation functions itself emphasizes the need to look at more than the diffusive motion permitted by simple continuum theories.^{2,13} More to the point, the fact that experiments are now considering the evolution in time from inertial to diffusive behavior^{3,13,14} moves the discussion beyond the level of any theory which does not have individual molecules accounting at least for the dynamics at the shortest times.

A rigorous way to go beyond the hydrodynamic models while still preserving the basic idea of a rotational friction is to express the rotational dynamics through a rotational generalized Langevin equation (GLE).^{47,60–65} For a linear or spherical top molecule, such an equation takes the form

$$I \dot{\vec{\omega}}(t) = - \int_0^t d\tau \eta(t-\tau) \vec{\omega}(\tau) + \vec{N}(t), \quad (1.3)$$

where the function $\eta(t)$ generalizes the Langevin equation (memory-less) friction to a time-dependent version, $\vec{N}(t)$ is the so-called fluctuating torque, and I is the solute moment of inertia. Physically, we can think of this equation as dividing the torque felt by a solute into a direct (fluctuating) portion, the component the solute would feel even if its own motion had no effect on the solvent, and an indirect (friction) portion, the component caused by the back reaction of the solvent opposing the solute's motion. The fact that real (molecular) solvents have to move real distances means that this back reaction cannot be instantaneous. Hence adding time dependence to the friction serves to build in the physically correct time lag between solute angular velocity $\vec{\omega}(\tau)$ and the torque at any later time t .

The formal statistical mechanical underpinnings behind equations such as Eq. (1.3) are well established.^{66,67} The difficulty is that in order for us to apply Eq. (1.3) we need to have a fully molecular prescription for both the friction and the fluctuating torque. It is true that these two ingredients have to be intimately connected, as evidenced by the second fluctuation-dissipation theorem

$$\eta(t) = (2k_B T)^{-1} \langle \vec{N}(t) \cdot \vec{N}(0) \rangle, \quad (1.4)$$

a result which follows from the formal derivation of the GLE, as well as from more physical considerations.^{66,67} But, the abstract projections involved in partitioning the torque into its direct and indirect components makes both portions somewhat unphysical. The time evolution of the fluctuating torque, for example, can no longer be followed by solving Newton's laws using the microscopic forces.

The common solution to this dilemma in problems involving vibrational relaxation^{68,69} and reaction kinetics⁷⁰ is to make the approximation that the fluctuating solvent quantity (in vibrational relaxation examples, the force on a bond) can be replaced by the corresponding physical quantity evaluated with the dynamical variable of interest (the solute bond length) held fixed. With vibrational examples in particular, the intrinsic dynamics of the vibration is so much faster than that of the solvent motion that this approximation is usually going to be extremely accurate. Indeed, it is possible to show that this approximation becomes exact in the limit that the vibrational frequency becomes infinitely large.⁶⁸ Much the same approximation has appeared in the literature for the rotational friction; *fixed-orientation* frictions have been constructed by applying Eq. (1.4) with the actual torques replacing the fluctuating torques.^{64,71,72} Here, however, it is not obvious that there is any such separation of time scales. If our goal is to understand the molecular basis of rotational friction, we need to ask why (and even whether) such an ansatz should work in rotational problems.

In a sense, our work here is based on the purely mathematical observation by Zwanzig that a dynamical variable linearly coupled to a harmonic bath will obey a GLE whose friction (and fluctuating force) can be written explicitly in terms of the bath variables.^{73,74} This realization has been at the heart of some of the classic studies of both vibrational

relaxation^{75,76} and chemical reaction dynamics,^{77,78} but, with a few notable exceptions,^{79,80} the applications have been more schematic than physical because of the lack of a molecular identification of the harmonic modes. What we want to show in this paper is that by representing the solvent by an appropriately molecular set of harmonic modes, we too end up with a GLE describing reorientational motion, but with a clear molecular interpretation of the terms in the equation.

Consistent with our desire to elucidate molecular mechanisms, the GLE we derive is what we shall call an *instantaneous* generalized Langevin equation. That is, we shall be looking for the rotational dynamics launched from an arbitrary instantaneous liquid configuration, rather than from the more commonplace, fully averaged, set of initial conditions. As a result, the harmonic portrait of the solvent that we need to employ is based on the instantaneous-normal-mode (INM) representation of solution dynamics.^{81–83} This same strategy of using INMs to derive instantaneous GLEs has actually been used before in conjunction with vibrational relaxation^{84–86} and the resulting expressions for the vibrational friction have proven to be a considerable help in understanding the mechanisms of vibrational relaxation in liquids.^{87–89} In this and the following paper,⁹⁰ we shall endeavor to see if we can obtain the same kinds of physical insights for the more difficult problem of rotational relaxation.

The remainder of our presentation will be organized as follows: In Sec. II we show that one can indeed derive an instantaneous rotational GLE by using a Zwanzig-type analysis⁷³ on a short-time version of our Hamiltonian. The procedure is complicated by the intrinsic nonlinearity of the relationship between the angles describing the orientation and the angular velocity, but our desire to focus specifically on the short-time dynamics turns out to provide enough of a guide to proceed. We discuss some general features of this formulation in Sec. III, where we show that our equations do, in fact, embody the exact dynamics in the liquid at the earliest times and that the two-dimensional (θ and ϕ) equations necessitated by our instantaneous approach to a linear rotor do reduce, quite properly, to a single equation when we configurationally average. We also point out how the statistics of the instantaneous fluctuating torques ends up not being Gaussian, notwithstanding the harmonic character of a liquid's short-time dynamics. Section IV contains our first numerical results for the rotational friction and for the implied rotational dynamics. We compare these results to those derived from exact molecular dynamics and we demonstrate both the accuracy of the fixed-orientation approximation for the friction and the reasons why our formalism would predict that it would work so well. We conclude with a few comments in Sec. V, leaving for the companion paper⁹⁰ the next step of actually making use of our instantaneous rotational friction to understand the molecular mechanism of rotation in liquids.

II. DERIVATION OF THE INSTANTANEOUS GENERALIZED LANGEVIN EQUATION

The system we shall consider here is a single, linear, solute molecule dissolved in an atomic solvent. The gener-

alization to molecular solvents is straightforward, but our simple example probably suffices to reveal the essential issues. The information of interest to us, the orientation of our solute, is specified in the laboratory frame by the angles θ and ϕ , so we can represent all of the remaining degrees of freedom—those of the ‘‘bath’’—by $\mathbf{R} \equiv (\vec{r}_0, \vec{r}_1, \dots, \vec{r}_N)$, with \vec{r}_0 the position vector of the solute's center of mass and the remaining $\vec{r}_j (j=1, \dots, N)$ the position vectors of the N solvent atoms. Within this notation the total Hamiltonian of the system can be written

$$H = \frac{I}{2} (\dot{\phi}^2 \sin^2 \theta + \dot{\theta}^2) + \frac{1}{2} \sum_{j=0}^N m_j \dot{r}_j^2 + V(\phi, \theta, \mathbf{R}), \quad (2.1)$$

where I is the solute's moment of inertia, and the m_j are the masses of the solute molecule ($j=0$) and the solvent atoms ($j \geq 1$).

The reader may recognize that despite our having blithely invoked the concept of a bath, there will rarely be a unique way to partition the total potential energy of the system, $V(\phi, \theta, \mathbf{R})$, into a bath potential, V_b , and a potential coupling the bath and orientational degrees of freedom, V_c

$$V(\phi, \theta, \mathbf{R}) = V_b(\mathbf{R}) + V_c(\phi, \theta, \mathbf{R}). \quad (2.2)$$

With site–site intermolecular pair potentials, for example, each pair potential governing the interaction of a solute site with a solvent atom will contribute to the energies of both the solute translation and rotation. However once we decide to focus on the short-time rotational dynamics, it becomes clear how to proceed. In the following sections, we construct an approximate Hamiltonian by first defining instantaneous bath and coupling potentials and then writing the time evolution of each of these in terms of the instantaneous normal modes of the bath. Straightforward application of the classical laws of motion then lead to a generalized Langevin equation for the reorientation of the solute.⁸⁵

A. The short-time Hamiltonian for the system

We can define an instantaneous bath potential by evaluating the total potential energy with the solute fixed at its original ($t=0$) orientation

$$V_b(\mathbf{R}) = V(\phi_0, \theta_0, \mathbf{R}), \quad (2.3)$$

a choice which defines the coupling potential by difference

$$V_c(\phi, \theta, \mathbf{R}) = V(\phi, \theta, \mathbf{R}) - V(\phi_0, \theta_0, \mathbf{R}). \quad (2.4)$$

To look at the time evolution governed by these potentials, we now ask how these potentials change as the system moves away from its initial configuration $(\phi_0, \theta_0, \mathbf{R}_0)$.

