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REGULAR ARTICLE

Stochastic modelling of roto-translational motion of dyes in micellar environment

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Abstract Time decay of the fluorescence anisotropy ratio due to diffusion of dyes in micelles is usually interpreted by decoupling the reorientational dynamics of the molecule with respect to the local director from the translational diffusion of the dye. However, while such a kind of assumption is justified in other contexts (like for reorientations of a small mobile fragment in a macromolecule, decoupled from the motion of the macromolecule as a whole, as invoked in the well-known model by Lipari and Szabo), here it is not based on physical grounds. In this work we develop the stochastic model for the full description of the roto-translational dynamics of a dye in the micellar environment, by employing the Fokker–Planck–Smoluchowski equation for the positional and orientational variables. Then we simplify the model to the situation of strong confinement of the molecule at the micelle interface. Finally, by employing a time-scale separation between fast reorientational dynamics and slow lateral diffusion of the dye (which holds if the micelle radius is much larger than the size of the dye), and by resorting to a model like the "wobbling in a cone", we show that a bi-exponential form can be obtained for the fluorescence anisotropy ratio, but with the remarkable difference that the fast-relaxing component is not affected by the slow motion.

Keywords Fluorescence depolarization · Fokker–Planck equation · Micelles · Molecular diffusion

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1 Introduction

Time-dependent fluorescence depolarization of dyes confined to the interface of micelles are usually interpreted by assuming independent contributions of the librational motion with respect to a local director, and of the dye translational diffusion at the interface [1–4]. This allows the factorization of the transition dipole correlation function into a slow component, due to reorientations driven by the dye diffusion at the interface, and a fast component, associated to the dye librational motion. If a simplified model like the wobbling in cone [5,6] is employed for the latter process, then the fluorescence depolarization is described according to three independent parameters: (1) the correlation time for the interface diffusion of the dye, (2) the correlation time for the librational motion, and (3) the order parameter describing the degree of alignment of the dye with respect to the local director. Often, the overall rotational tumbling of the micelle is also taken into account, even if its contribution is negligible [1,3]. In practice the time dependence of the fluorescence anisotropy is fitted by the sum of two exponential decays and, from the corresponding time-constants and relative intensities, the three independent parameters of the model are evaluated [1–4].

To justify such a procedure, the "model-free" approach of Lipari and Szabo [7] is invoked. Such a model was elaborated for the analysis of the rotational relaxation in macromolecules when a small mobile fragment is observed. In this case, the assumption of independent contributions for the overall macromolecule rotations and the relative motion of the small fragment is well justified, as long as the motion of the fragment does not perturb significantly the dynamics of the overall macromolecule. In our opinion such a hypothesis cannot be taken for granted in the case of dyes in micelles, since the two independent motions cannot be assigned to bodies of different size. Furthermore, the separation of motions is not imposed by the need of simplifying the analysis of a very complex dynamical problem like macromolecular systems with a large number of internal degrees of freedom. As a matter of fact, the coupled translational and rotational motions of a rigid dye molecule are the only required ingredients for the analysis of the fluorescence anisotropy, and they can be treated according to standard stochastic methods based on the Fokker–Planck equation [8], or the Fokker–Planck–Smoluchowski equation for the overdamped regime. The complexity of the problem arises from the need of taking into account the dynamical effects of the ordered environment provided by micelles. These can be conveniently modelled by including in the evolution operator a suitable mean-field potential acting on both the translational and orientational degrees of freedom of the dye. In conclusion, the Fokker–Planck–Smoluchowski equation for the coupled translational and rotational motions of a rigid molecule with a proper mean-field potential can provide a self consistent description of dye fluorescence anisotropy in micelles. This, however, requires suitable procedures for the analysis of stochastic models in the presence of a mean-field potential.

In the past, the Theoretical Chemistry Group of Padua University, starting from the classical contributions by Nordio and coworkers on the rotational diffusion in nematic liquid crystals [9–11], has developed theoretical and computational methods for the analysis of Fokker–Planck equations of different kinds arising in several fields of Physical Chemistry. To summarize our past work, we would like to recall the analysis of (1) molecular models of the roto-translational dynamics in liquid crystals of nematic, smectic and cholesteric type [12–15]; (2) the conformational dynamics of flexible molecules [16–27]; (3) activated rate processes [28–36]; (4) electron transfer processes [37–44]; (5) cage effects in molecular fluids [45–51]; (6) effects of director fluctuations on spectroscopic observables [52–56]. Moreover, these applications required the development of computational algorithms [57–60]. In all the cases the basic formalism is provided by Fokker–Planck equations for the stochastic variables specific for a given problem, with a suitable potential reproducing the ordering due to environment or the internal coordinates.

In the present work, these theoretical methods will be applied to develop a molecular model for dye dynamics in micelles of spherical shape. In the next section we introduce the Fokker–Planck–Smoluchowski equation for the complete description of the rotational and translational dynamics of a rigid molecule in the micellar environment. A simplified model is derived in the third section by projecting out the radial dependence under the assumption of strong confinement at the interface of the micelle. In the fourth section we analyse when the roto-translational decoupling holds in order to make contact with the standard procedure of fitting the fluorescence depolarization [1–4]. We have also included some appendices with the specific mathematical tools employed in the analysis.

2 Roto-translational diffusion in micelles

Let us first describe the main reference systems employed in the modelling (see Fig. 1 for a geometric schematization). We introduce a *Laboratory Frame*, LF $\equiv (\mathbf{x}_{\mathrm{L}}, \mathbf{y}_{\mathrm{L}}, \mathbf{z}_{\mathrm{L}})$, whose origin is placed at the centre of the micelle, while the axes' orientation can be arbitrarily chosen due to the spherical symmetry of the system; then we consider a *Molecular Frame*, MF $\equiv (\mathbf{x}_{\mathrm{M}}, \mathbf{y}_{\mathrm{M}}, \mathbf{z}_{\mathrm{M}})$, tethered to the probe-molecule. With reference to LF, the stochastic variables for the roto-translational dynamics of the probe are denoted by the collective array $\mathbf{Q} = (\mathbf{r}, \mathbf{\Omega}_{\mathrm{LM}})$, where $\mathbf{r} = (r_x, r_y, r_z)$ are the coordinates of the molecular centre in the LF, and $\mathbf{\Omega}_{\mathrm{LM}} = (\alpha_{\mathrm{LM}}, \beta_{\mathrm{LM}}, \gamma_{\mathrm{LM}})$ is the set of Euler angles which specifies the molecular orientation through the transformation LF → MF encoded according to Rose's convention [62].

By considering the roto-translational motions as a stationary stochastic process, all information about dynamics (and equilibrium properties as well) are contained in the non-equilibrium probability density $p(\mathbf{Q}, t)$ normalized as $\int \mathrm{d}\mathbf{Q}\, p(\mathbf{Q}, t) = 1$, where $\mathrm{d}\mathbf{Q} = \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{\Omega}_{\mathrm{LM}}$ with $\mathrm{d}\mathbf{\Omega}_{\mathrm{LM}} = \mathrm{d}\alpha_{\mathrm{LM}}\, \mathrm{d}\beta_{\mathrm{LM}} \sin\beta_{\mathrm{LM}}\, \mathrm{d}\gamma_{\mathrm{LM}}$. The stationary limit $\lim_{t\to\infty} p(\mathbf{Q}, t) = p_{\mathrm{eq}}(\mathbf{Q})$ determines the equilibrium distribution which can be specified as the Maxwell–Boltzmann distribution for a given mean-field potential $V(\mathbf{Q})$:

$$p_{\mathrm{eq}}(\mathbf{Q}) = \frac{\mathrm{e}^{-V(\mathbf{Q})/k_{\mathrm{B}}T}}{\int \mathrm{d}\mathbf{Q}\mathrm{e}^{-V(\mathbf{Q})/k_{\mathrm{B}}T}} \tag{1}$$

By modelling the roto-translational dynamics as a diffusive process, the evolution of the non-equilibrium probability density is described by the Fokker–Planck–Smoluchowski equation [8]

$$\frac{\partial}{\partial t} p(\mathbf{Q}, t) = -\Gamma(\mathbf{Q}) p(\mathbf{Q}, t) \tag{2}$$

