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*Invited Lecture*

# Uncorrelated jumps model for orientational relaxation in liquid crystals – nanosecond and picosecond time domains

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A generalized theoretical model to interpret the orientational relaxation in uniaxially aligned systems is suggested. The proposed approach is more general than those existing so far, which can be derived from our approach as particular cases at a constant residence time. It is compared with the results obtained by strong collision and small step rotational diffusion models.

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## 1. Introduction

The complex character of the reorientational processes in anisotropic systems (e.g. mesomorphic materials, polymers, membranes, etc.) limit the plausible choice of an adequate theoretical approach. It is usually assumed that the molecular orientation $\Omega$ 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 an arbitrary correlation between $\tilde{\Omega}$ and $\Omega$ ($\tilde{\Omega}$ and $\Omega$ being the orientations before and after the jumps) and it has been applied to a large number of different physical problems. For anisotropic fluids, only two simple limiting cases, namely the small step rotational diffusion model (SSRD) [2] and the strong collision one (SC) [3] for the correlation between $\tilde{\Omega}$ and $\Omega$, have been considered and applied so far. A very strong correlation between the orientations before and after the jumps in the small step rotational diffusion model is assumed. From an experimentalist's point of view, a disadvantage of the SSRD model is the complicated form of the orientational correlation functions – they are multi-exponential and their correlation times are order-dependent. The strong collision model accepts that $\Omega$ 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 both models are sometimes not consistent with experiments [3], they are attractive due to their simplicity and havebeen applied to interpretation of some studies [4].

The purpose of this paper is to present a generalized uncorrelated jumps model for the reorientation of anisotropic molecules (spherical and symmetrical rotors) in anisotropic media. The suggested approach is to develop further the investigation of reorientational processes in nematics formed by rigid rod-shaped molecules [5] Our theoretical model is discussed and compared with the SSRD and SC approaches.

## 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 an orientation $\Omega$ at time $t$ if at $t = 0$, $P(\Omega_0 | \Omega t) = \delta(\Omega - \Omega_0)$. We start from the Feller equation [6] where $F(\tilde{\Omega}, \Omega)$ is the probability density for changing the orientation from $\tilde{\Omega}$ to $\Omega$ in given jump, and $\tau(\Omega)$ is the average time between the jumps at orientation $\Omega$. In isotropic liquids, due to the symmetry of the phase, $F(\tilde{\Omega}, \Omega) = F(\tilde{\Omega} - \Omega)$ and $\tau(\Omega) = const$.

Taking into account that the equilibrium orientation distribution function $f(\Omega)$ is a stationary solution of the Feller equation, we obtain the usual condition [7, 8] restricting the possible choices of $F(\tilde{\Omega}, \Omega)$ and $\tau(\Omega)$:

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

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

$$\frac{\partial}{\partial t}P(\Omega_0\mid\Omega\, t)=\frac{1}{\tau(\widetilde{\Omega})}P(\Omega_0\mid\Omega\, t)+ \\ +F(\Omega)\int d\widetilde{\Omega}\,\frac{1}{\tau(\widetilde{\Omega})}P(\Omega_0\mid\widetilde{\Omega}\, t) \tag{2}$$

The detailed balance condition becomes:

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

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 $\Omega$ -dependent. The SC model can be obtained from our approach, assuming $\tau(\Omega)=const$, although this assumption seems very doubtful and arbitrary. In fact, $\tau(\Omega)=const$ (along with $F(\Omega)=const$ ) is a natural choice only for isotropic liquids. In anisotropic systems, the orientational dependence of both the residence time $\tau(\Omega)$ and the rate of reorientation $F(\Omega)$, is physically reasonable – molecules with different orientations $\Omega$ interact in different ways 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 [5]

$$G_{mn}^{\ell k}(t)= \\ =\int d\Omega_0\int d\Omega D_{mn}^{\ell}(\Omega_0)D_{mn}^{k*}(\Omega)f(\Omega_0)P(\Omega_0/\Omega\, t) \tag{4}$$

