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Uncorrelated jumps model for molecular orientational relaxation in liquid crystals

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Abstract

Molecular reorientation in anisotropic fluids is considered as Markov's stochastic process. Uncorrelated angular jumps and orientational-dependent residence time $\tau(\Omega)$ are assumed. The proposed model is more general than the strong collision one, which can be derived from our approach as a particular case at $\tau(\Omega) = \text{const}$. New solutions describing molecular reorientation (spherical and symmetric rotor) in anisotropic media are proposed and compared with the results obtained by strong collision and small step rotational diffusion models.

Keywords: Dynamic reorientational processes; Anisotropic systems

1. Introduction

The complex character of the reorientational processes in anisotropic systems (e.g. mesomorphic materials, polymers, membranes, etc.) limit the plausible choice of adequate theoretical approach. It is usually assumed that the molecular orientation Ω is a Markov's stochastic variable and that the reorientation proceeds by instantaneous jumps. In the isotropic phase this model has been studied by Ivanov and Valiev [1] for arbitrary correlation between $\tilde{\Omega}$ and Ω ($\tilde{\Omega}$ and Ω being the orientations before and after the jumps) and it has been applied to large number of different physical problems. For anisotropic fluids only two simple limiting cases, namely the small step rotational diffusion model (SSRD) [2–5] and the strong collision model (SC) [4,6–13] for the correlation between $\tilde{\Omega}$ and Ω, have been considered and applied so far.

(i) A very strong correlation between the orientations before and after the jumps in the small step rotational diffusion model is assumed. This model refers to both, the molecular and microscopic anisotropies of the reorientation and, at least qualitatively, it is in satisfactory agreement with the experimental data. From experimentalist's point of view, a disadvantage of the SSRD model is the complicated form of the orientational correlation functions – they are multiexponential and their correlation times are order-dependent. On the other hand, the number of the dynamical parameters (the rotational diffusion coefficients) is very restricted, which is helpful for the data treatment. That is why this method has been widely applied for interpretation of the results in numerous experimental studies of the reorientational dynamics in liquid crystals and membranes [5–11].

(ii) The strong collision model accepts that Ω does not depend upon $\tilde{\Omega}$, i.e. the jumps are uncorrelated. In the simplest version of this model (it does not concern the anisotropy of the rotational molecular mobility) the orientational correlation functions are exponential with the same order-dependent correlation time. Although this result is not

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consistent with some experiments [4], it is attractive because of its simplicity and therefore has been applied for data interpretation in some studies [6,12,14].

A phenomenological attempt to introduce the molecular anisotropy into SC model has been carried out by Luckhurst and Sanson [13]. Their approach reveals exponential functions with different correlation times, which should be considered as unknown parameters. The large number of these independent dynamical characteristics and their unknown dependence on the orientational order impede the data treatment. Nevertheless, due to the simple exponential form of the correlation functions, this model has been often applied to the experimental data interpretation [6,12,13].

The purpose of this paper is to develop a general uncorrelated jumps model for the reorientation of anisotropic molecules (spherical and symmetrical rotors) in anisotropic media. Our theoretical model is compared with SSRD and SC approaches already existing in the literature.

2. Results and discussion

Let $\Omega = (\alpha, \beta, \gamma)$ be the set of Euler angles defining the molecular orientation in the laboratory frame of reference. $P(\Omega_0|\Omega t)$ is the conditional probability density for the molecule to have orientation Ω at time t if at $t = 0$, $P(\Omega_0|\Omega 0) = \delta(\Omega - \Omega_0)$. We start from the Feller equation [15] where $F(\tilde{\Omega}, \Omega)$ is the probability density for changing the orientation from $\tilde{\Omega}$ to Ω, at given jump, and $\tau(\Omega)$ is the average time between the jumps at orientation Ω. In the isotropic liquids, due to the symmetry of the phase, $F(\tilde{\Omega}, \Omega) = F(\tilde{\Omega} - \Omega)$ and $\tau(\Omega) = \text{const}$.

Taking into account that the equilibrium orientation distribution function $f(\Omega)$ is a stationary solution of Feller equation, we obtain the usual condition [16,17], restricting the possible choices of $F(\tilde{\Omega}, \Omega)$ and $\tau(\Omega)$:

$$\frac{f(\Omega)}{\tau(\Omega)} = \int \mathrm{d}\tilde{\Omega} \frac{f(\tilde{\Omega})}{\tau(\tilde{\Omega})} F(\tilde{\Omega}, \Omega) \tag{1}$$