For time scales short compared to those required for significant rearrangement of the bath, we can imagine expanding the bath potential in powers of the bath-coordinate displacements, truncating the expansion at second order. This step, of course, defines the instantaneous normal modes of our bath. Briefly, from the (mass-weighted) dynamical matrix, $\mathbf{D}(\mathbf{R}_0)$, for a given initial configuration of the bath, \mathbf{R}_0 ,

$$D_{j\mu, k\nu}(\mathbf{R}_0) = \frac{1}{\sqrt{m_j m_k}} \left. \frac{\partial^2 V}{\partial r_{j\mu} \partial r_{k\nu}} \right|_{\mathbf{R}_0}, \quad (2.5)$$

where the $r_{j\mu}$ denotes the μ th ($\mu = x, y, z$) Cartesian component of the position vector of the j th atom, we can construct a set of independent collective coordinates $q_\alpha(t)$, the INMs, which provide a molecular description of the subsequent dynamics.⁸² If the eigenvector matrix is $\mathbf{U}(\mathbf{R}_0)$, the characteristic frequencies of the modes ω_α are prescribed by the eigenvalues of the dynamical matrix,

$$[\mathbf{U}^T(\mathbf{R}_0)\mathbf{D}(\mathbf{R}_0)\mathbf{U}(\mathbf{R}_0)]_{\alpha\beta} = \omega_\alpha^2 \delta_{\alpha\beta}, \quad (2.6)$$

and the modes themselves are defined by the eigenvectors

$$q_\alpha(t) = \sum_{j\mu} U_{j\mu,\alpha} \sqrt{m_j} [r_{j\mu}(t) - r_{j\mu}(0)]. \quad (2.7)$$

It is then straightforward to show that the bath-potential energy, V_b , is given in terms of these modes by

$$V_b(\mathbf{R}_t) \approx V_b(\mathbf{R}_0) + \sum_\alpha [-f_\alpha q_\alpha(t) + \frac{1}{2} \omega_\alpha^2 q_\alpha^2(t)], \quad (2.8)$$

where the f_α are the transformed forces,

$$f_\alpha = \sum_{j\mu} U_{j\mu,\alpha} F_{j\mu}, \quad F_{j\mu}(\mathbf{R}_0) = -\frac{1}{\sqrt{m_j}} \left. \frac{\partial V}{\partial r_{j\mu}} \right|_{\mathbf{R}_0}. \quad (2.9)$$

Since the instantaneous normal modes are a natural basis for dynamics of the bath, the short-time dynamics is revealed by expanding the coupling in powers of them as well. The leading term is just $V_c(\phi, \theta, \mathbf{R}_0)$, what the coupling would be for a frozen bath, but each successive term brings in higher powers of the bath INMs. In much the same way, we can watch the early evolution of the solute orientation by expanding simultaneously in successive powers of the angle displacements. Note that, by construction, the coupling term corresponding to having the bath evolve at fixed solute orientation, $V_c(\phi_0, \theta_0, \mathbf{R})$, is identically zero, so that the entire expansion is of what we might call the purely *dynamical* portion of the coupling.⁸⁵

Explicitly then, if we keep just the leading short-time terms, the coupling potential can be written

$$\begin{aligned} V_c(\phi, \theta, \mathbf{R}) = & V_c(\phi, \theta, \mathbf{R}_0) + \sum_{j\mu} \sqrt{m_j} [c_{\phi,j\mu}(\phi(t) - \phi_0) \\ & \times (r_{j\mu}(t) - r_{j\mu}(0)) + c_{\theta,j\mu}(\theta(t) - \theta_0) \\ & \times (r_{j\mu}(t) - r_{j\mu}(0))], \end{aligned} \quad (2.10)$$

where the coupling coefficients $c_{\phi,j\mu}$ and $c_{\theta,j\mu}$ are

$$\begin{aligned} c_{\phi,j\mu} = & \frac{1}{\sqrt{m_j}} \left. \frac{\partial^2 V}{\partial \phi \partial r_{j\mu}} \right|_{\phi_0, \theta_0, \mathbf{R}_0}, \\ c_{\theta,j\mu} = & \frac{1}{\sqrt{m_j}} \left. \frac{\partial^2 V}{\partial \theta \partial r_{j\mu}} \right|_{\phi_0, \theta_0, \mathbf{R}_0}. \end{aligned} \quad (2.11)$$

Rewriting this equation in terms of INMs and adding the result to Eq. (2.8) gives us a short-time expression for the total potential energy of the system

$$\begin{aligned} V(\phi, \theta, \mathbf{R}) \approx & V(\phi, \theta, \mathbf{R}_0) + \sum_\alpha [c_{\phi,\alpha}(\phi - \phi_0) \\ & + c_{\theta,\alpha}(\theta - \theta_0)] q_\alpha + \sum_\alpha \left[-f_\alpha q_\alpha + \frac{\omega_\alpha^2}{2} q_\alpha^2 \right], \end{aligned} \quad (2.12)$$

with $c_{\phi,\alpha}$ and $c_{\theta,\alpha}$ the transformed coupling coefficients

$$\begin{aligned} c_{\phi,\alpha} = & \sum_{j\mu} U_{j\mu,\alpha} c_{\phi,j\mu} = \left. \frac{\partial^2 V}{\partial \phi \partial q_\alpha} \right|_{\phi_0, \theta_0, \mathbf{R}_0}, \\ c_{\theta,\alpha} = & \sum_{j\mu} U_{j\mu,\alpha} c_{\theta,j\mu} = \left. \frac{\partial^2 V}{\partial \theta \partial q_\alpha} \right|_{\phi_0, \theta_0, \mathbf{R}_0} \end{aligned} \quad (2.13)$$

Adding the kinetic energy⁹¹ then provides us with our desired short-time formulation for the whole Hamiltonian of our system,

$$\begin{aligned} H = & \frac{I}{2} (\dot{\phi}^2 \sin^2 \theta + \dot{\theta}^2) + V(\phi, \theta, \mathbf{R}_0) \\ & + \sum_\alpha [c_{\phi,\alpha}(\phi - \phi_0) + c_{\theta,\alpha}(\theta - \theta_0)] q_\alpha \\ & + \frac{1}{2} \sum_\alpha \dot{q}_\alpha^2 + \sum_\alpha \left[-f_\alpha q_\alpha + \frac{\omega_\alpha^2}{2} q_\alpha^2 \right]. \end{aligned} \quad (2.14)$$

Because of the instantaneous character of our approach, this Hamiltonian actually depends on the initial configuration of the system. Any properly formulated calculation of an experimental observable based on Eq. (2.14) should therefore include an average over the equilibrium distribution of these configurations. Nonetheless, by being careful to order terms in powers of displacements from the initial configuration (rather than say, powers of the coordinates themselves), our the total Hamiltonian ends up being divided naturally into three physically distinguishable terms: a *solute* Hamiltonian in which the bath variables are fixed at initial configuration, \mathbf{R}_0 , a *bath* Hamiltonian where the solute orientation is fixed at initial value (ϕ_0, θ_0) , and a dynamic coupling between the solute rotation and the bath INMs. Equation (2.14) is the starting point for our derivation of a GLE for solute rotation.

B. Derivation of a rotational generalized Langevin equation

Our object here is to derive an effective equation of motion for the solute rotation from the short-time Hamiltonian constructed in the preceding section. We begin with the familiar equation for the classical time evolution of the angular velocity of a linear top. The angular velocity is dictated by the torque, \vec{N} , which in turn is related to the angular gradient of the total potential,

$$I \dot{\omega}_\gamma = N_\gamma = - \frac{\partial V}{\partial \psi_\gamma}, \quad (2.15)$$

where $d\psi_\gamma$ is the *infinitesimal* rotation angle around the γ th laboratory frame axis. Inserting the short-time potential, Eq. (2.12), into Eq. (2.15), gives us an equation of motion for the angular velocity,

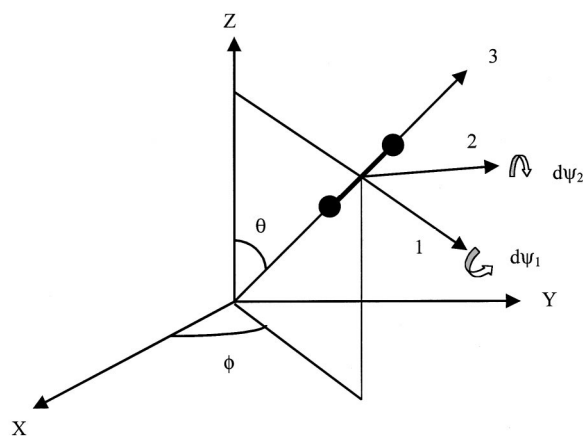


FIG. 1. Coordinate systems for studying the rotational dynamics of a linear molecule (portrayed here as a diatomic). The laboratory frame is indicated by the X, Y, and Z axes; our choice for an instantaneous frame is defined by the axes numbered 1, 2, and 3, with the infinitesimal twist angles $d\psi_1$ and $d\psi_2$ defined as shown.

