

A many-body stochastic approach to rotational motions in liquids: a reassessment of the Hubbard–Einstein relation \star

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A multidimensional Fokker–Planck–Kramers equation for rotational relaxation of small solutes in complex liquids is developed wherein collective solvent effects are explicitly represented by rotating torques and stochastic fields. A simplified version of the model is applied to interpret the breakdown of the Hubbard–Einstein relation at high viscosities.

1. Introduction

The usual approach for modeling rotational relaxation of solute molecules in molecular liquids is based on the classical treatment of a Brownian object rotating in a homogeneous fluid. Based upon the original contribution due to Debye [1], the only relevant set of degrees of freedom for the system of solute molecule + solvent is the set of Euler angles (α, β, γ) determining the orientation of the molecular frame of reference with respect to a fixed laboratory one, or the equivalent [2]. Any solvent effect on the probe dynamics is included as a constant damping term and/or a mean field potential in which the particle reorients. A Smoluchowski equation [2], or a Fokker–Planck equation [3] when the conjugate momentum L is included, can readily be written and solved numerically to obtain any correlation function of interest.

Although a qualitative resemblance of simulation with experimental data can often be achieved within this simple scheme, optical [4] and magnetic resonance [5,6] experiments performed in complex liquids show that the simplified picture of a continuous, homogeneous fluid providing a simple viscous background for the rotating object is insufficient. This

is also supported by molecular dynamics simulations [7]. It is clearly unrealistic to expect that the complex phenomenon of stochastic torques acting on the probe would yield simple relaxation behavior for the probe, especially in extreme regimes of temperatures and pressure.

In the past, many attempts have been made to improve the Debye approach and to retain the conceptual simplicity of a stochastic model, without introducing excessive complications. In this Letter we present preliminary results based on a systematic multimode procedure, in which explicit additional solvent degrees of freedom, having correlation times comparable to the rotating molecule under investigation, are included in order to simulate the complexity of a real liquid environment but with a limited set of “relevant” parameters or modes. Our approach is in the spirit of various attempts at modeling complex liquids with a multibody or “mesoscopic” description. Thus Coffey and Evans [8] have considered a planar two-body description and Grigolini and co-workers have tried to simulate a complex stochastic environment with a small set of variables [9]: An interesting recent contribution in this spirit is due to Kivelson and Miles [4]. Several years ago a systematic attempt was initiated by Stillman and Freed [10] to develop a general stochastic multibody methodology within the formalism of the “augmented” Fokker–Planck equations.

One may contrast such a multi-mode or “mesoc-

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opic" approach with that of a molecular dynamics (or Brownian dynamics) simulation. One can always try to devise such simulations or "computer experiments" to be as close to reality as possible. However informative molecular dynamics may be, it, like an actual experiment, requires interpretation to provide physical insight. One would like to use information available from laboratory and/or computer experiments in conjunction with physical insights to define a reduced set of variables, able to describe the main features of the effect of the solvent upon the solute without having to resort to the full many-body description of all the degrees of freedom of the liquid. Whereas it is very difficult, purely on the basis of formal theory, to define appropriate "collective" degrees of freedom, reasonable choices can be made by defining solvent coordinates of a mesoscopic nature, i.e. those more or less related to well-defined properties of the solvent. Thus, for example, one can include a dynamic equivalent of the static "solvation sphere" widely used in the thermodynamics of solutions, and/or a fluctuating polarization by analogy with the reaction field used in interpreting dielectric relaxation in polar solvents.

Our basic hypothesis is that the solvent environment is described by a few local structures (or "cages") relaxing with correlation times τ_{c1} , τ_{c2} etc. of similar order of magnitude as the intrinsic correlation time τ_R for the probe, and described formally as other rotating tops or more precisely as torque and force fields, interacting via a given potential. We regard such a model as an approximate and convenient one that can be expected to reproduce the level of complexity of the role of the solvent as observed in many experiments and simulations. Clearly the degree of success must ultimately be judged on the basis of its ability to correlate a range of experimental results in a consistent fashion.

Our current objective is to provide a framework for modeling solvent-solute interactions using multibody Fokker-Planck-Kramers (FPK) equations. A stochastic multidimensional equation is written and numerically solved for the conditional probability density of the system, including all the angular and linear momenta. A detailed study of our method applied to different physical systems will be presented elsewhere, together with a comparison with previous theoretical studies [11]. Here we empha-

size how some key weaknesses of the classic one-body model may be overcome by a proper choice of additional degrees of freedom in conjunction with accurate computations.

