

Rotational dynamics of axially symmetric solutes in isotropic solvents. II. The stochastic model

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In paper I of this series, a molecular dynamics (MD) study of liquid chlorine was performed, and it includes the definition and observation of operational cage variables. These cage variables were used to describe the local environment of a rotating axially symmetric molecule, or probe. Probe and cage properties of interest, such as rotational correlation functions and momentum correlation functions, were computed, together with an effective distribution of librational cage frequencies. In the second part of this work, we develop a stochastic model which includes the relevant elementary relaxation processes previously identified by the MD study. This stochastic model is based upon a multi-dimensional Fokker–Planck equation for the coupled dynamics of the probe and cage orientations, the angular momentum of the probe, and the librational frequencies for the probe in the cage. Semi-analytical approximations, based upon a “Born–Oppenheimer”-type separability of fast and slow variables, are used in order to calculate probe and cage correlation functions, and they are found to be in reasonable agreement with the MD results. In an appendix the Born–Oppenheimer approximation for stochastic operators is developed. © 1996 American Institute of Physics. [S0021-9606(96)01203-5]

I. INTRODUCTION

In a previous work (Ref. 1 hereafter denoted as paper I), a Molecular Dynamics (MD) simulation of liquid chlorine has been performed in order to characterize the solvent cage confining a solute. The method employed was a generalization to molecular systems of the procedure originally applied to atomic liquids.² In order to introduce operational definitions of cage properties which can be extracted from a MD simulation, the interaction potential between the solute and the solvent (a probe molecule and the rest of the sample, respectively, when considering pure liquids) is considered as a function of the solute coordinates for a given solvent configuration sampled during the simulation. The parametrization of such a cage potential, through its curvatures and the location of its minimum, provides an ensemble of parameters which can be easily determined during the MD simulation and which describe the effects on the solute of the surrounding solvent cage.

As shown in paper I, a general analysis of the cage potential can be performed for axially symmetric solutes, by including both translational and rotational coordinates, but it leads to a very large set of cage parameters whose interpretation in terms of solute–solvent interactions is difficult. Therefore, a reduced form of the cage potential was derived in paper I under the assumption that probe translations within the cage are dynamically uncoupled, at least approximately,

to the probe rotations because of their short time scale. In this way only the following parameters are required to describe the rotational effects of the solvent cage: the cage frequencies $\omega \equiv (\omega_x, \omega_y)$ and the orientation $\Omega^c \equiv (\alpha^c, \beta^c, \gamma^c)$ of the cage frame. The two cage frequencies ω_x and ω_y determine the independent frequencies for the librational motion of the probe in the presence of the confining potential due to the surrounding molecules, and therefore their magnitude measures the strength of solute–solvent interactions. The z -axis of the cage frame determines the probe’s stationary orientation for a fixed cage configuration, while the x - and y -axes are fixed along the principal directions of probe librational motions. The probe motion would then be represented by the superposition of fast librational fluctuations about the equilibrium configuration described by Ω^c , and a slower rotational diffusion driven by reorientations of the cage frame, in agreement with a picture proposed by Hill.³

Given the operational character of our definition of cage parameters, their evolution can be followed during a MD simulation with the opportunity of deriving detailed information about the distribution and the relaxation times of the cage parameters. This has been done in paper I for liquid chlorine near the triple point, thereby recovering for this specific system the statistical distribution of the librational frequencies and the relaxation times of both probe and cage variables from the corresponding time correlation functions. As expected, a time scale separation exists between the fast librational processes within the cage (as revealed by correlation functions of the probe angular momentum and of the

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probe relative orientation with respect to the cage frame) and the slower evolution of both the cage orientation and the cage frequencies, with the rotation of the principal librational axes around the z -direction of the cage frame in the intermediate range.

In this work, we intend to develop a theoretical model for the probe rotational dynamics coupled to the solvent cage. In the past this problem has been tackled from different points of view (see Sec. I of paper I for a review). Our method is based on a Markovian representation which includes explicitly both the probe degrees of freedom and the cage parameters as independent stochastic variables.^{4,5} A Fokker–Planck (FP) equation will be defined for the ensemble of these independent variables, by using the MD results as a guideline for the choice of the equilibrium distribution and of the transport coefficients. A similar procedure has been applied to liquid argon with a satisfactory agreement when compared with the correlation functions of the MD simulation.⁶ Here we shall examine specifically the solute-cage rotational problem on the basis of information derived in paper I from the MD simulation of liquid chlorine.

Given the complexity of the problem, with the interference of several relaxation mechanisms, a detailed representation of all the features of the MD simulation is not possible. A more reasonable objective is the representation of the most important features of the solute-cage dynamical coupling by means of a simple enough model to allow a transparent description of the underlying physical processes. For instance, the MD simulation of liquid chlorine has shown that cage frequencies have a complex dynamics with superimposed fast and slow decay processes. To account for this behavior in paper I, we have separated the fast and slow components of the overall cage frequencies. In principle both of these parameters should be considered as independent variables to be treated on an equal footing, in order to fully reproduce the MD correlation functions. But this would require an enlarged set of independent variables with a too complex theoretical model to permit reasonably accurate predictions. Therefore, we shall treat explicitly only the slow components of the cage frequencies, which are essential to describe the long time behavior of the system, while their fast fluctuating parts are included among the processes leading to frictional dissipation.

Even if the stochastic model in its essential form is developed with a proper choice of the independent variables, its solution for the calculation of the relevant correlation functions would still be a formidable task because of the intrinsic couplings between a large number of variables. No exact analytical solutions are available and also complete numerical solutions are not realistic because of the huge matrices that would be required. The only reasonable way to tackle the problem is to benefit from the time scale separation between different variables in order to derive reasonably accurate approximations. We shall employ a specific technique based on the Born–Oppenheimer (BO) approximation often applied to quantum mechanical problems. By properly adapting the BO approximation to stochastic operators, an efficient method is derived for separating the effects of fast

and slow relaxation processes in the correlation functions. Given the generality of this approach, we expect it might also be useful in the study of other stochastic problems.

In Sec. II, the Fokker–Planck equation is introduced for the solute-cage rotational problem by isolating the contribution of each independent relaxation mechanism. Particular care is taken in the derivation of a compact representation of the time evolution operator, which should allow straightforward formal manipulations, for example when a change of variables is required. In the following sections the FP model is analyzed in order to derive the correlation functions of interest by employing the BO approximation whose general application to stochastic operators is described in Appendix B. The relaxation behavior of the slow cage variables is analyzed in Section III on the basis of the projected evolution operator which allows straightforward calculations of correlation functions for the cage orientation and for the librational frequencies. The analysis of the dynamics of the fast variables, like the probe angular momentum, is performed in Section IV by using an asymptotic technique justified by the strength of the cage potential. The probe orientational correlation functions are then reconstructed by superimposing both the fast and the slow components. The general conclusions of this work are finally presented in Section V.

II. STOCHASTIC MODEL FOR SOLUTE AND CAGE DYNAMICS

As shown in paper I, a general picture of the evolution of both cage and probe variables can be obtained from MD simulations. The next step is the formulation of a stochastic model for the dynamics of these variables, with the objective of analyzing the solute rotational motion and its coupling with the cage dynamics. The required information is provided by correlation functions from a MD simulation, which allows one to identify the time scales of the independent relaxation mechanisms. Considerable freedom still exists in choosing a particular model for the time evolution operator. Highly accurate representations would require complex models with a large set of independent parameters to be optimized (that is transport coefficients mainly, since the equilibrium distribution can be obtained directly from MD simulations, cf. paper I). On the other hand, given the intrinsic complexity of the problem to be analyzed, a primary objective of any theoretical description should be the identification of the contribution of each elementary process to the relaxation of the relevant observables. This calls for simple models in order to allow semi-analytical calculation of the correlation functions. In the present theory we have attempted to balance these opposite requisites.

In the definition of the stochastic model it is convenient to use the following set of independent variables (following the same notation of paper I):

$$\mathbf{Y} \equiv (\boldsymbol{\Omega}^o, \mathbf{L}, \boldsymbol{\Omega}^c, \boldsymbol{\omega}) \quad (1)$$

since it allows a straightforward identification of the independent contributions to the time evolution operator. The sets of Euler angles $\boldsymbol{\Omega}^c \equiv (\alpha^c, \beta^c, \gamma^c)$ and $\boldsymbol{\Omega}^o \equiv (\alpha^o, \beta^o, \gamma^o)$ de-

scribe the orientation of the cage frame (CF) and of the probe molecule, respectively, with respect to the laboratory frame (LF), while \mathbf{L} is the angular momentum of the probe with components in the molecular frame (MF) of the solute. In order to describe the fluctuations in the strength of solute-solvent interactions, we have included also the two independent librational frequencies of the cage, which are denoted by $\boldsymbol{\omega}=(\omega_x, \omega_y)$. We recall that in the MD simulation of paper I, we have identified both fast and slow fluctuating components of these librational frequencies, which must be treated separately because of the different time scales. Whereas a more general theory should include both these components, we will consider explicitly only the slower ones in order to minimize the set of independent variables. On the other hand, only these librational frequencies are essential to account for the long time behavior of the system. Hereafter, ω_i with $i=x, y$ will denote the slow components of the librational frequencies (or cage frequencies), which are characterized by the same distribution function $P(\omega_i)$ because of their statistical equivalence.

An important ingredient of the problem is the interaction potential between solute and solvent. As shown in paper I, it can be represented by a cage potential $V_c(\boldsymbol{\Omega}, \boldsymbol{\omega})$ which depends explicitly on the molecular orientation $\boldsymbol{\Omega}=(\alpha, \beta, \gamma)$ with respect to the cage frame, and on the set $\boldsymbol{\omega}$ of librational frequencies describing the strength of solute-solvent interactions for a given configuration of the solvent cage. In paper I we have discussed in detail the procedures for deriving from MD data the cage potential and its parametrized forms. For the moment we do not choose a particular cage potential, since we intend to introduce the stochastic model in a rather general framework. For a given cage potential, the equilibrium distribution is derived as

$$P(\mathbf{Y}) = \frac{\exp\{-[\mathbf{L}^t \mathbf{I}^{-1} \mathbf{L}/2 + V_c(\boldsymbol{\Omega}, \boldsymbol{\omega})]/k_B T\} P(\omega_x) P(\omega_y)}{16\pi^3 k_B T I_{\perp} (2\pi k_B T I_{\parallel})^{1/2} \int d\boldsymbol{\Omega} \exp\{-V_c(\boldsymbol{\Omega}, \boldsymbol{\omega})/k_B T\}}, \quad (2)$$

where \mathbf{I} is the inertia tensor in the molecular frame

$$\mathbf{I} = \begin{pmatrix} I_{\perp} & 0 & 0 \\ 0 & I_{\perp} & 0 \\ 0 & 0 & I_{\parallel} \end{pmatrix} \quad (3)$$

and the $P(\omega_i)$ is the equilibrium distribution function for the librational frequencies along the i th molecular axis. Transpose arrays or matrices are labeled in Eq. (2) as well in the following by the superscript $(\dots)^t$. Distribution $P(\mathbf{Y})$ allows the calculation of equilibrium averages of functions $f(\mathbf{Y})$ of stochastic variables:

$$\bar{f} = \int d\mathbf{Y} f(\mathbf{Y}) P(\mathbf{Y}), \quad (4)$$

where $d\mathbf{Y} = d\boldsymbol{\Omega}^o d\mathbf{L} d\boldsymbol{\Omega}^c d\boldsymbol{\omega}$ is the infinitesimal volume element, with $d\boldsymbol{\Omega}^o$ and $d\boldsymbol{\Omega}^c$ including integration factors $\sin \beta^o$ and $\sin \beta^c$, respectively.