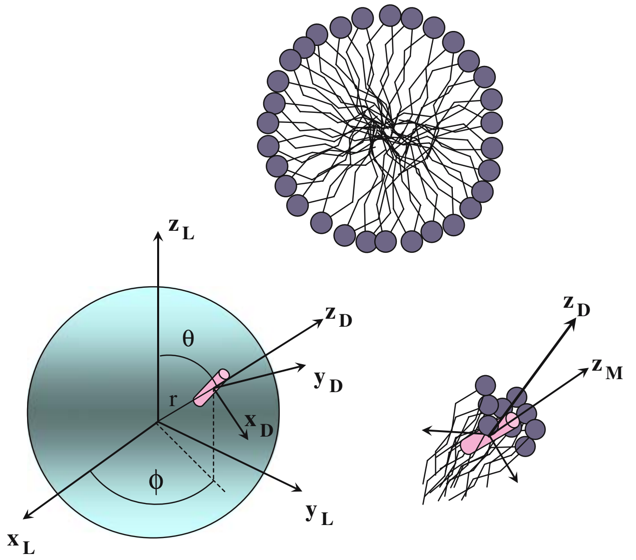

Fig. 1 Schematic representation of a spherical micelle, and reference systems employed in the analysis: the Laboratory Frame LF $\equiv (\mathbf{x}_\mathrm{L}, \mathbf{y}_\mathrm{L}, \mathbf{z}_\mathrm{L})$, the Director Frame DF $\equiv (\mathbf{x}_\mathrm{D}, \mathbf{y}_\mathrm{D}, \mathbf{z}_\mathrm{D})$ specified at the location of the dye, and the Molecular Frame MF $\equiv (\mathbf{x}_\mathrm{M}, \mathbf{y}_\mathrm{M}, \mathbf{z}_\mathrm{M})$ tethered to the dye

where $\Gamma(\mathbf{Q})$ is the evolution operator, acting on variables $\mathbf{Q}$, given by

$$\Gamma(\mathbf{Q}) = \nabla^\dagger(\mathbf{Q})\mathbf{D}(\mathbf{Q})p_\mathrm{eq}(\mathbf{Q})\nabla(\mathbf{Q})p_\mathrm{eq}(\mathbf{Q})^{-1} \tag{3}$$

with $\mathbf{D}(\mathbf{Q})$ the 6×6 roto-translational diffusion matrix, and $\nabla(\mathbf{Q})$ the gradient operator built as

$$\nabla(\mathbf{Q}) = \begin{pmatrix} \nabla_\mathrm{T}(\mathbf{r}) \\ \nabla_\mathrm{R}(\mathbf{\Omega}_\mathrm{LM}) \end{pmatrix} \tag{4}$$

where $\nabla_\mathrm{T}(\mathbf{r})$ and $\nabla_\mathrm{R}(\mathbf{\Omega}_\mathrm{LM})$ are, respectively, its positional-gradient and orientational-gradient components

$$\nabla_\mathrm{T}(\mathbf{r}) \equiv \frac{\partial}{\partial \mathbf{r}}, \quad \nabla_\mathrm{R}(\mathbf{\Omega}_\mathrm{LM}) \equiv \mathbf{M}_\mathrm{L}(\mathbf{\Omega}_\mathrm{LM}) \tag{5}$$

The operator $\mathbf{M}_\mathrm{L}(\mathbf{\Omega}_\mathrm{LM})$ is the generator of infinitesimal rotations (applied to functions of $\mathbf{\Omega}_\mathrm{LM}$) with Cartesian components referred to the Laboratory Frame; its form, involving derivatives with respect to the Euler angles, is specified in the Appendix A. Finally, the symbol "†" in Eq. (3) denotes the adjoint-operator, introduced in the context of the scalar product defined as $\langle f(\mathbf{Q}) \mid g(\mathbf{Q})\rangle \equiv \int \mathrm{d}\mathbf{Q} f(\mathbf{Q})^* g(\mathbf{Q})$ for generic pairs of functions f and g, by means of $\langle f(\mathbf{Q}) \mid \mathcal{O}(\mathbf{Q})g(\mathbf{Q})\rangle \equiv \langle(\mathcal{O}(\mathbf{Q})^\dagger f(\mathbf{Q})) \mid g(\mathbf{Q})\rangle$ for a generic operator $\mathcal{O}(\mathbf{Q})$; with reference to gradient operators, integration by parts yields the general rule $\nabla(\mathbf{Q})^\dagger \equiv -\nabla(\mathbf{Q})^\mathrm{Tr}$ with "Tr" denoting the transposed array.

The knowledge of $p(\mathbf{Q}, t)$ allows one to evaluate (time-dependent) averages of generic *observables*, i.e., $\overline{f}(t) = \int \mathrm{d}\mathbf{Q}\, p(\mathbf{Q}, t) f(\mathbf{Q})$ for functions $f(\mathbf{Q})$ probing the actual state of the stochastic variables. Moreover one can calculate time-correlation functions between generic pairs of observables $f(\mathbf{Q})$ and $g(\mathbf{Q})$ evaluated at two times t_1 and t_2; for a stationary process, the correlation functions depend only on the time-separation $t = t_2 - t_1$, and can be casted in the form

$$\overline{f(\mathbf{Q})^*_t g(\mathbf{Q})_0} = \int \mathrm{d}\mathbf{Q}\, f(\mathbf{Q})^* \mathrm{e}^{-\Gamma(\mathbf{Q})t} p_\mathrm{eq}(\mathbf{Q}) g(\mathbf{Q}) \tag{6}$$

In particular, in the context of this work we are interested in evaluating the anisotropy ratio of the fluorescence emission for dye-probes, which is expressed as [1–4].

$$r(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)} \tag{7}$$

where $I_\parallel(t)$ and $I_\perp(t)$ are the intensities of the emission detected on planes parallel and perpendicular to the polarization plane. On assuming that both the absorption- and emission- dipole transition moments are collinear to the molecular axis individuated by the unit vector $\boldsymbol{\mu} \equiv \mathbf{z}_\mathrm{M}$, then Eq. (7) becomes

$$r(t) = \frac{2}{5}\overline{P_2(\boldsymbol{\mu}(t) \cdot \boldsymbol{\mu}(0))} = \frac{2}{5}\sum_m \overline{\mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM})^*_t \mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM})_0} \tag{8}$$

where $P_2(\cdot)$ denotes the second-rank Legendre polynomial, and $\mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM})$ are second-rank rotational Wigner functions [62]. From Eq. (8) one gets immediately that the initial-time value is $r(0) = 2/5$ and, since the diffusion occurs in a spherically symmetric environment where all orientations are equally sampled at equilibrium, the long-time limit is $\lim_{t\to\infty} r(t) = 0$. In summary, the general problem requires the evaluation of the characteristic correlation functions entering the sum Eq. (8) by employing the integral form Eq. (6).

The structure of Eq. (3) is here simplified by considering the model-case of uniaxial probe molecules (for which there are no roto-translational coupling blocks in the diffusion matrix), and assuming isotropic translational diffusion in the local viscous environment with unique coefficient D^T. Thus, in our model we shall deal with

$$\mathbf{D}(\mathbf{Q}) = \begin{pmatrix} D^\mathrm{T}\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{D}^\mathrm{R}_\mathrm{L}(\mathbf{Q}) \end{pmatrix} \tag{9}$$

where $\mathbf{1}$ denotes the 3×3 identity matrix and $\mathbf{D}^\mathrm{R}_\mathrm{L}$ is the rotational diffusion tensor expressed with reference to the LF axes. Such a tensor depends only on the molecular orientation $\mathbf{\Omega}_\mathrm{LM}$ through

$$\mathbf{D}^\mathrm{R}_\mathrm{L}(\mathbf{\Omega}_\mathrm{LM}) = \mathbf{E}(\mathrm{LF} \leftarrow \mathrm{MF})\mathbf{D}^\mathrm{R}_\mathrm{M}\mathbf{E}(\mathrm{LF} \leftarrow \mathrm{MF})^\mathrm{Tr} \tag{10}$$

where $\mathbf{E}(\mathrm{LF} \leftarrow \mathrm{MF})$ is the Euler matrix [62] for the transformation of vector's coordinates under rotation of the reference axes from MF to LF, and $\mathbf{D}_{\mathrm{M}}^{\mathrm{R}}$ is the tensor expressed in the Molecular Frame. For probes of uniaxial symmetry about $\mathbf{z}_{\mathrm{M}}$, $\mathbf{D}_{\mathrm{M}}^{\mathrm{R}}$ takes the form

$$\mathbf{D}_{\mathrm{M}}^{\mathrm{R}} = \begin{pmatrix} D_{\perp}^{\mathrm{R}} & 0 & 0 \\ 0 & D_{\perp}^{\mathrm{R}} & 0 \\ 0 & 0 & D_{\parallel}^{\mathrm{R}} \end{pmatrix} \tag{11}$$

where $\parallel$ refers to the spinning about the symmetry axis, while $\perp$ refers to the tumbling motions of the molecule about transverse axes.

According to Eq. (9), the evolution operator Eq. (3) reduces to

$$\Gamma(\mathbf{Q}) = \Gamma^{\mathrm{T}}(\mathbf{r}) + \Gamma^{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{LM}}) \tag{12}$$

where $\Gamma^{\mathrm{T}}(\mathbf{r})$ is the component related to translational diffusion ("T") of the molecular centre, while $\Gamma^{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{LM}})$ refers to the reorientational motions ("R") with respect to the Laboratory Frame, and they are explicitly given by

$$\Gamma^{\mathrm{T}}(\mathbf{r}) = D^{\mathrm{T}} \nabla_{\mathrm{T}}(\mathbf{r})^{\dagger} p_{\mathrm{eq}}(\mathbf{Q}) \nabla_{\mathrm{T}}(\mathbf{r}) p_{\mathrm{eq}}(\mathbf{Q})^{-1} \tag{13}$$

$$\begin{aligned} \Gamma^{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{LM}}) &= \nabla_{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{LM}})^{\dagger} p_{\mathrm{eq}}(\mathbf{Q}) \mathbf{D}_{\mathrm{L}}^{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{LM}}) \\ &\quad \times \nabla_{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{LM}}) p_{\mathrm{eq}}(\mathbf{Q})^{-1} \end{aligned} \tag{14}$$

We stress here a fundamental point which emerges from the structure of Eqs. (13) and (14): the two operators (and hence the corresponding dynamical processes) are coupled by the equilibrium distribution which depends on both the positional and orientational variables. In other words, the orientational-positional coupling in the mean-field potential (*statics*) induces a roto-translational coupling (*dynamics*) so to prevent, in principle, the separation between the two kinds of motions.