The problem we consider concerns the well-known Hubbard-Einstein relation [12]

$$\tau_R \tau_J = \frac{I}{6k_B T}, \quad (1)$$

which relates the (second-rank) rotational correlation time τ_R to the angular momentum correlation time τ_J for a Brownian rotor. In eq. (1), I is the moment of inertia of the Brownian particle, T is the temperature and k_B is Boltzmann's constant. In ESR studies [5,6] of linewidths (or T_2) and of spin-lattice relaxation, T_1 one finds that whereas $\tau_R \propto \eta/T$ (where η is the solvent viscosity), $\tau_J \propto T/\eta$ only at high temperatures. At lower temperatures τ_J is more nearly temperature and viscosity independent (provided that the measured T_1 is appropriately attributed to spin-rotational relaxation). Similar T_1 observations have been made in NMR studies [13]. Finally, τ_J is, in general, found to be larger than predicted by eq. (1), even when $\tau_J \propto T/\eta$.

Hwang et al. [5] report that the changeover from behavior consistent with eq. (1) to the "anomalous" behavior occurs for the probe PD-Tempone in several solvents for $\tau_R > 10^{-11}$ s, corresponding to $\tau_J < 5 \times 10^{-14}$ s according to eq. (1), with similar results for the dianion radical peroxyamine disulfonate [14]. They point out that "such values (of τ_J) are already of the order of, or faster than molecular vibrational periods. Thus, one can question the interpretation and physical meaning of τ_J ...". In fact, it is unrealistic to think that τ_J can continue to decrease in accordance with eq. (1) as τ_R increases with viscosity. Hwang et al. proposed a simple model wherein the finite relaxation time of the fluctuating torques was taken into account, but to lowest order. Such a perturbation approach did not predict any breakdown in eq. (1).

It has remained as an open problem whether a systematic treatment of stochastic solvent modes (either considered as fast fluctuating torques or slowly relaxing local structures, cf. refs. [5,6,10]) would be able to account for this and other weaknesses of the classic one-body approach. In the following we present some computational results based on a simplified

multidimensional stochastic model that suggests, at least partially, a positive answer to this question.

2. General formulation

We shall denote by Ω_1 a set of Euler angles defining the orientation of the solute molecule (hereafter body 1). Since we explicitly consider inertial effects, the momentum vector L_1 is included in the relevant set of degrees of freedom. A second rotating top, described by an analogous set of coordinates and momenta Ω_2 and L_2 , is coupled to the probe. It might be thought of as a collective structure of solvent molecules reorienting at roughly the same range of rates at which the probe moves. In order to explicitly model the dissipative interaction of the probe and the solvent cage with the rest of the solvent, a stochastic field X and its conjugate momentum P is included, coupled both to body 1 and body 2. For a simple electrostatic representation of the solvent, one can think in terms of a polarization variable, or to the stochastic analogue of the static Onsager reaction field [15]. However, the physical interpretation of the third set of coordinates should be considered as less precise. In fact, we could alternatively treat the "third body" by rotational rather than translational degrees of freedom with no substantial changes in the qualitative nature of the final results, in view of the lowest order treatment (cf. below) accorded to them [11]. Its major role is to account for the fast (but not very fast) stochastic processes due to the solvent and affecting the probe. A small damping term is also included, due to the interaction with all the remaining unspecified very fast solvent degrees of freedom.

The field X behaves as the source of "fluctuating torques" [10,16] acting on both the probe and the "slowly relaxing local structure" (or second body) [10,16], and it is identified with the solvent structure. It should also be stressed that this minimal "three-body" picture could easily be generalized, and the number of interacting objects increased in order to better reproduce the complex range of stochastic processes in the solvent, although the numerical computations become more and more difficult.