$$I\dot{\omega}_\gamma = -\frac{\partial V(\phi, \theta, \mathbf{R}_0)}{\partial \psi_\gamma} - \sum_\alpha \left[c_{\phi, \alpha} \frac{\partial \phi}{\partial \psi_\gamma} \Big|_t + c_{\theta, \alpha} \frac{\partial \theta}{\partial \psi_\gamma} \Big|_t \right] q_\alpha(t), \quad (2.16)$$

which also depends on the dynamics of the bath INMs. However, the time evolution of each INM, $\ddot{q}_\alpha = -(\partial V / \partial q_\alpha)$, is simply that of a forced harmonic oscillator, which we can evaluate, at least formally, as

$$q_\alpha(t) = \dot{q}_\alpha(0) \frac{\sin \omega_\alpha t}{\omega_\alpha} + \frac{f_\alpha}{\omega_\alpha^2} (1 - \cos \omega_\alpha t) - \int_0^t d\tau \frac{1 - \cos[\omega_\alpha(t - \tau)]}{\omega_\alpha^2} [c_{\phi, \alpha} \dot{\phi}(\tau) + c_{\theta, \alpha} \dot{\theta}(\tau)]. \quad (2.17)$$

With this expression we could derive an effective equation for the solute orientation simply by substituting the $q_\alpha(t)$'s into Eq. (2.16). Indeed precisely this strategy was used by Zwanzig in his derivation of a GLE from a general harmonic bath,⁷³ and by us in our derivation of an instantaneous GLE for vibrational relaxation based on INMs.^{84,85} In the present case, however, the result would be a complicated nonlinear equation which would not easily lend itself to writing in a GLE form. For us to obtain an equation with the structure of a GLE we shall need some further approximations, ones actually suggested by our short-time perspective.

We can obtain precisely the rotational GLE we desire by choosing a special coordinate system for the resolution of angular velocity and by making a short-time approximation for the dynamics of the angle displacements. For a given initial orientation of the solute (Fig. 1), let us resolve the angular velocity, $\vec{\omega}$, along the three mutually perpendicular axes 1, 2, and 3, where the axis 3 parallels the bond axis of the linear top, and the axis 1 is in the plane made by the bond axis and the z axis of the laboratory-fixed frame. That is, for a given initial orientation we switch to a special laboratory

frame which coincides with the instantaneous body coordinates. By inspection, we see that the infinitesimal rotation angles around the axes 1 and 2 at that instant, $d\psi_1(0)$ and $d\psi_2(0)$, are related to the differential angles, $d\theta_0$ and $d\phi_0$, by

$$d\psi_1(0) = -\sin \theta_0 d\phi_0, \quad d\psi_2(0) = d\theta_0. \quad (2.18)$$

The 3 component of the angular velocity, $\omega_3(0)$, is zero, since we have taken axis 3 to be along the bond axis of the linear top. The other components of angular velocity, $\omega_\gamma = d\psi_\gamma/dt$, are obtained from Eq. (2.18) as $\omega_1(0) = -\dot{\phi}_0 \sin \theta_0$, $\omega_2(0) = \dot{\theta}_0$. The crucial assumption that brings us a GLE is the idea that, for short times, when the orientation has not changed all that much from its initial angles, the infinitesimal twist angles are given at time t by⁹²

$$d\psi_1(t) = -\sin \theta_0 d\phi_t, \quad d\psi_2(t) = d\theta_t. \quad (2.19)$$

The angular velocity then follows as

$$\omega_1(t) = -\dot{\phi}_t \sin \theta_0, \quad \omega_2(t) = \dot{\theta}_t, \quad (2.20)$$

and the 3 component of the angular velocity is assumed to remain zero.

The short-time approximations, Eqs. (2.19) and (2.20), together with the solution for the bath INMs, Eq. (2.17), allow us to eliminate $\omega_3(t)$ and rewrite Eq. (2.16) as a rotational GLE,

$$I\dot{\omega}_\gamma = N_\gamma(\phi, \theta, \mathbf{R}_0) - \sum_{\lambda=1}^2 \int_0^t \eta_{\gamma\lambda}(t-\tau) \cdot \omega_\lambda(\tau) d\tau + \mathcal{N}_\gamma(t) \quad (\gamma=1,2), \quad (2.21)$$

with each term on the right-hand side of the equation having a suggestive physical meaning. The *frozen-bath torque*, $N_\gamma(\phi, \theta, \mathbf{R}_0)$, defined as

$$N_\gamma(\phi, \theta, \mathbf{R}_0) = -\frac{\partial V}{\partial \psi_\gamma} \Big|_{\mathbf{R}_0}, \quad (2.22)$$

represents the torque the solute would feel if the bath were frozen at the initial configuration, \mathbf{R}_0 . The *fluctuating torque*, $\mathcal{N}_\gamma(t)$,

$$\mathcal{N}_\gamma(t; \phi_0, \theta_0, \mathbf{R}_0, \dot{\mathbf{R}}_0) = -\sum_\alpha c_{\gamma, \alpha} \left[\dot{q}_\alpha(0) \frac{\sin \omega_\alpha t}{\omega_\alpha} + \frac{f_\alpha}{\omega_\alpha^2} (1 - \cos \omega_\alpha t) \right], \quad (2.23)$$

arises from the solvent fluctuations one would see with the solute orientation fixed at its initial angles, ϕ_0 and θ_0 . Finally, the self-consistent dynamical interaction between the bath and the solute appears as a convolution of the angular velocity and the *rotational friction matrix*, defined as

$$\eta_{\gamma\lambda}(t; \phi_0, \theta_0, \mathbf{R}_0) = \sum_\alpha c_{\gamma, \alpha} c_{\lambda, \alpha} \frac{\cos \omega_\alpha t - 1}{\omega_\alpha^2}, \quad (2.24)$$

with the $c_{\gamma, \alpha}$'s in Eqs. (2.23) and (2.24) the coupling strengths of each mode α ,

$$c_{\gamma,\alpha}(\phi_0, \theta_0, \mathbf{R}_0) = - \left. \frac{\partial N_\gamma}{\partial q_\alpha} \right|_{\phi_0, \theta_0, \mathbf{R}_0}. \quad (2.25)$$

Note that as far as the solute orientation goes, Eq. (2.21) is a properly nonlinear generalized Langevin equation; the frozen-bath torque contains all the nonlinear dependence on orientation necessary to give the exact torque on the solute for a fixed bath configuration, \mathbf{R}_0 . Consistent with the rest of our short-time development though, we know that if we desire no more than short-time results we would also be justified in expanding this torque to low order in the angle displacements (justified, that is, to precisely the same extent that the linearization of intermolecular forces in the bath to produce INMs is justified).⁸⁵ Consider what happens if we do so.

Expanding the frozen-bath torque, $N_\gamma(\phi, \theta, \mathbf{R}_0)$, up to linear terms in the angle displacements yields

$$\begin{aligned} N_\gamma(\phi, \theta, \mathbf{R}_0) &\approx N_\gamma(\phi_0, \theta_0, \mathbf{R}_0) + \frac{1}{\sin \theta_0} \left. \frac{\partial N_\gamma}{\partial \phi} \right|_{\phi_0, \theta_0, \mathbf{R}_0} \\ &\quad \times (\sin \theta_0)(\phi - \phi_0) + \left. \frac{\partial N_\gamma}{\partial \theta} \right|_{\phi_0, \theta_0, \mathbf{R}_0} (\theta - \theta_0) \\ &\approx N_\gamma(\phi_0, \theta_0, \mathbf{R}_0) + \left. \frac{\partial N_\gamma}{\partial \psi_1} \right|_{\phi_0, \theta_0, \mathbf{R}_0} \int_0^t d\tau \omega_1(\tau) \\ &\quad + \left. \frac{\partial N_\gamma}{\partial \psi_2} \right|_{\phi_0, \theta_0, \mathbf{R}_0} \int_0^t d\tau \omega_2(\tau). \end{aligned} \quad (2.26)$$

With this expansion, which would be exact if we had purely harmonic libration, we get a linearized GLE,

$$\begin{aligned} I\dot{\omega}_\gamma &= N_\gamma(\phi_0, \theta_0, \mathbf{R}_0) - \sum_{\lambda=1}^2 \int_0^t d\tau [I\Omega_{\gamma\lambda}^2 + \eta_{\gamma\lambda}(t-\tau)] \\ &\quad \times \omega_\lambda(\tau) + \mathcal{N}_\gamma(t), \end{aligned} \quad (2.27)$$

where the *instantaneous librational frequency* matrix, $\Omega_{\gamma\lambda}$, is defined as

$$\Omega_{\gamma\lambda}^2 = \frac{1}{I} \left. \frac{\partial^2 V}{\partial \psi_\gamma \partial \psi_\lambda} \right|_{\mathbf{R}_0, \phi_0, \theta_0}. \quad (2.28)$$

Parenthetically, were we to turn off both the friction and fluctuating torque in the GLE, freezing the dynamics of the solvent completely, Eq. (2.27) would portray the rotation of the solute within each separate static solvent configuration as a libration:

$$\ddot{\omega}_\gamma + \sum_{\lambda=1}^2 \Omega_{\gamma\lambda}^2 \omega_\lambda = 0.$$

More generally, what a GLE gives under such circumstance is the purely inhomogeneous contribution of the solvent to the dynamics of the solute. Our instantaneous perspective therefore identifies our friction (and our fluctuating torque) as the source of rotational dephasing for each liquid configuration.