For a spherical rotor in anisotropic media we have:

$$G_{mn}^{\ell k}(s)=\int d\Omega\,\frac{D_{mn}^{\ell}(\Omega)D_{mn}^{k*}(\Omega)f(\Omega')}{s+1/\tau(\Omega)}+ \\ +\frac{\delta_{m0}\delta_{n0}}{\overline{\tau^{-1}}-\int d\Omega\,\dfrac{f(\Omega)}{\tau(\Omega)(1+s\,\tau(\Omega))}} \tag{5}$$

$$\int d\Omega\,\frac{f(\Omega)D_{00}^{k}(\Omega)}{1+s\,\tau(\Omega)}\int d\Omega_0\,\frac{f(\Omega_0)D_{00}^{\ell}(\Omega_0)}{1+s\,\tau(\Omega_0)}$$

where

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

In the particular case $\tau(\Omega)=const$, the formal solution of Eq. (5) reproduces the results of the SC model.

The approximation of the orientation of a highly anisotropic molecule as a 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 (rotation time usually a few picoseconds) and much slower reorientation of the axis itself (tumbling motion in the time domain of nanoseconds), and further we will consider the dynamics of a 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 the 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 the sum of rotations, where $\Omega''=(0,\ 0,\ \gamma)$ defines the molecular orientation in the "transferring" frame and $\Omega'(t)$ describes the spinning reorientation. The statistical independence of the $\Omega'$ and $\Omega''$ relaxations, 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. without rotation around the long molecular axis. At $t\to\infty$ we obtain:

$$f(\Omega)=f_2(\Omega')f_1(\Omega'') \tag{7}$$

where

$$f_1(\Omega'')=\frac{1}{2\pi} \tag{8}$$

The correlation functions for the spinning and tumbling relaxations are, respectively:

$$G_{(1)in}^{\ell k}(t)= \\ =\int d\Omega_0''\int d\Omega'' f_1(\Omega_0'')\,P_1(\Omega_0''|\,\Omega'' t)\,D_{in}^{\ell}(\Omega_0'')\,D_{in}^{k*}(\Omega'') \tag{9 a}$$

$$G^{\ell k}_{(2)mi}(t)= \tag{9 b}$$
$$=\int d\Omega_0'\int d\Omega' f_2(\Omega_0')\,P_2(\Omega_0'|\,\Omega' t)\,D^{\ell}_{mi}(\Omega_0')\,D^{k*}_{mi}(\Omega')$$

Taking into account that $\tau(\Omega'')=const=\tau_\gamma$, due to the cylindrical symmetry of the molecules, $f_1(\Omega'')$ and $F(\Omega'')$ are orientation independent. The solution of Eqs. (9) is:

$$P_1(\Omega_0''\,|\Omega'' t)= \tag{10}$$
$$=\delta(\gamma-\gamma_0)\exp[-t/\tau_\gamma]+\frac{1}{2\pi}\left(1-\exp[-t/\tau_\gamma]\right)$$

and the orientational correlation function is:

$$G^{\ell k}_{(1)mn}(t)=\delta_{mn}\left[\delta_{n0}\left(1-\exp[-t/\tau_\gamma]\right)+\exp[-t/\tau_\gamma]\right]= \tag{11}$$
$$=\delta_{mn}\exp\left[-\left(1-\delta_{n0}\right)t/\tau_\gamma\right]$$

Laplace transformation of Eq. (11) gives for the tumbling motion:

$$G^{\ell k}_{mn}(s)=\int d\Omega' \frac{D^{\ell}_{mn}(\Omega')D^{k*}_{mn}(\Omega')f(\Omega')}{s+1/\tau(\Omega')}+$$
$$+\frac{1}{2\pi}\frac{\delta_{m0}\delta_{n0}}{\overline{\tau^{-1}}-\int d\Omega' \dfrac{f(\Omega')}{\tau(\Omega')\,(1+s\,\tau(\Omega'))}} \tag{12}$$
$$\int d\Omega\,\frac{f(\Omega)D^{k}_{00}(\Omega)}{1+s\,\tau(\Omega)}\int d\Omega_0\,\frac{f(\Omega_0)D^{\ell}_{00}(\Omega_0)}{1+s\,\tau(\Omega_0)}$$

For $n=0$, the correlation functions are sensitive only to tumbling reorientation, and Eqs. (5) and (12) are equivalent. For $n\neq 0$, however, the results for the spherical and linear rotor differ substantially (note that $d\Omega'=d\alpha\, d\beta$, while $d\Omega=d\Omega'\, d\Omega''=d\Omega'\, d\gamma$).