The time evolution of the probability density for

the system is assumed to be governed by a FPK operator \hat{F}

$$\hat{F} = \hat{F}_1 + \hat{F}_2 + \hat{F}_X, \quad (2)$$

where \hat{F}_1 and \hat{F}_2 are the rotational Kramers operators for the first and second tops and \hat{F}_X is the translational operator in (X, P) . An isotropic fluid, corresponding to spherical symmetry is assumed for simplicity; the explicit form of the rotational operator for the n th body ($n=1, 2$) is

$$\hat{F}_n = \frac{i}{I_n} L_n J_n + T_n \nabla_n - k_B T \zeta_n^0 \nabla_n \left(\nabla_n + \frac{1}{I_n k_B T} L_n \right). \quad (3)$$

Here J_n is the operator (defined according Hwang and Freed [17]), proportional to the infinitesimal rotation operator and L_n is the angular momentum; ∇_n is the gradient operator in L_n ; I_n is the (scalar) moment of inertia, ζ_n^0 is the friction acting on the body due to the very fast solvent degrees of freedom. Finally $T_n = -iJ_n V$ is the torque on body n due to the interaction potential V expressed as a sum of pair potentials involving the three bodies. An analogous form is written for the Cartesian term \hat{F}_X ,

$$\hat{F}_X = \frac{1}{M} P \nabla_X + F \nabla_P - k_B T \zeta_X \nabla_P \left(\nabla_P + \frac{1}{M k_B T} P \right). \quad (4)$$

∇_X, ∇_P are the gradient operators respectively on X and P , M and ζ_X are the scalar mass and friction associated with the stochastic field; $F = -\nabla_X V$ is the force acting on X and due to V .

The potential function V has been taken according to the following general form:

$$V = V_0(\Omega_1, \Omega_2) - \lambda_1 u_1 X - \lambda_2 u_2 X + \frac{1}{2} \varepsilon^2 X^2 \quad (5)$$

and it is a two-body analogue of the potential defined for a single-body problem in ref. [15]. Here $V_0(\Omega_1, \Omega_2)$ is the direct interaction between the solute and its immediate surroundings, i.e. the solvent cage. It is always possible to write it explicitly as a multipole expansion in terms of first, second rank etc., depending only on the relative orientation between the top bodies, i.e. $\Omega_2 - \Omega_1$ [6]. The last term in eq. (5) is a minimal description of the stochastic isotropic fluctuations of the field X , whose averaged amplitude depends on the unique parameter ε [15].

Finally a simple linear coupling between the field and the n th body is realized via the scalar product of the field and a unitary vector \mathbf{u}_n fixed in the body; an obvious electrostatic analogue being the dipole-field interaction between the dipole $\lambda_n \mathbf{u}_n$ and the electric field X .

Eq. (5) obeys all the requirements of detailed balance as described by Stillman and Freed [10]; the probability density tends to the equilibrium function defined by the Boltzmann distribution with respect to the total energy of the system given by

$$E = V + \frac{1}{2I_1} L_1^2 + \frac{1}{2I_2} L_2^2 + \frac{1}{2M} P^2. \quad (6)$$

Note that it is possible to establish equivalences between the present multidimensional FPK equations and the "augmented" FP equations [10] by means of a projection procedure [11].

3. Reduced expressions

In the following, we will further simplify the time evolution operator \hat{F} of eq. (2), under the hypothesis that both X and P are much faster than the rotational motions of the two tops. Our principal interest is in the averaged effect of the fast stochastic field on the rotating solute. For this purpose a projection procedure [10] can be applied to the original operator, and a reduced system of only two interacting bodies is obtained, governed by a modified FPK operator whose structure exhibits the presence of new interaction terms due to residual effects of the averaged field. First of all, there is a modified interaction potential given by

$$\bar{V} = V_0(\Omega_1, \Omega_2) - \frac{\lambda_1^2 + \lambda_2^2}{\Xi^2} - \frac{\lambda_1 \lambda_2}{\Xi^2} \mathbf{u}_1 \mathbf{u}_2, \quad (7)$$

from which the new torques T_1 and T_2 are calculated instead of from eq. (5). The two new potential terms in eq. (7) are obtained from averaging the original terms linear in X in the total energy of eq. (6). They represent the solvation energy of the composite system of solute + cage due to the undifferentiated "rest of the solvent".