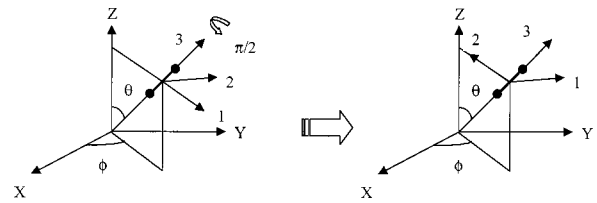


FIG. 2. A useful symmetry operation: rotation of the linear molecule by $\pi/2$ around axis 3. Under this operation, the total Hamiltonian and the configuration of the system are unchanged, but the infinitesimal twist angles around the axes 1 and 2 vary as shown in Eq. (3.1).

The instantaneous linearized rotational generalized Langevin equation, Eq. (2.27), along with the microscopic definitions of the rotational friction, Eq. (2.24), and the fluctuating torque Eq. (2.23), constitute the primary results of this paper. Using the explicit representation of the bath dynamics provided by INMs, we have reduced the calculation of the short-time reorientational dynamics of a solute to a single integro-differential equation for each configuration, one relying on nothing but the equilibrium properties of that configuration. However, we still need to establish in what sense this result is really correct for short times—and just how we can make use of the equation in practice. To do so we need to investigate a number of the special features of our instantaneous GLE.

III. CHARACTERISTIC FEATURES OF THE INSTANTANEOUS GLE

A. Some useful symmetries

In formulating our dynamics we were careful to choose a set of laboratory coordinates coinciding with those of the solute's time-zero body-fixed frame. Because of this special choice, and because of the linear geometry of our rotor, we can derive a number of symmetry properties that greatly simplify the further analysis of our GLE. These symmetries will not only help us investigate the exact short-time behavior of the angular velocity time correlation function generated from our GLE, but they will also allow us to study the configuration-averaged rotational-friction and instantaneous-librational-frequency matrices. The symmetry arguments will also be helpful in the looking at the distribution of fluctuating torques.

Consider the symmetry operation of a $\pi/2$ rotation of the linear top around axis 3 (Fig. 2). Under this operation, the infinitesimal twist angles change as

$$d\psi_1 \rightarrow -d\psi_2, \quad d\psi_2 \rightarrow d\psi_1, \quad (3.1)$$

but the Hamiltonian and the configuration of the system remain unchanged. The transformations of the torque, $N_\gamma = -(\partial V / \partial \psi_\gamma)$, and the angular velocity, $\omega_\gamma = d\psi_\gamma / dt$, follow directly as

$$N_1 \rightarrow -N_2, \quad N_2 \rightarrow N_1, \quad \omega_1 \rightarrow -\omega_2, \quad \omega_2 \rightarrow \omega_1. \quad (3.2)$$

Using the fact that any ensemble average we compute should be invariant to these transforms,⁹³ one can prove that

TABLE I. Transformations of various quantities under the symmetry operation which rotates a linear molecule by $\pi/2$ around axis 3.

From	$c_{1,\alpha}$	$c_{2,\alpha}$	$\eta_{11}(t)$	$\eta_{22}(t)$	$\eta_{12}(t)$	Ω_{11}^2	Ω_{22}^2	Ω_{12}^2	$\mathcal{N}_1(t)$	$\mathcal{N}_2(t)$
To	$-c_{2,\alpha}$	$c_{1,\alpha}$	$\eta_{22}(t)$	$\eta_{11}(t)$	$-\eta_{12}(t)$	Ω_{22}^2	Ω_{11}^2	$-\Omega_{12}^2$	$-\mathcal{N}_2(t)$	$\mathcal{N}_1(t)$

$$\begin{aligned}\langle N_1(0)^2 \rangle &= \langle N_2(0)^2 \rangle = \frac{1}{2} \langle \vec{N}(0)^2 \rangle, \\ \langle \omega_1(0)^2 \rangle &= \langle \omega_2(0)^2 \rangle = \frac{1}{2} \langle \vec{\omega}(0)^2 \rangle,\end{aligned}\quad (3.3)$$

and that the corresponding cross terms, such as $\langle N_1(0)N_2(0) \rangle$, are zero. Thus we have the general principle that axes 1 and 2 must be statistically equivalent.

What happens under this same transformation to the key quantities in the instantaneous GLE, the coupling constants, $c_{\gamma,\alpha}$, the friction matrix, $\eta_{\gamma\lambda}(t)$, the instantaneous-librational-frequency matrix, $\Omega_{\gamma\lambda}$, and the fluctuating torques, $\mathcal{N}_\gamma(t)$, is described in Table I. From the table, we see that the average diagonal elements of the friction and librational-frequency matrices are also identical,

$$\langle \eta_{11}(t) \rangle = \langle \eta_{22}(t) \rangle, \quad \langle \Omega_{11}^2 \rangle = \langle \Omega_{22}^2 \rangle, \quad (3.4)$$

and the off-diagonal elements such as $\langle \eta_{12}(t) \rangle$ and $\langle \Omega_{12}^2 \rangle$ are zero. We see that the mean fluctuating torque must vanish as well.

$$\langle \mathcal{N}_1(t) \rangle = \langle \mathcal{N}_2(t) \rangle = 0. \quad (3.5)$$

In an average sense, then, our instantaneous rotational generalized Langevin equation looks much the same as the traditional, diagonal, GLE given in Eq. (1.3). Similar symmetry arguments based on π rotations about the laboratory axes can be used to show how the more conventional GLE (derived formally via projection operator techniques) can always be reduced to a diagonal form for linear and spherical top rotors.⁹⁴

B. Comparison with the exact short-time behavior

Though we hope the development here will be appropriate for 100's of fs rather than 10's of fs, it is important that we know how the formalism behaves at the latter, ultrashort, time scales—time short enough that a low-order power series in t suffices. We therefore need to compare the leading terms in the expansion of an exact correlation function with those predicted by our instantaneous GLE.⁸⁵ The exact short-time expansion of the angular velocity time correlation function, $C_{\omega\omega}(t)$, for a linear top is, for example, well known,⁹⁵

$$C_{\omega\omega}(t) = 1 - \frac{t^2}{2} \frac{\langle \vec{N}(0)^2 \rangle}{2Ik_B T} + \frac{t^4}{4!} \frac{\langle \dot{\vec{N}}(0)^2 \rangle}{2Ik_B T} + \dots \quad (3.6)$$

To evaluate this same time correlation function from our GLE, we first obtain expressions for the initial time derivatives of the angular velocity, $\dot{\omega}_\gamma(0), \ddot{\omega}_\gamma(0), \dots$ from the INM-GLE, Eq. (2.27), and its successive time derivatives. After expanding Eq. (1.2) in a powers series in t , a little algebra then yields the equivalent INM-GLE correlation function, $C_{\omega\omega}^{\text{INM}}(t)$,

$$\begin{aligned}C_{\omega\omega}^{\text{INM}}(t) &= 1 - \frac{t^2}{2} \langle \Omega_{11}^2 \rangle + \frac{t^4}{4!} \left[\sum_{\lambda=1}^2 \langle \Omega_{1\lambda}^4 \rangle \right. \\ &\quad \left. + \frac{1}{I} \left\langle \sum_{\alpha} c_{1,\alpha}^2 \right\rangle \right] + \dots\end{aligned}\quad (3.7)$$

But, if we evaluate the ϕ integration in the mean-squared-instantaneous-librational frequency, $\langle \Omega_{11}^2 \rangle = (1/I) \times \langle \csc^2 \theta (\partial^2 V / \partial \phi^2) \rangle$, by integration by parts⁸² we find

$$\begin{aligned}\langle \Omega_{11}^2 \rangle &= \frac{1}{Ik_B T} \left\langle \left(\csc \theta \frac{\partial V}{\partial \phi} \right)^2 \right\rangle = \frac{1}{Ik_B T} \left\langle \left(\frac{\partial V}{\partial \psi_1} \right)^2 \right\rangle \\ &= \frac{\langle \vec{N}(0)^2 \rangle}{2Ik_B T},\end{aligned}\quad (3.8)$$

where the symmetry property, Eq. (3.3), is used to derive the last identity. Therefore we see that the t^2 coefficient of $C_{\omega\omega}^{\text{INM}}(t)$ is exact.

