Separation of Fast and Slow Processes from a Stochastic Cage Model of Molecular Dynamics†

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The linear solute cage model (LSCM) has been proposed in the past [Moro, G. J., Polimeno, A. *J. Chem. Phys.* **1997**, *107*, 7884] to account for the action of the confining potential generated by neighboring solvent molecules on a linear solute, in the presence of fluctuations of the resulting cage structure. Rotational correlation functions, directly related to spectroscopic observables such as dielectric permittivity and far-infrared spectra in molecular liquids, can be calculated from the numerical solution of the model. However, to understand the influence of different relaxation processes on the solute dynamics, it is useful to explore semianalytical approximations, able to connect directly predictions with physical ingredients of the model. In this work, we present a detailed analysis of LSCM based on the application of a Born−Oppenheimer time-scale separation procedure, which allows a complete description of the probe fast libration motions and the cage slow rotation and restructuring modes.

I. Introduction

A major source of complexity in molecular dynamics phenomena in liquids derives from the local cage structure formed by the solvent surrounding a given solute or a given solvent molecule taken as the probe. The local structure is responsible for the fast librational motions observed with far-infrared spectra[1] or more recently with the optically detected Kerr effect (OKE) technique.[2] A complete description of the molecular motions, including both the fast librational motions and the slow reorientations as detected in magnetic resonance experiments, represents a challenging objective for our understanding of the liquid state of the matter. Standard Brownian motion theory,[3] with the solvent appearing as a mere source of frictional drag, is not sufficient as long as it neglects the persistent (on the short time scale of the librational motions) torques due to the cage structure. In recent works,[4−7] the method of the stochastic cage model has been developed with the purpose of describing the effects of the local solvent structure in the framework of a Markovian representation. Specific stochastic variables are employed for describing the instantaneous configuration of the local solvent structure: the cage orientation (i.e., the equilibrium orientation within the cage of the solute or of the probe) and the librational frequency as a measure of the strength of solute−solvent interactions. This method can be applied to both the translational motion[4] and the rotational motion[5−7] at different levels of approximation depending, on one hand, on the detail in the description of the cage dynamics and, on the other hand, on the accuracy in the calculation of the relevant observables.

The most advanced model for the rotational motion is that of ref 7 (hereafter denoted as I) for the case of a linear solute, where two independent processes were considered for the cage dynamics: diffusion cage rotation and random restructuring process of the cage structure which randomizes both the cage orientation and the solute librational frequency. Moreover, the exact solution of the model was achieved by using efficient numerical methods. The linear solute cage model (LSCM) has been shown to be able to reproduce the characteristic features of time correlation functions, and of the corresponding spectral densities, as seen in experiments or molecular dynamics (MD) simulations[8] at both the short time-scale of the librational motions and the long-time scale of wide angle reorientations of the solute. However, the availability of numerical solutions of the model is not sufficient for an useful comparison with experimental data and for the analysis of the model dependence upon physical parameters. In the effort of providing a faithful description of real systems, several elementary processes have to be included in the stochastic cage model with correspondingly a large set of independent variables, in particular those for the distributions on the librational frequency and on the cage reorientation during the restructuring process, as well as the rate constant of each independent relaxation mechanism. It is extremely difficult on the basis of the numerical solution alone to establish a correlation between the parameters of the model and specific features of the observables, thus preventing the rationalization of experimental results in terms of the contributions of elementary processes. This calls for semianalytical but approximate solutions of the model in order to establish a transparent relation between its ingredients and the predicted behavior of the dynamical observables.

The present work has precisely such an objective: given the LSCM defined in I, we intend to develop the approximate methods of solution which allow a simple evaluation of the relevant correlation functions. The separation between the slow cage processes and the fast probe librational motions is the major step invoked in our analysis. Formally, this can be achieved by employing a general method already presented in ref 6 and which constitutes the stochastic counterpart of the Born−Oppenheimer procedure of molecular quantum mechanics. Then the two classes of dynamical processes can be analyzed separately in order to determine their contribution to the orientational and angular velocity correlation functions. As a result of this procedure, the important role of the cage restructuring process emerges in the analysis of the long time behavior of

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the orientational correlation functions by differentiating their rank dependence from that of the simple diffusion model. In the case of the fast librational motions, approximations at different levels of accuracy are employed in order to link the confined solute relaxation with the dispersion of librational frequency, i.e., the inhomogeneity of the local cage structures.[1]

The paper is organized as follows. In the next section, we recall the basic definitions of the LSCM, previously introduced in I. The slow processes alone are analyzed in section III with the purpose of separating the effects of cage rotations and cage restructuring processes in the long time behavior of orientational correlation functions. In section IV, the methods for the analysis of fast librational processes are presented in relation to the orientational relaxation and angular velocity correlation functions. A summary of the main results of the work are presented in the final section.

II. The Model

The cage model for the rotational motion of a linear molecule is based on a series of hypotheses concerning the static and dynamic properties of the system: (a) the solute (probe) is represented as a linear inertial rotator by neglecting the coupling with its translational degrees of freedom;[9] (b) the solvent local environment is made by a cluster of molecules (cage) and it behaves as a diffusive rigid body, subjected to random changes in its internal structure; (c) the interaction potential between probe and cage is responsible for fast librations of the probe. Then the overall motion of the probe is determined by the superposition of its librations within the cage and the reorientations due to the cage dynamics. The same picture can be applied to pure liquids, by considering a given molecule as the probe. After defining the phase space and the model of the time evolution of the system, we shall identify the fast and slow variables whose dynamics is analyzed separately in the following sections. According to I, the phase space describing a linear molecule rotating in the field generated by a cage solvent structure is given by the following set of variables:

$$\mathbf{X} = (\Omega, L, \Omega_c, \omega) \tag{1}$$

where $\Omega = (\alpha,\beta,\gamma)$ are the Euler angles which specify the orientation with respect to the cage frame (CF) of the molecular frame (MF) having the z axis along the symmetry axis and the y axis along the instantaneous direction of the angular momentum; L is the modulus of the angular momentum vector of the probe; $\Omega_c = (\alpha_c,\beta_c,\gamma_c)$ are the Euler angles determining the orientation of the cage frame with respect to the laboratory frame (LF); and finally, ω is the frequency of the librational motions of the solute about the x or y axes of the cage frame. In general, two librational frequencies ω_x and ω_y would be required, but here, we consider the model within the axial cage approximation $\omega = \omega_x = \omega_y$. The calculation of the orientational correlation functions requires also the absolute orientation Ω_0 of the probe with respect to the laboratory frame (LF), which can be derived once the relative probe orientation Ω with respect to the cage frame and Ω_c is given. In Figure 1a, sketch of the reference frames employed in the model is shown.

The potential function for the solute within the cage is written by including only the leading term with respect to the rank j of Wigner functions $D^j_{p,q}(\Omega)$ in the following form:

$$V_c(\Omega,\omega) = -I\omega^2 D^1_{0,0}(\Omega) = -I\omega^2 \cos\beta \tag{2}$$

This can be justified by performing an expansion of the intermolecular potential between probe and solvent with respect to the librational displacement β,[6] so identifying the librational frequency ω with the strength of the probe interactions with the solvent cage. The equilibrium distribution for the system is then given by

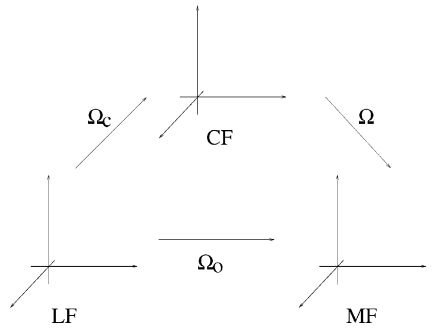

Figure 1. Reference frames which define the combined system of solute molecule and cage: LF = laboratory frame, MF = molecular frame, and CF = cage frame.

$$P(\mathbf{X}) = \frac{\exp\{-[L^2/2I + V_c(\Omega,\omega)]/k_BT\}P(\omega)}{8\pi^2 I k_B T \int d\Omega \exp\{-V_c(\Omega,\omega)/k_BT\}} \tag{3}$$

The structural inhomogeneity of the solvent cage is taken into account by the distribution $P(\omega)$ on the librational frequency. We adopt the following Gaussian distribution:

$$P(\omega) = \frac{\exp[-(\omega - \bar{\omega})^2/2\sigma_\omega{}^2]}{\sigma_\omega\sqrt{\pi/2}[1 + \mathrm{erf}(\bar{\omega}/\sigma_\omega\sqrt{2})]} \tag{4}$$

which is normalized for $\omega \geq 0$. This is a very simple form requiring the specification of only two parameters $\bar{\omega}$ and σ_ω for the most probable librational frequency and the width of the distribution. We emphasize, however, that the following theory can be applied to any other parametrization of the librational frequency distribution. The equilibrium distribution eq 3 is conveniently factorized in the following form:

$$P(\mathbf{X}) = P(L)P(\omega)P(\omega|\Omega)/8\pi^2 \tag{5}$$

where $P(L)$ and $P(\omega|\Omega)$ denote the angular momentum distribution and the conditional probability of Ω for a given librational frequency ω, respectively

$$P(L) = \frac{\exp[-L^2/2Ik_BT]}{Ik_BT} \tag{6}$$

$$P(\omega|\Omega) = \frac{\exp[-V_c(\Omega,\omega)/k_BT]}{\int d\Omega' \exp[-V_c(\Omega',\omega)/k_BT]} = \frac{\omega^2 \exp[\omega^2 D^1_{0,0}(\Omega)/\omega_s{}^2]}{8\pi^2\omega_s{}^2 \sinh(\omega^2/\omega_s{}^2)} \tag{7}$$

with $\omega_s = (k_BT/I)^{1/2}$ being the streaming frequency for free rotations of the probe.

