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Deuteron NMR resolved mesogen vs crosslinker molecular order and reorientational exchange in liquid single crystal elastomers

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In this Electronic Supplementary Information we provide a more detailed description of the model of static orientational disorder and reorientational exchange, employed to describe ^{2}H quadrupole-perturbed NMR spectra in liquid single crystal elastomers (LSCEs).

Theoretical Calculations

Distribution of domain directors. In oriented LSCEs, the distribution of orientations of domain director, $w_{stat}(u,\sigma_u)$, is assumed to be spherical Gaussian:

$$w_{\text{stat}}(u,\sigma_u)=\frac{e^{-\frac{1-u^2}{2\,\sigma_u^2}}}{e^{-\frac{1}{2\,\sigma_u^2}}\sqrt{2\pi}\,\sigma_u\,\text{erfi}\left(\frac{1}{\sqrt{2}\,\sigma_u}\right)}. \quad (1)$$

Here $u=\cos\theta\in[-1,1]$, with θ denoting the orientation of a given domain, whereas $\sigma_u\in[0,\infty]$ represents the dispersion of the distribution. By introducing $\tan\sigma_\theta=\sigma_u$, dispersion can be quantified by $\sigma_\theta\in[0,90°]$. Erfi is the imaginary error function. $w_{\text{stat}}(u,\sigma_\theta=90°)=1/2$ corresponds to isotropic distribution of domains, a situation found in polydomain samples. Relation (1) implies cylindrical symmetry of domain misalignments.

Domain orientational order parameter $Q_{\text{stat}}\equiv\overline{P_2(cos\theta)}$ can be expressed as

$$Q_{\text{stat}}(\sigma_u)=\int_{-1}^{1}w_{\text{stat}}(u,\sigma_u)\frac{(3u^2-1)}{2}\,\mathrm{d}u=-\frac{1}{2}-\frac{3\sigma_u^2}{2}+\frac{3\,e^{-\frac{1}{2\sigma_u^2}}\sigma_u}{\sqrt{2\pi}\,\text{erfi}\left(\frac{1}{\sqrt{2}\,\sigma_u}\right)}. \quad (2)$$

Transversal precession of magnetization in the case of reorienting nematic director. The Bloch equation for the magnetization *M*, precessing in the plane perpendicular to the external magnetic field, and nematic director subject to RMTD or RMTD-equivalent director reorientation process, is expressed as[1–3]:

$$\frac{\partial M}{\partial t}=i2\pi\nu^{\pm}M-\frac{M}{\widetilde{T}_2}+\omega_D\frac{\partial^2 M}{\partial u^2}, \quad (3)$$

with ω_D representing the angular diffusion and $\widetilde{T}_2$ the spin-spin (transverse) relaxation rate of the magnetization.
In the following, we will solve the differential Eq. (3) in a discrete approximation[4]. For arbitrary distribution $w_{\text{stat}}(u,\sigma_u)$, we introduce a new "isoprobability" variable $v(u,\sigma_u)$ with respect to which the probability density $w_{stat}(v,\sigma_u)$ is constant:

$$v(u,\sigma_u)=\int_{-1}^{u}w(u',\sigma_u)du'=\frac{1}{2}\left[1+\frac{\text{erfi}\left(\frac{u}{\sqrt{2}\sigma_u}\right)}{\text{erfi}\left(\frac{1}{\sqrt{2}\sigma_u}\right)}\right]. \quad (4)$$

The isoprobability variable v is introduced in order to simplify the calculation, specifically to allow for the use of a relatively simple form of discrete exchange matrix $\mathbf{K}$ (Ref. 4) adapted to the case where, in the equilibrium, all the discrete orientational states are equally probable. We discretize the problem by dividing the $[0,1]$ range of variable v into N equidistant intervals $[(k-1)\Delta v,k\Delta v]$ of lengths $\Delta v=1/N$ and equal discrete probabilities $P_{\text{stat},k}=1/N$, indexed by $k=1,\cdots,N$. Such use of variable v is equivalent to dividing the $[-1,1]$ range of variable u into N non-equidistant intervals $[u_k^-,u_k^+]$ of lengths $\Delta u_k=u_k^+-u_k^-$, containing discrete probabilities independent of k,

$$P_{\text{stat},k}=\int_{u_k^-}^{u_k^+}w_{\text{stat}}(u,\sigma_u)\,\mathrm{d}u=\frac{1}{N}, \quad (5)$$

with integration limits $u_k^-=u(v=(k-1)\Delta v)$ and $u_k^+=u(v=k\Delta v)$ where $u(v)$ is the inverse function of $v(u)$ (Eq. (4)).