A Markovian time evolution equation is assumed for the non-equilibrium distribution $P(\mathbf{Y}; t)$:

$$\partial P(\mathbf{Y}; t) / \partial t = -\hat{\Gamma} P(\mathbf{Y}; t). \quad (5)$$

In order to model the time evolution operator $\hat{\Gamma}$, we shall include several contributions identified on physical grounds with the various independent dynamical processes.

Let us first consider the solute. We shall include the streaming operator $\hat{\Gamma}_s$ for its conservative rotational motion in the presence of the cage potential, and the collisional operator $\hat{\Gamma}_c$ describing the frictional relaxation of the angular momentum. The streaming operator is written in the following standard form⁷:

$$\hat{\Gamma}_s = \mathbf{L}^t \mathbf{I}^{-1} \hat{\mathbf{M}}(\boldsymbol{\Omega}^o) + (\mathbf{T} + \mathbf{P})^t \partial / \partial \mathbf{L}, \quad (6)$$

where $\hat{\mathbf{M}}(\boldsymbol{\Omega}^o)$ is the rotation operator acting on $\boldsymbol{\Omega}^o$ with components in the molecular frame. The torque \mathbf{T} due to the cage potential and the precessional torque \mathbf{P} are given as:

$$\mathbf{T} = -\hat{\mathbf{M}}(\boldsymbol{\Omega}^o) V_c(\boldsymbol{\Omega}, \boldsymbol{\omega}), \quad \mathbf{P} = \mathbf{L}_{\times} \mathbf{I}^{-1} \mathbf{L}, \quad (7)$$

where the 3×3 matrix \mathbf{L}_{\times} is derived from the vector \mathbf{L} on the basis of its identity with the vector product $\mathbf{L}_{\times} \mathbf{v} \equiv \mathbf{L} \times \mathbf{v}$ with any vector \mathbf{v} .^{8,6}

In order to specify unambiguously the rotation operator $\hat{\mathbf{M}}(\boldsymbol{\Omega}^o)$, let us consider an infinitesimal rotation of the molecular frame from $\boldsymbol{\Omega}^o$ to $\boldsymbol{\Omega}^o + d\boldsymbol{\Omega}^o$ with $d\boldsymbol{\Omega}^o \equiv (d\alpha^o, d\beta^o, d\gamma^o)^t$. It can be represented by an infinitesimal Cartesian vector with components $d\boldsymbol{\varphi}^o \equiv (d\varphi_x^o, d\varphi_y^o, d\varphi_z^o)^t$ in the molecular frame. Then the infinitesimal change of a given function $f(\boldsymbol{\Omega}^o)$ can be specified as:

$$df(\boldsymbol{\Omega}^o) \equiv f(\boldsymbol{\Omega}^o + d\boldsymbol{\Omega}^o) - f(\boldsymbol{\Omega}^o) = (d\boldsymbol{\varphi}^o)^t \hat{\mathbf{M}}(\boldsymbol{\Omega}^o) f(\boldsymbol{\Omega}^o) \quad (8)$$

and this equation implicitly defines the rotation operator $\hat{\mathbf{M}}(\boldsymbol{\Omega}^o)$ in the molecular frame. By means of the linear relation⁹

$$d\boldsymbol{\Omega}^o = \mathbf{R}(\boldsymbol{\Omega}^o) d\boldsymbol{\varphi}^o, \quad \mathbf{R}(\boldsymbol{\Omega}^o) = \begin{pmatrix} -\cos \gamma^o / \sin \beta^o & \sin \gamma^o / \sin \beta^o & 0 \\ \sin \gamma^o & \cos \gamma^o & 0 \\ \cos \beta^o \cos \gamma^o / \sin \beta^o & -\cos \beta^o \sin \gamma^o / \sin \beta^o & 1 \end{pmatrix}. \quad (9)$$

it can be written explicitly in terms of the Euler angle derivatives as

$$\hat{\mathbf{M}}(\boldsymbol{\Omega}^o) = \mathbf{R}(\boldsymbol{\Omega}^o)^t \partial / \partial \boldsymbol{\Omega}^o. \quad (10)$$

The rotation operator in the laboratory frame would be recovered by inserting in Eq. (8) the components of $d\boldsymbol{\varphi}^o$ in the laboratory frame. The same procedure can be applied to the relative orientation of two arbitrary frames, thus generating the corresponding rotation operators.

If all solute-solvent interactions were taken into account by the cage potential $V_c(\boldsymbol{\Omega}, \boldsymbol{\omega})$, then the streaming operator $\hat{\Gamma}_s$ alone would be sufficient to represent the solute rotational motion. However, a parabolic expansion about the minimum is required in order to derive a simple parametrization of the

cage potential (cf. paper I). Thus the anharmonic contributions to the cage potential are neglected. Even if small in magnitude, these anharmonic interactions might influence the solute, by generating additive torques with respect to \mathbf{P} of Eq. (7) due to $V_c(\mathbf{\Omega}, \boldsymbol{\omega})$. In the hypothesis that torques of anharmonic origin are rapidly fluctuating, they act as a source of frictional drag on the angular momentum. Fluctuations of the fast components of the librational frequencies should have similar effects. Therefore, we introduce the collisional operator describing angular momentum relaxation due to frictional effects:

$$\hat{\Gamma}_c = -k_B T \frac{\partial}{\partial \mathbf{L}} \boldsymbol{\xi} P(\mathbf{Y}) \frac{\partial}{\partial \mathbf{L}} P(\mathbf{Y})^{-1} \quad (11)$$

in order to include in the stochastic model the dynamical effects of those interactions with the thermal bath which are not accounted for by cage potential $V_c(\mathbf{\Omega}, \boldsymbol{\omega})$. The following friction matrix in the molecular frame

$$\boldsymbol{\xi} = \begin{pmatrix} \xi_{\perp} & 0 & 0 \\ 0 & \xi_{\perp} & 0 \\ 0 & 0 & \xi_{\parallel} \end{pmatrix} \quad (12)$$

will be used for axially symmetric solutes.

Let us now discuss the cage dynamics. One should differentiate the collective behavior of the ensemble of solvent particles, which is described by a variety of time scales, from the dynamics of solvent particles surrounding the solute and which have the major influence on the cage potential. A simplified treatment with few relaxation times appears to be sufficient in the latter case as long as only short range fluctuations need to be described. A model is easily generated by directly considering the variables $\mathbf{\Omega}^c$ and $\boldsymbol{\omega}$ which describe at each instant the configuration of the cage potential. In fact, one can introduce stochastic operators for their time evolution without the need to describe in detail the solvent particle motions that determine the changes in the cage potential. In our model, we shall include two independent contributions that describe i) rotations of the cage frame orientations $\mathbf{\Omega}^c$ and ii) fluctuations of the librational frequencies $\boldsymbol{\omega}$. A rotational diffusion operator for axially symmetric particles will be used for the former:

$$\hat{\Gamma}_D = -\hat{\mathbf{M}}(\mathbf{\Omega}^c) \dagger \mathbf{D}^c P(\mathbf{Y}) \hat{\mathbf{M}}(\mathbf{\Omega}^c) P(\mathbf{Y})^{-1}, \quad (13)$$

where $\hat{\mathbf{M}}(\mathbf{\Omega}^c)$ denotes the rotation operator acting on the $\mathbf{\Omega}^c$ variables and with its components in the cage frame (CF). Two coefficients are required to specify the diffusion matrix in the cage frame

$$\mathbf{D}^c = \begin{pmatrix} D_{\perp} & 0 & 0 \\ 0 & D_{\perp} & 0 \\ 0 & 0 & D_{\parallel} \end{pmatrix}. \quad (14)$$

The coefficient D_{\perp} is the reorientation rate of CF z -axis that determines the most favorable orientation of the solute. Also, D_{\parallel} determines the exchange rate of the principal librational axes (i.e. the rotations of the CF x - and y -axes around the CF z -axis which are described by the angle γ^c). A diffusion operator will also be employed for the fluctuations of the librational frequencies ω_x and ω_y :

$$\hat{\Gamma}_{\omega} = -\sum_i \frac{\partial}{\partial \omega_i} D^{\omega} P(\mathbf{Y}) \frac{\partial}{\partial \omega_i} P(\mathbf{Y})^{-1} \quad (15)$$

with a unique diffusion coefficient D^{ω} because of the statistical equivalence of the two librational frequencies.

The overall evolution operator is finally recovered from the superposition of all the previous contributions

$$\hat{\Gamma} = \hat{\Gamma}_s + \hat{\Gamma}_c + \hat{\Gamma}_D + \hat{\Gamma}_{\omega}. \quad (16)$$

Note that equilibrium distribution Eq. (2) is the stationary solution to $\hat{\Gamma}$ as well as to each term on the right-hand side of Eq. (16). Therefore, relaxation to the correct equilibrium distribution must be recovered from time dependent solutions of Eq. (5). In the following sections this stochastic model will be analyzed with the purpose of interpreting the relaxation of both solute and cage variables. This requires the calculation of correlation functions of the form

$$\begin{aligned} G(t) &\equiv \overline{f[\mathbf{Y}(t)] * f[\mathbf{Y}(0)]} \\ &= \int d\mathbf{Y} f(\mathbf{Y}) * \exp(-\hat{\Gamma}t) f(\mathbf{Y}) P(\mathbf{Y}) \end{aligned} \quad (17)$$

for a set of observables $f(\mathbf{Y})$ specified as functions of the stochastic variables. The major obstacle derives from the large number of stochastic variables which are intrinsically coupled by the time evolution operator. Of course, simplified models can be obtained by reducing the set of stochastic variables. For instance, in the presence of negligible fluctuations in the librational frequencies, one may substitute $\boldsymbol{\omega}$ with their averages. The resulting model with the set of $(\mathbf{\Omega}^c, \mathbf{L}, \mathbf{\Omega}^c)$ variables has been previously discussed by Polimeno and Freed.⁵

A more compact representation of the full Fokker-Planck operator is derived by introducing the gradient $\hat{\nabla}_{\mathbf{Y}}$ with respect to the ensemble of stochastic variables \mathbf{Y} :

$$\hat{\nabla}_{\mathbf{Y}} \equiv \begin{pmatrix} \hat{\mathbf{M}}(\mathbf{\Omega}^c) \\ \partial / \partial \mathbf{L} \\ \hat{\mathbf{M}}(\mathbf{\Omega}^c) \\ \partial / \partial \boldsymbol{\omega} \end{pmatrix}. \quad (18)$$

Then the time evolution operator can be recasted in the following form

$$\hat{\Gamma} = -\hat{\nabla}_{\mathbf{Y}}^{\text{tr}} \mathbf{A}_{\mathbf{Y}} P(\mathbf{Y}) \hat{\nabla}_{\mathbf{Y}} P(\mathbf{Y})^{-1} \quad (19)$$

with matrix $\mathbf{A}_{\mathbf{Y}}$ given by:

$$\mathbf{A}_{\mathbf{Y}} = \begin{pmatrix} \mathbf{0} & -k_B T \mathbf{1} & \mathbf{0} & \mathbf{0} \\ k_B T \mathbf{1} & k_B T (\xi - \mathbf{L}_{\times}) & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{D}^{\mathcal{E}} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & D^{\omega} \mathbf{1} \end{pmatrix}. \quad (20)$$

In this way a diffusion-like operator is recovered for $\hat{\Gamma}$, even if $\mathbf{A}_{\mathbf{Y}}$ cannot be identified with a true diffusion matrix, since it is neither symmetric nor positive definite. The matrix $\mathbf{A}_{\mathbf{Y}}$ describes the dynamical coupling among the different variables. It should be emphasized that the coupling between solute variables (Ω^o, \mathbf{L}) and cage variables (Ω^c, ω) is determined by the equilibrium distribution $P(\mathbf{Y})$ through the explicit dependence of the cage potential on the librational frequencies ω and on the solute orientation Ω with respect to the cage frame. This clearly prevents any factorization of $P(\mathbf{Y}; t)$ with respect to the two sets of variables.