A Markovian representation is introduced for the evolution of the nonequilibrium probability $P(\mathbf{X}, t)$

$$\frac{\partial}{\partial t}P(\mathbf{X}, t) = -\hat{\Gamma}P(\mathbf{X}, t) \tag{8}$$

with the time evolution operator $\hat{\Gamma}$ decomposed according to

the elementary dynamical processes of the system

$$\hat{\Gamma} = \hat{\Gamma}_{\text{solute}} + \hat{\Gamma}_{\text{cage rot}} + \hat{\Gamma}_{\text{cage rest}} \tag{9}$$

The first term describes the solute dynamics under the action of the cage potential according to the Fokker−Planck operator

$$\hat{\Gamma}_{\text{solute}} = -\frac{T_x}{L}\hat{M}_z(\Omega) + T_y\frac{\partial}{\partial L} + \frac{L}{I}\hat{M}_z(\Omega) + -\xi k_B T\left[\frac{1}{L^2}\hat{M}_z{}^2(\Omega) + \left(\frac{\partial}{\partial L} + \frac{1}{L}\right)\left(\frac{\partial}{\partial L} + \frac{L}{Ik_BT}\right)\right] \tag{10}$$

where ξ is the friction coefficient for the angular momentum relaxation and $\mathbf{T} = -\hat{\mathbf{M}}(\Omega)V(\Omega,\omega)$ is the torque. The rotational diffusion of the cage without modification of its structure (i.e., of the librational frequency ω) is accounted for by the operator

$$\hat{\Gamma}_{\text{cage rot}} = -[\hat{\mathbf{M}}(\Omega) - \mathbf{E}(\Omega)\hat{\mathbf{M}}(\Omega)]^{\text{tr}}\mathbf{D}P(\mathbf{X})[\hat{\mathbf{M}}(\Omega) - \mathbf{E}(\Omega)\hat{\mathbf{M}}(\Omega)]P(\mathbf{X})^{-1} \tag{11}$$

with an axial diffusion tensor

$$\mathbf{D} = \begin{pmatrix} D_\perp & 0 & 0 \\ 0 & D_\perp & 0 \\ 0 & 0 & D_{||} \end{pmatrix} \tag{12}$$

In eqs 11 and 12, $\mathbf{E}(\Omega)\hat{\mathbf{M}}(\Omega)$ and $\hat{\mathbf{M}}(\Omega_c)$ denote the vector rotation operator components in the cage frame (CF) acting on the Euler angles Ω and Ω_c respectively. The term $\mathbf{E}(\Omega)\hat{\mathbf{M}}(\Omega)$ in eq 11 derives from a change of variable from the absolute orientation Ω_0 to the relative orientation Ω[7] for the probe, $\mathbf{E}(\Omega)$ being the Euler matrix transforming the vector components from the molecular frame (MF) to the cage frame. The third term of eq 9 describes the restructuring of the cage which randomizes both its orientation Ω_c and the librational frequency ω, and it is specified as a master equation

$$\hat{\Gamma}_{\text{cage rest}}P(\mathbf{X}, t) = \int d\mathbf{X}'\,[P(\mathbf{X}, t)W(\mathbf{X} \rightarrow \mathbf{X}') - P(\mathbf{X}', t)W(\mathbf{X}' \rightarrow \mathbf{X})] \tag{13}$$

where $W(\mathbf{X} \rightarrow \mathbf{X}')$ is the rate for the transition from $\mathbf{X}$ to $\mathbf{X}'$ configurations. Two constraints are imposed to the transition kernel: the detailed balance condition[14] and the condition that changes of the solvent cage, which are supposed to be instantaneous, do not modify the solute configuration, i.e., that the absolute orientation Ω_0 of the probe and its angular momentum remain constant during cage restructuring. Correspondingly we choose the following rate kernel of BGK type:

$$W(\mathbf{X} \rightarrow \mathbf{X}') \equiv W(\Omega,L,\Omega_c,\omega \rightarrow \Omega',L',\Omega_c',\omega') = F(\Delta\Omega_c)\delta(\Omega_0' - \Omega_0)\delta(L' - L)P(\omega')P(\omega'|\Omega') \tag{14}$$

where Ω_0 (Ω_0') is the absolute orientation of the probe before (after) the transition as derived form Euler angles Ω_c and Ω (Ω_c' and Ω'). An effective rate w can be assigned to the process of cage rearrangement as the average transition rate

$$w = \int d\mathbf{X}\,d\mathbf{X}'\,P(\mathbf{X})W(\mathbf{X} \rightarrow \mathbf{X}') \tag{15}$$

In eq 14 the function $F(\Delta\Omega_c)$ has been inserted in order to control the distribution of cage reorientations Ω_c during the restructuring process. The Euler angles $\Delta\Omega_c$ specify the orientation of the cage frame in the arrival state $\mathbf{X}'$ with respect to the cage frame in the starting state $\mathbf{X}$. In I, we have performed the calculation with a simple constant function, i.e.

$$F(\Delta\Omega_c) = w \tag{16}$$

However, realistic modeling of cage dynamics requires a more careful choice of such a function. To this aim, it is convenient to introduce the distribution $\rho(\Delta\Omega_c)$ of cage frame reorientations due to transitions, by considering the average rate for fixed $\Delta\Omega_c$, i.e., for an arbitrary argument Ξ of the distribution

$$\rho(\Xi) = \frac{1}{w}\int d\mathbf{X}\,d\mathbf{X}'\,P(\mathbf{X})W(\mathbf{X} \rightarrow \mathbf{X}')\delta(\Delta\Omega_c - \Xi) \tag{17}$$

with the factor $1/w$ ensuring the correct normalization

$$\int d\Xi\,\rho(\Xi) = 1 \tag{18}$$

By inserting the rate kernel eq 14, one derives a reduced form for the distribution ρ

$$\rho(\Delta\Omega_c) = \frac{F(\Delta\Omega_c)}{w}\int d\Omega\,d\omega\,d\omega'\,P(\omega)P(\omega|\Omega)P(\omega')P(\omega'|\Omega') \tag{19}$$

where, for a given Ω, the Euler angles Ω' denote the relative orientation of the probe after a reorientation $\Delta\Omega_c$ of the cage frame. By means of the expansion of $P(\omega|\Omega)$ on the basis of Wigner functions of Ω, the following more explicit relation is obtained:

$$\rho(\Delta\Omega_c) = \frac{F(\Delta\Omega_c)}{w}\sum_j \frac{2j+1}{8\pi^2}\overline{D^j_{0,0}(\Omega)^2}D^j_{0,0}(\Delta\Omega_c) \tag{20}$$

When the constant function $F(\Delta\Omega_c) = w$ is employed, ρ depends only on the angle $\Delta\beta_c$ of $\Omega_c = (\alpha_c,\beta_c,\gamma_c)$. Figure 2 displays such a distribution as recovered from the Gaussian form eq 4 for $P(\omega)$ with parameters $\bar{\omega}/\omega_s = 4$ and $\sigma_\omega/\omega_s = 2.5$.

It should be mentioned that function $\rho(\Delta\beta_c)$ depends strongly on the librational frequency distribution, and in particular, it becomes narrower when $P(\omega)$ is shifted to higher librational frequencies. On the other hand, one can choose the rate w and the distribution $\rho(\Delta\Omega_c)$ and then derive according to eq 20 the function $F(\Delta(\Omega_c))$. This allows a more flexible use of the model by selecting the distribution of cage frame reorientations independently of the librational frequency distribution. Because of the axial symmetry of the cage, only the dependence on $\Delta\beta_c$ is significant, and a convenient parametric form is given as

$$\rho(\Delta\Omega_c) = \frac{\exp(\lambda\cos\Delta\beta_c)}{\int d\Delta\Omega_c\exp(\lambda\cos\Delta\beta_c)} \tag{21}$$

with λ derivable from a chosen value of the average

$$\overline{\cos\Delta\beta_c} = \int d\Delta\Omega_c\,\rho(\Delta\Omega_c)\cos\Delta\beta_c \tag{22}$$

This average can be considered as an "order parameter" of such a distribution, with the two limits: $\overline{\cos\Delta\beta_c} = 1$ (i.e., $\lambda \rightarrow \infty$) for small steps reorientations of the cage and $\overline{\cos\Delta\beta_c} = 0$ (i.e., $\lambda \rightarrow 0$) for random jumps of arbitrary size of the cage frame during restructuring. In Figure 2, we have represented also the distribution eq 21 for $\overline{\cos\Delta\beta_c} = 0.3$, which appears to be appropriate for a pure liquid of linear molecules when cage reorientations of significant size are expected, but with a reduced probability for complete reorientations $\Delta\beta_c = \pi$.