The dynamical effects of the orientational-positional coupling can be highlighted by applying a suitable change of reference system, as illustrated in the following. Let us consider the spherical coordinates which identify the actual location of the probe-molecule, $\mathbf{r} \equiv (r, \theta, \phi)$, and introduce a new frame, the *Director Frame* DF $\equiv (\mathbf{x}_{\mathrm{D}}, \mathbf{y}_{\mathrm{D}}, \mathbf{z}_{\mathrm{D}})$, identified by the transformation LF $\rightarrow$ DF specified by the set of Euler angles $\boldsymbol{\Omega}_{\mathrm{LD}} = (\phi, \theta, 0)$. In particular, the longitudinal axis of DF points along the actual radial direction, which is taken as the local director of molecular alignment experienced by the probe-molecule in the micelle: $\mathbf{z}_{\mathrm{D}} = \mathbf{r}/r$. The molecular orientation referred to DF is denoted as $\boldsymbol{\Omega}_{\mathrm{DM}} = (\alpha_{\mathrm{DM}}, \beta_{\mathrm{DM}}, \gamma_{\mathrm{DM}})$. By specifying the molecular orientation with respect to DF, the state of the molecule is fully specified by the new set of stochastic variables $\mathbf{Q}' = (r, \theta, \phi, \boldsymbol{\Omega}_{\mathrm{DM}})$. The relations between the three systems of axes up to now introduced are summarized by the following scheme:

$$\begin{tikzcd} \mathrm{LF} \arrow[rr, "\boldsymbol{\Omega}_{\mathrm{LM}}"] \arrow[dr, "\boldsymbol{\Omega}_{\mathrm{LD}}"'] & & \mathrm{MF} \\ & \mathrm{DF} \arrow[ur, "\boldsymbol{\Omega}_{\mathrm{DM}}"'] & \end{tikzcd} \quad , \quad \boldsymbol{\Omega}_{\mathrm{LD}} = (\phi, \theta, 0) \tag{15}$$

At given distance r from the centre, the orientational equilibrium distribution with respect to the DF is invariant under migration of the dye across the micelle, because of the spherical symmetry of the system. Thus, $p_{\mathrm{eq}}(\mathbf{Q}')$ depends explicitly only on r and $\boldsymbol{\Omega}_{\mathrm{DM}}$, and in terms of mean-field potential one has that $V(\mathbf{Q}') \equiv V(r, \boldsymbol{\Omega}_{\mathrm{DM}})$. A parametric form of such a function can be obtained as expansion on the basis of Wigner functions,

$$V(r, \boldsymbol{\Omega}_{\mathrm{DM}}) = \sum_{j \geq 0} v^{(j)}(r)\, \mathcal{D}_{0,0}^{j}(\boldsymbol{\Omega}_{\mathrm{DM}}) \tag{16}$$

where for uniaxial molecules embedded in a locally uniaxial mean-field environment only Wigner functions with null values of both the projection indices have to be accounted. At the lowest level of detail, a model form for the mean-field potential is

$$\begin{aligned} V(r, \boldsymbol{\Omega}_{\mathrm{DM}}) &= v^{(0)}(r) + v^{(1)}(r)\, \mathcal{D}_{0,0}^{1}(\boldsymbol{\Omega}_{\mathrm{DM}}) \\ &= v^{(0)}(r) + v^{(1)}(r) \cos \beta_{\mathrm{DM}} \end{aligned} \tag{17}$$

where $v^{(0)}(r)$ is an orientation-independent contribution which sets the intrinsic modulation of the molecular confinement on moving along the radial direction, while the other contribution introduces a polar alignment of the molecule with respect to the local director, weighted by the position-dependent coefficient $v^{(1)}(r)$.

We shall focus now on the global transformation of the time evolution operator according to the employed change of variables $\mathbf{Q} \rightarrow \mathbf{Q}'$. In the Appendix B we demonstrate that the positional-and orientational- gradient operators transform to

$$\begin{aligned} \nabla_{\mathrm{T}}(\mathbf{Q}') &= \mathbf{S}_{\mathrm{TT}}(r, \theta, \phi)^{\mathrm{Tr}} \begin{pmatrix} \partial/\partial r \\ \partial/\partial \phi \\ \partial/\partial \theta \end{pmatrix} \\ &\quad + \mathbf{S}_{\mathrm{RT}}(r, \theta, \phi)^{\mathrm{Tr}} \mathbf{M}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \end{aligned} \tag{18}$$

$$\nabla_{\mathrm{R}}(\mathbf{Q}') = \mathbf{E}(\mathrm{LF} \leftarrow \mathrm{DF}) \mathbf{M}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \tag{19}$$

with the transposed of matrices $\mathbf{S}_{\mathrm{TT}}$ and $\mathbf{S}_{\mathrm{RT}}$ explicitly given in Eqs. (B9) and (B12). The transformed operator is then

$$\Gamma(\mathbf{Q}') = \Gamma^{\mathrm{T}}(\mathbf{Q}') + \Gamma^{\mathrm{R}}(\mathbf{Q}') \tag{20}$$

with the translational term given by

$$\Gamma^{\mathrm{T}}(\mathbf{Q}') = D^{\mathrm{T}}\nabla_{\mathrm{T}}(\mathbf{Q}')^{\dagger} p_{\mathrm{eq}}(\mathbf{Q}')\nabla_{\mathrm{T}}(\mathbf{Q}')p_{\mathrm{eq}}(\mathbf{Q}')^{-1} \tag{21}$$

while, by considering also Eq. (10), the rotational part is

$$\Gamma^{\mathrm{R}}(\mathbf{Q}') = \mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{DM}})^{\dagger}\mathbf{D}^{\mathrm{R}}_{\mathrm{M}} p_{\mathrm{eq}}(\mathbf{Q}')\mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{DM}})p_{\mathrm{eq}}(\mathbf{Q}')^{-1} \tag{22}$$

It should be evident that the complex structures of these evolution operators, and the coupling between rotational and translational degrees of freedom, do not allow a direct solution of the stochastic problem. A simplification can be introduced, as described in the next section, by assuming a strong confinement of the molecule at the micelle interface.

3 Strong confinement at the micelle interface

The degree of radial confinement of the molecule can be described by the reduced distribution $\rho_{\mathrm{eq}}(r) = 4\pi\int \mathrm{d}\mathbf{\Omega}_{\mathrm{DM}}\, p_{\mathrm{eq}}(\mathbf{Q}')$ normalized as $\int \mathrm{d}r\, r^2\, \rho_{\mathrm{eq}}(r) = 1$. Let us assume that $\rho_{\mathrm{eq}}(r)$ is highly "peaked" at the distance r_{m} from the micelle centre (which can be identified as the "micelle radius"). Correspondingly one can eliminate the radial coordinate by projecting the probability density onto the functional space spanned by the remaing variables $\mathbf{q} = (\theta, \phi, \mathbf{\Omega}_{\mathrm{DM}})$, with the starting variable set specified as $\mathbf{Q}' = (r, \mathbf{q})$. Formally, the projected non-equilibrium probability density is given by

$$p(\mathbf{q}, t) = \int \mathrm{d}r\, r^2\, p(\mathbf{Q}', t) \tag{23}$$

with the projected equilibrium distribution

$$p_{\mathrm{eq}}(\mathbf{q}) = p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}})/4\pi, \qquad \int \mathrm{d}\mathbf{\Omega}_{\mathrm{DM}}\, p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}}) = 1 \tag{24}$$

where $p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}})$ is the orientational distribution of the molecule with respect to the DF. In particular, by using Eq. (17) for the mean-field potential one gets

$$p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}}) \propto \mathrm{e}^{-v^{(1)}(r_{\mathrm{m}})\cos\beta_{\mathrm{DM}}/k_{\mathrm{B}}T} \tag{25}$$

where it has been assumed that the coefficient $v^{(1)}(r)$ depends weakly on the radial coordinate, so to be allowed to evaluate it at the distance r_{m}. The evolution of $p(\mathbf{q}, t)$ is still described by a Fokker–Planck–Smoluchowski equation,

$$\frac{\partial}{\partial t} p(\mathbf{q}, t) = -\Gamma(\mathbf{q})p(\mathbf{q}, t) \tag{26}$$

where $\Gamma(\mathbf{q})$ is the projected operator, acting on $\mathbf{q}$, implicitly defined through the following identity to be satisfied by a generic function $f(\mathbf{q})$ [63]:

$$\Gamma(\mathbf{q})f(\mathbf{q})p_{\mathrm{eq}}(\mathbf{q}) = \int \mathrm{d}r\, r^2\, \Gamma(\mathbf{Q}')f(\mathbf{q})p_{\mathrm{eq}}(\mathbf{Q}') \tag{27}$$