The orientation Ω^o of the solute with respect to the laboratory frame is not a convenient variable for the analysis of the model. In fact its relaxation is driven by two processes with very different time scales: the fast librational motion within the cage potential and the slow reorientation of the cage frame. In order to take into account the time scale separation, it is useful to replace Ω^o by the relative solute orientation Ω with the cage orientation Ω^c already included in the set of stochastic variables. Therefore, in the analysis of the model we shall employ the following set of variables:

$$\mathbf{X} = (\Omega, \mathbf{L}, \Omega^c, \omega). \quad (21)$$

The Fokker-Planck equation for the non-equilibrium distribution $P(\mathbf{X}; t)$ must now be derived for the new set of variables. A detailed discussion of the procedure is given in Appendix A, where the new time evolution operator is derived in the following form:

$$\hat{\Gamma} = -\hat{\nabla}_{\mathbf{X}}^{\text{tr}} \mathbf{A}_{\mathbf{X}} P(\mathbf{X}) \hat{\nabla}_{\mathbf{X}} P(\mathbf{X})^{-1}, \quad (22)$$

$P(\mathbf{X})$ being the equilibrium distribution with respect to the new set of variables. The gradient operator and the coupling matrix are now:

$$\hat{\nabla}_{\mathbf{X}} = \begin{pmatrix} \hat{\mathbf{M}}(\Omega) \\ \partial/\partial \mathbf{L} \\ \hat{\mathbf{M}}(\Omega^c) \\ \partial/\partial \omega \end{pmatrix},$$

$$\mathbf{A}_{\mathbf{X}} = \begin{pmatrix} \mathbf{E} \mathbf{D}^{\mathcal{E}} \mathbf{E}^{\text{tr}} & -k_B T \mathbf{1} & -\mathbf{E} \mathbf{D}^{\mathcal{E}} & \mathbf{0} \\ k_B T \mathbf{1} & k_B T (\xi - \mathbf{L}_{\times}) & \mathbf{0} & \mathbf{0} \\ -\mathbf{D}^{\mathcal{E}} \mathbf{E}^{\text{tr}} & \mathbf{0} & \mathbf{D}^{\mathcal{E}} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & D^{\omega} \mathbf{1} \end{pmatrix}, \quad (23)$$

where $\hat{\mathbf{M}}(\Omega)$ is the rotation operator on angles Ω whose components are expressed in the molecular frame, while

$\mathbf{E} = \mathbf{E}(\Omega)$ is the Euler matrix transforming vector components from the cage frame to the molecular frame. The following analysis will be confined to the operator $\hat{\Gamma}$ in the form of Eq. (22) without further change of variables, and the subscript \mathbf{X} of the gradient operator and of the coupling matrix will be omitted.

When convenient we shall use the symmetrized time evolution operator

$$\tilde{\Gamma} \equiv P(\mathbf{X})^{-1/2} \hat{\Gamma} P(\mathbf{X})^{1/2} \\ = -P(\mathbf{X})^{-1/2} \hat{\nabla}^{\text{tr}} \mathbf{A} P(\mathbf{X}) \hat{\nabla} P(\mathbf{X})^{-1/2} \quad (24)$$

which enables the calculation of correlation functions in the following form:

$$G(t) \equiv \overline{f(\mathbf{X}(t)) * f(\mathbf{X}(0))} \\ = \langle f(\mathbf{X}) P(\mathbf{X})^{1/2} | \exp(-\tilde{\Gamma} t) | f(\mathbf{X}) P(\mathbf{X})^{1/2} \rangle \quad (25)$$

with the scalar product $\langle \dots \rangle$ defined as an integration over the set of stochastic variables \mathbf{X} . Specific calculations will be performed with the following cage potential, written in terms of the Wigner rotation matrices for Ω :

$$V_c(\Omega, \omega) = -(I_{\perp}/6) \{ (\omega_x^2 + \omega_y^2) D_{0,0}^2(\Omega) \\ + \sqrt{3/2} (\omega_x^2 - \omega_y^2) [D_{2,0}^2(\Omega) + D_{-2,0}^2(\Omega)] \} \quad (26)$$

which has been derived for liquid chlorine studied in the MD simulation of paper I. In the same work the simulation results were analyzed in order to recover the distribution of the slow librational frequencies. A bell-shaped distribution was found with the center at $\bar{\omega}_i = 7.5 \text{ ps}^{-1}$ and width $\sigma = 1.6 \text{ ps}^{-1}$. In order to simplify the calculations with the stochastic model, a Gaussian distribution will be employed for the librational frequencies:

$$P(\omega_i) = \frac{1}{\sigma \sqrt{2\pi}} \exp\{-(\omega - \bar{\omega}_i)^2 / 2\sigma^2\} \quad (27)$$

with the previously given parameters $\bar{\sigma}_i$ and σ . The other required parameter $\sqrt{k_B T / I_{\perp}} = 1.47 \text{ ps}^{-1}$ is obtained from the moment of inertia of Cl_2 and the temperature $T = 178 \text{ K}$ used in the Molecular Dynamics simulation.

III. SLOWLY RELAXING PROCESSES

A rather complex model with a large set of variables is required in order to represent in a complete fashion the dynamics of both the solute and the solvent cage. Exact solutions cannot be derived analytically because of the inherent coupling between all the variables. Also a complete numerical solution of the problem becomes prohibitive because of the huge dimension of the matrix required to represent the time evolution operator.^{10,5} Therefore it is necessary to search for solutions of an approximate nature, which properly take into account the physical features of the problem, in particular the time scale separation between the elementary relaxation mechanisms.

In paper I we have obtained the correlation functions for different observables from the MD simulation of chlorine.

Those data allow the identification of the characteristic relaxation time τ_z for each variable z , which can be summarized in the following form:

$$(\tau_L, \tau_\Omega \sim 0.1 \text{ ps}) < (\tau_{\gamma^c} \sim 0.6 \text{ ps}) < (\tau_\omega \sim 3 \text{ ps}) \\ < (\tau_{\alpha^c, \beta^c} \sim 5 \text{ ps}). \quad (28)$$

A definite time scale separation exists between the fast solute variables $(\mathbf{\Omega}, \mathbf{L})$ and the slow cage variables $(\boldsymbol{\omega}, \alpha^c, \beta^c)$, with the azimuthal Euler angle γ^c for the cage orientation in the intermediate range. A rather simple picture of the dynamics of the system is suggested by these characteristic times. Only the slow cage variables are essential to describe dynamical correlations at long enough times when the fast variables have almost equilibrated. On the other hand, the behavior at short times is dominated by the evolution of the fast solute variables which experience a substantially frozen field of interactions due to the cage. In other words, the two sets of variables are to a large extent dynamically uncoupled, except for the presence of a “static” coupling due to the cage potential $V_c(\mathbf{\Omega}, \boldsymbol{\omega})$.

Given this physical picture we seek an efficient method of solution that takes into account the time scale separation, such as the Born–Oppenheimer (BO) approximation. A BO approximation has previously been utilized to treat time-scale separations in stochastic models of solute dynamics in liquid-crystalline media.¹¹ Appendix B presents the general procedure to be applied to stochastic problems when the independent variables \mathbf{X} can be partitioned into sets of slow \mathbf{X}_S and fast \mathbf{X}_F variables

$$\mathbf{X} = (\mathbf{X}_S, \mathbf{X}_F) \quad (29)$$

with a well-defined time scale separation. This method will be applied to the solute–solvent cage problem with the following partition of the variables:

$$\mathbf{X}_S = (\boldsymbol{\Omega}^c, \boldsymbol{\omega}), \quad \mathbf{X}_F = (\mathbf{L}, \boldsymbol{\Omega}). \quad (30)$$

Because of the intermediate time scale for the γ^c variable, an alternative choice with the inclusion of γ^c among the fast variables is also legitimate. But in this case the application of the BO approximation would be much more complicated, and preliminary calculations have shown that the general features of the resulting correlation functions are not modified.

It should be mentioned that the cage potential Eq. (26) for centrosymmetric linear molecules might induce a slow decay in the correlation function of $D_{0,0}^1(\boldsymbol{\Omega})$ as a result of β -angle flips between 0 and π with a barrier crossing at $\beta = \pi/2$.¹² This process would eliminate the time scale separation between slow variables \mathbf{X}_S of Eq. (30) and the solute relative orientation $\boldsymbol{\Omega}$. However, the MD simulation of chlorine has shown that, because of the height of the barrier, such a flipping process is much too infrequent to have significant effects on the rotational relaxation of the solute over time scales of interest. Thus we shall exclude it in our analysis by constraining the angle β to the following range:

$$0 \leq \beta \leq \pi/2. \quad (31)$$

As a result, the correlation function for $D_{0,0}^1(\boldsymbol{\Omega})$ will be devoid of any slow component from the barrier crossing, and the time scale separation between variables $\boldsymbol{\Omega}$ and \mathbf{X}_S of Eq. (30) will be fulfilled. Notice that the constraint Eq. (31) does not limit the available configurations for the solute, since the same physical situation obtained after a π -flip of the solute is recovered by means of a π rotation of the z -axis of the cage frame, keeping the angle β fixed.

The rest of this section will be confined to the analysis of the slowly relaxing processes. This can be done by isolating the slow components of the correlation functions from the more general expressions given in Appendix B. An alternative and equivalent method is supplied simply by the projection of the full stochastic equation onto the subspace for the slow variables \mathbf{X}_S . The general definition of the distribution function $P_S(\mathbf{X}_S; t)$ for the slow variables is obtained by integrating over the set of fast variables:

$$P_S(\mathbf{X}_S; t) \equiv \int d\mathbf{X}_F P(\mathbf{X}; t). \quad (32)$$

Correspondingly, the reduced equilibrium distribution $P_S(\mathbf{X}_S)$ for the slow variables is obtained by integration of the full equilibrium distribution Eq. (2), and an isotropic distribution over the cage orientation is recovered

$$P_S(\mathbf{X}_S) = P(\omega_x)P(\omega_y)/2\pi. \quad (33)$$

Let us consider the subspace ϵ_S spanned by functions of \mathbf{X}_S having $P_S(\mathbf{X}_S)$ as the weighting factor in integrations. By projecting the full FP equation onto the ϵ_S subspace,^{13,6} the time evolution equation for the reduced distribution is derived as

$$\partial P_S(\mathbf{X}_S; t)/\partial t = -\hat{\Gamma}_S P_S(\mathbf{X}_S; t) \quad (34)$$

with the projected operator $\hat{\Gamma}_S$ implicitly defined by the following equation:

$$\hat{\Gamma}_S f(\mathbf{X}_S) P_S(\mathbf{X}_S) = \int d\mathbf{X}_F \hat{\Gamma} P(\mathbf{X}) f(\mathbf{X}_S) \quad (35)$$

[see also Eq. (B22) of Appendix B]. By applying this procedure to the full FP operator of Eq. (22), one obtains the explicit form of the projected operator:

$$\hat{\Gamma}_S = -\hat{\mathbf{M}}(\boldsymbol{\Omega}^c)^\dagger \mathbf{D}^c \hat{\mathbf{M}}(\boldsymbol{\Omega}^c) + \hat{\Gamma}_\omega \quad (36)$$

with a rotational diffusion operator for the cage orientation $\boldsymbol{\Omega}^c$, and the following Smoluchowski-type of diffusion operator for the librational frequencies:

$$\hat{\Gamma}_\omega = -D_\omega \sum_{i=x,y} (\partial/\partial\omega_i) P(\omega_i) (\partial/\partial\omega_i) P(\omega_i)^{-1}. \quad (37)$$