Some simple features of the rotational correlation functions (e.g. their behaviour at $t\,\overline{\tau^{-1}}<<1$) can be easily obtained by Eq. (5). The same equation allows us to calculate $G^{\ell k}_{mn}(t)$ numerically, taking the integrals at a given $\tau(\Omega)$. However, this procedure, due to its significant technical difficulties, is not convenient for our purpose. Here we shall use another approach, similar to that already applied for the numerical (or approximate analytical) solution of the equations in the SSRD model [2, 5]. Let us define:

$$W^{\ell}_{mn}(\Omega,t)=\frac{1}{f(\Omega)}\int d\Omega_0\, f(\Omega_0)D^{\ell}_{mn}(\Omega_0)P(\Omega_0|\Omega t) \tag{13}$$

Multiplying Eq. (2) by $f(\Omega_0)D^{\ell}_{mn}(\Omega_0)$ and integrating over $\Omega_0$, we obtain:

$$f(\Omega)\frac{\partial}{\partial t}W^{\ell}_{mn}(\Omega,t)= \tag{14}$$
$$=\overline{\tau^{-1}}F(\Omega)\left[-W^{\ell}_{mn}(\Omega,t)+\int d\tilde{\Omega}\,F(\tilde{\Omega})\,W^{\ell}_{mn}(\tilde{\Omega},t)\right]$$

where $F(\Omega)$ is the rate of reorientation (see Eq. (3)). Taking into account the molecular and microscopic symmetry, we expand all functions in Eq. (14) as a series of Wigner matrices and obtain a set of linear differential expressions:

$$\sum_i b^{ik}_{mn}\frac{d}{dt}V^{\ell i}_{mn}(t)=-\sum_i a^{ik}_{mn}\frac{d}{dt}V^{\ell i}_{mn}(t) \tag{15}$$

$$V^{\ell i}_{mn}(t)=\frac{2I+1}{8\pi^2}\int W^{\ell}_{mn}(\Omega,t)\,\left[D^{i}_{mn}(\Omega)\right]^{*}d\Omega \tag{16}$$

$$b^{\ell k}_{mn}=\lim_{t\to 0}G^{ik}_{mn}(t)= \tag{17}$$
$$=\sum_{s-even}(2s+1)\langle P_s\rangle(-1)^{m+n}\varpi^{isk}_{m}\varpi^{isk}_{n}$$

$$a^{\ell k}_{mn}=-\lim_{t\to 0}\frac{d}{dt}G^{ik}_{mn}(t)= \tag{18}$$
$$=\overline{\tau^{-1}}\left[\sum_{s-even}(2s+1)F_s(-1)^{m+n}\varpi^{isk}_{m}\varpi^{isk}_{n}-\delta_{m0}\delta_{n0}F_\ell F_k\right]$$

where

$$\varpi^{isk}_{m}=\begin{pmatrix} i & s & k\\ m & 0 & -m\end{pmatrix} \text{ and } \varpi^{isk}_{n}=\begin{pmatrix} i & s & k\\ n & 0 & -n\end{pmatrix}$$

are the Wigner 3J-coefficients, $\langle P_s\rangle$ - the usual order parameters and

$$F_s=\int d\Omega\, F(\Omega)D^{S}_{00}(\Omega) \tag{19}$$

- the phenomenological parameters of our model.

From Eqs. (4) and (13) we have:

$$G^{\ell k}_{mn}(t)=\int d\Omega\, f(\Omega)\,D^{k*}_{mn}(\Omega)W^{\ell}_{mn}(\Omega,t)= \tag{20}$$
$$=\sum_i b^{ik}_{mn}\,V^{\ell i}_{mn}(t)$$

The Laplace transforms of Eqs. (18) and (20) are:

$$\sum_i\left(a^{ik}_{mn}+s\,b^{ik}_{mn}\right)V^{\ell i}_{mn}(s)=b^{\ell k}_{mn} \tag{21}$$

$$G^{\ell k}_{mn}(s)=\sum_i b^{ik}_{mn}\,V^{\ell i}_{mn}(s) \tag{22}$$

These equations are similar to (although more complicated than) those already derived in SSRD model

[5]. The main difference is the explicit form of the coefficients $a_{mn}^{\ell k}$. The correlation functions $G_{mn}^{\ell k}(t)$ can be obtained from Eq. (22) as a sum of exponentials. In our case we might conclude, under the reasonable assumption $F_s < \langle P_s \rangle$, that the sum converges fast and only a few exponentials are necessary to obtain a good approximation.