Due to the coupling of the initial torques T_1 and T_2 with T_X , a second interaction term arises in the reduced operator, which is strictly dynamical in na-

ture (i.e. it does not affect the final energy distribution expressed by eq. (6)). It appears as new frictional contributions which are orientation dependent and proportional to the square of the coupling parameters λ_1 and λ_2 , but they are the averaged effect of the stochastic fluctuation of the fast field X . The interesting feature of this new frictional effect is that not only is there a large additional friction acting on each isolated body, but there is also a frictional coupling between the bodies that is of the same order of magnitude, i.e. the total viscosity on body 1 depends on the orientation and angular velocity of body 2 and vice versa. The overall friction tensor may be written in the form of a partitioned matrix

$$\begin{bmatrix} \xi_{11} & \xi_{12} \\ \xi_{21} & \xi_{22} \end{bmatrix} = \begin{bmatrix} \xi_1^0 \mathbf{1} + \xi_1 \mathbf{U}_1 \mathbf{U}_1^T & (\xi_1 \xi_2)^{1/2} \mathbf{U}_1 \mathbf{U}_2^T \\ (\xi_1 \xi_2)^{1/2} \mathbf{U}_2 \mathbf{U}_1^T & \xi_2^0 \mathbf{1} + \xi_2 \mathbf{U}_2 \mathbf{U}_2^T \end{bmatrix}, \quad (8)$$

where each ξ_n is proportional to ξ_X

$$\xi_n = \frac{\lambda_n^2}{\Xi^4} \xi_X. \quad (9)$$

\mathbf{U}_1 and \mathbf{U}_2 are 3×3 matrices depending on the instantaneous orientations of \mathbf{u}_1 and \mathbf{u}_2 respectively, defined simply as

$$\mathbf{U}_n = -i\mathbf{J}_n \otimes \mathbf{u}_n, \quad (10)$$

where the \otimes sign implies that the pq component of \mathbf{U}_n is given by the p component of $-i\mathbf{J}_n$ applied to the q component of \mathbf{u}_n . If each vector and vector operator is defined in a fixed laboratory frame, the implicit definition of \mathbf{U}_n given in ref. [15] holds.

It is interesting to note that if the total friction tensor of eq. (8) is referred to a molecular frame fixed on body 1 (or 2), the diagonal friction block for body 1 (or 2) becomes a constant diagonal matrix, whereas the diagonal friction block for body 2 (or 1) and the coupling friction blocks are only dependent on the relative orientation $\Omega_2 - \Omega_1$, i.e. the friction is easily separated into a constant contribution and a time-dependent one, that is a function only of the absolute orientations of the two bodies.

One of our principal goals in this Letter is to investigate the effect of this dissipative interaction on rotational correlation times, such as the second-rank correlation function, τ_K and the angular momentum correlation time, τ_J . The averaged operator \hat{F} can now be written explicitly as

$$\begin{aligned} \hat{L} = & \frac{i}{I_1} L_1 J_1 + T_1 \nabla_1 - k_B T \nabla_1 \xi_1 \left(\nabla_1 + \frac{1}{I_1 k_B T} L_1 \right) \\ & + \frac{i}{I_2} L_2 J_2 + T_2 \nabla_2 - k_B T \nabla_2 \xi_2 \left(\nabla_2 + \frac{1}{I_2 k_B T} L_2 \right) \\ & - k_B T \nabla_1 \xi_{12} \left(\nabla_2 + \frac{1}{I_2 k_B T} L_2 \right) \\ & - k_B T \nabla_2 \xi_{21} \left(\nabla_1 + \frac{1}{I_1 k_B T} L_1 \right). \end{aligned} \quad (11)$$

This is still a very large system (12 degrees of freedom) to be treated numerically by the FPK approach.

One is interested in evaluating correlation functions for the reorientational relaxation of the probe

$$G_{jm}^R(t) \equiv \langle Y_{jm}^*(t) | Y_{jm}(0) \rangle, \quad (12)$$

with $j=2$, and correlation functions for the relaxation of the momentum vector L_1 components

$$G_m^J(t) \equiv \langle L_m^*(t) | L_m(0) \rangle \quad (13)$$

as well as the associated spectral densities $J_{jm}^R(\omega)$ and $J_m^J(\omega)$, given by the real parts of the Fourier-Laplace transforms of eqs. (12) and (13). Due to the spherical symmetry (i.e. isotropic liquids) both eqs. (12) and (13) are the same for all values of m . Finally we note that $\tau_R \equiv J_{2m}^R(0)$ and $\tau_J \equiv J_m^J(0)$.