The projected evolution operator $\hat{\Gamma}_S$ can be used to calculate correlation functions for functions $f(\mathbf{X}_S)$ of the slow variables. Moreover one can compute the slowly decaying component of the correlation function $G(t)$ relative to a generic observable $f(\mathbf{X})$ by considering its projection $f_S(\mathbf{X}_S)$ onto the ϵ_S subspace:

$$f_S(\mathbf{X}_S) \equiv \int d\mathbf{X}_F f(\mathbf{X}) P(\mathbf{X}_S | \mathbf{X}_F), \quad (38)$$

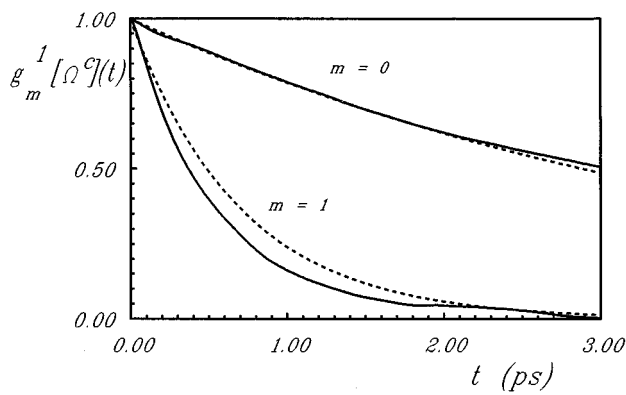


FIG. 1. First rank orientational correlation functions of the cage from MD simulation (continuous lines) and from the stochastic model (dashed lines).

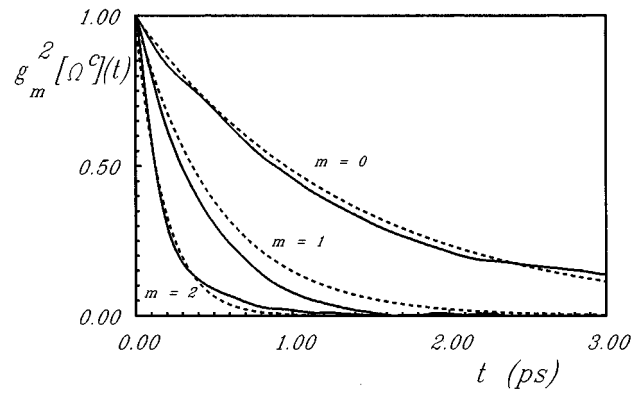


FIG. 2. Second rank orientational correlation functions of the cage from MD simulation (continuous lines) and from the stochastic model (dashed lines).

where $P(\mathbf{X}_S|\mathbf{X}_F)$ is the equilibrium conditional probability of \mathbf{X}_F for a given \mathbf{X}_S :

$$P(\mathbf{X}_S|\mathbf{X}_F) \equiv P(\mathbf{X})/P_S(\mathbf{X}_S). \quad (39)$$

The slow component $G_S(t)$ of $G(t)$ is derived as the correlation function of $f_S(\mathbf{X}_S)$:

$$\begin{aligned} G_S(t) &\equiv \overline{f_S(\mathbf{X}_S(t)) * f_S(\mathbf{X}_S(0))} \\ &= \int d\mathbf{X}_S f_S(\mathbf{X}_S) * \exp(-\hat{\Gamma}_S t) f_S(\mathbf{X}_S) P_S(\mathbf{X}_S). \end{aligned} \quad (40)$$

Of course $G_S(t) = G(t)$ if $f_S(\mathbf{X}_S) = f(\mathbf{X}_S)$, i.e. if f is a function of the slow variables only. Otherwise $G(t)$ would also contain a fast component $G_F(t)$ which can be calculated according to the methods of Appendix B (see Section IV).

As applications we shall consider the correlation functions which have been determined from the MD simulation of Cl_2 , with the purpose of testing the capability of our stochastic model to interpret the dynamics of solute-solvent cage interactions. For the cage orientation, the correlation function of $D_{l,m}^j(\Omega^c)$ is readily obtained from the isotropic diffusion operator of Eq. (36) in the following standard form

$$\begin{aligned} G_m^j[\Omega^c](t) &\equiv \overline{D_{l,m}^j(\Omega^c(t)) * D_{l,m}^j(\Omega^c(0))} \\ &= \exp\{-[j(j+1)D_{\perp} + m^2(D_{\parallel} - D_{\perp})]t\} / (2j+1). \end{aligned} \quad (41)$$

In Figures 1 and 2 the predicted behavior is compared with the MD results for correlation functions of the first ($j=1$) and second ($j=2$) ranks, respectively. Diffusion coefficients $D_{\perp} = 0.12 \text{ ps}^{-1}$ and $D_{\parallel} = 1.3 \text{ ps}^{-1}$ have been employed. The fair agreement supports the attribution of a diffusional motion to the cage rotation, as emphasized in paper I. Notice that in Figures 1 and 2, as well as in the following ones, correlation functions normalized with respect to their initial values

$$g(t) \equiv G(t)/G(0) \quad (42)$$

are reported.

Let us consider now the correlation function for the deviations $\delta\omega_i \equiv \omega_i - \bar{\omega}_i$ of the librational frequencies from

their average. Because of the factorization in $\hat{\Gamma}_S$ of $\hat{\Gamma}\omega$ and of the cage rotational part, its calculation can be confined to the subspace of functions of the librational frequencies

$$\begin{aligned} G[\omega](t) &\equiv \sum_i \overline{\delta\omega_i(t) \delta\omega_i(0)} \\ &= \int d\omega \sum_i \delta\omega_i \exp(-\hat{\Gamma}_\omega t) \delta\omega_i P(\omega) \end{aligned} \quad (43)$$

and by inserting the Gaussian distribution Eq. (27), the following analytical result for the Gaussian-Markov process is recovered

$$G[\omega](t) = 2\sigma^2 \exp(-D_\omega t / \sigma^2). \quad (44)$$

Therefore, a simple exponential decay is predicted for the slow cage frequency, as has been found in the MD simulation (see Fig. 9 of paper I). The observed value 2.87 ps of the corresponding correlation time τ_ω^s allows the determination of the unknown coefficient as $D_\omega = 0.13 \text{ ps}^{-3}$. The same method can be applied to the calculation of correlation functions of any observable $f(\omega)$ that is a function of the librational frequencies, after expanding $f(\omega)$ about the average $\bar{\omega}$.¹⁴ The rather narrow width of the distribution $P(\omega_i)$ allows one to truncate the expansion at the first order terms

$$\begin{aligned} f(\omega) &\approx f(\bar{\omega}) + \sum_{i=x,y} \delta\omega_i f_i(\bar{\omega}), \\ f_i(\bar{\omega}) &\equiv [\partial f(\omega) / \partial \omega_i]_{\omega=\bar{\omega}}, \end{aligned} \quad (45)$$

yielding the correlation function in the following form:

$$\begin{aligned} \overline{f(\omega(t)) * f(\omega(0))} &\approx |f(\bar{\omega})|^2 + \sum_i |f_i(\bar{\omega})|^2 \sigma^2 \\ &\quad \times \exp(-D_\omega t / \sigma^2). \end{aligned} \quad (46)$$

Finally we examine the correlation functions for the probe observables. In the case of the angular momentum \mathbf{L} , no slow component $G_S(t)$ of its correlation function is recovered because its projection Eq. (38) vanishes. Similarly one excludes slow components in the case of functions $f(\Omega)$ of the relative probe orientation, since their projections

are at most constant. However a significant slow component is recovered for functions of the absolute probe orientation $\mathbf{\Omega}^o$ with respect to the laboratory frame. Because of their direct relation with experimental observables of spectroscopic origin, these are the most important correlation functions for the probe orientation. Let us consider the correlation function

$$G^j[\mathbf{\Omega}^o](t) \equiv \overline{D_{l,0}^j(\mathbf{\Omega}^o(t)) * D_{l,0}^j(\mathbf{\Omega}(0))} \quad (47)$$

for the Wigner function $f = D_{l,0}^j(\mathbf{\Omega}^o)$ which is conveniently expanded as

$$f = \sum_m D_{l,m}^j(\mathbf{\Omega}^c) D_{m,0}^j(\mathbf{\Omega}). \quad (48)$$

Its projection onto ϵ_S according to Eq. (38) is given as

$$f_S = \sum_m D_{l,m}^j(\mathbf{\Omega}^c) d_m^j(\boldsymbol{\omega}) \quad (49)$$

with

$$d_m^j(\boldsymbol{\omega}) \equiv \int d\mathbf{\Omega} D_{m,0}^j(\mathbf{\Omega}) \exp\{-V_c(\mathbf{\Omega}, \boldsymbol{\omega})/k_B T\} / \int d\mathbf{\Omega} \times \exp\{-V_c(\mathbf{\Omega}, \boldsymbol{\omega})/k_B T\}. \quad (50)$$

Notice that $d_m^j(\bar{\omega}) = \delta_{m,0} d_0^j(\bar{\omega})$ because of the axial symmetry of the cage potential Eq. (26) for $\omega_x = \omega_y$.

The corresponding correlation function is easily calculated because of the factorization in $\hat{\Gamma}_S$ of orientational and librational terms. By taking into account only the first order contributions in the librational frequency expansion as in Eq. (46), the following explicit relation is found

$$\begin{aligned} G_m^j[\mathbf{\Omega}^o]_S(t) &\equiv \overline{f_S(t) * f_S(0)} \\ &= (2j+1)^{-1} |d_0^j(\bar{\omega})|^2 \exp\{-j(j+1)D_{\perp} t\} \\ &\quad + (2j+1)^{-1} \sum_m \sum_{i=x,y} \sigma^2 |d_{m,i}^j(\bar{\omega})|^2 \\ &\quad \times \exp\{-[j(j+1)D_{\perp} + m^2(D_{\parallel} - D_{\perp}) \\ &\quad + D_{\omega}/\sigma^2]t\} \end{aligned} \quad (51)$$

with coefficients $d_{m,i}^j(\bar{\omega})$ for $i=x,y$ defined according to Eq. (45). In general the slow component of the orientational correlation function for the probe should display a multi-exponential decay with rates depending on the diffusion coefficients D_{\perp} and D_{\parallel} of the cage and on the coefficient D_{ω} for the diffusion of the librational frequencies. The weights of the different exponential decays are determined by the distribution $P(\omega_i)$ of the librational frequencies through coefficients $d_0^j(\bar{\omega})$ and $d_{m,i}^j(\bar{\omega})$. Table I provides the non-vanishing values of these coefficients for the case of chlorine explicitly considered here. In this case the weights $|\sigma d_{m,i}^j(\bar{\omega})|^2$ are much smaller than that $|d_0^j(\bar{\omega})|^2$ of the leading term (we remind the reader that $\sigma = 1.6 \text{ ps}^{-1}$). Therefore Eq. (51) can be approximated as

$$G^j[\mathbf{\Omega}^o]_S(t) \approx (2j+1)^{-1} |d_0^j(\bar{\omega})|^2 \exp\{-j(j+1)D_{\perp} t\} \quad (52)$$

TABLE I. Averages $d_m^j(\bar{\omega})$ and derivatives.

j	m	$d_m^j(\bar{\omega})$	$d_{m,x}^j(\bar{\omega})$	$d_{m,y}^j(\bar{\omega})$
1	0	0.957	0.0064	0.0064
2	0	0.878	0.0174	0.0174
2	2	0	0.0071	-0.0071

which has the simple behavior expected from a rotational diffusion model for the probe motion with the same diffusion coefficient as that of the cage rotation. This corresponds to the physical situation of a solvent exerting a rather strong cage potential, so that the probe orientation at long times simply follows the slow rotational motion of the cage. Such a result, however, cannot be extended to the possible systems. In particular, noticeable effects of the multi-exponential decay of the probe orientational correlation function should be detected a) in the presence of a weaker cage potential leading to smaller values of the $d_0^j(\bar{\omega})$ coefficients and correspondingly increasing $d_{m,i}^j(\bar{\omega})$ terms, or b) with a broader distribution of cage frequencies which increases the width σ .