By inserting $\Gamma(\mathbf{Q}')$ as given in Eq. (20), together with Eqs. (21) and (22), and by elaborating the integral at the right-hand side, one derives the following expression for the projected operator

$$\Gamma(\mathbf{q}) = \Gamma^{\mathrm{T}}(\mathbf{q}) + \Gamma^{\mathrm{R}}(\mathbf{\Omega}_{\mathrm{DM}}) \tag{28}$$

where the translational term results as

$$\Gamma^{\mathrm{T}}(\mathbf{q}) = D^{\mathrm{T}}\nabla_{\mathrm{T}}(\mathbf{q})^{\dagger} p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}})\nabla_{\mathrm{T}}(\mathbf{q})p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}})^{-1} \tag{29}$$

with the gradient operator

$$\nabla_{\mathrm{T}}(\mathbf{q}) \simeq \frac{1}{r_{\mathrm{m}}}\begin{pmatrix} -\dfrac{\sin\phi}{\sin\theta}\dfrac{\partial}{\partial\phi} + \cos\theta\cos\phi\dfrac{\partial}{\partial\theta} \\ \dfrac{\cos\phi}{\sin\theta}\dfrac{\partial}{\partial\phi} + \cos\theta\sin\phi\dfrac{\partial}{\partial\theta} \\ -\sin\theta\dfrac{\partial}{\partial\theta} \end{pmatrix} + \mathbf{S}^{\mathrm{Tr}}_{\mathrm{RT}}(r_{\mathrm{m}}, \theta, \phi)\mathbf{M}_{\mathrm{D}}(\mathbf{\Omega}_{\mathrm{DM}}) \tag{30}$$

while for rotational term one gets

$$\Gamma^{\mathrm{R}}(\mathbf{\Omega}_{\mathrm{DM}}) = \mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{DM}})^{\dagger}\mathbf{D}^{\mathrm{R}}_{\mathrm{M}} p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}}) \times\mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{DM}})p_{\mathrm{eq}}(\mathbf{\Omega}_{\mathrm{DM}})^{-1} \tag{31}$$

which is nothing but the usual form of a rotational diffusion operator for a molecule reorienting with respect to a (local) Director Frame.

It should be emphasized that the rotational evolution operator Eq. (31) is independent of the polar angles (θ, ϕ) for the translational coordinates. On the contrary, a similar condition does not hold for the translational operator Eq. (29), since the positional-gradient in Eq. (30) includes a contribution by the rotation operator $\mathbf{M}_{\mathrm{D}}(\mathbf{\Omega}_{\mathrm{DM}})$ through the matrix $\mathbf{S}_{\mathrm{RT}}(r_{\mathrm{m}}, \theta, \phi)$. As long as the matrix $\mathbf{S}_{\mathrm{RT}}$ is not vanishing, the translational dynamics of the probe at the micelle interface, described by the variables (θ, ϕ), and the rotational motion of the dye with respect to the director, accounted by the Euler angles $\mathbf{\Omega}_{\mathrm{DM}}$, are intrinsically coupled. Therefore, the assumption of independent contributions by the two types of motions, as usually invoked in the analysis of fluorescence anisotropy of dyes in micelles [1–4], is not legitimate. It should be mentioned that a completely different situation arises in the analysis of small fragment motions with respect to a large macromolecule, where the independence of the overall rotational motion and the relative motion of the fragment can be justified on the basis of the different size of the moving bodies, as assumed in the "model-free" approach of Lipari and Szabo [5,6].

In conclusion, a different route has to be followed in order to derive, on a sound physical basis, an explicit solution for the dye dynamics in micelles. This can be achieved, as shown in the next section, by invoking a separation of time-scales for the two types of motion.

4 Time-scale separation: fast reorientations and slow lateral diffusion

Let us invoke a time-scale separation between slow migration of the probe molecule on the spherical surface at distance r_m from the micelle centre, and much faster reorientations of the molecule about the local director. In other words, the molecule reorients fast about the local “quenched” director, which in turn reorients much slower with respect to the LF axes. Accordingly, the decay of the correlation functions contributing to the anisotropy ratio $r(t)$ is expected to present a fast-relaxing component due to the fast reorientations at fixed location of the molecular centre, superimposed to a slow-relaxing component corresponding to the slower loss of orientational correlation driven by the diffusion across the surface. The formal procedure to evaluate the fast- and the the slow-components of the correlation functions, at the formal level of a Born–Oppenheimer-like approximation, is illustrated in the appendix B of ref. [63], while in Appendix C of the present work we only summarize the leading expressions applied hereafter.

Let us make a partition of $\mathbf{q}$ into the set of *slow* variables $\mathbf{q}^\mathrm{s} \equiv (\theta, \phi)$ and the set of *fast* variables $\mathbf{q}^\mathrm{f} \equiv \mathbf{\Omega}_\mathrm{DM}$. In the present application we are interested in evaluating the following self-correlation functions

$$G_\mathrm{m}(t) = \overline{\mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM})^*_t \mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM})_0} \tag{32}$$

where, by application of the closure relation for Wigner functions [62] with reference to the scheme in Eq. (15), the following substitution has to be performed

$$\mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM}) = \sum_k \mathcal{D}^2_{\mathrm{m},k}(\mathbf{\Omega}_\mathrm{LD}) \mathcal{D}^2_{k,0}(\mathbf{\Omega}_\mathrm{DM}) \tag{33}$$

We shall now evaluate the slow- and fast- relaxing components, $G^\mathrm{s}_\mathrm{m}(t)$ and $G^\mathrm{f}_\mathrm{m}(t)$, respectively, such that $G(t) \simeq G^\mathrm{s}_\mathrm{m}(t) + G^\mathrm{f}_\mathrm{m}(t)$. By adopting Eq. (C2), and recalling that $p_\mathrm{eq}(\mathbf{q}) = p_\mathrm{eq}(\mathbf{\Omega}_\mathrm{DM})/4\pi$, the equilibrium distribution projected onto the subspace of the slow variables is $p^\mathrm{s}_\mathrm{eq}(\theta, \phi) = 1/4\pi$ for isotropic distribution of the directors. Moreover, application of Eq. (C8) yields the following form of projected operator referring to the slow lateral diffusion

$$\Gamma^\mathrm{s}(\theta, \phi) = (D^\mathrm{T}/r^2_\mathrm{m})\mathcal{L}^2 \tag{34}$$

where

$$\mathcal{L}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{35}$$

is (proportional to) the angular momentum operator of a point-like particle [62]. Then, by means of Eq. (C4) applied to Eq. (33), we isolate the projection of the observable-function onto the space of the slow variables, to obtain

$$\begin{aligned}
&\mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LM})^\mathrm{s} \\
&\quad = \sum_k \mathcal{D}^2_{\mathrm{m},k}(\mathbf{\Omega}_\mathrm{LD}) \int \mathrm{d}\mathbf{\Omega}_\mathrm{DM}\, p_\mathrm{eq}(\mathbf{\Omega}_\mathrm{DM}) \mathcal{D}^2_{k,0}(\mathbf{\Omega}_\mathrm{DM}) \\
&\quad = \mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LD})\, \overline{P_2}
\end{aligned} \tag{36}$$

where for the last identity we have considered that, because of the uniaxial local alignment, averages of Wigner functions with $k \neq 0$ vanish; the factor $\overline{P_2} = \int \mathrm{d}\mathbf{\Omega}_\mathrm{DM}\, p_\mathrm{eq}(\mathbf{\Omega}_\mathrm{DM})\mathcal{D}^2_{0,0}(\mathbf{\Omega}_\mathrm{DM})$, which corresponds to the average of the Legendre polynomial $P_2(\cos\beta_\mathrm{DM})$ over the local equilibrium distribution, is the second-rank order parameter usually employed to quantify the degree of alignment in uniaxial phases. Application of Eq. (C6) yields the slow-relaxing component as

$$\begin{aligned}
G^\mathrm{s}_\mathrm{m}(t) = (\overline{P_2})^2 &\int \mathrm{d}\theta \sin\theta \mathrm{d}\phi\, \mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LD})^* \\
&\times \mathrm{e}^{-(D^\mathrm{T}/r^2_\mathrm{m})\mathcal{L}^2 t} \mathcal{D}^2_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LD})/4\pi
\end{aligned} \tag{37}$$