Once the stochastic model is defined, one can evaluate the auto-correlation function for the generic observable $f(\mathbf{X})$

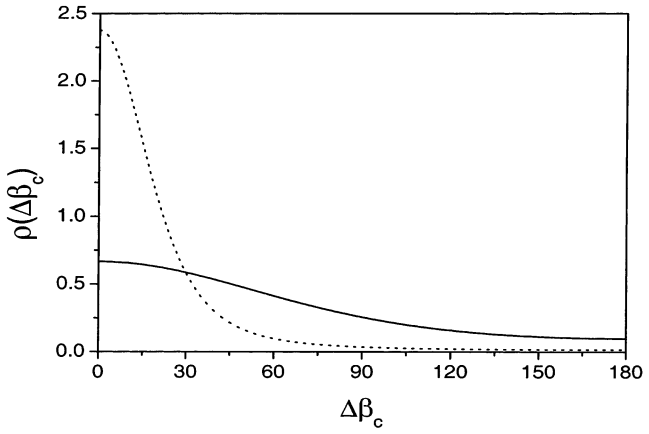

Figure 2. Distribution $\rho(\Delta\beta_c)$ for cage frame reorientations due to cage restructuring. Continuous line: distribution with $\overline{\cos\Delta\beta_c} = 0.3$; dashed line: distribution for $F(\Delta\Omega_c) = w$.

$$G(t) = \overline{f[\mathbf{X}(0)]^* f[\mathbf{X}(t)]} = \int d\mathbf{X}\, f(\mathbf{X})^* \exp(-\hat{\Gamma}t) f(\mathbf{X}) P(\mathbf{X}) \tag{23}$$

We shall specifically analyze the correlation functions probing the solute dynamics and which are required in the interpretation of spectroscopic observations.[10] For the solute orientation, we shall consider the spherical harmonics which can be specified as Wigner functions of the first two angles of $\Omega_0 = (\alpha_0,\beta_0,\gamma_0)$ (the third angle γ_0 is required only for the determination of the angular momentum orientation). The jth rank correlation function denoted as

$$G^j(t) = (2j+1)\overline{D^j_{m,0}[\Omega_0(0)]^* D^j_{m,0}[\Omega_0(t)]} \tag{24}$$

is independent of the index m because of the isotropy with respect to the laboratory frame. Another relevant correlation function is defined for the angular momentum observable

$$G^L(t) = \overline{\mathbf{L}(0)\cdot\mathbf{L}(t)}/2Ik_BT = \overline{L(0)\mathbf{y}(0)\cdot\mathbf{y}(t)L(t)}/2Ik_BT \tag{25}$$

where $\mathbf{y}$ is the axis of the molecular frame determined by the instantaneous direction of the angular momentum. To deal with correlation functions equal to one at $t = 0$, a suitable normalization factor has been inserted in definitions (24) and (25).

To summarize, the LSCM is fully specified once a value is attributed to the parameters $\omega_s = (k_BT/I)^{1/2}$ (streaming frequency), $\tau_c = \xi/I$ (collision time), $D_\perp$ (cage diffusion coefficient), and functional forms have been defined for $P(\omega)$ and $\rho(\Delta\Omega_c)$. Notice that the dependence upon $D_\parallel$ is absent due to the axial symmetry of the cage potential. Given the complexity of the stochastic model, exact solutions for the correlation functions are derivable only numerically. This has been worked out in I through (i) the matrix representation of the time evolution operator on a complete set of basis functions and (ii) the direct diagonalization of the resulting matrix. The procedure was shown to be effective, although the number of coupled degrees of freedom is rather large. However, the exploration of the effects of different parameters and the characterization of the possible dynamical regimes predicted by the model can be better accomplished by approximate treatments able to correlate in a transparent way the different ingredients of the model with the observed behavior of the correlation functions. A full numerical solution can be used for fine-tuning of the model, to reproduce accurately the experimental measurements.

We shall examine the typical situation of molecular liquids when the librational motion controls only the short time behavior of the molecular rotational motion, whereas the much slower cage dynamics determines the long time relaxation.[1] This condition is achieved when the average librational frequency $\bar{\omega}$ and the rate $1/\tau_c$ of angular momentum relaxation are both much larger than the rates for rotation and the restructuring process of the cage, i.e., $\bar{\omega}$, $1/\tau_c \gg D_\perp$, w. Then one can apply the methods of ref 6 for treating separately the different processes on the basis of their time scales. Correspondingly the stochastic variables $\mathbf{X} = (\mathbf{X}_F,\mathbf{X}_S)$ are partitioned into the set of fast variables for the angular momentum and the relative probe orientation, $\mathbf{X}_F = (\Omega, L)$, and the set of slow variables for the cage configuration, $\mathbf{X}_S = (\Omega_c,\omega)$. For later use, we introduce the equilibrium distribution on the slow variables only

$$P_S(\mathbf{X}_S) = \int d\mathbf{X}_F\, P(\mathbf{X}_F,\mathbf{X}_S) = P(\omega)/8\pi^2 \tag{26}$$

Correspondingly the full equilibrium distribution is conveniently factorized as

$$P(\mathbf{X}) = P_S(\mathbf{X}_S)P(\mathbf{X}_S|\mathbf{X}_F) = P_S(\mathbf{X}_S)P(L)P(\omega|\Omega) \tag{27}$$

where $P(\mathbf{X}_S|\mathbf{X}_F)$ is the conditional probability of fast variables $\mathbf{X}_F$ for a given set of values of the slow variables $\mathbf{X}_S$.

III. Slow Cage Dynamics

The behavior of the system at long time scales is determined by the relaxation of the slow variables only, and it can be described by the time-dependent distribution averaged on the fast variables $\mathbf{X}_F$

$$P_S(\mathbf{X}_S, t) = \int d\mathbf{X}_F P(\mathbf{X}, t) \tag{28}$$

the projection onto the subspace of functions of slow variables supplies the required time evolution equation[6]

$$\frac{\partial}{\partial t} P_S(\mathbf{X}_S, t) = -\hat{\Gamma}_S P_S(\mathbf{X}_S, t) \tag{29}$$

with the projected operator $\hat{\Gamma}_S$ defined implicitly by the identity

$$\hat{\Gamma}_S g(\mathbf{X}_S) P_S(\mathbf{X}_S) \equiv \int d\mathbf{X}_F\, \hat{\Gamma} P(\mathbf{X}) g(\mathbf{X}_S) \tag{30}$$

for any function $g(\mathbf{X}_S)$ of the slow variables only. Given an observable $f(\mathbf{X})$ its component along the functional subspace of slow variables is extracted in the following way

$$fs(\mathbf{X}_S) \equiv \int d\mathbf{X}_F\, f(\mathbf{X}) P(\mathbf{X}_S|\mathbf{X}_F) \tag{31}$$

In the autocorrelation function $G(t)$ of eq 23, a slow component $G_S(t)$ is identified by the relation[6]

$$G_S(t) = \int d\mathbf{X}_S f_S(\mathbf{X}_S)^* \exp(-\hat{\Gamma}_S t) f_S(\mathbf{X}_S) P_S(\mathbf{X}_S) \tag{32}$$