In the uncorrelated jumps correlation, the dependence of $F(\tilde{\Omega}, \Omega)$ on the previous orientation is neglected $(F(\tilde{\Omega}, \Omega) = F(\Omega))$ and we obtain:

$$\frac{\partial}{\partial t} P(\Omega_0|\Omega t) = \frac{1}{\tau(\tilde{\Omega})} P(\Omega_0|\Omega t) + F(\Omega) \times \int \mathrm{d}\tilde{\Omega} \frac{1}{\tau(\tilde{\Omega})} P(\Omega_0|\tilde{\Omega} t) \tag{2}$$

The detailed balance condition becomes:

$$\frac{f(\Omega)}{F(\Omega)\tau(\Omega)} = \frac{f(\tilde{\Omega})}{F(\tilde{\Omega})\tau(\tilde{\Omega})} = \int \mathrm{d}\tilde{\Omega} \frac{f(\tilde{\Omega})}{\tau(\tilde{\Omega})} \tag{3}$$

The only difference between Eqs. (2) and (3) and the corresponding expressions in the SC model [**4**] is that our residence time $\tau(\Omega)$ is Ω dependent. The SC model can be obtained from our approach, assuming $\tau(\Omega) = \text{const}$, although this assumption seems very doubtful and arbitrary. In fact, $\tau(\Omega) = \text{const}$ (along with $F(\Omega) = \mathit{const}$) is a natural choice only for isotropic liquids. In the anisotropic systems the orientational dependence of both, residence time $\tau(\Omega)$ and the rate of reorientation $F(\Omega)$, is physically reasonable – the molecules with different orientation Ω interact in different way with the medium. For example, at $\beta = 0$ the molecule is in deep potential well of the mean orienting potential of the medium and for its reorientation, collisions much stronger than for the reorientation of a molecule with $\beta = \pi/2$ are necessary. Naturally, the residence time for $\beta = 0$ is expected to be longer than for $\beta = \pi/2$.

From the usual definition of the orientational correlation functions [18]

$$G^{\ell k}_{mn}(t) = \int \mathrm{d}\Omega_0 \int \mathrm{d}\Omega D^{\ell}_{mn}(\Omega_0) D^{k^*}_{mn}(\Omega) f(\Omega_0) P(\Omega_0/\Omega t) \tag{4}$$

we have for spherical rotor in anisotropic media:

$$G^{\ell k}_{mn}(s) = \int \mathrm{d}\Omega \frac{D^{\ell}_{mn}(\Omega) D^{k^*}_{mn}(\Omega) f(\Omega')}{s + 1/\tau(\Omega)} + \frac{\delta_{m0}\delta_{n0}}{\overline{\tau^{-1}} - \int \mathrm{d}\Omega \frac{f(\Omega)}{\tau(\Omega)(1+s\tau(\Omega))}} \times \int \mathrm{d}\Omega \frac{f(\Omega) D^{k}_{00}(\Omega)}{1 + s\tau(\Omega)} \int \mathrm{d}\Omega_0 \frac{f(\Omega_0) D^{\ell}_{00}(\Omega_0)}{1 + s\tau(\Omega_0)} \tag{5}$$

where

$$\overline{\tau^{-1}} = \int \mathrm{d}\Omega \frac{f(\Omega)}{\tau(\Omega)} \tag{5a}$$

In the particular case $\tau(\Omega) = \text{const}$ the formal solution of Eq. (5) reproduces the results of the SC model. The approximation of the orientation of a highly anisotropic molecule as spherical rotor is obviously very idealistic. In fact, both inertial and steric anisotropy of the molecule lead to fast rotation around the long molecular axis (spinning motion) and much slower reorientation of the axis itself (tumbling motion) and further we will consider the dynamics of symmetric rotor in anisotropic media.

We assume hereafter that the spinning and tumbling reorientations are statistically independent. This reasonable approximation is physically equivalent to the usual assumption in SSRD model that the reorientational diffusion tensor is diagonal and constant in the molecular frames of reference. Let us introduce a "transferring" frame of reference, related to tumbling reorientation, and defined in the laboratory coordinate system by a set of Euler angles $\Omega' = (\alpha, \beta, 0)$. We have then $\Omega = \Omega' + \Omega''$ in the sense of sum of rotation, where $\Omega'' = (0,0,\gamma)$ defines the molecular orientation in the "transferring" frame Ω'(t) and describes the spinning reorientation. The statistical independence of Ω' and Ω'' relaxation assumed by us, leads to factorization of the conditional probability:

$$P(\Omega_0|\Omega t) = P_2(\Omega'_c|\Omega t') P_1(\Omega''_0|\Omega t'') \tag{6}$$

where $P_1(\Omega''_0|\Omega''_t)$ describes the spinning reorientation, and the most natural choice for $P_2(\Omega'_0|\Omega'_t)$ is the conditional probability for the "pure" tumbling reorientation, i.e.