By taking into account that the Wigner functions are eigenfunctions of the angular momentum operator with $\mathcal{L}^2\mathcal{D}^j_{\mathrm{m,k}}(\mathbf{\Omega}_\mathrm{LD}) = j(j+1)\mathcal{D}^j_{\mathrm{m,k}}(\mathbf{\Omega}_\mathrm{LD})$, then

$$\begin{aligned}
&\mathrm{e}^{-(D^\mathrm{T}/r^2_\mathrm{m})\mathcal{L}^2 t}\mathcal{D}^j_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LD}) = \mathrm{e}^{-t/\tau_\mathrm{D}}\, \mathcal{D}^j_{\mathrm{m},0}(\mathbf{\Omega}_\mathrm{LD}), \\
&\qquad\qquad \tau^{-1}_\mathrm{D} = 6D^\mathrm{T}/r^2_\mathrm{m}
\end{aligned} \tag{38}$$

and Eq. (37) reduces to

$$G^\mathrm{s}_\mathrm{m}(t) = (\overline{P_2})^2 \frac{1}{5}\mathrm{e}^{-t/\tau_\mathrm{D}} \tag{39}$$

Let us turn now to the fast-relaxing component. The equilibrium distribution at “quenched” slow variables (i.e., the conditional distribution on $\mathbf{\Omega}_\mathrm{DM}$ at fixed $\mathbf{\Omega}_\mathrm{LD}$) is here given by $p^\mathrm{f}_\mathrm{eq}(\mathbf{q}) = p_\mathrm{eq}(\mathbf{\Omega}_\mathrm{DM})$. Then, the operator $\Gamma^\mathrm{f}(\mathbf{\Omega}_\mathrm{DM})$, which describes the evolution of the non-equilibrium density for the fast variables, is obtained from the original $\Gamma(\mathbf{q})$ by extracting the terms which act only on the fast variables; explicitly it takes the form

$$\begin{aligned}
\Gamma^\mathrm{f}(\mathbf{\Omega}_\mathrm{DM}) = D^\mathrm{T}&[\mathbf{S}^\mathrm{Tr}_\mathrm{RT}(r_\mathrm{m}, \theta, \phi)\mathbf{M}_\mathrm{D}(\mathbf{\Omega}_\mathrm{DM})]^\dagger p_\mathrm{eq}(\mathbf{\Omega}_\mathrm{DM}) \\
&\times[\mathbf{S}^\mathrm{Tr}_\mathrm{RT}(r_\mathrm{m}, \theta, \phi)\mathbf{M}_\mathrm{D}(\mathbf{\Omega}_\mathrm{DM})]p_\mathrm{eq}(\mathbf{\Omega}_\mathrm{DM})^{-1} \\
&+\Gamma^\mathrm{R}(\mathbf{\Omega}_\mathrm{DM})
\end{aligned} \tag{40}$$

in which a parametric dependence on the slow variables θ, ϕ is conserved. Let us consider now the part of the observable-function $\mathcal{D}^2_{\mathrm{m},0}(\boldsymbol{\Omega}_{\mathrm{LM}})$, which is complementary to its slow component $\mathcal{D}^2_{\mathrm{m},0}(\boldsymbol{\Omega}_{\mathrm{LM}})^{\mathrm{s}}$, that is,

$$\begin{aligned}\delta\mathcal{D}^2_{\mathrm{m},0}(\boldsymbol{\Omega}_{\mathrm{LM}})^{\mathrm{f}} &= \mathcal{D}^2_{\mathrm{m},0}(\boldsymbol{\Omega}_{\mathrm{LM}}) - \mathcal{D}^2_{\mathrm{m},0}(\boldsymbol{\Omega}_{\mathrm{LM}})^{\mathrm{s}} \\ &= \sum_k \mathcal{D}^2_{\mathrm{m},k}(\boldsymbol{\Omega}_{\mathrm{LD}})[\mathcal{D}^2_{k,0}(\boldsymbol{\Omega}_{\mathrm{DM}}) - \delta_{k,0}\overline{P_2}] \end{aligned} \quad (41)$$

Notice that $\delta\mathcal{D}^2_{\mathrm{m},0}(\boldsymbol{\Omega}_{\mathrm{LM}})^{\mathrm{f}}$ keeps a parametric dependence on the slow variables; such a dependence leads to a $\boldsymbol{\Omega}_{\mathrm{LD}}$-dependendent contribution to the fast-relaxing component of the correlation function, which is explicitated by means of Eq. (C9) as

$$\begin{aligned} G^{\mathrm{f}}_{\mathrm{m}}(\boldsymbol{\Omega}_{\mathrm{LD}}, t) &\simeq \sum_{k,k'} \mathcal{D}^2_{\mathrm{m},k}(\boldsymbol{\Omega}_{\mathrm{LD}})^* \mathcal{D}^2_{\mathrm{m},k'}(\boldsymbol{\Omega}_{\mathrm{LD}}) \\ &\times \int \mathrm{d}\boldsymbol{\Omega}_{\mathrm{DM}} \, [\mathcal{D}^2_{k,0}(\boldsymbol{\Omega}_{\mathrm{DM}}) - \delta_{k,0}\overline{P_2}]^* \mathrm{e}^{-\Gamma^{\mathrm{f}}(\Omega_{\mathrm{DM}})t} \\ &\times p_{\mathrm{eq}}(\boldsymbol{\Omega}_{\mathrm{DM}})[\mathcal{D}^2_{k',0}(\boldsymbol{\Omega}_{\mathrm{DM}}) - \delta_{k',0}\overline{P_2}] \end{aligned} \quad (42)$$

Then, as expressed by Eq. (C10), the effective fast-relaxing component can be obtained as a weighted superposition of the "static" responses $G^{\mathrm{f}}_{\mathrm{m}}(\boldsymbol{\Omega}_{\mathrm{LD}}, t)$ over the equilibrium distribution on the slow variables, i.e.,

$$G^{\mathrm{f}}_{\mathrm{m}}(t) \simeq \int \mathrm{d}\theta \sin\theta \mathrm{d}\phi \, G^{\mathrm{f}}_{\mathrm{m}}(\boldsymbol{\Omega}_{\mathrm{LD}}, t)/4\pi \quad (43)$$

Finally, by recalling Eq. (8), one completes the derivation to achieve

$$r(t) = \frac{2}{5}\sum_m G_{\mathrm{m}}(t), \quad G_{\mathrm{m}}(t) = G^{\mathrm{s}}_{\mathrm{m}}(t) + G^{\mathrm{f}}_{\mathrm{m}}(t) \quad (44)$$

with $G^{\mathrm{s}}_{\mathrm{m}}(t)$ given in Eq. (39) and $G^{\mathrm{f}}_{\mathrm{m}}(t)$ in Eq. (43).

Furthermore, we are allowed to simplify the form of $G^{\mathrm{f}}_{\mathrm{m}}(t)$ by applying the condition of time-scale separation between lateral diffusion and local reorientations. By making the reliable assumption that such a separation is mainly due to very different magnitudes of the related diffusion coefficients, then all terms proportional to $D^{\mathrm{T}}/r^2_{\mathrm{m}}$ can be neglected in Eq. (40) with respect to those involving the elements $D^{\mathrm{R}}_{\perp}, D^{\mathrm{R}}_{\parallel}$ of the rotational diffusion tensor if

$$D^{\mathrm{T}}/r^2_{\mathrm{m}} \ll D^{\mathrm{R}}_{\perp}, D^{\mathrm{R}}_{\parallel} \quad (45)$$

Thus,

$$\Gamma^{\mathrm{f}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \simeq \Gamma^{\mathrm{R}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \quad (46)$$

so that the parametric dependence on θ and ϕ is lost, and the fast component of the evolution operator reduces to that which describes the local reorientational dynamics. By employing Eq. (46) in Eq. (42), by recalling the definition of the order parameter $\overline{P_2}$, and finally by integrating as specified in Eq. (43), with some algebraic elaborations one gets

$$G^{\mathrm{f}}_{\mathrm{m}}(t) \simeq \frac{1}{5}\left[\sum_k \overline{\mathcal{D}^2_{k,0}(\boldsymbol{\Omega}_{\mathrm{DM}})^*_0 \mathcal{D}^2_{k,0}(\boldsymbol{\Omega}_{\mathrm{DM}})_t} - (\overline{P_2})^2\right] \quad (47)$$

It can be easily verified that $G^{\mathrm{f}}_{\mathrm{m}}(0) = [1 - (\overline{P_2})^2]/5$ and $\lim_{t\to\infty} G^{\mathrm{f}}_{\mathrm{m}}(t) = 0$. By including also the slow-relaxing component given in Eq. (39), the complete fluorescence anisotropy ratio is finally expressed as

$$\begin{aligned} r(t) &= \frac{2}{5}(\overline{P_2})^2 \mathrm{e}^{-t/\tau_{\mathrm{D}}} \\ &+ \frac{2}{5}\left[\sum_k \overline{\mathcal{D}^2_{k,0}(\boldsymbol{\Omega}_{\mathrm{DM}})^*_0 \mathcal{D}^2_{k,0}(\boldsymbol{\Omega}_{\mathrm{DM}})_t} - (\overline{P_2})^2\right] \end{aligned} \quad (48)$$

where the initial value $r(0) = 2/5$ and the limit $\lim_{t\to\infty} r(t) = 0$ are correctly reproduced. Now, in order to obtain explicitly the time-depencence of $r(t)$, only the librational diffusion problem has to be solved. An analytical approximation can be recovered by employing asymptotic methods with respect to the orientational potential [61] or, like in refs. [1–4,7], by invoking a simplified model like the "wobbling in a cone" to describe the librational motion, in which case the following explicit relation is found

$$r(t) = \frac{2}{5}(\overline{P_2})^2 \mathrm{e}^{-t/\tau_{\mathrm{D}}} + \frac{2}{5}(1 - \overline{P_2}^2)\mathrm{e}^{-t/\tau_{\mathrm{w}}} \quad (49)$$

where τ_{w} is the time-constant for the wobbling motion. Notice that, according to such a derivation, the fast component does not include any contribution from the lateral diffusion.