The discrete form of Eq. (3) is obtained by rewriting the derivatives in terms of differences[4]:

$$\dot{\boldsymbol{M}}^{\pm}(t) = \left(i\underline{\boldsymbol{\Omega}}^{\pm} - \frac{1}{\widetilde{T}_2}\underline{\mathbf{I}} + \frac{1}{\tau}\underline{\mathbf{K}}\right)\cdot \boldsymbol{M}(0) = \underline{\boldsymbol{\mathcal{K}}}^{\pm}\cdot \boldsymbol{M}(0)\ . \tag{6}$$

$\underline{\boldsymbol{\mathcal{K}}}^{\pm} = \left(i\underline{\boldsymbol{\Omega}}^{\pm} - \widetilde{T}_2^{-1}\underline{\mathbf{I}} + \tau^{-1}\underline{\mathbf{K}}\right)$ represents magnetization exchange matrix in inverse second units (s^{-1}). $\underline{\boldsymbol{\Omega}}^{\pm} = 2\pi\underline{\boldsymbol{\nu}}^{\pm}$ is the diagonal matrix of the effective magnetization precession frequencies, averaged within respective intervals Δu_k,

$$\langle \nu\rangle_k^{\pm} = N\int_{u_k^-}^{u_k^+} \nu^{\pm}(u) w_{\text{stat}}(u,\sigma_u)\,\mathrm{d}u\ , \tag{7}$$

where $\nu^{\pm}(u) = \pm 3\bar{\nu}_q S\,(3u^2-1)/8$ as defined by Eq. (3) of the Manuscript.

$\underline{\mathbf{I}}$ is the identity matrix and $\underline{\mathbf{K}}$ the dimensionless population exchange matrix[4] (only nonzero elements shown)

$$\underline{\mathbf{K}} = \begin{bmatrix} -1 & 1 & & & & & & \\ 1 & -2 & 1 & & & & & \\ & 1 & -2 & 1 & & & & \\ & & & \ddots & & & & \\ & & & 1 & -2 & 1 & & \\ & & & & 1 & -2 & 1 & \\ & & & & & 1 & -1 & \end{bmatrix}. \tag{8}$$

With $\pm$ we take into account the two components of the ^{2}H quadrupole-perturbed spectrum. The nominal exchange time is given by $\tau = 4\Delta\nu^2/\omega_D = (N^2\omega_D/4)^{-1}$. The equilibrium dimensionless magnetization equals

$$\boldsymbol{M}(0) = (1,1,\cdots,1,1)/N \tag{9}$$

since the magnetization states are parametrized by the isoprobability variable v and are therefore equally probable. The formal solution to equation (6) is in terms of matrix exponent of magnetization exchange matrix $\underline{\boldsymbol{\mathcal{K}}}^{\pm}$,

$$\boldsymbol{M}^{\pm}(t) = \exp\left(\underline{\boldsymbol{\mathcal{K}}}^{\pm}t\right)\cdot \boldsymbol{M}(0)\ . \tag{10}$$

Generalized dimensionless population exchange matrix. The above tridiagonal population exchange matrix is suitable for modeling reorientational processes in the "weak-collision" limit where the exchange only takes place between two neighboring sites ($\Delta N = 1$). Nevertheless, the "strong-collision" case, where the exchange is effective between a general pair of states ($1 \le \Delta N \le N-1$), can as well be addressed, by solely generalizing the exchange matrix to include more distant off-diagonal terms, provided that it satisfies the principle of detailed balance[5]. In our specific case of homogeneous equilibrium (stationary) state (expression (9)), this requires that the sum of all elements in any row or column vanishes.

Relaxation dynamics of the orientational order parameter. As discussed above, any dynamic reorientation of nematic director, with characteristic time of the order of or shorter than the inverse rigid lattice line width, should result in the motional narrowing of the spectra. Let us now relate this reorientational process with the exchange modelling presented above. We conjure that at time $t = 0$, the system is ideally ordered, $w(u, t=0) = w_0(u) = (\delta(u-1) + \delta(u+1))/2$, and relaxes in the course of time towards the stationary distribution, $w(u, t\to\infty) \to w_{\text{stat}}(u,\sigma_u)$ (relation (1)). Within the discrete exchange model, introduced above, this is equivalent to the initial probability vector

$$\boldsymbol{P}(0) = (1,0,0,\cdots 0,0,1)/2\ , \tag{11}$$

subject to exchange dynamics

$$\dot{\boldsymbol{P}}(\tilde{t}) = \underline{\mathbf{K}}\cdot \boldsymbol{P}(0) \tag{12}$$

solving to

$$\boldsymbol{P}(\tilde{t}) = \left(P_1(\tilde{t}), P_2(\tilde{t}), \cdots, P_{N-1}(\tilde{t}), P_N(\tilde{t})\right) = \exp\left(\underline{\mathbf{K}}\,\tilde{t}\right) \cdot \boldsymbol{P}(0)\,. \tag{13}$$