It is possible to perform this task effectively by adopting a matrix representation for the FPK operator of eq. (11) using an efficient set of basis functions, which are obtained by the systematic application of standard angular momentum coupling techniques [11]. In this manner, one may benefit from the full spherical symmetry. In the appropriate coupled representation we find that only 8 coupled degrees of freedom are relevant [11]. The desired spectral densities can be evaluated very efficiently by means of an iterative algorithm, especially appropriate for the treatment of large sparse matrices, such as the Lanczos or conjugate gradient algorithm [18,19]. In general, very large basis sets are required (up to order 10^3) for this task. However this is actually the case only for physical regimes with strong potential effects and low frictions (i.e. inertial regimes). In this Letter we present computational results for quasi-diffusional conditions, in which the effective frictional parameters are quite large (i.e.

low temperatures), so that only matrices of order 10^3 – 10^4 were necessary. Only 100–200 s of super-computer CPU time were required for each spectral density calculation.

4. Results and discussion

In this Letter we limit ourselves to investigate the effect of additional solvent degrees of freedom on the Hubbard–Einstein relation, eq. (1), for two limiting cases. We have chosen them to make contact with previous similar, but more approximate, models. (A more general exploration of various extended models will be given elsewhere [11].) In the first case only a “slowly relaxing local structure” (SRLS) is included. It involves the orientation-dependent potential (i.e. $V_0(\Omega_1, \Omega_2)$ in eq. (5)) between the probe and the solvent cage. (The role of the third body is ignored here by setting $\lambda_1 = \lambda_2 = 0$.) In this limiting model the reorienting probe is affected by its interaction with the solvent cage, which relaxes with a correlation time that is slower than that of the probe itself [10,11]. The explicit form of the potential we used is

$$V_0 = \bar{V} = -u_2 P_2(\Omega_2 - \Omega_1), \quad (14)$$

where $P_2(\Omega_2 - \Omega_1)$ is the second-rank Legendre polynomial in the relative orientations of bodies 1 and 2, and u_2 specifies the magnitude of the interaction. We also consider the overdamped or (nearly) Smoluchowski regime, but the full FPK form has been retained to obtain angular momentum correlation functions and to allow for any residual inertial effects on rotational reorientation due to the restoring potential. (This SRLS model has previously been considered in the Smoluchowski limit [10,16], but that precluded the calculation of angular momentum correlation functions and inertial effects.) The “solvent cage” is taken to be both larger ($I_2/I_1 = 10$) and slower ($\xi_2^0/\xi_1^0 = 10$) than the solute molecule.

As a second case, we consider the effects of the frictional coupling between the two bodies as given by eq. (8). This case may be referred to as a “fluctuating torque” (FT) one [5,10]. For simplicity we neglect the interaction potential (i.e. \bar{V} may be set equal to zero). The FT acting on bodies 1 and 2 are the cause of the orientation-dependent friction ten-

tor (measured by parameters ξ_1 and ξ_2) that are in addition to the "zero-order" friction (ξ_1^0 and ξ_2^0). Note that the frictional coupling has no effect on the final equilibrium distribution. In fact, since $\bar{V}=0$ the equilibrium properties are those of two Brownian rotors. (As noted in section 1, the earlier FT model of Hwang et al. [5] was only to lowest order in perturbation theory and could not predict any breakdown in eq. (1). Furthermore, our result given by eq. (8) provides a precise source for the FT, whereas the Hwang et al. treatment was for a very simple and ad hoc quasi-one-dimensional orientation-independent form.)

We show in table 1 results on τ_R and τ_J for the SRLS case for a range of values of the potential parameter, u_2 with all other parameters kept constant. The inertial and frictional coefficients used for body 1 ($(k_B T/I_1)^{1/2} = 10^{12} \text{ s}^{-1}$ and $\xi_1^0/I_1 = 10^{14} \text{ s}^{-1}$, respectively) are in the range appropriate for a moderately small solute molecule (e.g. PD-Tempone [5,6]) in solvents of moderate viscosity. In fig. 1 we show the spectral densities for the rotational and the momentum relaxation at $u_2=0$ (no coupling) and $u_2=2k_B T$. In the limit of $u_2=0$, the numerical results are in complete agreement with eq. (1) and a simple Debye model for τ_R , as they should. As u_2 is increased, τ_R substantially increases, where τ_J only decreases slightly. This leads to a substantial breakdown of eq. (1). The increase in τ_R is the SRLS effect discussed previously [6,10,16] in the context of the Smoluchowski limit for which one can write