In conclusion, explicit relations for the fluorescence depolarization are recovered under the time-scale separation described by the condition Eq. (45). By taking into account that the translational and rotational components of the diffusion matrix scale according to the size a of the dye as

$$D^{\mathrm{T}}/D^{\mathrm{R}}_{\perp} \sim D^{\mathrm{T}}/D^{\mathrm{R}}_{\parallel} \sim a^2 \quad (50)$$

then the condition Eq. (45) implies that

$$r^2_{\mathrm{m}} \gg a^2 \quad (51)$$

i.e., the size of the dye must be much smaller that the radius of the micelle.

5 Concluding remarks

In this work we have shown that a self-consistent representation of dye dynamics in the micellar environment can be obtained, if roto-translational coupling and the effects of the mean-field potential are properly taken into account. Such a general description, however, does not provide directly an explicit equation for the relevant observables like the time-dependent fluorescence anisotropy, even if the approximation of strong confinement at the micellar interface is invoked. The assumption of independent contributions of the librational motion with respect to the local director, and translational diffusion at the micellar interface, clearly results to be unjustified. A more reasonable procedure relies on the time-scale separation between the fast librational motion and the slow translational diffusion at the micellar interface. This allows the derivation of an explicit relation, Eq. (48), for the fluorescence depolarization. If the "wobbling in a cone" model is employed for the librational motion, the resulting Eq. (49) is similar to the parameterized form usually employed for the analysis of the fluorescence depolarization [1–4], with the notable difference that the fast component is devoid of any contribution by the slow diffusion process.

Besides the possibility of making contact with the standard procedure of analysis of fluorescence depolarization, our method allows the treatment of the dynamical problem in more general conditions, for instance in the absence of strong confinement, or when the time-scale separation is missing when dealing with a large-size dye. In these cases, the full solution of the model is required by employing suitable computational procedures which have been developed in the past for analogous complex stochastic problems.

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Appendix A: About the rotation operators

Consider a function $f(\mathbf{\Omega}_{\mathrm{LM}})$ evaluated at the molecular orientation specified by the set of Euler angles $\mathbf{\Omega}_{\mathrm{LM}} = (\alpha_{\mathrm{LM}}, \beta_{\mathrm{LM}}, \gamma_{\mathrm{LM}})$ which encodes the transformation from the Laboratory Frame (LF) to the Molecular Frame (MF) [62]. Under the infinitesimal change of molecular orientation $\mathrm{d}\mathbf{\Omega}_{\mathrm{LM}} = (\mathrm{d}\alpha_{\mathrm{LM}}, \mathrm{d}\beta_{\mathrm{LM}}, \mathrm{d}\gamma_{\mathrm{LM}})$, the function changes as

$$\begin{aligned} \mathrm{d}f(\mathbf{\Omega}_{\mathrm{LM}}) &= f(\mathbf{\Omega}_{\mathrm{LM}} + \mathrm{d}\mathbf{\Omega}_{\mathrm{LM}}) - f(\mathbf{\Omega}_{\mathrm{LM}}) \\ &= \mathrm{d}\mathbf{\Omega}_{\mathrm{LM}}^{\mathrm{Tr}} \frac{\partial}{\partial \mathbf{\Omega}_{\mathrm{LM}}} f(\mathbf{\Omega}_{\mathrm{LM}}) \\ &\equiv \mathrm{d}\alpha_{\mathrm{LM}} \frac{\partial}{\partial \alpha_{\mathrm{LM}}} f(\mathbf{\Omega}_{\mathrm{LM}}) + \mathrm{d}\beta_{\mathrm{LM}} \frac{\partial}{\partial \beta_{\mathrm{LM}}} f(\mathbf{\Omega}_{\mathrm{LM}}) \\ &\quad + \mathrm{d}\gamma_{\mathrm{LM}} \frac{\partial}{\partial \gamma_{\mathrm{LM}}} f(\mathbf{\Omega}_{\mathrm{LM}}) \end{aligned} \tag{A1}$$

Let us introduce the infinitesimal Cartesian vector $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{LM}}(\mathbf{\Omega}_{\mathrm{LM}})$ describing the infinitesimal rotation due to the $\mathrm{d}\mathbf{\Omega}_{\mathrm{LM}}$ of MF with respect to LF, and whose components are expressed in the LF. Explicitly one has that

$$\mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}})\mathrm{d}\boldsymbol{\varphi}_L(\mathbf{\Omega}_{\mathrm{LM}}) = \mathrm{d}\mathbf{\Omega}_{\mathrm{LM}} \tag{A2}$$

for the matrix $\mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}})$ given by

$$\mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}}) = \begin{pmatrix} -\cos\gamma_{\mathrm{LM}}/\sin\beta_{\mathrm{LM}} & \sin\gamma_{\mathrm{LM}}/\sin\beta_{\mathrm{LM}} & 0 \\ \sin\gamma_{\mathrm{LM}} & \cos\gamma_{\mathrm{LM}} & 0 \\ \cos\beta_{\mathrm{LM}}\cos\gamma_{\mathrm{LM}}/\sin\beta_{\mathrm{LM}} & -\cos\beta_{\mathrm{LM}}\sin\gamma_{\mathrm{LM}}/\sin\beta_{\mathrm{LM}} & 1 \end{pmatrix} \tag{A3}$$

By substituting Eq. (A2) into Eq. (A1) we obtain

$$\begin{aligned} \mathrm{d}f(\mathbf{\Omega}_{\mathrm{LM}}) &= \mathrm{d}\boldsymbol{\varphi}_L(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \frac{\partial}{\partial \mathbf{\Omega}_{\mathrm{LM}}} f(\mathbf{\Omega}_{\mathrm{LM}}) \\ &= \mathrm{d}\boldsymbol{\varphi}_L(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \mathbf{M}_{\mathrm{L}}(\mathbf{\Omega}_{\mathrm{LM}}) f(\mathbf{\Omega}_{\mathrm{LM}}) \end{aligned} \tag{A4}$$

where we have introduced

$$\mathbf{M}_{\mathrm{L}}(\mathbf{\Omega}_{\mathrm{LM}}) \equiv \mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \frac{\partial}{\partial \mathbf{\Omega}_{\mathrm{LM}}} \tag{A5}$$

which is the *rotation operator* (with respect to the molecular state $\mathbf{\Omega}_{\mathrm{LM}}$) whose Cartesian components are expressed in the LF.

Now consider the following change of representation of the infinitesimal rotation vector under change of the reference frame from LF to MF:

$$\mathrm{d}\boldsymbol{\varphi}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}}) \equiv \mathbf{E}(\mathrm{MF} \leftarrow \mathrm{LF}) d\boldsymbol{\varphi}_L(\mathbf{\Omega}_{\mathrm{LM}}) \tag{A6}$$

where $\mathbf{E}(\mathrm{MF} \leftarrow \mathrm{LF})$ is the Euler matrix employed in the transformation of vector's Cartesian components under this specific change of reference frame [62]. The use of Eq. (A6) in Eq. (A2) leads to

$$\begin{aligned} \mathrm{d}\mathbf{\Omega}_{\mathrm{LM}} &= \mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}})\mathbf{E}(\mathrm{LF} \leftarrow \mathrm{MF})\mathrm{d}\boldsymbol{\varphi}_M(\mathbf{\Omega}_{\mathrm{LM}}) \\ &= \mathbf{R}'(\mathbf{\Omega}_{\mathrm{LM}})\mathrm{d}\boldsymbol{\varphi}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}}) \end{aligned} \tag{A7}$$

where we have introduced the matrix

$$\mathbf{R}'(\mathbf{\Omega}_{\mathrm{LM}}) \equiv \mathbf{R}(\mathbf{\Omega}_{\mathrm{LM}})\mathbf{E}(\mathrm{LF} \leftarrow \mathrm{MF}) \tag{A8}$$