IV. FAST PROCESSES

As shown in Appendix B, the correlation function for a generic observable $f(\mathbf{X})$

$$G(t) \equiv \overline{f(\mathbf{X}(0)) * f(\mathbf{X}(t))} = G_S(t) + G_F(t) \quad (53)$$

can be decomposed into a slow component $G_S(t)$ to be calculated according to the procedure of Sec. III, and a fast component $G_F(t)$ associated with operator $\hat{\Gamma}_F$ driving the relaxation of the fast variables \mathbf{X}_F when the slow variables are kept frozen. In this section the fast component of the correlation function for the different observables of interest will be derived by neglecting the small effects due to the evolution of the slow variables. Therefore the fast component $G_F(t)$ will be calculated as an average over \mathbf{X}_S as shown in Eq. (B26), of the correlation function $G_F(\mathbf{X}_S; t)$, that is derived by solving the dynamical problem for only the fast variables according to Eq. (B27). That is:

$$G_F(\mathbf{X}_S; t) = \int d\mathbf{X}_F \delta f(\mathbf{X}) * \exp(-\hat{\Gamma}_F t) \delta f(\mathbf{X}) P(\mathbf{X}_S | \mathbf{X}_F) \quad (54)$$

with a parametric dependence on the ‘‘static’’ variables \mathbf{X}_S . In the previous equation $\delta f(\mathbf{X}) \equiv f(\mathbf{X}) - f_S(\mathbf{X}_S)$ is the orthogonal component of the observable $f(\mathbf{X})$ with respect to the ϵ_S subspace. In order to avoid a very cumbersome notation, we shall always leave implicit the parametric dependence on \mathbf{X}_S of Eq. (54), as well as the average over \mathbf{X}_S to be performed on $G_F(\mathbf{X}_S; t)$, by focusing on the solution of the dynamical problem for the operator $\hat{\Gamma}_F$ which is chosen according to constraints Eqs. (B2) and (B3). This choice is done by selecting from the complete time evolution operator of Eq. (22) those components of the gradient operator $\hat{\nabla}_{\mathbf{X}}$ acting explicitly onto the fast variables $\mathbf{X}_F = (\boldsymbol{\Omega}, \mathbf{L})$. Then one derives the following operator

$$\hat{\Gamma}_F = \hat{\Gamma}_s + \hat{\Gamma}_c + \hat{\Gamma}_{D,F} \quad (55)$$

with three independent contributions. Operator $\hat{\Gamma}_s$ denotes the streaming operator for the variables \mathbf{X} of Eq. (21), and it has the same form as Eq. (6) except for the substitution of rotation operator $\hat{\mathbf{M}}(\mathbf{\Omega}^o)$ by rotation operator $\hat{\mathbf{M}}(\mathbf{\Omega})$ acting on the relative solute orientation $\mathbf{\Omega}$. A similar substitution should be performed on Eq. (7) for the torque \mathbf{T} . The collisional operator $\hat{\Gamma}_c$ is the same as Eq. (11) after substitution of the equilibrium distribution by $P(\mathbf{X})$. Finally, $\hat{\Gamma}_{D,F}$ accounts for the contributions deriving from operator $\hat{\Gamma}_D$ of Eq. (13) for the cage rotational diffusion. This is the most complicated part because of the presence of several terms, which can be partitioned according to their proportionality to the parallel component D_{\parallel} or the perpendicular component D_{\perp} of the diffusion matrix Eq. (14), which have been previously determined by analyzing the correlation function for the cage rotation. Given the small value of $D_{\perp} = 0.12 \text{ ps}^{-1}$, one expects that the corresponding components of $\hat{\Gamma}_{D,F}$ have negligible effects on the relaxation of fast variables occurring on a time scale of few tenths of picosecond. Then it is legitimate to neglect these contributions and to keep in $\hat{\Gamma}_{D,F}$ only the terms proportional to D_{\parallel} , thereby deriving a much simpler operator:

$$\tilde{\Gamma}_{D,F} = -D_{\parallel} \frac{\partial}{\partial \alpha} P(\mathbf{X}) \frac{\partial}{\partial \alpha} P(\mathbf{X})^{-1}. \quad (56)$$

In this way the evolution operator for the fast variables is fully specified.

First we analyze the correlation function for the angular momentum component \mathbf{L}_{\perp} which is orthogonal to the probe symmetry axis

$$\mathbf{L}_{\perp} \equiv \mathbf{n}_M^x L_x + \mathbf{n}_M^y L_y, \quad (57)$$

where $(\mathbf{n}_M^x, \mathbf{n}_M^y, \mathbf{n}_M^z)$ are the unit vectors of the molecular frame (MF). This observable does not have a slow component in its correlation function, since its average over \mathbf{X}_F according to Eq. (38) vanishes. Therefore, only the fast component of the correlation function

$$G[L](t) = \overline{\mathbf{L}_{\perp}(t) \cdot \mathbf{L}_{\perp}(0)} \quad (58)$$

needs to be calculated according to the method previously discussed. Observable \mathbf{L}_{\perp} of Eq. (57) has an implicit angular dependence because of the rotational motion of the molecular frame axis. In order to make explicit such an orientational dependence, it is necessary to express \mathbf{L}_{\perp} in terms of the cage frame axis $(\mathbf{n}_C^x, \mathbf{n}_C^y, \mathbf{n}_C^z)$, which can be considered immobile during the relaxation of the fast variables. The spherical tensor notation¹⁵:

$$\mathbf{n}_A^{(1,\pm 1)} \equiv \mp (\mathbf{n}_A^x \pm i \mathbf{n}_A^y), \quad \mathbf{n}_A^{(1,0)} \equiv \mathbf{n}_A^z \quad (59)$$

for $A = C$ and $A = M$, allows a convenient representation of the relation between the frame axis in the following form

$$\mathbf{n}_M^{(1,m)} = \sum_{l=0,\pm 1} D_{l,m}^1(\mathbf{\Omega}) \mathbf{n}_C^{(1,l)}. \quad (60)$$

By also introducing the spherical tensor components $L^{(1,\pm 1)} = \mp (L_x \pm i L_y)$ of the angular momentum, the observable can be written as

$$\mathbf{L}_{\perp} = \sum_{m=\pm 1} L^{(1,m)} * \mathbf{n}_M^{(1,m)} = \sum_{l=0,\pm 1} f^{(1,l)}(\mathbf{\Omega}, \mathbf{L}) * \mathbf{n}_C^{(1,l)} \quad (61)$$

with

$$f^{(1,l)}(\mathbf{\Omega}, \mathbf{L}) \equiv \sum_{m=\pm 1} D_{l,m}^1(\mathbf{\Omega}) * L^{(1,m)}. \quad (62)$$

Substitution into Eq. (58) and using the orthogonality relation

$$\mathbf{n}_C^{(1,l)} * \mathbf{n}_C^{(1,l')} = \delta_{l,l'} \quad (63)$$

leads to a correlation function without explicit reference to any frame axis

$$G[\mathbf{L}](t) = \sum_{l=0,\pm 1} \overline{f^{(1,l)}(\mathbf{\Omega}(t), \mathbf{L}(t)) * f^{(1,l)}(\mathbf{\Omega}(0), \mathbf{L}(0))}. \quad (64)$$

However, its calculation cannot be performed analytically and also a full numerical computation would be extremely difficult because of the requirement of a complete representation of the $\hat{\Gamma}_F$ operator in the space of functions of both $\mathbf{\Omega}$ and \mathbf{L} variables.⁷ On the other hand we are investigating the case in which the cage potential is rather strong, such that only small fluctuations of the azimuthal angle β are allowed. Correspondingly one could perform an asymptotic expansion by retaining only linear functions of β , which are directly coupled to linear functions of angular momentum components L_x and L_y . In order to extend the analysis to the case of finite, albeit large, librational frequencies, one can adopt the same strategy employed in Ref. 12, that is to represent the evolution operator into a finite set of functions with the correct boundary conditions, but which mimic the asymptotic behavior. In the present case one should consider the subspace ϵ_{lin} of functions with a linear dependence on the angular momentum components or functions with a linear expansion with respect to β as $\beta \rightarrow 0$. Therefore only the terms $D_{m,m}^1(\mathbf{\Omega}) * L^{(1,m)}$ with $m = \pm 1$ are retained in Eq. (62) for functions $f^{(1,l)}$ in the correlation function Eq. (64), because of the following behavior of the Wigner rotation matrices for $\beta \rightarrow 0$:

$$D_{l,m}^j \propto \beta^{|l-m|} \exp(-il\alpha - im\gamma). \quad (65)$$

The ϵ_{lin} subspace will include these functions, as well as the other elements of the Krylov sequence^{10,16} generated by the $\hat{\Gamma}_F$ operator, which belong to ϵ_{lin} . The following set of functions is selected in this way: $D_{m,m}^j(\mathbf{\Omega}) * L^{(1,m)}$ and $D_{m,0}^j(\mathbf{\Omega}) *$ for $m = \pm 1$ without any constraint on the index j . That is, because of Eq. (65), these latter functions have the same β dependence independent of the index j , which then can be chosen according to the rank of the observable ($j=1$ for the angular momentum correlation). Therefore the following four functions, which are neither orthogonal nor normalized [cf. the weighting functions expressed in Eq. (25)] are sufficient to span the ϵ_{lin} subspace

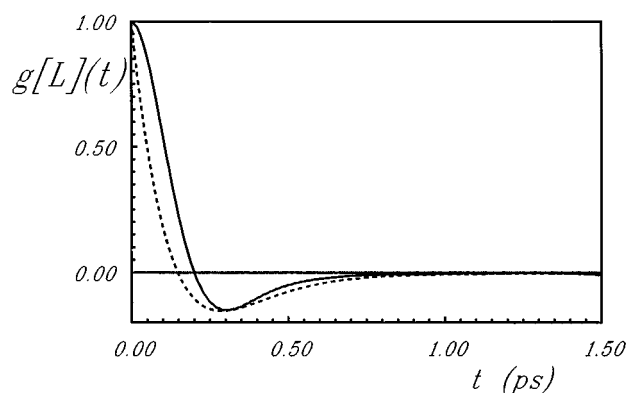


FIG. 3. Correlation function for the probe angular momentum \mathbf{L}_\perp . Continuous lines: MD simulation, dashed lines: result of the stochastic model.

$$\begin{aligned} h_1 &= D_{-1,0}^j(\boldsymbol{\Omega})^*, \\ h_2 &= D_{-1,-1}^j(\boldsymbol{\Omega})^* L^{(1,-1)}, \\ h_3 &= D_{1,1}^j(\boldsymbol{\Omega})^* L^{(1,1)}, \\ h_4 &= D_{1,0}^j(\boldsymbol{\Omega})^*. \end{aligned} \quad (66)$$

After evaluating the overlap matrix and the matrix representation of $\hat{\Gamma}_F$, which are, respectively:

$$C_{n,n'} = \int d\mathbf{X}_F h_n(\mathbf{X}_F)^* P(\mathbf{X}_S|\mathbf{X}_F) h_{n'}(\mathbf{X}_F), \quad (67)$$

$$B_{n,n'} = \int d\mathbf{X}_F h_n(\mathbf{X}_F)^* \hat{\Gamma}_F P(\mathbf{X}_S|\mathbf{X}_F) h_{n'}(\mathbf{X}_F), \quad (68)$$

one is left with a simple expression for the desired correlation function

$$G[L](t) = \mathbf{e}_2^{\text{tr}} \exp(-\mathbf{B}\mathbf{C}^{-1}t) \mathbf{C}\mathbf{e}_2 + \mathbf{e}_3^{\text{tr}} \exp(-\mathbf{B}\mathbf{C}^{-1}t) \mathbf{C}\mathbf{e}_3, \quad (69)$$

where \mathbf{e}_k is the four-dimensional array with null elements except for the unity in the k th position. Notice that the two terms at the right-hand side of Eq. (69) are complex conjugates of each other, so that the resulting function is real in spite of the presence of complex elements in the \mathbf{B} and \mathbf{C} matrices. These elements are readily calculated in terms of integrals of exponential and Bessel functions. Of course both matrices depend parametrically on the set \mathbf{X}_S of slow variables and, therefore, the results of Eq. (69) should be averaged as in Eq. (B26) in order to obtain the complete correlation function.