What about the t^4 coefficient? We note

$$\begin{aligned}\dot{N}_1(0) &= \sum_{j\mu} \frac{\partial N_1}{\partial r_{j\mu}} \dot{r}_{j\mu}(0) + \sum_{\lambda=1}^2 \frac{\partial N_1}{\partial \psi_\lambda} \omega_\lambda(0) \\ &= \sum_{j\mu} \frac{\partial N_1}{\partial r_{j\mu}} \dot{r}_{j\mu}(0) + \sum_{\lambda=1}^2 I \Omega_{1\lambda}^2 \omega_\lambda(0),\end{aligned}\quad (3.9)$$

enabling us to write the t^4 coefficient from the exact MD as⁹⁶

$$\frac{\langle \dot{\vec{N}}(0)^2 \rangle}{2Ik_B T} = \left\langle \sum_{\lambda=1}^2 \Omega_{1\lambda}^4 \right\rangle + \frac{1}{I} \sum_{j\mu} \left\langle \frac{1}{m_j} \left(\frac{\partial N_1}{\partial r_{j\mu}} \right)^2 \right\rangle. \quad (3.10)$$

This equation matches the corresponding coefficient from INM-GLE, except for the second term on the right-hand side. But if we notice the identity,

$$\begin{aligned}\left\langle \sum_{\alpha} c_{1,\alpha}^2 \right\rangle &= \left\langle \sum_{\alpha} \left(\frac{\partial N_1}{\partial q_{\alpha}} \right)^2 \right\rangle \\ &= \left\langle \sum_{\alpha} \left(\sum_{j\mu} U_{j\mu,\alpha} \frac{1}{\sqrt{m_j}} \frac{\partial N_1}{\partial r_{j\mu}} \right)^2 \right\rangle \\ &= \left\langle \sum_{j\mu} \frac{1}{m_j} \left(\frac{\partial N_1}{\partial r_{j\mu}} \right)^2 \right\rangle,\end{aligned}\quad (3.11)$$

arising from the orthogonality of the \mathbf{U} eigenvector matrix, we see that the t^4 coefficient of $C_{\omega\omega}^{\text{INM}}(t)$ is also exact. Thus, despite the approximations used in deriving it, the INM-GLE is guaranteed to produce the exact short time behavior for the angular velocity time correlation function through order t^4 . Higher orders are, of course, also included, but not with the same quantitative accuracy.

C. Distribution of the fluctuating torque

The fact that our fluctuating torque is defined by a fully molecular expression instead of by just the typical set of statistical properties one normally sees with a GLE means that we cannot take these statistical properties for granted. Indeed, the ability of the instantaneous approach to incorporate realistic non-Gaussian features of the statistics^{69,85} is part of its power. We therefore conclude this section by deriving some formal properties of our fluctuating torque from our instantaneous GLE and by studying its statistical distribution within a specific numerical example.

We first note that, consistent with standard usage, our fluctuating torque, $\vec{N}(t)$, is uncorrelated with the initial angular velocity, $\vec{\omega}(0)$:

$$\langle \vec{\omega}(0) \cdot \vec{N}(t) \rangle = 0, \quad (3.12)$$

since $\vec{N}(t)$ is a function of configuration only. Moreover, as with the usual expectations, we can show that the fluctuating torque autocorrelation function is related to the rotational friction. Note, however, that our instantaneous friction and fluctuating torque are defined so as to vanish at time zero, meaning that their strict analogues in conventional GLE formalisms would be the displacements, $\eta(t) - \eta(0)$ and $\vec{N}(t) - \vec{N}(0)$. As discussed in the previous work,⁸⁵ this choice is not unique, but it suits the short time nature of our approach. At time zero, the torque on the solute is given by the exact instantaneous torque, $\vec{N}(\theta_0, \phi_0, \mathbf{R}_0)$, but the fluctuating torque and the friction grow in as the system evolves, bringing in the dynamics of the interaction between the solute and the bath—bringing in, in particular, the torque on the solute caused by the bath's own dynamics and the ‘reaction-field’ torque generated by the bath's response to the solute rotation, respectively. With this feature in mind, we can understand why Eqs. (2.23) and (2.24) tell us that the INM version of the second fluctuation-dissipation theorem is

$$\frac{d^2}{dt^2} \langle \eta_{\gamma\gamma}(t) \rangle = -\frac{1}{k_B T} \langle \dot{N}_\gamma(t) \dot{N}_\gamma(0) \rangle \quad (3.13)$$

(where we have used the equipartition of the initial INM velocities, $\langle \dot{q}_\alpha(0) \dot{q}_\beta(0) \rangle = k_B T \delta_{\alpha\beta}$, and the fact that the off-diagonal elements of the friction matrix vanish by symmetry), rather than the usual, twice-integrated, version of the same equation.

We turn, finally, to the distribution of the fluctuating torque itself, $D(N)$,

$$D(N) = \langle \delta[N - \mathcal{N}_\gamma(t; \phi_0, \theta_0, \mathbf{R}_0, \dot{\mathbf{R}}_0)] \rangle. \quad (3.14)$$

(In this and all the remaining equations in this section, the subscript γ is meant to denote either of the two axes 1 and 2 shown in Fig. 1; the final answers are invariant to the choice.) In contrast to the friction and librational frequency, which rely solely on the initial configuration, our fluctuating torque has an additional dependence on the initial velocities of the bath, $\dot{\mathbf{R}}_0$. This dependence is easily integrated analytically though, and as we might have expected, when we perform the velocity average indicated in Eq. (3.14) we do find a Gaussian distribution. The nontrivial feature is that the

Gaussian is different for each liquid configuration; our final result is actually a configurational average of Gaussians

$$D(N) = \left\langle \frac{1}{\sqrt{2\pi\sigma_\gamma^2(t)}} \exp\left[-\frac{(N - \bar{\mathcal{N}}_\gamma(t))^2}{2\sigma_\gamma^2(t)}\right] \right\rangle, \quad (3.15)$$

with time- and configuration-dependent means,

$$\bar{\mathcal{N}}_\gamma(t) = -\sum_\alpha \frac{c_{\gamma,\alpha} f_\alpha}{\omega_\alpha^2} (1 - \cos \omega_\alpha t), \quad (3.16)$$

and variances,

$$\sigma_\gamma^2(t) = k_B T \sum_\alpha \left(\frac{c_{\gamma,\alpha}}{\omega_\alpha} \sin \omega_\alpha t \right)^2. \quad (3.17)$$

Our distribution of fluctuating torques, therefore will not, in general, be Gaussian despite the harmonic character of our formalism.⁸⁵

The defining property of a Gaussian distribution is, of course, that all the cumulants higher than the second order disappear. To see just what our distribution looks like, we compare the full distribution, Eq. (3.15), to the outcome from a second-order cumulant expansion. The first cumulant, $\langle \mathcal{N}_\gamma(t) \rangle$, is zero by symmetry (Sec. III A), and the second cumulant is given by

$$C_2 = \langle \sigma_\gamma(t)^2 \rangle + \left\langle \left[\sum_\alpha \frac{c_{\gamma,\alpha} f_\alpha}{\omega_\alpha^2} (\cos \omega_\alpha t - 1) \right]^2 \right\rangle. \quad (3.18)$$

In Fig. 3 we plot the distribution of the fluctuating torque and the Gaussian approximation for it for a homonuclear diatomic in an atomic solvent. As the time increases, the rather sharp distribution seen at the shortest time (21.6 fs) appears to stretch out to a nearly uniform distribution at the longest time (2.16 ps). [The distribution actually broadens without a limit for an infinite time, because the variance for each configuration, Eq. (3.17), diverges, a consequence of the short-time character of our theory.⁹⁷] The interesting point for us, though, is that the Gaussian distribution is found to be noticeably broader than the exact distribution at the shortest times, but the differences seem to become less pronounced at the two longer times displayed.⁹⁸

IV. THE AVERAGE ROTATIONAL FRICTION

A. The rotational friction spectrum

The most physically revealing quantity arising out of our generalized Langevin formalism is the instantaneous rotational friction, Eq. (2.24); it is what sets the time scales and mechanisms for rotational relaxation. However, as we shall see presently, most of the physical content of the instantaneous friction is embodied in its configurational average. We will therefore focus on this average for the remainder of this paper.