Moreover, by means of Eq. (A6), Eq. (A4) changes to

$$\begin{aligned} \mathrm{d}f(\mathbf{\Omega}_{\mathrm{LM}}) &= \mathrm{d}\boldsymbol{\varphi}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \mathbf{R}'(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \frac{\partial}{\partial \mathbf{\Omega}_{\mathrm{LM}}} f(\mathbf{\Omega}_{\mathrm{LM}}) \\ &= \mathrm{d}\boldsymbol{\varphi}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}}) f(\mathbf{\Omega}_{\mathrm{LM}}) \end{aligned} \tag{A9}$$

where

$$\mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}}) \equiv \mathbf{R}'(\mathbf{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}} \frac{\partial}{\partial \mathbf{\Omega}_{\mathrm{LM}}} \tag{A10}$$

is the rotation operator (with respect to the Euler Angles $\mathbf{\Omega}_{\mathrm{LM}}$) with Cartesian components now expressed in the MF. The relation between $\mathbf{M}_{\mathrm{L}}(\mathbf{\Omega}_{\mathrm{LM}})$ in Eq. (A5) and $\mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}})$ in Eq. (A10) is the simple transformation of vector's coordinates under rotation of the reference frame, i.e.,

$$\mathbf{M}_{\mathrm{M}}(\mathbf{\Omega}_{\mathrm{LM}}) = \mathbf{E}(\mathrm{MF} \leftarrow \mathrm{LF})\mathbf{M}_{\mathrm{L}}(\mathbf{\Omega}_{\mathrm{LM}}) \tag{A11}$$

Appendix B: Change of representation $\mathbf{Q} \rightarrow \mathbf{Q}'$ in the gradient operators

With reference to the notation introduced in Sect. 2, let us consider a function $f(\mathbf{Q})$ of the coordinates $\mathbf{Q} = (\mathbf{r}, \boldsymbol{\Omega}_{\mathrm{LM}})$. Under the infinitesimal change of variables $\mathrm{d}\mathbf{Q}$, the function changes according to

$$\begin{aligned} \mathrm{d}f(\mathbf{Q}) &= f(\mathbf{Q}+\mathrm{d}\mathbf{Q}) - f(\mathbf{Q}) \\ &= \mathrm{d}\mathbf{r}^{\mathrm{Tr}}\nabla_{\mathrm{T}}(\mathbf{r})f(\mathbf{Q}) + \mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}})^{\mathrm{Tr}}\mathbf{M}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}})f(\mathbf{Q}) \end{aligned} \tag{B1}$$

with $\mathrm{d}\mathbf{r} = (\mathrm{d}r_x, \mathrm{d}r_y, \mathrm{d}r_z)$, and where $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}})$ is the infinitesimal rotation vector due to $\mathrm{d}\boldsymbol{\Omega}_{\mathrm{LM}}$, with Cartesian components expressed in the LF (see Eq. (A4) of Appendix A); thus, the orientational-gradient operator is $\nabla_{\mathrm{R}}(\mathbf{Q}) \equiv \mathbf{M}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}})$. Consider now the change of representation $\mathbf{Q} \rightarrow \mathbf{Q}' = (r, \theta, \phi, \boldsymbol{\Omega}_{\mathrm{DM}})$, where $\boldsymbol{\Omega}_{\mathrm{DM}}$ denotes the molecular orientation with respect to the Director Frame (DF). Of course one has that $f(\mathbf{Q}') = f(\mathbf{Q})\,|_{\mathbf{Q}=\mathbf{Q}(\mathbf{Q}')}$. Our purpose is to explicitate the positional- and orientational-gradient operators acting on the new coordinates, $\nabla_{\mathrm{T}}(\mathbf{Q}')$ and $\nabla_{\mathrm{R}}(\mathbf{Q}')$, respectively. We start by considering that the infinitesimal change of the function due to the change $\mathrm{d}\mathbf{Q}'$ is given by

$$\begin{aligned} \mathrm{d}f(\mathbf{Q}') &= f(\mathbf{Q}'+\mathrm{d}\mathbf{Q}') - f(\mathbf{Q}') \\ &= \mathrm{d}r\frac{\partial}{\partial r}f(\mathbf{Q}') + \mathrm{d}\phi\frac{\partial}{\partial \phi}f(\mathbf{Q}') + \mathrm{d}\theta\frac{\partial}{\partial \theta}f(\mathbf{Q}') \\ &\quad + \mathrm{d}\boldsymbol{\varphi}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}})^{\mathrm{Tr}}\mathbf{M}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}})f(\mathbf{Q}') \end{aligned} \tag{B2}$$

where $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}})$ is the infinitesimal rotation vector due to $\mathrm{d}\boldsymbol{\Omega}_{\mathrm{DM}}$ with Cartesian components in the DF. First one has the following relations,

$$\begin{aligned} \mathrm{d}r &= \sin\theta\cos\phi\,\mathrm{d}r_x + \sin\theta\sin\phi\,\mathrm{d}r_y + \cos\theta\,\mathrm{d}r_z \\ \mathrm{d}\phi &= -\frac{\sin\phi}{r\sin\theta}\mathrm{d}r_x + \frac{\cos\phi}{r\sin\theta}\mathrm{d}r_y \\ \mathrm{d}\theta &= \frac{\cos\theta\cos\phi}{r}\mathrm{d}r_x + \frac{\cos\theta\sin\phi}{r}\mathrm{d}r_y - \frac{\sin\theta}{r}\mathrm{d}r_z \end{aligned} \tag{B3}$$

Then, the infinitesimal rotation of MF with respect to LF given by $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}})$ can be replaced by the infinitesimal rotation of DF specified by vector $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LD}})$, followed by the rotation of MF with respect to DF specified by the vector $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{DM}})$. By exploiting the additive property of infinitesimal rotation vectors, one obtains

$$\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}}) = \mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LD}}) + \mathbf{E}(\mathrm{LF} \leftarrow \mathrm{DF})\mathrm{d}\boldsymbol{\varphi}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \tag{B4}$$

On the basis of the LF unit vectors, $\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LD}})$ is given by

$$\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LD}}) = \mathrm{d}\phi\mathbf{z}_{\mathrm{L}} + \mathrm{d}\theta\mathbf{u}, \quad \mathbf{u} = \cos\phi\mathbf{y}_{\mathrm{L}} - \sin\phi\mathbf{x}_{\mathrm{L}} \tag{B5}$$

that is, the whole infinitesimal rotation of DF with respect to LF is decomposed as an anti-clockwise rotation of $\mathrm{d}\phi$ about $\mathbf{z}_{\mathrm{L}}$, followed by an anti-clockwise rotation of $\mathrm{d}\theta$ about the vector $\mathbf{u}$ which is coincident with the azimuthal unit vector of the Spherical orthogonal set of axes at the location r, ϕ, θ. From Eqs. (B4) and (B5) one gets

$$\begin{aligned} \mathrm{d}\boldsymbol{\varphi}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}}) = \mathbf{E}(\mathrm{DF} \leftarrow \mathrm{LF})[&\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{LM}}) - \mathrm{d}\theta\cos\phi\mathbf{y}_{\mathrm{L}} \\ &+ \mathrm{d}\theta\sin\phi\mathbf{x}_{\mathrm{L}} - \mathrm{d}\phi\mathbf{z}_{\mathrm{L}}] \end{aligned} \tag{B6}$$

Now, from Eqs. (B4) and (B6) one can establish the following connection between infinitesimal changes of the "new" variables and those of the "old" ones,

$$\begin{pmatrix} \mathrm{d}r \\ \mathrm{d}\phi \\ \mathrm{d}\theta \end{pmatrix} = \mathbf{S}_{\mathrm{TT}}\mathrm{d}\mathbf{r} + \mathbf{S}_{\mathrm{TR}}\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \tag{B7}$$

$$\mathrm{d}\boldsymbol{\varphi}_{\mathrm{D}}(\boldsymbol{\Omega}_{\mathrm{DM}}) = \mathbf{S}_{\mathrm{RT}}\mathrm{d}\mathbf{r} + \mathbf{S}_{\mathrm{RR}}\mathrm{d}\boldsymbol{\varphi}_{\mathrm{L}}(\boldsymbol{\Omega}_{\mathrm{DM}}) \tag{B8}$$

with the the matrices

$$\mathbf{S}_{\mathrm{TT}}^{\mathrm{Tr}} = \begin{pmatrix} \sin\theta\cos\phi & -\dfrac{\sin\phi}{r\sin\theta} & \dfrac{\cos\theta\cos\phi}{r} \\ \sin\theta\sin\phi & \dfrac{\cos\phi}{r\sin\theta} & \dfrac{\cos\theta\sin\phi}{r} \\ \cos\theta & 0 & -\dfrac{\sin\theta}{r} \end{pmatrix} \tag{B9}$$

$$\mathbf{S}_{\mathrm{TR}} = \mathbf{0} \tag{B10}$$

$$\mathbf{S}_{\mathrm{RR}} = \mathbf{E}(\mathrm{DF} \leftarrow \mathrm{LF}) \tag{B11}$$

$$\mathbf{S}_{\mathrm{RT}}^{\mathrm{Tr}} = \begin{pmatrix} A_1\frac{\cos\theta\cos\phi}{r} + B_1\frac{\sin\phi}{r\sin\theta} & A_2\frac{\cos\theta\cos\phi}{r} + B_2\frac{\sin\phi}{r\sin\theta} & A_3\frac{\cos\theta\cos\phi}{r} + B_3\frac{\sin\phi}{r\sin\theta} \\ A_1\frac{\cos\theta\sin\phi}{r} - B_1\frac{\cos\phi}{r\sin\theta} & A_2\frac{\cos\theta\sin\phi}{r} - B_2\frac{\cos\phi}{r\sin\theta} & A_3\frac{\cos\theta\sin\phi}{r} - B_3\frac{\cos\phi}{r\sin\theta} \\ -A_1\frac{\sin\theta}{r} & -A_2\frac{\sin\theta}{r} & -A_3\frac{\sin\theta}{r} \end{pmatrix} \tag{B12}$$

where

$$\begin{aligned} A_j &= [\mathbf{E}(\mathrm{DF} \leftarrow \mathrm{LF})\mathbf{x}_{\mathrm{L}}]_j\sin\phi - [\mathbf{E}(\mathrm{DF} \leftarrow \mathrm{LF})\mathbf{y}_{\mathrm{L}}]_j\cos\phi \\ B_j &= [\mathbf{E}(\mathrm{DF} \leftarrow \mathrm{LF})\mathbf{z}_{\mathrm{L}}]_j \end{aligned} \tag{B13}$$

with the index $j = 1, 2, 3$ labelling the axes of DF.