In Figure 3 the angular momentum correlation function obtained from the MD simulation of chlorine is compared with the theoretical one calculated with $\xi_\perp/I_\perp = 8 \text{ ps}^{-1}$ (the other parameters having already been determined). The overall agreement should be considered rather satisfactory, taking into account the simplifications introduced in our stochastic model. Note that for early times the stochastic model is unable to reproduce the well-known Gaussian behavior of the momentum correlation function,¹⁷ since we have neglected any explicit description of the rapidly fluctuating

TABLE II. Equilibrium averages $\overline{|D_{m,0}^j(\boldsymbol{\Omega}) - d_m^j(\boldsymbol{\omega})|^2}$.

j	m	$\overline{ D_{m,0}^j(\boldsymbol{\Omega}) - d_m^j(\boldsymbol{\omega}) ^2}$
1	0	0.0055
1	1	0.0497
2	0	0.0293
2	1	0.1116
2	2	0.0086

forces (i.e. $\dot{\mathbf{L}}$) acting on the probe molecule. Inclusion of such a feature would substantially complicate the stochastic model.

Finally we examine the fast component of the correlation function Eq. (47) for the overall probe rotation. Therefore Eq. (54) should be computed using

$$\delta f = \sum_m D_{l,m}^j(\boldsymbol{\Omega}^c) [D_{m,0}^j(\boldsymbol{\Omega}) - d_m^j(\boldsymbol{\omega})] \quad (70)$$

and it can be decomposed into the sum of contributions for different values of the index m in Eq. (70). The cross terms will be eliminated by the subsequent average over the slow variables $\boldsymbol{\Omega}^c$. Even in this case the full numerical calculation cannot be performed easily given the large size of the functional space to be considered. Therefore we shall employ the same technique used for the angular momentum. In Table II the averages of $\overline{|D_{m,0}^j(\boldsymbol{\Omega}) - d_m^j(\boldsymbol{\omega})|^2}$ are reported in order to show that only the contributions with $m = \pm 1$ are the most significant, and they correspond to functions with a linear expansion in the azimuthal angle β . Therefore the same basis functions of Eq. (66) with the index j fixed according to the rank of the observable, can be employed for computing such a correlation function

$$\begin{aligned} (2j+1)G^j[\boldsymbol{\Omega}^o]_F(t) &= \mathbf{e}_1^{\text{tr}} \exp(-\mathbf{B}\mathbf{C}^{-1}t) \mathbf{C}\mathbf{e}_1 + \mathbf{e}_4^{\text{tr}} \\ &\quad \times \exp(-\mathbf{B}\mathbf{C}^{-1}t) \mathbf{C}\mathbf{e}_4. \end{aligned} \quad (71)$$

The overall correlation function, which includes both this fast component and the slow component analyzed in the previous section, are displayed in Fig. 4 for ranks $j=1,2$. These results reproduce the general trend found in the MD simula-

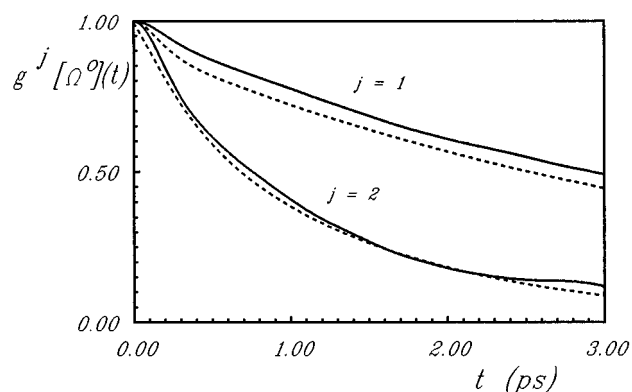


FIG. 4. Correlation functions of ranks $j=1$ and $j=2$ for the probe orientation $\boldsymbol{\Omega}^c$. Continuous lines: MD simulation, dashed lines: stochastic model.

tion, with a small component decaying in short times, and the long time tail accounted for by the cage rotational diffusion.

It should be mentioned that one parameter of the stochastic model has not been determined: the parallel component, ξ_{\parallel} , of the friction. Of course it has no physical meaning in the case of linear molecules like chlorine since their rotations about the symmetry axes are not defined. In the more general case of a molecule having a well defined parallel component I_{\parallel} of the moment of inertia and with, at least approximately, axially symmetric interactions with the solvent molecules, it can be determined by examining the correlation function for the parallel component $L_{\parallel} \equiv L_z$ of the angular momentum. Because of the axial symmetry, L_{\parallel} is not coupled to other variables by the complete evolution operator Eq. (22). Therefore

$$\overline{L_{\parallel}(t)L_{\parallel}(0)} = I_{\parallel}k_B T \exp(-t\xi_{\parallel}/I_{\parallel}) \quad (72)$$

and by comparison with MD data one can extract the unknown ξ_{\parallel} friction coefficient.

V. CONCLUSIONS

In order to analyze theoretically the molecular rotational motion coupled to the solvent cage, a rather complex treatment is required even when attention is focused on the principal correlation functions. The physical origin of such a complexity is the presence of several competing relaxation processes which are essential to determine the overall behavior of the observables. Correspondingly, a large number of independent variables needs to be considered in the stochastic model for the solute-cage interactions, and efficient techniques are required in order to derive the relevant time-dependent observables. This has been possible in our specific case because of the compact representation, Eq. (19) of the time evolution operator, which facilitates the formal elaborations required, for example, by the change of variables, and because of the applicability of the BO approximation which allows a separation of fast and slow variables in computing a given correlation function.

The set of derived results provides a rationalization of the findings of the MD simulation of paper I, thereby demonstrating that a stochastic model which explicitly includes a suitable set of cage parameters as independent variables is able to account for the general features of solute-solvent interactions. Given the efficiency of the theoretical tools, it is possible in our opinion to develop even more detailed models by including, for example, the fast cage frequencies among the independent variables, in order to recover a more accurate agreement with the MD simulations particularly in the short time scale.

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APPENDIX A: CHANGE OF ORIENTATIONAL VARIABLES

The transformation of the representation from the \mathbf{Y} variables of Eq. (1) to the variables \mathbf{X} of Eq. (21) requires that the absolute probe orientation $\boldsymbol{\Omega}^o$ be substituted by the relative orientation $\boldsymbol{\Omega}$ with respect to the cage frame. This change of orientational variables is conveniently done by employing the method of Ref. 8. Let us introduce the differential $d\tilde{\mathbf{Y}}$ conjugate to the gradient operator $\hat{\nabla}_{\mathbf{Y}}$ [cf. Eq. (18)]:

$$d\tilde{\mathbf{Y}} \equiv \begin{pmatrix} d\boldsymbol{\varphi}^o \\ d\mathbf{L} \\ d\boldsymbol{\varphi}^c \\ d\boldsymbol{\omega} \end{pmatrix}, \quad (A1)$$

where $d\boldsymbol{\varphi}^o$ has already been specified in relation to Eq. (8), while $d\boldsymbol{\varphi}^c$ denotes the components in the cage frame of the infinitesimal rotation vector of the cage frame with respect to the laboratory frame. Correspondingly, the change of an arbitrary function $f(\mathbf{Y})$ after an infinitesimal increment $d\mathbf{Y}$ of the variables is written as:

$$df = f(\mathbf{Y} + d\mathbf{Y}) - f(\mathbf{Y}) = d\tilde{\mathbf{Y}}^t \hat{\nabla}_{\mathbf{Y}} f(\mathbf{Y}). \quad (A2)$$

Note that $d\mathbf{Y}$ and $d\tilde{\mathbf{Y}}$ differ in their rotational components; cf. Eq. (1) and (A1).

In a similar way the differential $d\tilde{\mathbf{X}}$ conjugate to gradient operator $\hat{\nabla}_{\mathbf{X}}$ of Eq. (23) is introduced in the following form

$$d\tilde{\mathbf{X}} = \begin{pmatrix} d\boldsymbol{\varphi} \\ d\mathbf{L} \\ d\boldsymbol{\varphi}^c \\ d\boldsymbol{\omega} \end{pmatrix}, \quad (A3)$$

where $d\boldsymbol{\varphi}$ denotes the components in the molecular frame of the infinitesimal rotation vector of the molecular frame. From the additivity of infinitesimal rotation vectors, one immediately derives

$$d\boldsymbol{\varphi}^o = \mathbf{E}d\boldsymbol{\varphi}^c + d\boldsymbol{\varphi}, \quad (A4)$$

where the Euler matrix $\mathbf{E} = \mathbf{E}(\boldsymbol{\Omega})$ transforms vector components from the cage frame to the molecular frame. Therefore differentials $d\tilde{\mathbf{Y}}$ and $d\tilde{\mathbf{X}}$ are linearly related as:

$$d\tilde{\mathbf{X}} = \mathbf{S}d\tilde{\mathbf{Y}}, \quad \mathbf{S}(\boldsymbol{\Omega}) = \begin{pmatrix} \mathbf{1} & \mathbf{0} & -\mathbf{E}(\boldsymbol{\Omega}) & \mathbf{0} \\ \mathbf{0} & \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{1} \end{pmatrix}. \quad (A5)$$

As in Eq. (A2), the infinitesimal change of a function $f(\mathbf{X}) = [f(\mathbf{Y})]_{\mathbf{Y}=\mathbf{Y}(\mathbf{X})}$ is written as:

$$df = f(\mathbf{X} + d\mathbf{X}) - f(\mathbf{X}) = d\tilde{\mathbf{X}}^{\text{tr}} \hat{\nabla}_{\mathbf{X}} f(\mathbf{X}). \quad (\text{A6})$$

Under the condition of the same initial and final states, equations (A2) and (A6) are equivalent and, by taking into account Eq. (A5), one derives the following relation for the transformation of the gradient operator

$$\hat{\nabla}_{\mathbf{Y}} = \mathbf{S}^{\text{tr}} \hat{\nabla}_{\mathbf{X}}. \quad (\text{A7})$$