The discussion of our results in their most general form is difficult, due to the large number ofphenomenological parameters $F_S$. However, the main features of our model are easy to understand when we apply the following particular cases:

i) Let us assume $\tau(\Omega) = const = \tau$. Evidently, in this case our expressions reduce to those of SC model [3]. The correlation functions are exponential

$$G_{mn}^{\ell k}(t) = \delta_{m0}\delta_{n0}\langle P_\ell \rangle \langle P_k \rangle + \left[G_{mn}^{\ell k}(0) - \delta_{m0}\delta_{n0}\langle P_\ell \rangle \langle P_k \rangle\right] \exp(-t/\tau) \tag{23}$$

with the correlation time $\tau$, and independent of $\ell, k, m, n$ and of the order parameters, as well. This result does not coincide with many experimental data, demonstrating that $\tau$ is order dependent. This dependence is usually different at various $\ell$ and $k$ [3], $\tau$ itself depends on $\ell$ and $k$ [3, 5] and at $\ell = k = 1$ and $n = 0$ (i.e. when the spinning motion does not influence the data and the spherical rotor is a good approximation) it depends on the subscript $m$ [4].

ii) Let us assume that $F(\Omega) = \dfrac{1}{8\pi^2}$ [5, 7, 8]. In this case, the orientational dependence in our model is due only to the residence time $\tau(\Omega)$

$$\tau(\Omega) = \frac{f(\Omega)}{\overline{\tau^{-1}} F(\Omega)} = \frac{8\pi^2}{\overline{\tau^{-1}}} f(\Omega) \tag{24}$$

From Eq. (19) we obtain $F_s = \delta_{s0}$ [5] and Eq. (18) gives

$$a_{mn}^{\ell k} = \overline{\tau^{-1}} \left[ \frac{\delta_{ik}}{2i+1} - \delta_{m0}\delta_{n0}\delta_{i0}\delta_{k0} \right] \tag{25}$$

The first (uni-exponential) approximated solution of Eqs. (21) and (22) is:

$$G_{mn}^{\ell k}(t) = \delta_{m0}\delta_{n0}\langle P_l \rangle \langle P_k \rangle + \left(b_{mn}^{\ell k} - \delta_{m0}\delta_{n0}\langle P_k \rangle \langle P_\ell \rangle\right) \exp\left[-t/\tau_{mn}^{\ell k}\right] \tag{26}$$

where

$$\tau_{mn}^{\ell k} = \frac{\left(b_{mn}^{\ell k} - \delta_{m0}\delta_{n0}\langle P_k \rangle \langle P_\ell \rangle\right)}{a_{mn}^{\ell k}} \tag{27}$$

Eq. (26) can be very useful for investigations of the short time behaviour ($t\, \overline{\tau^{-1}} << 1$) of the correlation functions (e.g. for interpretation of data obtained by IR and Raman bandshape analysis [4]).

For the interpretation of data obtained by some other techniques (polarized optical spectroscopy), $G_{mn}^{\ell k}(t)$ should be calculated for a large time-window. For this purpose, Eqs. (21) and (22) can be used and $G_{mn}^{\ell k}(t)$ are obtained to good a approximation as the sum of a few exponentials. Fig. 1 presents the numerical results for $G_{mn}^{11}(t)$, calculated in this way with one-, two- and three-exponential approximations. The order parameters $\langle P_s \rangle$, necessary for this calculation have been theoretically generated using a Maier-Saupe [9] potential for $\langle P_2 \rangle$ = 0.43 and $\langle P_2 \rangle$ = 0.82; $a_{mn}^{\ell k}$ = - 0.43, $b_{mn}^{\ell k}$ = - 0.82.