As we have written it, the instantaneous rotational friction is given as a 2×2 matrix. When averaged over the configurations, though, the friction matrix becomes diagonal by symmetry, with the diagonal elements of the matrix identical to one another. Thus the average friction reduces to a purely one-dimensional quantity (meaning that we can drop

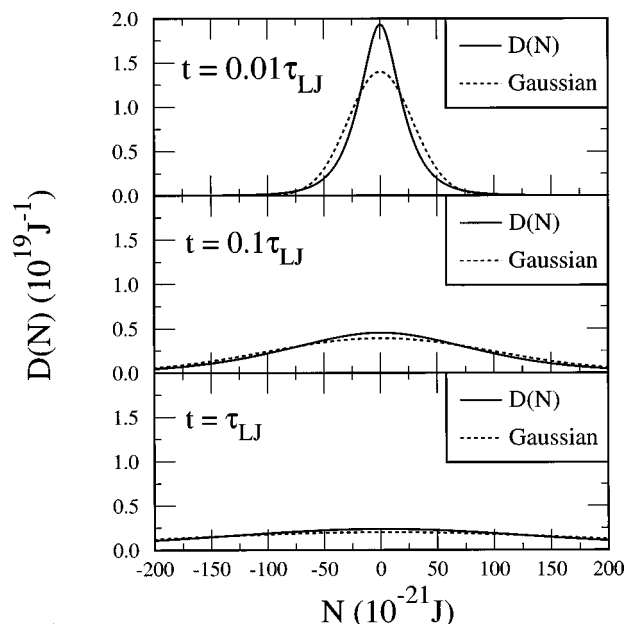


FIG. 3. Distribution of the fluctuating torque calculated from our instantaneous GLE for a homonuclear diatomic dissolved in an atomic fluid. For comparison we also plot the Gaussian distributions with zero mean and the same variances as those predicted by our GLE. In this and all succeeding figures, the solvent is Lennard-Jonesium under dense, supercritical conditions (reduced temperature $k_B T/\epsilon=2.50$ and reduced density $\rho\sigma^3=1.05$, with ϵ and σ being the Lennard-Jones well depth and diameter, respectively) and the diatomic is modeled as two Lennard-Jones atoms, identical in mass and Lennard-Jones parameters with those of the solvent. For this example, the atoms in the diatomic are separated by a rigid bond length $d=1.25\sigma$. The three different panels correspond to the distribution evaluated at three different times, 21.6 fs, 216 fs, and 2.16 ps, averaging each over 40 000 configurations. The numerical values shown are those for an Ar solvent ($\epsilon=119.8$ K and $\sigma=3.405$ Å), for which the natural time scale $\tau_{LJ}=2.16$ ps.

the subscripts in our subsequent use). The diagonal element of the average matrix, $\eta^{\text{INM}}(t)=\langle\eta_{11}(t)\rangle=\langle\eta_{22}(t)\rangle$, can be written as

$$\eta^{\text{INM}}(t)=\left\langle\sum_{\alpha}(c_{\alpha})^2\frac{\cos\omega_{\alpha}t-1}{\omega_{\alpha}^2}\right\rangle, \quad (4.1)$$

where $c_{\alpha}=(\partial N/\partial q_{\alpha})$ and N is the torque along an axis perpendicular to the axis of the linear top.

It is useful, as in other INM treatments of solute relaxation,⁸⁷ to introduce the *rotational friction spectrum*, $\rho_{\text{fric}}(\omega)$,

$$\rho_{\text{fric}}(\omega)=\left\langle\sum_{\alpha}(c_{\alpha})^2\delta(\omega-\omega_{\alpha})\right\rangle, \quad (4.2)$$

which lets us write the average friction, $\eta^{\text{INM}}(t)$, and its Fourier transform, $\tilde{\eta}^{\text{INM}}(\omega)$, as

$$\eta^{\text{INM}}(t)=\int d\omega\rho_{\text{fric}}(\omega)\frac{\cos\omega t-1}{\omega^2} \quad (4.3)$$

and

$$\tilde{\eta}^{\text{INM}}(\omega)=\int_0^{\infty} dt\cos\omega t\eta(t)=\frac{\pi}{2}\frac{\rho_{\text{fric}}(\omega)}{\omega^2}, \quad \omega\neq 0. \quad (4.4)$$

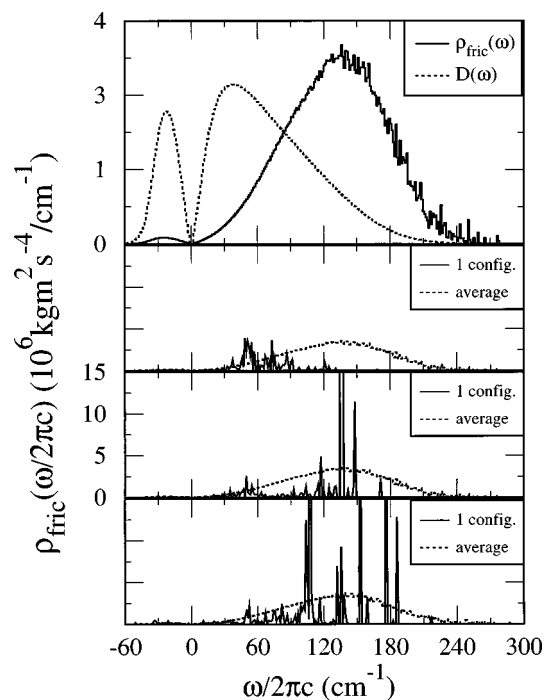


FIG. 4. The average rotational friction spectrum $\rho_{\text{fric}}(\omega)$ (top) and three representative instantaneous (single-configuration) friction spectra (bottom) for a homonuclear diatomic dissolved in a dense supercritical argon fluid. The model and thermodynamic conditions are as reported in Fig. 3, with configurational averaging carried out over 40 000 configurations. In the top panel, we also plot the solvent instantaneous-normal-mode density of states, $D(\omega)$, normalized so as to have the same area as the friction spectrum. The bottom three panels all have the same vertical scale as one another, 3.75 times that of the top panel, and include the average rotational friction spectrum for comparison.

The physical interpretation of the rotational friction spectrum is compelling: each mode with frequency ω_{α} contributes to the spectrum to an extent determined by its coupling strength, c_{α}^2 , and the final spectrum is simply the configurationally averaged sum of the contribution of each mode. The rotational friction spectrum is thus an *influence spectrum* of a kind familiar to us through the INM studies of solvation and vibrational relaxation.^{87,88,99,100} Its natural counterpart, and a useful comparison is the liquid's *density of states*, $D(\omega)$,

$$D(\omega)=\left\langle(3N+3)^{-1}\sum_{\alpha}\delta(\omega-\omega_{\alpha})\right\rangle, \quad (4.5)$$

which has a constant weighting for every mode.

In Fig. 4 we show a typical rotational friction spectrum, one for a homonuclear diatomic dissolved in a dense supercritical fluid of argon. Despite the relatively low probability of seeing high-frequency modes (as evidenced by the density of states), high-frequency modes make a significant contribution to the rotational friction spectrum. The peak frequency of $\rho_{\text{fric}}(\omega)$ occurs at the relatively high frequency of 136 cm^{-1} , and the area under the imaginary branch, which amounts to 18.2% of the total area of the density of states, is almost negligible (less than 1% of the total area) in the rotational friction spectrum. This same kind of shift to a higher frequency compared to the density of states and this same near irrelevance of the imaginary branch have also been found in the vibrational friction and solvation spectra.^{88,100}

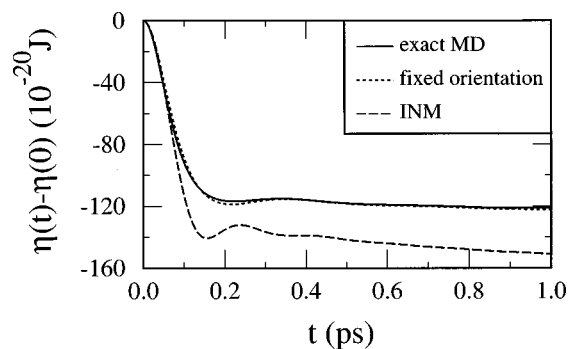


FIG. 5. The time-domain rotational friction for a homonuclear diatomic dissolved in a dense supercritical argon fluid. The model and thermodynamic conditions are as reported in Fig. 3. Plotted here are the friction kernels extracted from exact molecular dynamics simulations, both by rigorous inversion (solid line) and by using the fixed-orientation approximation (short-dashed line), as well as those predicted by the instantaneous-normal-mode theory (long-dashed line).

For comparison purposes, we illustrate at the bottom of the figure the friction spectra for several individual configurations. In contrast to the averaged spectrum, these spectra consist of well resolved peaks whose locations vary tremendously from configuration to configuration, making clear the role of the strong inhomogeneity in broadening the single-configuration spectra.^{87,88}

Once we evaluate the rotational friction spectrum, the time- and frequency-domain friction kernels can be calculated by using Eqs. (4.3) and (4.4). In Fig. 5 we compare the time-domain friction kernel from $\rho_{\text{fric}}(\omega)$ to the results from exact molecular dynamics (and to the results from the fixed-orientation molecular-dynamics calculations that will be discussed in Sec. VI B) for a homonuclear diatomic dissolved in an atomic solvent. (For this, and all of our subsequent calculations, we shall omit any contributions there might be from the imaginary modes.) We first notice that most of the essential dynamics of the exact friction occurs within 200 fs, illustrating short-time character of rotational friction. The INM friction precisely duplicates the abrupt falloff of the exact friction for short times, although it decays too quickly after 100 fs, and slowly diverges to negative infinity at longer times.⁸⁵ In the frequency domain, (Fig. 6), the INM frictions are much more appealing, nicely reproducing the basic frequency range and much of the qualitative behavior. They do slightly overestimate the exact frictions at intermediate frequencies (up to 175 cm^{-1}) and die too quickly beyond that frequency (Fig. 6). Moreover, at zero frequency, the INM frictions are qualitatively incorrect, with a ω^{-1} divergence setting in as the frequency approaches zero.¹⁰¹ Nonetheless, the INM frictions are in reasonable agreement with the exact results for all but the lowest frequencies. In particular, the INM theory, being a molecular theory, successfully captures the two-orders-of-magnitude change in friction created by varying the bond length of the diatomic.