In order to transform the evolution operator of the FP equation also, let us consider the time-dependent average of the function $f(\mathbf{Y})$

$$\overline{f(t)} \equiv \int d\mathbf{Y} f(\mathbf{Y}) P(\mathbf{Y}; t) \quad (\text{A8})$$

whose time evolution is given as:

$$\begin{aligned} \overline{df(t)/dt} &= - \int d\mathbf{Y} f(\mathbf{Y}) \hat{\Gamma} P(\mathbf{Y}; t) \\ &= \int d\mathbf{Y} P(\mathbf{Y}) [\hat{\nabla}_{\mathbf{Y}} f(\mathbf{Y})]^{\text{tr}} \mathbf{A}_{\mathbf{Y}} \\ &\quad \times \hat{\nabla}_{\mathbf{Y}} P(\mathbf{Y})^{-1} P(\mathbf{Y}; t), \end{aligned} \quad (\text{A9})$$

where Eq. (19) has been used for $\hat{\Gamma}$ followed by an integration by parts applied to the first gradient operator. The constant terms are omitted in such an integration by parts because of the assumed conservation of the probability norm. By changing the integration variables to \mathbf{X} , by then transforming the gradient operator according to Eq. (A7), and by a further integration by parts, one finally obtains:

$$\overline{df(t)/dt} = - \int d\mathbf{X} f(\mathbf{X}) \hat{\Gamma} P(\mathbf{X}; t) \quad (\text{A10})$$

with the time evolution operator in the new set of variables

$$\hat{\Gamma} = - \hat{\nabla}_{\mathbf{X}}^{\text{tr}} P(\mathbf{X}) \mathbf{A}_{\mathbf{X}} \hat{\nabla}_{\mathbf{X}} P(\mathbf{X})^{-1}. \quad (\text{A11})$$

The corresponding coupling matrix is given as

$$\mathbf{A}_{\mathbf{X}} = \mathbf{S} \mathbf{A}_{\mathbf{Y}} \mathbf{S}^{\text{tr}} \quad (\text{A12})$$

and by inserting Eq. (A5) for the transformation matrix \mathbf{S} , the final result Eq. (23) of the second section is recovered. Other kinds of change of variables can be performed in the same manner after transforming the gradient operator as in Eq. (A7).

APPENDIX B: THE BORN–OPPENHEIMER APPROXIMATION APPLIED TO STOCHASTIC OPERATORS

In this appendix we analyze in a general framework the separation of the contributions of fast \mathbf{X}_F and slow \mathbf{X}_S variables in the stochastic problem for $\mathbf{X} = (\mathbf{X}_S, \mathbf{X}_F)$. The basic method is the same as the Born–Oppenheimer approximation for the quantum mechanical treatment of the coupled motion of electrons and nuclei in molecules. However, a generalization of this procedure is required in the application to stochastic problems. Before applying the approximation, one should isolate from the complete evolution operator $\hat{\Gamma}$ its fast component $\hat{\Gamma}_F$ acting on the \mathbf{X}_F variables, which describes

their relaxation to equilibrium when the slow variables \mathbf{X}_S are frozen. Therefore, only a parametric dependence on slow variables \mathbf{X}_S is allowed for $\hat{\Gamma}_F$. Correspondingly one can introduce a time evolution equation for the \mathbf{X}_F variables only, by considering the conditional probability $P(\mathbf{X}_S | \mathbf{X}_F; t)$ of \mathbf{X}_F with respect to a fixed set \mathbf{X}_S :

$$\partial P(\mathbf{X}_S | \mathbf{X}_F; t) / \partial t = - \hat{\Gamma}_F P(\mathbf{X}_S | \mathbf{X}_F; t) \quad (\text{B1})$$

with the stationary solution provided by the equilibrium conditional probability Eq. (39)

$$\hat{\Gamma}_F P(\mathbf{X}_S | \mathbf{X}_F) = 0. \quad (\text{B2})$$

The following condition is required

$$\int d\mathbf{X}_F \hat{\Gamma}_F P(\mathbf{X}_S | \mathbf{X}_F; t) = 0 \quad (\text{B3})$$

in order to preserve the normalization

$$\int d\mathbf{X}_F P(\mathbf{X}_S | \mathbf{X}_F; t) = 1. \quad (\text{B4})$$

These are the mathematical constraints for the choice of $\hat{\Gamma}_F$. In the case of stochastic operators like Eq. (22), they can be met simply by including in $\hat{\Gamma}_F$ only the components of the gradient operator $\hat{\nabla}_{\mathbf{X}}$ with derivatives of \mathbf{X}_F variables. The remaining terms are collected in the residual operator $\delta\hat{\Gamma}$ such that

$$\hat{\Gamma} = \hat{\Gamma}_F + \delta\hat{\Gamma}. \quad (\text{B5})$$

In the classic Born–Oppenheimer approximation $\delta\hat{\Gamma}$ should only depend upon the \mathbf{X}_S variables. Then it supplies the characteristic separability of the solution into eigenvectors of $\hat{\Gamma}_F$ that depend parametrically on \mathbf{X}_S , and the eigenvectors for the \mathbf{X}_S depend explicitly on the particular eigenvalue of $\hat{\Gamma}_F$ as well as on $\delta\hat{\Gamma}$. We shall modify this procedure by allowing $\delta\hat{\Gamma}$ to also contain small terms dependent upon \mathbf{X}_F such that they are perturbations compared to $\hat{\Gamma}_F$, i.e. such that:

$$|\hat{\Gamma}_F| \gg |\delta\hat{\Gamma}|. \quad (\text{B6})$$

On the other hand this is an implicit condition for the separation of fast and slow variables, since only when Eq. (B6) is satisfied will the relaxation of the two sets of variables be characterized by very different time scales.

For the sake of convenience, we shall employ time evolution operators $\tilde{\Gamma}$, $\tilde{\Gamma}_F$ and $\delta\tilde{\Gamma}$ in their symmetrized form defined as in Eq. (24), and the integration restricted to fast and slow variables will be conveniently denoted as

$$\langle \cdots \rangle_F \equiv \int d\mathbf{X}_F \cdots, \langle \cdots \rangle_S \equiv \int d\mathbf{X}_S \quad (\text{B7})$$

so that

$$\langle \cdots \rangle \equiv \int d\mathbf{X} \cdots = \int d\mathbf{X}_S \int d\mathbf{X}_F \cdots = \langle \langle \cdots \rangle_F \rangle_S. \quad (\text{B8})$$

A biorthonormal basis for \mathbf{X}_F -functional space can be derived from eigenvectors of $\tilde{\Gamma}_F$ and its adjoint

$$\langle n|n'\rangle_F = \delta_{n,n'}. \quad (\text{B9})$$

Then the operator $\tilde{\Gamma}_F$ can be decomposed as

$$\tilde{\Gamma}_F = \sum_n |n\rangle_F E_n(\mathbf{X}_S) \langle n|, \quad (\text{B10})$$

where E_n for $n=0,1,2,\dots$, are the eigenvalues of $\tilde{\Gamma}_F$. These eigenvalues, as well as the corresponding eigenvectors, depend parametrically on \mathbf{X}_S variables. Notice that the first eigenvalue $E_0=0$ vanishes corresponding to the stationary solution derived according to Eqs. (B2) and (B3)

$$|0\rangle_F = |P(\mathbf{X}_S|\mathbf{X}_F)^{1/2}\rangle_F, \quad \langle 0| = \langle P(\mathbf{X}_S|\mathbf{X}_F)^{1/2}|. \quad (\text{B11})$$

By also introducing a biorthonormal basis $\langle q|q'\rangle_S = \delta_{q,q'}$ for the ϵ_S space of functions of \mathbf{X}_S only, a complete biorthonor-

mal set spanning the full functional space in $\mathbf{X}=(\mathbf{X}_F,\mathbf{X}_S)$ is recovered as the direct product of $|n\rangle_F$ and $|q\rangle_S$, i.e. $|n,q\rangle = |n\rangle_F |q\rangle_S$. Because of the assumed completeness and biorthonormality of the $|n,q\rangle$ basis, the correlation function Eq. (25) of a given observable $f(\mathbf{X})$ is decomposed as:

$$G(t) = \sum_{n,q,n',q'} \langle f(\mathbf{X})P^{1/2}(\mathbf{X})|n,q\rangle \langle n,q|e^{-\tilde{\Gamma}t}|n',q'\rangle \times \langle n',q'|f(\mathbf{X})P^{1/2}(\mathbf{X})\rangle. \quad (\text{B12})$$

The exponential operator in Eq. (B12) can be expanded in a Taylor series in time

$$\begin{aligned} \langle n,q|e^{-\tilde{\Gamma}t}|n',q'\rangle &= \sum_k \frac{(-t)^k}{k!} \langle n,q|(\tilde{\Gamma}_F + \delta\tilde{\Gamma})^k|n',q'\rangle \\ &= \sum_k \frac{(-t)^k}{k!} \sum'_{\alpha_1,\beta_1,\dots,\alpha_m,\beta_m} \langle n,q|\tilde{\Gamma}_F^{\alpha_1} \delta\tilde{\Gamma}^{\beta_1} \dots \tilde{\Gamma}_F^{\alpha_m} \delta\tilde{\Gamma}^{\beta_m}|n',q'\rangle \\ &= \sum_k \frac{(-t)^k}{k!} \sum'_{\alpha_1,\beta_1,\dots,\alpha_m,\beta_m} \sum_{n_1,q_1,\dots,n_{2m-1},q_{2m-1}} \langle n,q|\tilde{\Gamma}_F^{\alpha_1}|n_1,q_1\rangle \\ &\quad \times \langle n_1,q_1|\delta\tilde{\Gamma}^{\beta_1}|n_2,q_2\rangle \dots \langle n_{2m-2},q_{2m-2}|\tilde{\Gamma}_F^{\alpha_m}|n_{2m-1},q_{2m-1}\rangle \langle n_{2m-1},q_{2m-1}|\delta\tilde{\Gamma}^{\beta_m}|n',q'\rangle, \end{aligned} \quad (\text{B13})$$

where the primed sums are extended over all natural numbers α_i , β_i and m but with the constraint $\sum_{i=1}^m (\alpha_i + \beta_i) = k$. The completeness of $|n,q\rangle$ is invoked again to recover the final expression.

In this framework, the Born–Oppenheimer approximation is equivalent to 1) the use of the representation of $\hat{\Gamma}_F$ given by Eq. (B10) and the use of the direct product basis $|n,q\rangle$, plus 2) the retention of only diagonal elements of $\delta\tilde{\Gamma}$ with respect to the $|n\rangle_F$ basis

$$\langle n|\delta\tilde{\Gamma}|n'\rangle_F = \delta_{n,n'} \delta\tilde{\Gamma}_n^{\text{BO}}, \quad (\text{B14})$$

where $\delta\tilde{\Gamma}_n^{\text{BO}} = \langle n|\delta\tilde{\Gamma}|n\rangle_F$ is the averaged operator with respect to $|n\rangle_F$ and, therefore, it acts on \mathbf{X}_S only. This is based upon the condition of Eq. (B6) justifying a first order perturbation treatment. Such an approximation is self-consistently applied to generic powers of $\delta\tilde{\Gamma}$ as

$$\begin{aligned} \langle n|\delta\tilde{\Gamma}^\beta|n'\rangle_F &= \sum_{n''} \langle n|\delta\tilde{\Gamma}|n''\rangle_F \langle n''|\delta\tilde{\Gamma}^{\beta-1}|n'\rangle_F \\ &= \delta\tilde{\Gamma}_n^{\text{BO}} \langle n|\delta\tilde{\Gamma}^{\beta-1}|n'\rangle_F = \delta_{n,n'} (\delta\tilde{\Gamma}_n^{\text{BO}})^\beta. \end{aligned} \quad (\text{B15})$$

Notice that such an approximation is always required unless one is considering the simple case of a time evolution opera-

tor with complete separation of the slow and fast variables. Even when $\delta\tilde{\Gamma}$ is an operator on \mathbf{X}_S only, the off-diagonal elements do not in general vanish because of the parametric dependence of eigenvectors $|n\rangle_F$ on \mathbf{X}_S , so they will in general be modified by the operator $\delta\tilde{\Gamma}$.