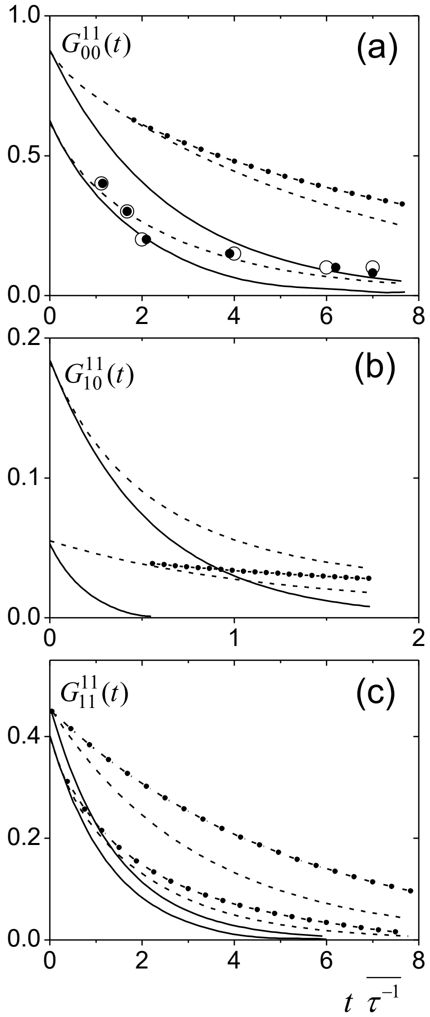


*Fig. 1. Calculated correlation functions $G_{00}^{11}(t)$ (part (a)); spherical rotor $G_{10}^{11}(t) = G_{01}^{11}(t)$ (part (b)) and spherical rotor $G_{11}^{11}(t)$ (part (c)), approximated by $i$ exponentials: $i = 1$ (solid lines); $i = 2$ (dashed lines); $i = 3$ (dash-dotted). The calculation parameters are given in the text. The circles are experimental Raman data; the points are experimental IR data for 4,n-pentylmethoxytolane.*

The experimental data $G_{mn}^{\ell k}(t)$ obtained by bandshape analysis of the Raman line at 2224 cm$^{-1}$ ($C \equiv C$ stretch vibration) and the IR band at 833 cm$^{-1}$ (CH aromatic-out-of-plane deformation) of 4,n-pentylmethoxytolane are also presented in Fig. 1. The coincidence between the numerical results and the experimental data is satisfactory within the limits of the errors (~ 10 %). The convergence of $G_{mn}^{11}(t)$ with the number of exponentials used in the calculation is slower than in the case of the SSRD model, and the time behaviour of the correlation functions is similar to that obtained by a diffusion model [5]. In particular, the decrease of $G_{00}^{11}(t)$ becomes slower at large $\langle P_2 \rangle$, in agreement with the experimental data [10].

For the most general case of the $\Omega$ -dependence of the reorientation rate $F(\Omega)$, we can expect that the parameters $F_s$ will be between $F_s = \langle P_s \rangle$ (case i) and $F_s = \delta_{s0}$ (case ii). The correlation functions can be calculated from Eqs. (26) and (27) for $t\,\overline{\tau^{-1}} << 1$ or for longer times. In general, it should be pointed out that the results are in better agreement with experiments than those of the simple SC model [3], but the data interpretation is much more difficult. In fact, at larger $\ell$ and $k$ and/or at longer times, in order to calculate $G_{mn}^{\ell k}(t)$, we should know more phenomenological parameters $F_s$.

## 3. Conclusions

Our approach seems quite promising for the investigation of the molecular relaxation in anisotropic media. It has a more sound physical basis than the strong collision one, and gives simple results with only one phenomenological parameter $\tau_\gamma$. It is difficult to distinguish which one of the models – SSRD or our approach is more suitable. At least for the tumbling motion, the SSRD seems more convincing. In fact, mesomorphic and polymeric molecules are highly anisotropic, and the large angular jumps of the long axis due to the big inertial moment and steric hindrance require a high energy.

With more data, it would be relatively easy to test the validity of our model compared to SSRD one. The proposed approach can be generalized for the case of an arbitrary correlation between the angular jumps around the long molecular axis, and/or for the equilibrium distribution function $f(\Omega) = f(\beta, \gamma)$, i.e. also taking into account the molecular biaxiality, and therefore it will be applicable to any anisotropic system with a rotational degree of freedom.

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