No slow component is recovered for the correlation function in eq 25 for the angular momentum, since the corresponding projected functions f_S vanish. On the contrary, a large contribution due to the slow cage dynamics is found for the solute rotation. The orientational observable in eq 24 is conveniently written as

$$f = D^j_{m,0}(\Omega_0) = \sum_k D^j_{m,k}(\Omega_c) D^j_{k,0}(\Omega) \tag{33}$$

from which the following slow component is derived

$$f_S = D^j_{m,0}(\Omega_c) d^j(\omega) \tag{34}$$

with coefficients

$$d^j(\omega) = \int d\Omega\, D^j_{0,0}(\Omega) P(\omega|\Omega) \tag{35}$$

As shown in Figure 3 these coefficients tend to one for large librational frequencies. On the other hand, from the asymptotic expansion about $\beta = 0$ of the previous average with distribution $P(\omega|\Omega)$ of eq 7, one derives the following estimates valid for $\omega \gg \omega_s$

$$d^j(\omega) \approx 1 - j(j+1)\frac{\omega_s^2}{2\omega^2} \tag{36}$$

By inserting into eq 30 the time evolution operator defined in the previous section, the following result is obtained

$$\hat{\Gamma}_S P_S(\mathbf{X}_S, t) = -\hat{\mathbf{M}}(\Omega_c)^{tr}\mathbf{D}\hat{\mathbf{M}}(\Omega_c) P_S(\mathbf{X}_S, t) + \int d\mathbf{X}'_S\, [P_S(\mathbf{X}_S, t) W_S(\mathbf{X}_S \rightarrow \mathbf{X}'_S) - P_S(\mathbf{X}'_S, t) W_S(\mathbf{X}'_S \rightarrow \mathbf{X}_S)] \tag{37}$$

without contribution from $\hat{\Gamma}_{solute}$ since it operates on fast variables only. The first term in the r.h.s. of eq 37 derives from the cage rotation operator, eq 11, after elimination of the rotation operator $\hat{\mathbf{M}}(\Omega)$ acting on the relative orientation Ω which belongs to the set of fast variables. The other term is the result of the projection of the master equation for the cage restructuring, with the following reduced kernel for transitions of slow variables

$$W_S(\mathbf{X}_S \rightarrow \mathbf{X}'_S) \equiv W_S(\Omega_c, \omega \rightarrow \Omega'_c, \omega') = \int d\mathbf{X}_F\, d\mathbf{X}'_F\, P(\mathbf{X}_S|\mathbf{X}_F) W(\mathbf{X} \rightarrow \mathbf{X}') = F(\Delta\Omega_c) P(\omega') \int d\Omega\, P(\omega|\Omega) P(\omega'|\Omega') \tag{38}$$

where Ω' is defined as in eq 14. Such a transition kernel does not depend on the individual cage orientations Ω_c and Ω'_c, but on the cage reorientation $\Delta\Omega_c$. Moreover only the dependence on $\Delta\beta_c$ of $\Delta\Omega_c$ is retained if one employs a cage reorientation distribution, eq 21, which is adequate for axial cages. Then, the evolution operator $\hat{\Gamma}_S$ results to be factorized with respect to the Wigner functions of cage orientation specifying the slow observable f_S of eq 34. Indeed, one can demonstrate the following relation for arbitrary functions $g(\omega)$

$$\hat{\Gamma}_S g(\omega) D^j_{m,0}(\Omega_c) = D^j_{m,0}(\Omega_c)[j(j+1) + \hat{\Gamma}_j] g(\omega) \tag{39}$$

where $\hat{\Gamma}_j$ is an integral operator for the librational frequency dependence only

$$\hat{\Gamma}_j g(\omega) = \int d\omega'\, [g(\omega) W_0(\omega \rightarrow \omega') - g(\omega') W_j(\omega' \rightarrow \omega)] \tag{40}$$

with the rate kernel depending on the rank $\boldsymbol{j}$ of the Wigner function

$$W_j(\omega \rightarrow \omega') = \int d\Delta\Omega_c D^j_{0,0}(\Delta\Omega_c) W_S(\Omega_c, \omega \rightarrow \Omega_c, \omega') \tag{41}$$

Correspondingly the orientational dependence of the correlation function is factorized as

$$G^j_S(t) = \exp[-j(j+1)D_\perp t] \int d\omega\, d^j(\omega) \exp(-\hat{\Gamma}_j t) d^j(\omega) P(\omega) \tag{42}$$

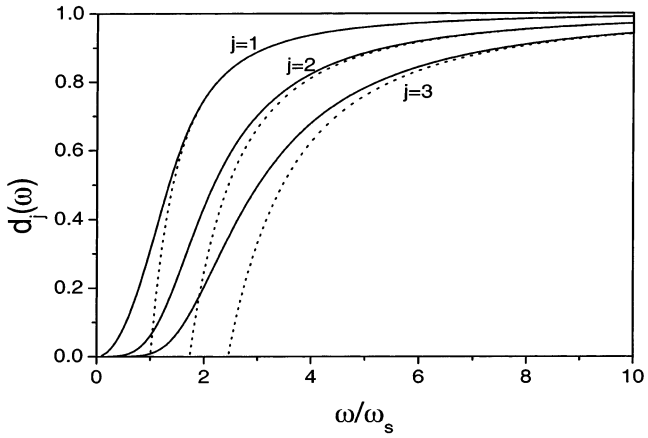

Figure 3. Dependence of coefficients $d^j(\omega)$ on the librational frequency. The asymptotic values, eq 36 (dashed lines), should be compared with the exact values (continuous line) calculated according to definition, eq 35.

The librational frequency contribution to this correlation function can be computed numerically after discretization of the variable ω into a set of equally spaced points.

Let us now disentangle the effects of the two independent mechanisms of cage dynamics (i.e., rotation and restructuring) on the slow component of orientational correlation function when a realistic distribution $\rho(\Delta\beta_c)$ of cage reorientations is employed. A simple situation is recovered when the cage rotation is comparably much faster ($D_\perp \gg w$), since according to eq 42 the cage restructuring bears a negligible contribution

$$G^j_S(t) = \overline{d^j(\omega)^2} \exp[-j(j+1)D_\perp t] \tag{43}$$

and the standard Debye behavior is recovered for the rank dependence of the relaxation times. A more complex situation arises when the cage restructuring contributions in eq 42 have a decay rate w comparable to $D_\perp$. Albeit on a general ground a multiexponential decay is expected, when the librational frequency distribution $P(\omega)$ is not exceedingly large one recovers a nearly single-exponential dependence

$$G^j_S(t) = \overline{d^j(\omega)^2} \exp[-j(j+1)D_\perp t - w_j t] \tag{44}$$

with the rate w_j well approximated by the first moment of $\hat{\Gamma}_j$ with respect to $d^j(\omega)$

$$w_j = \int d\omega\, d^j(\omega) \hat{\Gamma}_j d^j(\omega) P(\omega) / \overline{d^j(\omega)^2} \tag{45}$$

This can be verified by comparison with the full numerical solution of eq 42 shown in Figure 4, where a vanishing diffusion coefficient $D_\perp = 0$ has been employed to display the contribution of cage restructuring only. In Figure 4, and in the following ones, unless otherwise stated, we are employing the standard distribution of cage frequencies with parameters $\bar{\omega}/\omega_s = 4$ and $\sigma_\omega/\omega_s = 2.5$. Notice that at time $t = 0$ the correlation function is not unitary, since the fast relaxation term is still missing. Such a contribution will be analyzed in the next section. However, its weight can be estimated in advance by comparing the initial value of the full correlation function, $G^j(0) = 1$, with that of the slow component only, $G^j_S(0) = \overline{d^j(\omega)^2}$. Their difference is attributed to the fast variable contribution, which tends to vanish in the limit of a distribution $P(\omega)$ with components only for large librational frequencies, i.e., when the solvent generates tight structures around the solute.

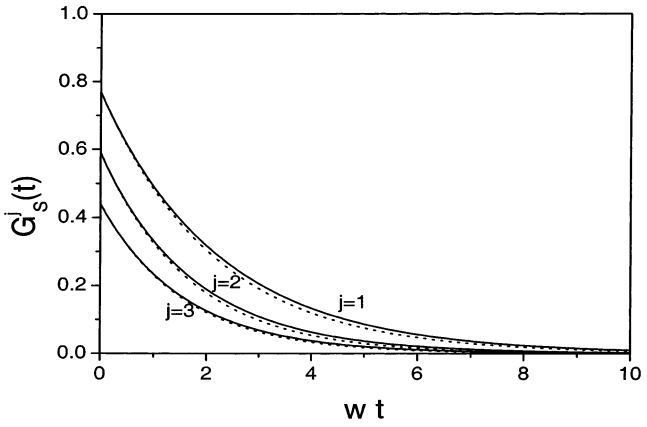

Figure 4. Slow components G_S^j for $D_\perp = 0$, $\overline{\cos\Delta\beta_c} = 0.3$. Continuous lines, numerical solution; dashed lines, approximate solution.