Table 1

τ_R and τ_J calculated for the SRLS model with different values of the potential coupling^{a)}

$u_2/k_B T$	S_j	$10^{10} \tau_R$ (s)	$10^{14} \tau_J$ (s)	$10^{24} \tau_R \tau_J$ (s ²)
0.0	0.000	0.167	1.000	0.167
0.5	0.106	0.349	0.982	0.342
1.0	0.220	0.928	0.926	0.859
1.5	0.334	1.877	0.841	1.578
2.0	0.434	3.092	0.741	2.291
2.5	0.530	4.394	0.646	2.838
3.0	0.605	5.638	0.566	3.191
3.5	0.664	6.724	0.504	3.388
4.0	0.711	7.607	0.461	3.506
4.5	0.748	8.268	0.431	3.563

^{a)} The values of the other parameters are: $(k_B T/I_1)^{1/2} = 10^{12} \text{ s}^{-1}$, $\xi_1^0/I_1 = 10^{14} \text{ s}^{-1}$ and $(k_B T/I_2)^{1/2} = 0.316 \times 10^{12} \text{ s}^{-1}$, $\xi_2^0/I_2 = 10^{15} \text{ s}^{-1}$.

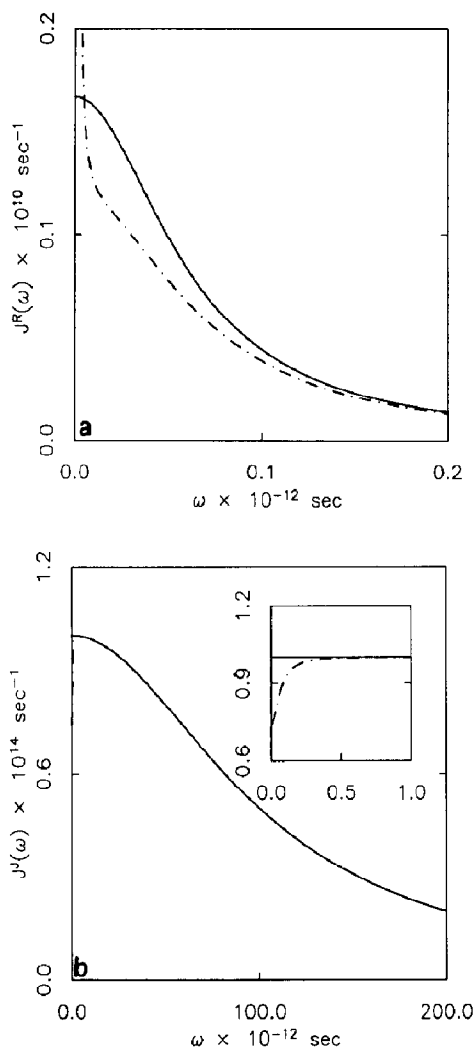


Fig. 1. Spectral densities for the SRLS model (cf. table 1). Solid lines: $u_2=0$; broken lines: $u_2=2k_B T$. (a) Rotational spectral densities (note $J^R(0) = 3.09 \times 10^{-10} \text{ s}$ for $u_2=2k_B T$); (b) angular momentum spectral densities.

$$\tau_R \approx (1 - S_j^2) \tau_R^0 + S_j^2 \tau_X, \quad (15)$$

where τ_R^0 is the intrinsic or Debye-model τ_R value in the limit of $u_2=0$ (i.e. $\tau_R^0 = \xi_1^0/6k_B T$), and τ_X is the correlation time of the solvent structure in the same limit. Also in eq. (15), $S_j \equiv \langle P_2(\Omega_1) \rangle$ is the order parameter of the solute relative to a fixed solvent cage at the given potential. The results of table 1 are in reasonable agreement with eq. (15), which shows that as u_2 increases, τ_R is increasingly determined by

the reorientation of the slower solvent cage; note that in table 1, $\tau_X/\tau_R^0 = 100$. There is a slight underestimation of computed τ_R versus eq. (15) that is probably due to the effect of librational motions within the potential well. This is a small effect given the strong damping, but it is of increasing importance as the potential is increased.