By taking into account that basis elements $|n\rangle_F$ are eigenfunctions of $\tilde{\Gamma}_F$, Eq. (B13) is reduced to the form:

$$\begin{aligned} \langle n,q|e^{-\tilde{\Gamma}t}|n',q'\rangle &= \sum_k \frac{(-t)^k}{k!} \sum'_{\alpha_1,\beta_1,\dots,\alpha_m,\beta_m} \sum_{q_1,\dots,q_{2m-1}} \\ &\quad \times \langle q|E_n^{\alpha_1}|q_1\rangle_S \langle q_1|\delta\tilde{\Gamma}_n^{\beta_1}|q_2\rangle_S \dots \\ &\quad \times \langle q_{2m-2}|E_n^{\alpha_m}|q_{2m-1}\rangle_S \langle q_{2m-1}|\tilde{\Gamma}_n^{\beta_m}|q'\rangle_S \delta_{n,n'}, \end{aligned} \quad (\text{B16})$$

which is written more concisely as

$$\langle n,q|e^{-\tilde{\Gamma}t}|n',q'\rangle = \langle q|e^{-(E_n + \delta\tilde{\Gamma}_n^{\text{BO}})t}|q'\rangle_S \delta_{n,n'}. \quad (\text{B17})$$

After substitution into Eq. (B13), the correlation function $G_{\text{BO}}(t)$ within the Born–Oppenheimer approximation is finally recovered as:

$$G_{\text{BO}}(t) = \sum_{n=0}^{\infty} \langle \langle fP^{1/2}|n\rangle_F e^{-(E_n + \delta\tilde{\Gamma}_n^{\text{BO}})t} \langle n|fP^{1/2}\rangle_F \rangle_S. \quad (\text{B18})$$

Notice that the only properties of the $|q\rangle_S$ basis required by this derivation are its completeness and biorthonormality.

One can partition the terms in the summation at the right-hand side of Eq. (B18) according to the presence (or the absence) in the exponents of contributions due to $\tilde{\Gamma}_F$, thereby defining a slow component $G_S(t)$ and a fast component $G_F(t)$ of the correlation function

$$G_{\text{Bo}}(t) = G_S(t) + G_F(t). \quad (\text{B19})$$

The slow component includes only the term with $n=0$ corresponding to the stationary mode $|0\rangle_F$ with vanishing eigenvalue $E_0=0$:

$$G_S(t) = \langle\langle fP^{1/2}|0\rangle_F e^{-\delta\tilde{\Gamma}_0 t} \langle 0|fP^{1/2}\rangle_F \rangle_S. \quad (\text{B20})$$

While the remaining terms are collected into $G_F(t)$

$$G_F(t) = \sum_{n=1}^{\infty} \langle\langle fP^{1/2}|n\rangle_F e^{-(E_n + \delta\tilde{\Gamma}_n)t} \langle n|fP^{1/2}\rangle_F \rangle_S. \quad (\text{B21})$$

By recalling Eq. (B11) and the definition of Eq. (38) of the projection $f_S(\mathbf{X}_S)$ of $f(\mathbf{X})$ onto the \mathbf{X}_S -functional space ϵ_S , one derives the result that $\langle 0|fP^{1/2}\rangle_F = f_S(\mathbf{X}_S)^{1/2} P_S(\mathbf{X}_S)^{1/2}$. Moreover the evolution operator in Eq. (B20) can be written as:

$$\delta\tilde{\Gamma}_0 \equiv \langle 0|\delta\tilde{\Gamma}|0\rangle_F = \langle 0|\tilde{\Gamma}|0\rangle_F = \tilde{\Gamma}_S, \quad (\text{B22})$$

where $\tilde{\Gamma}_S \equiv P_S^{-1/2} \hat{\Gamma}_S P_S^{1/2}$ is the symmetrized form of the projected operator $\hat{\Gamma}_S$ of Eq. (35) for the relaxation of the slow variables. In conclusion the slow component $G_S(t)$ can be rewritten as

$$G_S(t) = \langle f_S P_S^{1/2} | \exp(-\tilde{\Gamma}_S t) | f_S P_S^{1/2} \rangle_S, \quad (\text{B23})$$

which is equivalent to Eq. (40) already obtained in Section III by means of a direct projection onto ϵ_S of the full evolution operator.

In general, no further simplification can be made for the fast component given by Eq. (B21) unless the contributions from $\delta\tilde{\Gamma}_n$ are neglected by utilizing the condition given by Eq. (B6). Of course such an approximation might reduce the accuracy of the final results. On the other hand, by neglecting the $\delta\tilde{\Gamma}_n$ terms, one can perform analytically the summation over the eigenfunctions of $\tilde{\Gamma}_F$, thereby obtaining:

$$G_F(t) \approx \langle \delta f P^{1/2} | e^{-\tilde{\Gamma}_F t} | \delta f P^{1/2} \rangle, \quad (\text{B24})$$

where

$$\begin{aligned} \delta f(\mathbf{X}) &\equiv f(\mathbf{X}) - P(\mathbf{X})^{-1/2} |0\rangle_F \langle 0|fP^{1/2}\rangle_F \\ &= f(\mathbf{X}) - f_S(\mathbf{X}_S). \end{aligned} \quad (\text{B25})$$

Therefore the spectral resolution of $\tilde{\Gamma}_F$, i.e. the knowledge of its eigenfunctions and eigenvalues, would not be strictly required in the calculation of $G_F(t)$ from Eq. (B24). By taking into account that $\tilde{\Gamma}_F$ depends only parametrically on \mathbf{X}_S , Eq. (B24) can be rewritten as an average over \mathbf{X}_S

$$G_F(t) \approx \int d\mathbf{X}_S P_S(\mathbf{X}_S) G_F(\mathbf{X}_S, t) \quad (\text{B26})$$

of independent contributions $G_F(\mathbf{X}_S, t)$, which derive from the relaxation of the fast variables for fixed values of the set \mathbf{X}_S :

$$\begin{aligned} G_F(\mathbf{X}_S, t) &\equiv \int d\mathbf{X}_F \delta f(\mathbf{X}) * P(\mathbf{X}_S | \mathbf{X}_F)^{1/2} \\ &\quad \times \exp(-\tilde{\Gamma}_F t) \delta f(\mathbf{X}) P(\mathbf{X}_S | \mathbf{X}_F)^{1/2}. \end{aligned} \quad (\text{B27})$$

When analytical solutions of $\tilde{\Gamma}_F$ are not available, then one can perform a numerical calculation restricted to the space of \mathbf{X}_F variables only, with a simple superposition of the results at different \mathbf{X}_S (some examples are provided in Section IV). An equivalent result, from a more phenomenological approach, was obtained in Ref. 6.

Notice that according to Eq. (B27), $G_F(\mathbf{X}_S, t)$ would be the correlation function of $\delta f(\mathbf{X})$ for a fixed \mathbf{X}_S when the solution of Eq. (B1) for the dynamics of the fast variables only are taken into account. One can then provide a physical picture of the full correlation function, by considering that slow and fast variables are characterized by very different time scales $\tau_S \gg \tau_F$. Within a time window of the order of τ_F during which there are no significant changes of the slow variables, only the fast variables relax to the equilibrium consistent with the static values of \mathbf{X}_S . This process accounts for the fast component $G_F(t)$ of the correlation function, with the observable $f(\mathbf{X})$ relaxing to $f_S(\mathbf{X}_S)$, i.e. its average over \mathbf{X}_F conditioned by the static \mathbf{X}_S . Subsequently the evolution of the slow variable takes place on the time scale of τ_S , with the final relaxation of $f_S(\mathbf{X}_S)$ to \bar{f} described by the slow component $G_S(t)$ of the correlation function.

It is also possible to obtain the above results by introducing an approximate form of the conditional probability function. We write down such a form that immediately allows us to separate the slowly and rapidly relaxing terms. It is:

$$\begin{aligned} P(\mathbf{X}^0 | \mathbf{X}; t) &\approx \delta(\mathbf{X}_S - \mathbf{X}_S^0) [P(\mathbf{X}_S, \mathbf{X}_F^0 | \mathbf{X}_F; t) - P(\mathbf{X}_S | \mathbf{X}_F)] \\ &\quad + P(\mathbf{X}_S | \mathbf{X}_F) P_S(\mathbf{X}_S^0 | \mathbf{X}_S; t), \end{aligned} \quad (\text{B28})$$

where $P(\mathbf{X}_S, \mathbf{X}_F^0 | \mathbf{X}_F; t)$ describes the dynamics of the fast variables

$$P(\mathbf{X}_S, \mathbf{X}_F^0 | \mathbf{X}_F; t) \equiv \exp(-\hat{\Gamma}_F t) \delta(\mathbf{X}_F - \mathbf{X}_F^0), \quad (\text{B29})$$

the parametric dependence on \mathbf{X}_S deriving from operator $\hat{\Gamma}_F$, while $P(\mathbf{X}_S^0 | \mathbf{X}_S; t)$ is the conditional probability for the slow variables alone under the action of the projected operator $\hat{\Gamma}_S$ [cf. Eqs. (35) and (36)]:

$$P(\mathbf{X}_S^0|\mathbf{X}_S;t) \equiv \exp(-\hat{\Gamma}_S t) \delta(\mathbf{X}_S - \mathbf{X}_S^0). \quad (\text{B30})$$

In this way the separation of the dynamical contributions of the two types of variables appears evident also in the time-dependent probability. One can easily demonstrate that previous results are recovered utilizing Eq. (B29) by computing the correlation function by means of such a conditional probability, with the fast (approximate) component $G_F(t)$ [cf. Eq. (B27)] and the slow component $G_S(t)$ [cf. Eq. (B23)] deriving from the first term and the second term, respectively, on the right hand side of Eq. (B28). Simplified expressions are derived from Eq. (B28) in two limiting cases. For times $t \ll \tau_S$ when $P(\mathbf{X}_S^0|\mathbf{X}_S;t) \approx \delta(\mathbf{X}_S - \mathbf{X}_S^0)$ in the absence of significant displacements of the slow variables, one obtains

$$P(\mathbf{X}^0|\mathbf{X};t) \approx \delta(\mathbf{X}_S^0 - \mathbf{X}_S) P(\mathbf{X}_S, \mathbf{X}_F^0|\mathbf{X}_F;t), \quad (\text{B31})$$

where only the dynamics of the fast variables are effective. In the opposite limit $t \gg \tau_F$ when the fast variables have relaxed to equilibrium, i.e. $P(\mathbf{X}_S, \mathbf{X}_F^0|\mathbf{X}_F;t) \approx P(\mathbf{X}_S|\mathbf{X}_F)$, the following approximation holds

$$P(\mathbf{X}^0|\mathbf{X};t) \approx P(\mathbf{X}_S|\mathbf{X}_F) P(\mathbf{X}_S^0|\mathbf{X}_S;t), \quad (\text{B32})$$

with the evolution of the system driven by the slow variables only, since the fast variables are always equilibrated with respect to \mathbf{X}_S . Notice that the alternative approximation

$$P(\mathbf{X}^0|\mathbf{X};t) \approx P_S(\mathbf{X}_S^0|\mathbf{X}_S;t) P(\mathbf{X}_S, \mathbf{X}_F^0|\mathbf{X}_F;t) \quad (\text{B33})$$

which was used in the analysis of Ref. 11, does reproduce the same two limits.

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