B. The exact friction and the friction at fixed orientation

In order to obtain the last two figures, we computed the exact rotational friction, $\eta(t)$, from a molecular dynamics

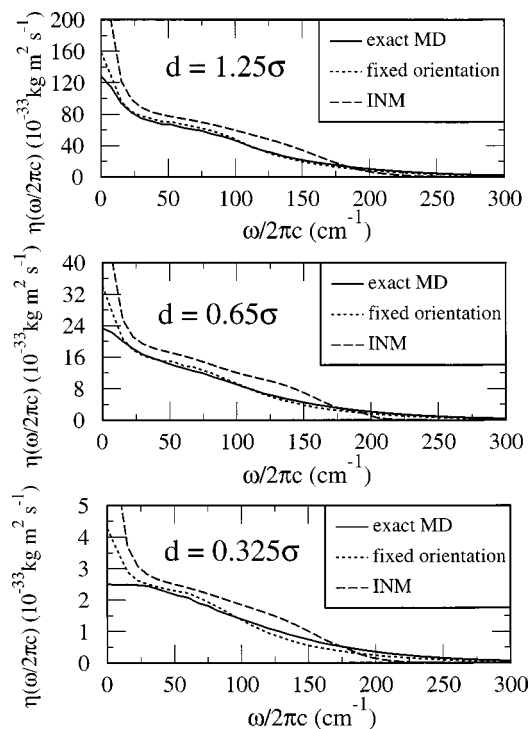


FIG. 6. The frequency-domain rotational friction for a homonuclear diatomic dissolved in a dense supercritical argon fluid. The model and thermodynamic conditions are as reported in Fig. 3, except that here we consider diatomics with three different bond lengths ($d = 1.25\sigma, 0.65\sigma, 0.325\sigma$). Note the significant differences in the magnitudes of the friction for the three examples. As in Fig. 5, the results from both exact (solid) and fixed-orientation (short dashed) molecular dynamics are compared with those from INM theory (long dashed).

simulation by a numerical method similar in spirit to Berne and Harp's⁹⁵ approach to calculating friction. Explicitly: differentiating Eq. (1.3) gives us a self-consistent equation for $\eta(t)$,

$$\eta(t) = -I\ddot{C}_{\omega\omega}(t) - \int_0^t d\tau \eta(\tau) \dot{C}_{\omega\omega}(t-\tau). \quad (4.6)$$

To calculate the time derivatives of $C_{\omega\omega}(t)$ needed in Eq. (4.6), we fit $C_{\omega\omega}(t)$ from the molecular dynamics with a sixth order polynomial in t and analytically differentiated the resulting functional form.^{102,103} With $\dot{C}_{\omega\omega}(t)$ and $\ddot{C}_{\omega\omega}(t)$ thus obtained, the friction kernel is calculated by propagating a discretized form of Eq. (4.6),

$$\eta(t_n) = -I\ddot{C}_{\omega\omega}(t_n) - dt \sum_{k=0}^{n-1} W_k \eta(t_k) \dot{C}_{\omega\omega}(t_n - t_k), \quad (4.7)$$

where Simpson's rule is used for the integral weightings, W_k .

This method of computing the exact friction is not only an indirect, numerically involved procedure, it makes the microscopic interpretation of the friction difficult. A much more physical and numerically practical approximation would result if we were allowed to use the second fluctuation-dissipation theorem [Eq. (1.4)] to compute the friction, but with the fluctuating torque replaced by the real torque of a hypothetical reference system in which the orientation of the solute was held fixed. As we noted in the

Introduction, the analogous calculation of a *rigid bond friction* is, in fact, commonplace in studies of vibrational relaxation. There however, the justification involves a presumed separation of time scales between the tagged (vibrating) degree of freedom and the surroundings.⁶⁸ Lacking any such separation for rotation, we need to examine whether this kind of approximation really provides a sensible alternative.

To produce the rotational version of the rigid-bond friction we evaluate the torque autocorrelation function holding the solute fixed at its initial orientation, ϕ_0 and θ_0 , giving us the *instantaneous fixed-orientation friction*, $\eta_{\text{fixed}}(t)$,

$$\eta_{\text{fixed}}(t) = \frac{1}{2k_B T} \langle \vec{N}(t) \cdot \vec{N}(0) \rangle_{\phi_0, \theta_0}, \quad (4.8)$$

where $\langle \rangle_{X_0}$ means the average with X fixed at the initial value X_0 and the torque is the real torque on the orientationally frozen solute. Clearly, fixed orientation friction kernels calculated from molecular dynamics (Figs. 5 and 6) do an exceptional job in replicating the exact results over the entire range of time and frequency: with the exception of frequencies less than 25 cm^{-1} or so, they are hardly distinguishable from the exact frictions.

Despite this quantitative success, we are left with the question of why the fixed-orientation friction *should* work as well as it does for rigid rotors in liquids. Unlike the situation with vibrational relaxation, the characteristic frequencies for rotation are rather low. In the gas-phase rotation is a zero-frequency excitation, and even in a liquid the librational frequencies ($\Omega_{\gamma\gamma}/2\pi c$) tend to be well under 100 cm^{-1} for all of the Ar solvent examples.⁹⁰ Within INM formalism, though, we can prove that this fixed orientation friction is identical (within a constant offset) to the average friction obtained from our instantaneous GLE: The torque on the nonrotating solute can be expanded to linear order in INMs,

$$N_\gamma(t) \approx N_\gamma(0) + \sum_\alpha \frac{\partial N_\gamma}{\partial q_\alpha} q_\alpha \quad (\gamma=1,2), \quad (4.9)$$

where we have chosen the special coordinates as before. Since the orientational variables of the solute are held fixed, the time evolution of q_α is given by Eq. (2.17) minus the convolution term

$$q_\alpha(t) = \dot{q}_\alpha(0) \frac{\sin \omega_\alpha t}{\omega_\alpha} + \frac{f_\alpha}{\omega_\alpha^2} (1 - \cos \omega_\alpha t), \quad (4.10)$$

so that

$$\langle \dot{N}_\gamma(t) \dot{N}_\gamma(0) \rangle_{\phi_0, \theta_0} = \left\langle \sum_\alpha \left(\frac{\partial N_\gamma}{\partial q_\alpha} \right)^2 \cos \omega_\alpha t \right\rangle_{\phi_0, \theta_0}. \quad (4.11)$$

Integrating Eq. (4.11) twice with respect to time,¹⁰⁴ gives us an expression for the fixed orientation friction within INM theory, $\eta_{\text{fixed}}^{\text{INM}}(t)$,

$$\eta_{\text{fixed}}^{\text{INM}}(t) = \frac{1}{k_B T} \langle N_\gamma(0)^2 \rangle_{\phi_0, \theta_0} + \left\langle \sum_\alpha \left(\frac{\partial N_\gamma}{\partial q_\alpha} \right)^2 \frac{\cos \omega_\alpha t - 1}{\omega_\alpha^2} \right\rangle_{\phi_0, \theta_0}. \quad (4.12)$$

However, using symmetry properties we can drop the subscript, γ in Eq. (4.12), leaving

$$\eta_{\text{fixed}}^{\text{INM}}(t) = \frac{1}{2k_B T} \langle \vec{N}(0)^2 \rangle_{\phi_0, \theta_0} + \int_0^\infty d\omega \rho_{\text{fixed}}(\omega) \frac{\cos \omega t - 1}{\omega^2}, \quad (4.13)$$

where the fixed-orientation friction spectrum, $\rho_{\text{fixed}}(\omega)$, is defined as

$$\rho_{\text{fixed}}(\omega) = \left\langle \sum_\alpha (c_\alpha)^2 \delta(\omega - \omega_\alpha) \right\rangle_{\phi_0, \theta_0}. \quad (4.14)$$

Furthermore, we can remove the constraint of fixed orientation in the averages of Eqs. (4.13) and (4.14), because the configuration spaces sampled are identical whether or not the orientation is fixed. Thus the fixed orientation friction within INM theory can be written as

$$\eta_{\text{fixed}}^{\text{INM}}(t) = \frac{1}{2k_B T} \langle \vec{N}(0)^2 \rangle + \eta^{\text{INM}}(t), \quad (4.15)$$

which, aside from the constant offset, is equal to the average friction, $\eta^{\text{INM}}(t)$, from the instantaneous rotational GLE. From the instantaneous perspective, then, configurationally averaging the friction is precisely equivalent to evaluating it by freezing the tagged solute degree of freedom.^{85,105}