For each computed correlation function and its related spectral density, it is possible to look at the full eigenvalue spectrum, i.e. the collection of distinct decay constants that contribute to it. Each eigenvalue λ_i contributes to the spectral density with a given weight c_i , according to the general expansion [18]

$$J(\omega) = \text{Re} \sum_i \frac{c_i}{i\omega + \lambda_i} \quad (16)$$

A study of the composition of the corresponding eigenvectors, in terms of the original basis set of functions, for the dominant modes in the expansion given by eq. (16) can be a very helpful instrument to understand the physical behavior of a complex system. In the present case, one finds that two dominant eigenmodes are present in the orientational spectral density: one of them is related to the free rotation of body 1 whereas the second is related to the free rotation of body 2. When the potential coupling is increased, the weight c_i associated with the second mode is increased, implying that the reorientational motion of the solute is more and more affected by the motion of the solvent structure. The fact that τ_j is hardly affected when the potential interaction is strengthened (by only a factor of two for u_2 going from 0 to 4.5 $k_B T$ units), may be understood by observing that the momentum relaxation process is dominated by eigenmodes that are essentially characteristic of an isolated Brownian rotor. Physically, this may be due to the fact that angular momentum relaxation occurs much more rapidly, and it is not affected by a solvent cage that is relatively static [11].

We show in table 2 results on τ_R and τ_j for the FT case, for a range of the renormalized friction parameters ξ_1 and ξ_2 , keeping the zero-order friction parameters ξ_1^0 and ξ_2^0 constant; in fig. 2 the spectral densities for $\xi_1/I_1 = 4.0 \times 10^{14}$ s and $\xi_1/I_1 = 0$ s are shown. One observes that τ_R increases with increase in the friction ξ_1 , becoming almost linearly dependent on ξ_1 when $\xi_1 \gg \xi_1^0$, i.e. the dominant friction

Table 2

τ_R and τ_j calculated for the FT model with different values of the frictional coupling ^{a)}

$10^{-14} \xi_1/I_1 (\text{s}^{-1})$	$10^{11} \tau_R (\text{s})$	$10^{13} \tau_j (\text{s})$	$10^{24} \tau_R \tau_j (\text{s}^2)$
0.0	0.167	1.000	0.167
100.0	0.641	0.515	0.330
200.0	0.907	0.485	0.439
300.0	1.142	0.471	0.537
400.0	1.369	0.464	0.635
500.0	1.591	0.461	0.733
600.0	1.765	0.458	0.808
700.0	2.016	0.457	0.921
800.0	2.228	0.455	1.013
900.0	2.439	0.453	1.104
1000.0	2.647	0.452	1.196
1100.0	2.858	0.452	1.291
1200.0	3.058	0.451	1.379

^{a)} The values of the other parameters are: $(k_B T/I_1)^{1/2} = 10^{12} \text{ s}^{-1}$, $\xi_1^0/I_1 = 10^{13} \text{ s}^{-1}$ and $(k_B T/I_2)^{1/2} = 0.316 \times 10^{12} \text{ s}^{-1}$, $\xi_2^0/I_2 = 10^{14} \text{ s}^{-1}$.

affecting the solute originates from the FT terms in this limit. On the other hand, τ_j becomes virtually independent of ξ_1 for large values of this parameter. Again the Hubbard–Einstein relation is violated. A simple interpretation of the behavior of τ_j in this case can be obtained by considering the full friction matrix given by eq. (8). In particular, τ_j is essentially determined by the eigenvalues of this matrix. The smallest eigenvalue is directly proportional to the core friction ξ_1^0 when ξ_1 and ξ_2 are large. Thus there is a cluster of decay constants (i.e. eigenvalues of the time evolution operator) close to ξ_1^0 in value. In this limit their associated eigenvectors are found to have the major effect in determining the spectral density for the angular momentum. If we consider the simpler planar analogue of the 3D case (i.e. two dipoles rotating in a plane), it is easy to write down, after averaging the fast reaction field, a simpler 2×2 friction matrix

$$\begin{bmatrix} \xi_1 & \xi_{12} \\ \xi_{21} & \xi_2 \end{bmatrix} = \begin{bmatrix} \xi_1^0 + \xi_1 & (\xi_1 \xi_2)^{1/2} \\ (\xi_1 \xi_2)^{1/2} & \xi_2^0 + \xi_2 \end{bmatrix} \quad (17)$$

after neglecting a residual orientation dependence. The correlation functions for the relaxation of both the momenta L_1 and L_2 can be computed analytically, and it is found that for large ξ_1 and ξ_2 they are controlled by ξ_1^0 and ξ_2^0 (note that eq. (17) is the sum of a diagonal matrix with elements ξ_1^0 and ξ_2^0