The comparison with the exact results in Figure 4 demonstrates that for the calculation of $G_S^j(t)$, the numerical solution of evolution operator $\hat{\Gamma}_j$ can be substituted by eq 44 with rates w_j evaluated by substitution of eqs 40 and 41 into eq 45. The final relation for w_j, however, is rather cumbersome, so preventing a direct identification of the rank j dependence of the cage restructuring contribution to the orientational correlation function. A simpler analysis can be performed in the limit of a vanishing width of $P(\omega)$, such that the fluctuations of the librational frequency ω have negligible effects. Then one can project out the dependence on ω of $P_S(\mathbf{X}_S, t) = P_S(\Omega_c,\omega, t)$, so obtaining a a reduced distribution on the cage orientation only

$$P_c(\Omega_c, t) = \int d\omega\, P_S(\Omega_c,\omega, t) \tag{46}$$

which is governed by the time evolution equation

$$\frac{\partial}{\partial t} P_c(\Omega_c, t) = -\hat{\Gamma}_c P_c(\Omega_c, t) = -\hat{\mathbf{M}}(\Omega_c)^{tr}\mathbf{D}\hat{\mathbf{M}}(\Omega_c)P_c(\Omega_c, t) + -\int d\Omega_c' \,[P_c(\Omega_c, t)W_c(\Omega_c \rightarrow \Omega_c') - P_c(\Omega_c, t)W_c(\Omega_c' \rightarrow \Omega_c)] \tag{47}$$

The reduced kernel for the transitions is given as

$$W_c(\Omega_c \rightarrow \Omega_c') = \int d\omega\, d\omega'\, W_S(\mathbf{X}_S \rightarrow \mathbf{X}_S') \tag{48}$$

which can be put in the simpler form

$$W_c(\Omega_c \rightarrow \Omega_c') = w\rho(\Delta\Omega_c) \tag{49}$$

with distribution $\rho(\Delta\Omega_c)$ controlling the size of cage reorientations. As a matter of fact, this reduced operator for cage restructuring is equivalent to the Ivanov jump model[15] for the cage frame orientation. The eigenfunction of the reduced operator $\hat{\Gamma}_c$ are simply the Wigner matrixes

$$\hat{\Gamma}_c D^j_{m,0}(\Omega_c) = [j(j+1)D_\perp + w_j]D^j_{m,0}(\Omega_c) \tag{50}$$

with the following explicit relation for the decay rates w_j due to cage restructuring

$$w_j = w[1 - \int d\Delta\, \Omega_c D^j_{0,0}(\Delta\Omega_c)\rho(\Delta\Omega_c)] \tag{51}$$

One recognizes two limiting cases: (i) the isotropic distribution, $\rho(\Delta\Omega_c) = \text{const.}$, when the rates w_j are independent of the rank j

$$w = w_j \tag{52}$$

and (ii) the small step rotation reorientation, $\overline{\cos\Delta\beta_c} \rightarrow 1$, when after an asymptotic expansion about $\Delta\beta_c = 0$ one derives

$$w_j = j(j+1)\frac{1 - \overline{\cos\Delta\beta_c}}{2}w \tag{53}$$

In the latter case, cage restructuring gives rise to a contribution with the same rank dependence of cage rotation, i.e., Debye-like behavior. On the contrary, contributions independent of the rank, as in random jump processes, are recovered in the former case. In Figure 5, we have represented the ratios w_j/w_1 as functions of the order parameter of cage reorientations distribution $\rho(\Delta\beta_c)$. To display the effects of the finite width of the librational frequency distribution, in the same Figure we have represented also the ratios w_j/w_1 with rates derived according to eq 45. Clear differences emerge only in the upper domain of the order parameter $\overline{\cos\Delta\beta_c}$, whereas in the opposite situation, the rates w_j tend to be independent of rank j. This latter case appears to be appropriate for normal liquids as long as cage reorientations of significant sizes are expected. Correspondingly, the rank dependence of the orientational relaxation (at long times) might deviate from the simple diffusion law, and the experimental observation of non-Debye behavior[16] can be interpreted as an effect of cage restructuring. However, this particular manifestation of cage restructuring processes requires that its rate is not too slow with respect to cage rotations. To illustrate this point, in Figure 6, we have plotted the relaxation times τ_j of different ranks j scaled by that of first rank τ_1 as functions of the ratio of rates $w/D_\perp$ of the two independent processes. These relaxation times are taken as time integral of the slow component of the orientational correlation function normalized with respect to its initial value

$$\tau_j = \int_0^\infty dt\, G_S^j(t)/G_S^j(0) \tag{54}$$

so that $1/\tau_j = j(j+1)D_\perp + w_j$ if eq 41 is adopted. When the cage restructuring is slow (i.e., $w < D_\perp/10$), the cage rotation process dominates in the orientation correlation functions with the Debye rank dependence. Significant deviations from the diffusion behavior emerge when the two processes have a comparable time scale, whereas if $w \gg D_\perp$, the relaxation times tend to be substantially independent of the rank, like in random jump processes.

IV. Fast Librational Motions

In the hypothesis that a well-defined separation exists between the time scales of cage dynamics and of solute librational motions, the evolution of fast variables $\mathbf{X}_F$ can be analyzed separately.[6] First one isolates from the full time evolution operator the part $\hat{\Gamma}_F$ which operates on the fast variables only. In the following we assume that

$$\hat{\Gamma}_F \equiv \hat{\Gamma}_{\text{solute}} \tag{55}$$

by neglecting contributions related to the cage, like the terms of $\hat{\Gamma}_{\text{cage rot}}$ in eq 11 acting on Ω. The separation of motions justifies such an approximation, as long as it requires the condition $|\hat{\Gamma}_{\text{solute}}| \gg |\hat{\Gamma}_{\text{cage rot}} + \hat{\Gamma}_{\text{cage rest}}|$ for their typical rates. However, eq 55 breaks down when friction ξ vanishes, and a purely conservative dynamics is described by $\hat{\Gamma}_{\text{solute}}$ without any relaxation to equilibrium. Then the cage-related terms become the main source of relaxation also for the probe coordinates,

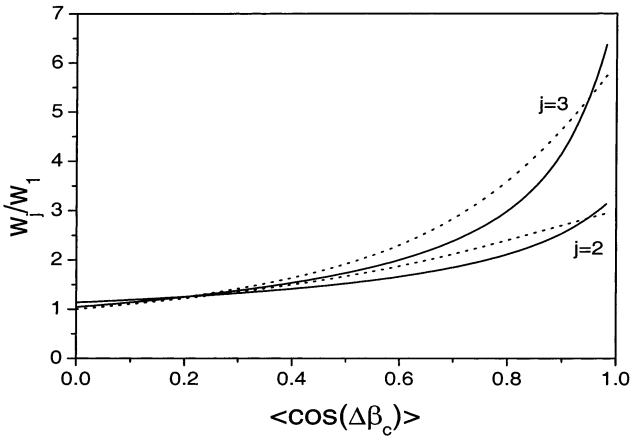

Figure 5. Ratios w_j/w_1 of the rank dependent rates for cage restructuring. Dashed lines: approximation for $P(\omega)$ of vanishing width; continuous line: exact form.

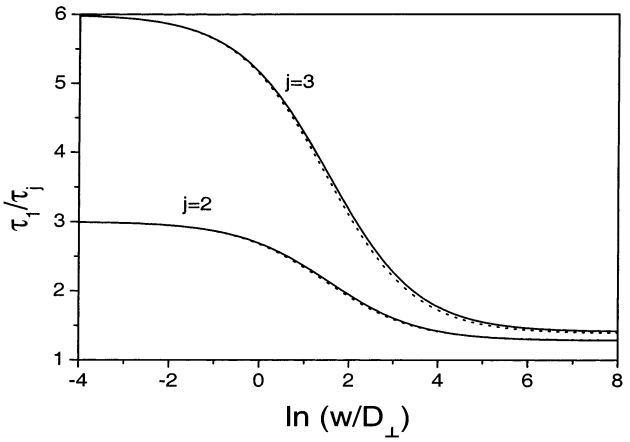

Figure 6. Relaxation times τ_j/τ_1 of the slow component of the orientational correlation function for $\overline{\cos\Delta\beta_c} = 0.3$. The numerical solution (continuous lines) and the approximate solution (dashed lines) are compared.

and their contribution cannot be neglected in $\hat{\Gamma}_F$. Therefore, approximation (55) is legitimate when the relaxation of fast variables is driven mainly by the frictional operator, that is if

$$1/\tau_c \gg D_\perp, w \tag{56}$$

where $1/\tau_c$ is the typical rate for the collisional part of $\hat{\Gamma}_{solute}$, and the typical rate of cage rotations and cage restructuring are estimated according to parameters $D_\perp$ and w, respectively.