C. Homogeneous dynamics from the average friction

Given the simplifications afforded by configurationally averaging, it is worth asking ourselves whether the average of our instantaneous friction might very well suffice as an ingredient in our instantaneous GLE. Certainly, in principle, one need not make any such approximation. One could, for example, solve our instantaneous GLE, Eq. (2.27), for each liquid configuration to obtain the angular-velocity autocorrelation function, $C_{\omega\omega}(t)$. Multiplying Eq. (2.27) by $\omega_\lambda(0)$ and taking the average over the initial angular velocities gives us a matrix equation for the correlation matrix, $\langle \omega_\gamma(t) \omega_\lambda(0) \rangle$, for a given initial configuration. By then solving for the correlation matrix for each configuration and taking the average of the results over configurations, we would get the desired, fully averaged, angular-velocity autocorrelation function. But instead of pursuing this complicated strategy, consider the much simpler route of replacing both the instantaneous friction and the instantaneous-square librational frequency in our GLE by their configurational averages:

$$I \dot{\omega}_\gamma(t) = - \int_0^t d\tau [I \bar{\Omega}^2 + \eta^{\text{INM}}(t-\tau)] \omega_\gamma(\tau) + \mathcal{N}_\gamma(t), \quad (4.16)$$

where $\bar{\Omega}$ is the rms value of the diagonal element of the instantaneous-librational frequency

$$\bar{\Omega}^2 = \langle \Omega_{11}^2 \rangle = \langle \Omega_{22}^2 \rangle. \quad (4.17)$$

This same approach has been found to be virtually exact in the INM study of vibrational relaxation.⁸⁵ Physically, it seems sensible that this preaveraging corresponds to the limiting case in which the solvent fluctuates rapidly compared

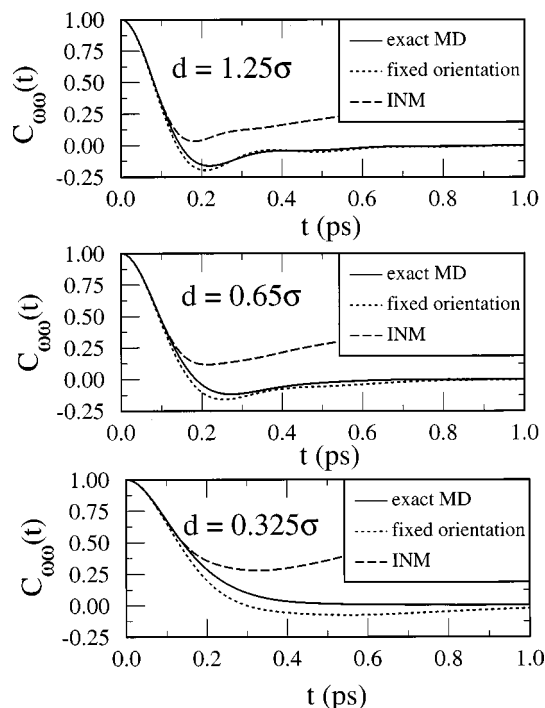


FIG. 7. Normalized angular-velocity autocorrelation functions for a homonuclear diatomic dissolved in a supercritical argon fluid. The models and thermodynamic conditions are as reported in Fig. 6. The correlation functions are calculated by using friction kernels derived from exact (solid) and fixed-orientation (short dashed) molecular dynamics, and from INM theory (long dashed). Imaginary mode contributions have been removed from the INM results in the standard fashion.

with the rotational relaxation of the solute, just as in Brownian motion of a heavy particle in a light solvent. The solute then sees the friction and instantaneous-librational frequency effectively averaged over these solvent fluctuations. To the extent to which this picture is correct, we need to think of the solute dynamics as falling into the *homogeneous* limit as opposed to a purely static solvent (inhomogeneous) limit, where, as discussed in Sec. II B, the solute rotates in a fixed solvent cage.

This homogeneous dynamics of the angular-velocity autocorrelation function, $C_{\omega\omega}(t)$, is governed by the integrodifferential equation,

$$\dot{C}_{\omega\omega}(t) = - \int_0^t d\tau [\bar{\Omega}^2 + (1/I)\eta^{\text{INM}}(t-\tau)] C_{\omega\omega}(\tau). \quad (4.18)$$

This equation is actually formally identical to the dynamics of the bond-velocity correlation of an oscillator with renormalized frequency $\bar{\Omega}$ and reduced mass I seen in GLE studies of vibrational relaxation.⁸⁶ Using the INM friction and the rms-librational frequency, we solved Eq. (4.18) numerically using the method of Berne and Harp.⁹⁵ In Fig. 7, we show the results: time correlation functions from the INM-, exact-MD, and fixed-orientation-MD friction kernels plotted for a homonuclear diatomic in dense supercritical argon. Note the relatively fast decay of the angular velocity correlation functions, especially for the two longer bond lengths displayed. The correlation functions from the INM-GLE precisely reproduce the exact correlation functions for times up to about 120 fs. They also mimic the overall features of

the exact results—the minima for the longer two bond lengths and the relatively slow and monotonic decay for the shortest bond length displayed. Betrayed by their fundamentally short-time character however, the INM correlation functions begin to deviate from the exact MD results after around 150 fs and fail to decay to zero at longer times.

V. CONCLUDING REMARKS

Our focus here has been on the influence of a liquid environment on how a linear solute reorients at short times. As in vibrational relaxation, the notion that we can describe much of the dynamics of the surrounding solvent by instantaneous normal modes lets us represent the complicated solute-solvent dynamical coupling with an instantaneous generalized Langevin equation for the solute coordinates of interest. More to the point, we are able to produce genuinely microscopic definitions for the rotational friction and the fluctuating torque. Our development of a GLE formalism has not been straightforward as it was with vibrational relaxation, both because of the need to represent the special geometry of rotational dynamics and because of the differences in how a solvent interacts with rotational degrees of freedom. Nonetheless, we find the resulting rotational friction and the consequent relaxation of the angular velocity to be similar to the vibrational friction and relaxation of the vibrational-mode velocity. More profound aspects of this similarity will be discussed in the companion paper.⁹⁰

The instantaneous rotational friction we calculate does seem to be reasonably accurate over a wide range of frequencies but, as with its vibrational counterpart, it has difficulty in reproducing the correct behavior at both very high and very low frequencies. Indeed, the low-frequency divergence of our friction seems to be a fundamental consequence of the short-time assumptions of the theory. However, our recent experiences with high-frequency vibrational relaxation suggest that the high-frequency deficiency can probably be remedied fairly easily within an instantaneous theory.¹⁰⁶ If the analogies hold, the physical events leading to the highest-frequency response are largely going to be rare but violent few-body interactions. As a result, the high frequencies are going to correspond to even shorter time scales than those that dominate the center of the solvent band, but with amplitudes for the relevant potentials, forces, and torques which are significantly larger. The bilinear (one-phonon) coupling assumed in Eq. (2.14) is therefore going to be strongly suspect; higher-order, multiphonon, couplings will undoubtedly be needed.

We do note that the use of bilinear coupling was critical to our derivation of the instantaneous rotational GLE, so much so that it is unclear how to go beyond this weak coupling assumption without losing the GLE structure. We can, however, include nonlinear couplings within the fixed-orientation approximation (which we have found to be virtually quantitative). To do so we observe that the torque perpendicular to the bond axis of the linear top, N , can be expanded to any desired order in the INMs,

$$N(t) = N(0) + \sum_{\alpha} \frac{\partial N}{\partial q_{\alpha}} q_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} \frac{\partial^2 N}{\partial q_{\alpha} \partial q_{\beta}} q_{\alpha} q_{\beta} + \dots \quad (5.1)$$

Keeping only the linear term in the expansion yields a friction identical to that derived from the instantaneous GLE, but there is nothing preventing us from keeping higher order terms, or even summing the series to infinite order. Doing so will still leave out the anharmonicity in the bath dynamics, but it will correctly preserve the nonlinear dependence of the torque on the bath variables. This kind of approach actually ended up being quite accurate in our vibrational relaxation studies, where we accomplished the infinite-order resummation by treating the coupling as being instantaneously exponential.¹⁰⁶

From a somewhat broader perspective, though, we really care less about having an exact numerical result for the rotational friction than about having some insight into the molecular mechanisms that underly rotational relaxation. With the realization that the fixed-orientation approximation provides a facile route to extracting rotational friction from conventional molecular dynamics simulations, there is, after all, little reason to choose an INM approach just to provide numerical values for the friction. The real advantage, as in the parallel studies of solvation and vibrational relaxation, lies in the prospects for analyzing specific molecular contributions to the friction. We are therefore ready to take up our basic physical question of which solvents, moving in which directions, most efficiently foster rotational relaxation. We will address this issue for a representative system in the following paper.⁹⁰

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