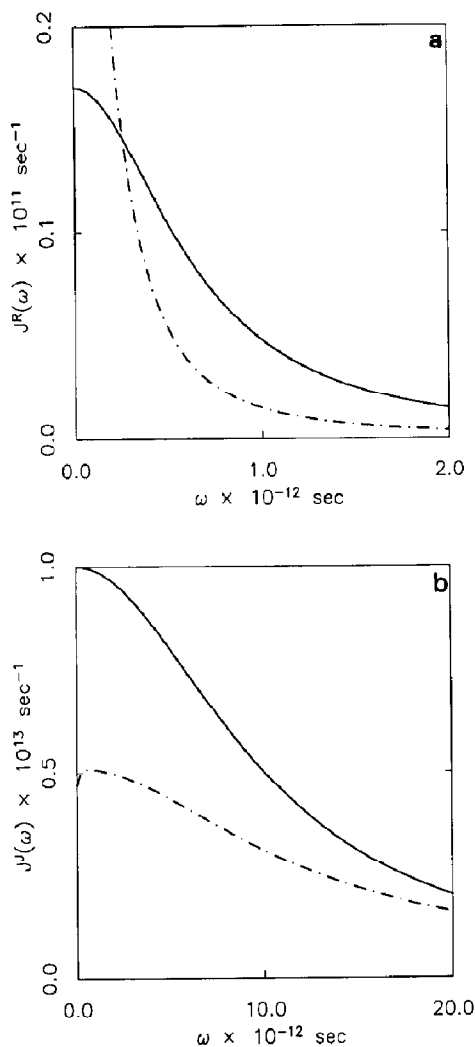


Fig. 2. Spectral densities for the FT model (cf. table 2). Solid lines: $\xi_1/I_1=0$; broken lines: $\xi_1/I_1=4.0 \times 10^{14} \text{ s}^{-1}$ (note $J^R(0)=1.37 \times 10^{-11} \text{ s}$ in the latter case); (b) angular momentum spectral densities.

and a $2 \otimes 2$ singular matrix, which leads to this property).

A different type of behavior is observed for the rotational correlation time τ_R . The spectral density is now dominated by an eigenfunction that can be related to a free rotation of the solute, with an increased friction proportional to ξ_1 (and an "intercept" given by the constant ξ_1^0), i.e. the fluctuating torque has the only effect of increasing the effective damping on the solute, without significantly en-

hancing the coupling with the solvent cage.

In both the SRLS and FT models the Hubbard-Einstein product $\tau_R \tau_J$ can be increased by orders of magnitude with respect to the theoretical value predicted by eq. (1) for the classic single-body model. One can try to infer what the effect of lowering the temperature would be for a physical system described either by the SRLS or the FT model. In the SRLS case, decreasing the temperature would cause both the friction and the order parameter to increase, so τ_R could initially increase somewhat faster than τ_J decreases. However, since at low temperatures τ_R should be roughly equal to τ_X , the product $\tau_R \tau_J$ should reach a limiting, nearly temperature-independent value that is greater than eq. (1) by the ratio of moments of inertia I_2/I_1 . As to the FT model, when the temperature is decreased the frictional parameters ξ_1^0 , ξ_2^0 and ξ_X increase. The relative importance of ξ_1 versus ξ_1^0 would be enhanced as the temperature is lowered (cf. eq. (9)) if (i) ξ_X increases faster than ξ_1^0 with inverse temperature, possibly because of enhanced collective effects (e.g. a larger "third body" which would have a larger friction), and/or if (ii) λ_1 increases faster than Ξ^2 . Thus the rate of increase of τ_R with temperature would be faster than the rate of decrease of τ_J (which is controlled only by the zero-order friction in the low temperature regime). In either case, the final outcome is that the $\tau_R \tau_J$ product is larger than the classic value predicted by the free Brownian rotator model.

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