Hereafter, we shall take for granted the condition of eq 56, by calculating nonequilibrium distributions on the fast variables according to eq 55. It should be emphasized that $\hat{\Gamma}_F$ operates on the $\mathbf{X}_F$ variables, but it keeps a parametric dependence on the slow variables, in particular on the librational frequency ω which determines the strength of the cage potential. Hence the conditional probability of $\mathbf{X}_F$ at time t with initial condition $\mathbf{X}_F^0$ at $t = 0$, with the time evolution determined by $\hat{\Gamma}_F$, depends also on the value of $\mathbf{X}_S$[6]

$$P(\mathbf{X}_S,\mathbf{X}_F^0|\mathbf{X}_F, t) = \exp(-\hat{\Gamma}_F t)\delta(\mathbf{X}_F - \mathbf{X}_F^0) \tag{57}$$

At asymptotically long times, the conditional probability is equal to the stationary distribution of $\mathbf{X}_F$ conditioned by $\mathbf{X}_S$

$$\lim_{t\to\infty} P(\mathbf{X}_S,\mathbf{X}_F^0|\mathbf{X}_F, t) = P(\mathbf{X}_S|\mathbf{X}_F) \tag{58}$$

Separation of fast and slow process is performed by employing the following approximation for the overall conditional probability

$$P(\mathbf{X}^0|\mathbf{X}, t) \approx \delta(\mathbf{X}_S - \mathbf{X}_S^0)[P(\mathbf{X}_S,\mathbf{X}_F^0|\mathbf{X}_F, t) - P(\mathbf{X}_S|\mathbf{X}_F)] + P(\mathbf{X}_S|\mathbf{X}_F)P(\mathbf{X}_S^0|\mathbf{X}_S, t) \tag{59}$$

where $P(\mathbf{X}_S^0|\mathbf{X}_S, t)$ is the conditional probability for the slow variables only to be derived as a solution of eq 29. The first term of the r.h.s. of eq 59 describes the relaxation of fast variables when the slow one are still frozen in correspondence of their initial value $\mathbf{X}_S^0$. Let us consider a time t^* which represent a time scale intermediate between those of the fast and slow motions. At such time, eq 59 is simplified as

$$P(\mathbf{X}^0|\mathbf{X}, t^*) \approx \delta(\mathbf{X}_S - \mathbf{X}_S^0)P(\mathbf{X}_S|\mathbf{X}_F) \tag{60}$$

that is the slow variables have still their initial value, whereas the conditional equilibrium distribution is recovered for the fast variables. At later times, the relaxation of slow variables becomes operative according to the second term of the r.h.s. of eq 59. Within this longer time scale the fast variables are always characterized by an equilibrium distribution $P(\mathbf{X}_S|\mathbf{X}_F)$ conditioned by the value of $\mathbf{X}_S$.

When calculating a generic autocorrelation function for an observable $f(\mathbf{X})$ according to eq 59, two different contributions are identified

$$G(t) = G_S(t) + G_F(t) \tag{61}$$

where $G_S(t)$ is the slow component already discussed in section 3. The time dependence of fast relaxing $G_F(t)$ is determined by operator $\hat{\Gamma}_F$ according to the expression

$$G_F(t) = \int d\mathbf{X}_S\, P_S(\mathbf{X}_S)\int d\mathbf{X}_F\, \delta f(\mathbf{X})^* \exp(-\hat{\Gamma}_F t)\delta f(\mathbf{X})P(\mathbf{X}_S|\mathbf{X}_F) \tag{62}$$

where $\delta f(\mathbf{X})$ is the observable devoid of its slow component $f_S(\mathbf{X}_S)$ provided by eq 31

$$\delta f(\mathbf{X}) = f(\mathbf{X}) - f_S(\mathbf{X}_S) \tag{63}$$

Notice that, because of eq 58, $G_F(t)$ vanishes outside the time window for the relaxation of fast variables.

It should be emphasized that, besides the previous phenomenological justification, a formal derivation of eqs 61 and 62 is possible by applying an adiabatic treatment to the initial stochastic operator $\hat{\Gamma}$, as shown in Appendix B of ref 6.

Following the same line of analysis employed in the previous section for the slow components of correlation functions, we proceed here by presenting an exact solution for the fast components and next obtaining approximate solutions. By taking into account the parametric dependence of $\hat{\Gamma}_F$ on the slow variables, eq 62 can be written as an average of $\mathbf{X}_S$ dependent elementary correlation functions defined in the $\mathbf{X}_F$ functional space. In the case of solute orientation observables, eq 33, one finds

$$\delta f = \sum_l D^j_{m,l}(\Omega_c)\delta D^j_{l,0}(\Omega) \tag{64}$$

where the ω dependence has been left implicit in the functions $\delta D^j_{k,0}(\Omega) \equiv D^j_{k,0}(\Omega) - d^j(\omega)\delta_{k,0}$. Therefore, the fast component of probe orientation correlation functions is obtained in the following form:

$$G_F^j(t) = (2j+1)\int d\omega\, P(\omega) \sum_l \int d\Omega L\, dL\, \delta D_{l,0}^j(\Omega)^* \exp(-\hat{\Gamma}_F t)\delta D_{l,0}^j(\Omega) P(\omega|\Omega, L) \quad (65)$$

where integration on the cage orientation has been performed analytically. In a similar way, an explicit form is derived for the correlation function of the angular momentum, which is devoid of a slow component

$$G^L(t) = G_F^L(t) = \frac{1}{4Ik_BT}\int d\omega\, P(\omega)\sum_l \int d\Omega L\, dL \times [\sum_{k\neq 0} D_{l,k}^{\ 1}(\Omega)^*]L \exp(-\hat{\Gamma}_F t)L[\sum_{k'\neq 0} D_{l,k'}^{\ 1}(\Omega)^*]P(\omega|\Omega, L) \quad (66)$$

Because of the torques deriving from the cage potential, no general analytical solution for the fast component of the correlation functions is available. A numerical estimate can be obtained by employing standard linear algebra methods, that is by generating the matrix representation of the operator in the following set of basis functions

$$|N\rangle = |J, M, K, n\rangle = D_{M,K}^J(\Omega)(L^2/2Ik_BT)^{|K|/2}\mathcal{L}_n^{|K|}(L^2/2Ik_BT)P(\omega|\Omega, L) \quad (67)$$

$$\langle N| = \langle J, M, K, n| = D_{M,K}^J(\Omega)^*(L^2/2Ik_BT)^{|K|/2}\mathcal{L}_n^{|K|}(L^2/2Ik_BT) \quad (68)$$

where N is a cumulative short-hand index for (J, M, K, n) and $\mathcal{L}_n^k(x)$ is the Laguerre polynomial of order k and degree n of argument x. These functions have been chosen by taking into account that their L functional part constitutes an eigenfunction of the collisional operator[11] and that the equilibrium distribution factor $P(\omega|\Omega, L)$ reproduces the correct localization about $\beta = 0$ of the angular dependence of the solutions of $\hat{\Gamma}_F$.[12] On the other hand these functions are *not* orthogonal with respect to the scalar product

$$\langle ... \rangle = \int d\mathbf{X}_F ... \quad (69)$$

because of the angular dependence of $P(\omega|\Omega, L)$. Thus, the numerical calculations require both the overlap matrix S and the matrix representation Γ of $\hat{\Gamma}_F$

$$S_{N,N'} = \langle N|N'\rangle, \quad \Gamma_{N,N'} = \langle N|\hat{\Gamma}_F|N'\rangle \quad (70)$$

whose elements are easily evaluated. Finally, for a generic function $f(\mathbf{X}_F)$, the correlation function derived from $\hat{\Gamma}_F$ is obtained as

$$G(\omega, t) = \overline{f[\mathbf{X}_F(0)]^* f[\mathbf{X}_F(t)]} = \mathbf{f}^\dagger \mathbf{S} \exp(-\mathbf{S}^{-1}\Gamma t)\mathbf{f} \quad (71)$$

where vector f is derived from the projection coefficients of $f(\mathbf{X}_F)$ on the basis functions

$$f(\mathbf{X}_F)^* = \sum_N \langle N| f_N^* \quad (72)$$

Function $G(\omega, t)$ is then integrated with respect to ω with weight $P(\omega)$ in eqs 65 or 66. The matrix elements for the overlap matrix and the time evolution operator are reported here for completeness. The generic overlap matrix element is

$$S_{N,N'} = \frac{(n+|K|)!\overline{D_{M,K}^{J*} D_{M,K}^{J'}}(\omega)}{n!}\delta_{M,M'}\delta_{K,K'}\delta_{n,n'} \quad (73)$$

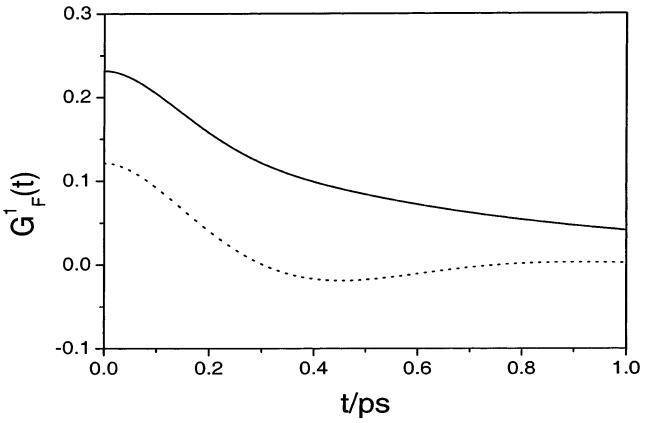

Figure 7. Fast component of first rank rotational correlation function $G_F^1(t)$ obtained via numerically exact matrix representation, for a wide distribution, $\sigma_\omega = 5$ ps^{-1} (continuous line) and sharp distribution, $\sigma_\omega = 0.1$ ps^{-1} (dashed line) of cage frequencies.