The final step consists in inserting Eqs. (B7) and (B8) into Eq. (B2), so that the infinitesimal change of the function, $\mathrm{d}f(\mathbf{Q}')$, is written in terms of the same infinitesimal changes of the "old" variables entering the expression for $\mathrm{d}f(\mathbf{Q})$ in Eq. (B1). Then, since the change of molecular state is the same, the expressions for the differences $\mathrm{d}f(\mathbf{Q})$ and $\mathrm{d}f(\mathbf{Q}')$ are compared yielding the following form of the transformed gradient operators acting on the new variables $\mathbf{Q}'$:

$$\nabla_{\mathrm{T}}(\mathbf{Q}') = \mathbf{S}_{\mathrm{TT}}^{\mathrm{Tr}} \begin{pmatrix} \partial/\partial r \\ \partial/\partial\phi \\ \partial/\partial\theta \end{pmatrix} + \mathbf{S}_{\mathrm{RT}}^{\mathrm{Tr}} \mathbf{M}_{\mathrm{D}}(\mathbf{\Omega}_{\mathrm{DM}}) \tag{B14}$$

$$\begin{aligned} \nabla_{\mathrm{R}}(\mathbf{Q}') &= \mathbf{S}_{\mathrm{TR}}^{\mathrm{Tr}} \frac{\partial}{\partial \mathbf{r}} + \mathbf{S}_{\mathrm{RR}}^{\mathrm{Tr}} \mathbf{M}_{\mathrm{D}}(\mathbf{\Omega}_{\mathrm{DM}}) \\ &= \mathbf{E}(\mathrm{LF} \leftarrow \mathrm{DF}) \mathbf{M}_{\mathrm{D}}(\mathbf{\Omega}_{\mathrm{DM}}) \end{aligned} \tag{B15}$$

Appendix C: Correlation functions under time-scale separation

In this appendix we summarize the main steps in the evaluation of time-correlation functions under the assumption of time-scale separation between different dynamic processes driving the relaxation. Here we collect the leading expressions which are applied in Sect. 4, while for the rigorous derivation and comments about the procedure we address the reader to the appendix B of ref. [63].

Let us divide the ensemble of stochatic variables $\mathbf{q}$, which are relevant in the description of a generic stochastic process, into a set of *slow* variables $\mathbf{q}^{\mathrm{s}}$ and a set of *fast* variables $\mathbf{q}^{\mathrm{f}}$. Accordingly, the decay of the correlation function $G(t) = \overline{f(\mathbf{q})_t^* g(\mathbf{q})_0}$ between a pair of generic observables depending on $\mathbf{q}$, shows a fast relaxing component $G^{\mathrm{f}}(t)$ and a low relaxing component $G^{\mathrm{s}}(t)$, with

$$G(t) = G^{\mathrm{s}}(t) + G^{\mathrm{f}}(t) \tag{C1}$$

The aim is to provide approximations to $G^{\mathrm{s}}(t)$ and $G^{\mathrm{f}}(t)$ starting from the knowledge of the evolution operator $\Gamma(\mathbf{q})$ and of the equilibrium distribution $p_{\mathrm{eq}}(\mathbf{q})$. The leading idea is that a Born-Oppenheimer-like approximation can be exploited, on assuming that a fast loss of correlation is due to fluctuations of $\mathbf{q}^{\mathrm{f}}$ at "quenched" $\mathbf{q}^{\mathrm{s}}$, followed by a much slower decay due to the stochastic modulation of $\mathbf{q}^{\mathrm{s}}$.

Let us start by projecting the equilibrium distribution onto the subspace ϵ^{s} of the slow variables (notice the superscript "s"),

$$p_{\mathrm{eq}}^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) = \int \mathrm{d}\mathbf{q}^{\mathrm{f}}\, p_{\mathrm{eq}}(\mathbf{q}) \tag{C2}$$

Then, the equilibrium distribution on the fast variables (superscript "f") is defined as the conditional distribution at fixed $\mathbf{q}^{\mathrm{s}}$,

$$p_{\mathrm{eq}}^{\mathrm{f}}(\mathbf{q}) \equiv p_{\mathrm{eq}}(\mathbf{q}^{\mathrm{s}} \mid \mathbf{q}^{\mathrm{f}}) \tag{C3}$$

Notice that $p_{\mathrm{eq}}^{\mathrm{f}}(\mathbf{q})$ may keep a parametric dependence on $\mathbf{q}^{\mathrm{s}}$. Now consider the projection of the observables $f(\mathbf{q})$ and $g(\mathbf{q})$ onto the subspace ϵ^{s},

$$f^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) p_{\mathrm{eq}}^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) = \int \mathrm{d}\mathbf{q}^{\mathrm{f}}\, f(\mathbf{q}) p_{\mathrm{eq}}(\mathbf{q}) \tag{C4}$$

and the correspondent orthogonal complement

$$\delta f^{\mathrm{f}}(\mathbf{q}) = f(\mathbf{q}) - f^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) \tag{C5}$$

[analogous relations hold for $g(\mathbf{q})$]. The slow relaxing component of the correlation function is obtained in the form

$$G^{\mathrm{s}}(t) = \int \mathrm{d}\mathbf{q}^{\mathrm{s}}\, f^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}})^* \mathrm{e}^{-\Gamma^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}})t} p_{\mathrm{eq}}^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) g^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) \tag{C6}$$

where $\Gamma^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}})$ is the projected evolution operator which defines the evolution of the projected non-equilibrium probability density $p^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}, t) = \int \mathrm{d}\mathbf{q}^{\mathrm{f}}\, p(\mathbf{q}, t)$ through the Fokker–Planck equation

$$\frac{\partial}{\partial t} p^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}, t) = -\Gamma^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) p^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}, t) \tag{C7}$$

The operator $\Gamma^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}})$ is implicitly defined by means of the following identity to be satisfied for generic functions $F(\mathbf{q}^{\mathrm{s}})$ of the slow variables,

$$\Gamma^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) F(\mathbf{q}^{\mathrm{s}}) p_{\mathrm{eq}}^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) = \int \mathrm{d}\mathbf{q}^{\mathrm{f}}\, \Gamma(\mathbf{q}) F(\mathbf{q}^{\mathrm{s}}) p_{\mathrm{eq}}(\mathbf{q}) \tag{C8}$$

Then, an approximation of the fast relaxing component of the correlation function (at quenched $\mathbf{q}^{\mathrm{s}}$) is found as

$$G^{\mathrm{f}}(\mathbf{q}^{\mathrm{s}}, t) \simeq \int \mathrm{d}\mathbf{q}^{\mathrm{f}}\, \delta f^{\mathrm{f}}(\mathbf{q})^* \mathrm{e}^{-\Gamma^{\mathrm{f}}(\mathbf{q})t} p_{\mathrm{eq}}^{\mathrm{f}}(\mathbf{q}) \delta g^{\mathrm{f}}(\mathbf{q}) \tag{C9}$$

where the operator $\Gamma^{\mathrm{f}}(\mathbf{q})$ is obtained from the global $\Gamma(\mathbf{q})$ by extracting the terms acting only on the fast variables $\mathbf{q}^{\mathrm{f}}$ (notice that a parametric dependence on $\mathbf{q}^{\mathrm{s}}$ may be kept). Finally, the fast relaxing component $G^{\mathrm{f}}(t)$ can be obtained by averaging Eq. (C9) over the distribution on $\mathbf{q}^{\mathrm{s}}$:

$$G^{\mathrm{f}}(t) \simeq \int \mathrm{d}\mathbf{q}^{\mathrm{s}}\, p_{\mathrm{eq}}^{\mathrm{s}}(\mathbf{q}^{\mathrm{s}}) G^{\mathrm{f}}(\mathbf{q}^{\mathrm{s}}, t) \tag{C10}$$

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