where the average $\bar{f}(\omega)$ of a generic function $f(\Omega)$ is defined with respect to the reduced distribution in Ω

$$\bar{f}(\omega) = \int d\Omega\, f(\Omega) \exp[-V_c(\Omega,\omega)/k_BT] / \int d\Omega \exp[-V_c(\Omega,\omega)/k_BT] \quad (74)$$

The matrix element of the time evolution operator is

$$\Gamma_{N,N'} = \frac{(2n+|K|)S_{N,N'}}{\tau_c} + \frac{\omega_S \gamma_{N,N'}}{2}\delta_{M,M'} \quad (75)$$

The reduced matrix element $\gamma_{N,N'}$ is calculated from the streaming part of the solute operator

$$\gamma_{N,N'} = \pm\delta_{K'-K,\pm 1}[c_{JK}^{\pm}\overline{D_{M,K'}^{J*} D_{M,K'}^{J'}}(\omega)a_{nK}^{\pm} + \sqrt{2}(\omega_j^2/\omega_s^2)D_{M,K}^{J*} D_{0,\mp 1}^{\ 1} D_{M,K\pm 1}^{J'}(\omega)b_{nK}^{\pm}] \quad (76)$$

where

$$c_{JK}^{\pm} = \sqrt{J(J+1) - K(K+1)}$$

and $a_{nK}^{\pm}$ and $b_{nK}^{\pm}$ are defined as

$$a_{nK}^{\pm} = \begin{cases} \sqrt{2}(n+|K|)!/n!(\delta_{n,n'} - \delta_{n,n'-1}) \\ \sqrt{2}(n'+|K|+1)!/n'!(\delta_{n,n'} - \delta_{n,n'+1}) \end{cases} \quad (77)$$

$$b_{nK}^{\pm} = \begin{cases} -\sqrt{2}(n+|K|)!/n!\delta_{n,n'} \\ \sqrt{(n'+|K|+1)!/n'!}\delta_{n,n'+1} \end{cases} \quad (78)$$

where the first expression holds for $K \geq 1$ for a_{nk}^- and b_{nK}^- and $K \leq -1$ for a_{nk}^+ and b_{nK}^+. Notice that due to the axial nature of the cage the M quantum number is diagonal. Finally, the vector element f_N is simply $\delta_{J,j}\delta_{K,0}\delta_{n,0}$ for the (unnormalized) rotational correlation function and $\delta_{J,1}(\delta_{M,0} + \delta_{|M|,1})\delta_{|K|,1}\delta_{n,0}$ for the (unnormalized) momentum correlation function. Few basis functions are needed to reach convergence. The following set of parameters has been chosen: $\omega_s = 2$ ps^{-1}, $1/\tau_c = 8$ ps^{-1}, and $P(\omega)$ as defined above. Correlation functions have been calculated up to the 4th decimal figure with truncations at values $J = 3$ and $n = 2$, resulting in 147 basis functions. A direct diagonalization of $\mathbf{S}^{-1}\Gamma$ is then feasible. In Figure 7, the fast component of the first rank rotational correlation function is

shown, obtained via numerically exact solution, for the same set of parameters adopted in section III. The smooth decay of the fast component shown in Figure 7 is a direct consequence of the averaging of oscillatory components in different cages: for comparison, in the same figure, the fast component is shown for the case of $P(\omega)$ with a small but finite value of $\sigma_\omega = 0.1$ ps^{-1}, for which only cages with frequency close to $\langle\omega\rangle$ contribute significantly.

Analytical approximations can be recovered for fast components of correlation functions, at a given cage frequency, $G(\omega, t)$, in the case of large cage potential, $\omega > \omega_s$. This condition is verified for most molecular liquids for which we can estimate that $P(\omega)$ is centered on frequencies 5−6 times larger than ω_s.[5] A large cage potential implies that the solute undergoes librations within a small range of orientations with respect to the z axis of the cage frame. As a consequence, it is natural to employ as effective coordinates

$$\mathbf{q} = \begin{cases} q_x = \cos\alpha \sin\beta \\ q_y = \sin\alpha \sin\beta \end{cases} \tag{79}$$

and their associated momenta, which can be expressed directly as functions of L and Ω

$$\mathbf{p} = \begin{cases} p_x = (\cos\alpha \cos\beta \sin\gamma + \sin\alpha \cos\gamma)L \\ p_y = (\sin\alpha \cos\beta \sin\gamma - \cos\alpha \cos\gamma)L \end{cases} \tag{80}$$

In the limit of small values of β angle, corresponding to small fluctuations around the z axis of the cage frame, the solute is approximately represented by the set of degenerate harmonic coordinates and momenta (q_x, p_x) and (q_y, p_y). For each oscillator, the equilibrium distribution $P(q, p)$ is defined with respect to the following total energy

$$H = \frac{I\omega^2}{2}q^2 + \frac{1}{2I}p^2 \tag{81}$$

where $q = q_x$ or q_y, $p = p_x$ or p_y, and the following time evolution operator, which is obtained by performing in $\hat{\Gamma}_{\text{solute}}$, eq 10, the change to variables defined by eqs 79 and 80, in the limit $\cos\beta \rightarrow 1$

$$\hat{\Gamma}_{\text{libr}} = \frac{p}{I}\frac{\partial}{\partial q} - I\omega^2 q\partial/\partial p - \xi k_B T \frac{\partial}{\partial p}\left(\frac{\partial}{\partial p} + \frac{p}{Ik_B T}\right) \tag{82}$$

To summarize, in the limit of strongly confining potential the solute is described by two librational normal modes, which relax independently; their time evolution is governed by the standard Fokker−Planck operator for Brownian oscillator.[13] The fast component for rotational observables can now be calculated approximately as follow: by expanding Wigner functions $D^j_{0,0}(\Omega)$ around $q_x = 0$ and $q_y = 0$ and keeping terms up to first order in q_x, q_y, the following asymptotic expression is obtained:

$$G^j_{\text{libr}}(\omega, t) = [1 - d^j(\omega)^2]\int \mathrm{d}q\, \mathrm{d}p\, q \exp(-\hat{\Gamma}_{\text{libr}}t)\, q\, P(q, p) = [1 - d^j(\omega)^2]g_q(\omega, t) \tag{83}$$

the factor $1 - d^j(\omega)^2$ is included to recover the correct dependence at time $t = 0$. Function $g_q(\omega, t)$ can be obtained in closed form[5]

$$g_q(\omega, t) = -\frac{\omega_-}{\omega_+ - \omega_-}e^{-\omega_+ t} + \frac{\omega_+}{\omega_+ - \omega_-}e^{-\omega_- t} \tag{84}$$

where $\omega_\pm$ are the decay frequencies of orientational libration of a linear solute in the limit of large cage potential, which are independent from rank j

$$\omega_\pm = 1/2\tau_c \pm \sqrt{1/4\tau_c^2 - \omega^2} \tag{85}$$

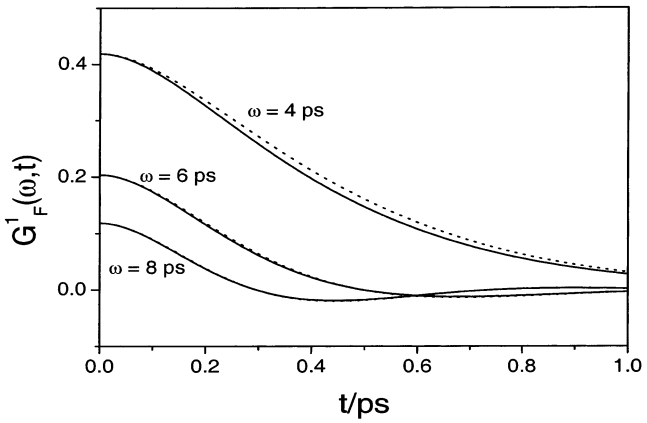

Figure 8. Fast component of first rank rotational correlation function at fixed cage, obtained via numerically exact matrix representation, $G^1_F(\omega, t)$ (continuous lines) and asymptotic approximation, $G^1_{\text{libr}}(\omega, t)$ (dashed lines).

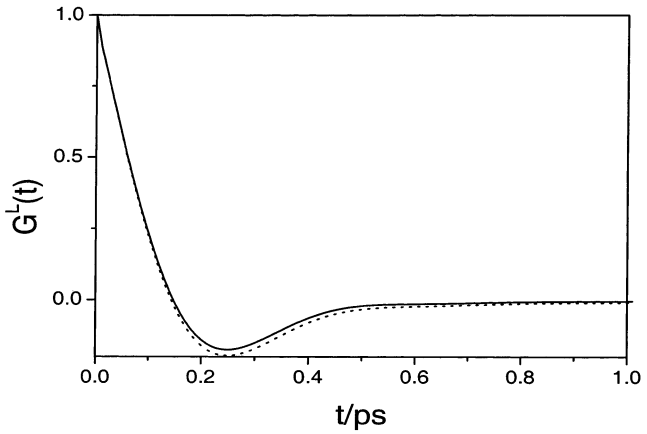

Figure 9. Angular momentum correlation function $G^L(t)$ obtained via numerically exact matrix representation, for a wide distribution, $\sigma_\omega = 5$ ps^{-1} (continuous line) and sharp distribution, $\sigma_\omega = 0.1$ ps^{-1} (dashed lines) of cage frequencies.

In Figure 8, the exact $G^j_F(\omega, t)$ and the asymptotic $G^j_{\text{libr}}(\omega, t)$ rotational correlation function are compared for different values of ω. The agreement is, as expected, satisfactory, albeit an increasing discrepancy is observed for decreasing values of ω, since to the validity of eqs 83 and 84 is limited to values of ω at least comparable to ω_s.

Finally, the same methodology can be applied to the calculation of the momentum correlation function. Although the angular momentum relaxation can be only indirectly related to spectroscopical observables, it is nevertheless a relevant tool for probing, for instance in MD simulations, the short time or inertial behavior of a solute. The characteristic presence of negative lobes is attributed on a physical ground to angular velocity reversal resulting from collisions with solvent molecules.[17] In the LSCM, the angular momentum is affected by librations within the cage, which are weighted by $P(\omega)$ and are independent from long time cage restructuring and rotation in the Born−Oppenheimer approximation. In Figure 9, we have plotted the momentum correlation function as obtained from the numerically exact solution: the large amplitude oscillations observed for the sharp distribution case are smeared out in the

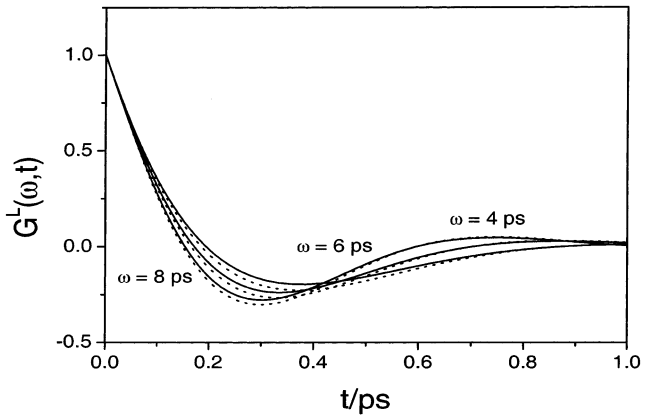

Figure 10. Angular momentum correlation function function at fixed cage, obtained via numerically exact matrix representation, $G^L_F(\omega, t)$ (continuous lines) and asymptotic approximation, $G^L_{libr}(\omega, t)$ (dashed lines).

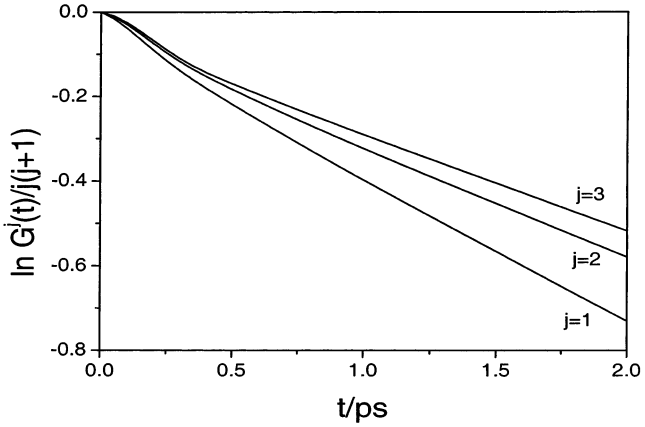

Figure 11. Plots of orientational correlation functions, $G^j(t) = G^j_S(t) + G^j_F(t)$, scaled to emphasize deviations from simple rotational diffusion model.

case of the broad distribution. The librational approximation can be easily extended to the case of momentum, and it provides for a given value of the cage frequency ω the following expression:

$$G^L_{libr}(\omega, t) = \int \mathrm{d}q\, \mathrm{d}p\, p \exp(-\hat{\Gamma}_{libr} t)\, p\, P(q, p) = g_p(\omega, t) \tag{86}$$

where function $g_p(\omega, t)$ is

$$g_p(\omega, t) = \frac{\omega_+}{\omega_+ - \omega_-} \mathrm{e}^{-\omega_+ t} - \frac{\omega_-}{\omega_+ - \omega_-} \mathrm{e}^{-\omega_- t} \tag{87}$$

Figure 10 shows the comparison between exact and approximate solution for the momentum correlation functions: the agreement is very satisfactory, even in the case of broad distribution of cage frequencies.

V. Discussion

The main purpose of this work was to elaborate simple approximations for the orientational correlation functions on the basis of a complex representation like the LSCM able to describe the main mechanisms of molecular relaxation in liquids, notably the probe librational motion within the cage, the cage rotation, and cage restructuring. By applying a Born−Oppenheimer type procedure justified by the separation on the time scale between the fast probe motions within the cage, and the slow cage relaxation processes, a correlation function is decomposed into the two corresponding independent contributions.

The fast decaying term is controlled by librational type motions of the probe within the confining potential generated by the solvent cage. In the harmonic approximation, simple analytical expressions are derived in analogy to a Brownian oscillator model. An important feature is due to the inhomogeneous character of the cage in liquids leading to a distribution of librational frequencies, which determines a complex time dependence, but independent from the rank j of the probed orientational function.

The slow branch of the correlation function derives from both the cage rotation and the cage restructuring process. The former leads to a diffusional (Debye-like) long time dependence with the $j(j + 1)$ scaling factor with respect the rank j, whereas the contribution of the latter brings a weaker dependence upon the rank j. Therefore, the rank dependence of the long time behavior of the correlation functions is determined by the relative rates of these two processes. In particular, if the cage restructuring is very slow, a Debye-like behavior is recovered. On the opposite case of cage restructuring faster than cage diffusion, a rank-independent decay is found like in strong collision mechanisms.

It should be emphasized that the basic assumption of a separation of time-scales between cage degrees of freedom and probe variables, which is taken for granted throughout this paper, should be considered a convenient approximation, able to describe at a low computational price the overall behavior of the system. However, the accuracy of such an approach can be estimated only via a direct comparison with computationally exact treatments of the model.[7] Previous studies carried on for the case of the spherical cage model[6] have shown that the general accordance between the approximate Born−Oppenheimer treatment and the numerically exact solution is rather good, provided that the characteristic decay times of the cage-related variables are at least 1 order of magnitude larger than the corresponding probe-related parameters. Notice that a broad cage frequency distribution $P(\omega)$, which has been observed in MD simulations of simple molecular liquids[5] does not appear to play such a crucial role in invalidating the correctness of the Born−Oppenheimer approximation. In fact, the contribution of slow probe librations, implied by the presence of shallow cages, is relatively small and does not affect significantly most correlation functions, at least in the range of parameters we have explored.

Nevertheless, in a quantitative comparison of the model predictions with actual experimental evidences, an exact solution of the cage model might be preferable to account for intermediate relaxation processes, which cannot be reproduced by the simple Born−Oppenheimer approach. On a more fundamental basis, our model has been limited to rotational probe and cage degrees of freedom: for interpreting spectroscopic techniques sensitive to the subpicosecond time-scale, the explicit description of translational degrees of freedom might be necessary.[4,5]

As a typical result of the theory, in Figure 11, we show the orientational correlation function of different ranks, as obtained by including both the fast and the slow components according to eq 61, with the standard distribution $P(\omega)$ of cage frequencies and the following set of dynamical parameters: $\omega_s = 2$ ps^{-1}, $1/\tau_c = 8$ ps^{-1}, $D_\perp = 0.2$ ps^{-1}, $w = 0.5$ ps^{-1}. In this figure, a logarithm scale has been employed for the correlation functions, with the $1/j(j + 1)$ scaling factor in order to show the departures from Debye-like behavior. The significant deviation from the diffusional behavior is due to the use of comparable values of

$D_\perp$ and w. Nearly coincident slopes in this type of diagram are obtained when $w \ll D_\perp$. This figure clearly displays also the short time decay due to the librational motions.

We think that this methodology, particularly in its simpler implementations, could provide an efficient tool for a global interpretation of spectroscopic measurements covering both the low frequency domain (magnetic resonance, for instance) and the fast time scale like in the modern developments of optical spectroscopies with pulsed techniques.

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