We have introduced dimensionless exchange time $\tilde{t} = t/\tau$. According to solution (12), there exist N characteristic dimensionless times $\tilde{\tau}_j$, $j = 1, \cdots, N$, of the exchange process, corresponding to negative inverse values of the dimensionless eigenvalues of the population exchange matrix, $\tilde{\tau}_j = -\kappa_j^{-1}$. In a system modelled with a general exchange matrix $\underline{\mathbf{K}}$ and a large number of sites N, these times span a broad range from short ones of the order of 1 towards very large values. The stationary state

$$\boldsymbol{P}_{\text{stat}} = \boldsymbol{P}(\tilde{t} \to \infty) = (1,1,\cdots,1,1)/N\,. \tag{14}$$

is associated with diverging characteristic time, equivalently with $\kappa = 0$ that solves $\dot{\boldsymbol{P}}(\tilde{t}) = \underline{\mathbf{K}} \cdot \boldsymbol{P}_{\text{stat}} = 0$.

It is rather tedious to quantify the reorientational exchange by a spectrum of relaxation times. We simplify the description by regarding this process in terms of the decay of the orientational order parameter

$$Q(t) = \int_{-1}^{1} \frac{(3u^2-1)}{2} w(u,t)du\,, \tag{15}$$

expressed in the framework of chemical exchange among N nematic director orientational states as

$$Q(\tilde{t}) = \sum_{k=1}^{N} \frac{P_k(\tilde{t})\,(3\langle u^2\rangle_k - 1)}{2}, \tag{16a}$$

$$\langle u^2\rangle_k = N \int_{u_k^-}^{u_k^+} u^2 w_{\text{stat}}(u,\sigma_u)\,\mathrm{d}u\,. \tag{16b}$$

Specifically, the evolution of $\boldsymbol{P}(\tilde{t})$ from $\boldsymbol{P}(0)$ to $\boldsymbol{P}_{\text{stat}}$ is associated with the evolution of $Q(\tilde{t})$ from the initial ideal order $Q(\tilde{t}=0) = 1$ towards $Q(\tilde{t} \to \infty) \to Q_{\text{stat}}$. The decay in $Q(\tilde{t})$ is inherently multi-exponential (N different characteristic times within the discrete chemical exchange approximation, see above) and can be expressed as

$$Q(\tilde{t}) - Q_{\text{stat}} = (1 - Q_{\text{stat}}) f(\tilde{t})\,. \tag{17}$$

The decay function $f(\tilde{t})$ is monotonously decreasing with time from the initial value $f(\tilde{t}=0) = 1$ to $f(\tilde{t} \to \infty) = 0$. We now introduce dimensionless nominal Q-decay time $\tilde{\tau}_Q = \tau_Q/\tau$ as the time during which $f(\tilde{t})$ decreases to 1/2:

$$Q\left(\tilde{\tau}_Q\right) - Q_{\text{stat}} = (1 - Q_{\text{stat}})/2 \;\Rightarrow\; \tilde{\tau}_Q(\sigma_u, N, \Delta N)\,. \tag{18}$$

As both $Q(\tilde{t})$ and Q_{stat} depend on σ_u, N, and ΔN, so does $\tilde{\tau}_Q = \tau_Q/\tau$. A representative $Q(\tilde{t})$ decay is shown in Fig. 1.

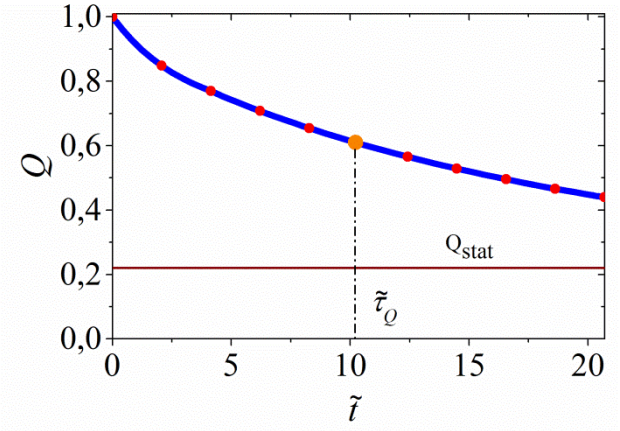

Figure 1. Time dependence of the dynamic orientational order parameter $Q(\tilde{t})$ in a partially-aligned sample with $\sigma_\theta = 30°$ ($\sigma_u = 0.58$) $\Rightarrow Q_{\text{stat}} = 0.22$. The point that determines nominal Q-decay time is marked with the orange dot. Points in red color were calculated using Eqs. (17) and (18) with $N = 100$ and $\Delta N = 3$. Blue solid line is an interpolated guide to the eyes.

It is noteworthy that, in the limit of large N and $\Delta N = 1$ (weak collision), the reorientational exchange model, introduced above, readily reproduces conventional diffusion with a Gaussian $w(u,\tilde{t})$ propagator profile

$$w_G(u,\tilde{t}) = \frac{1}{\sqrt{2\pi\sigma_u^2(\tilde{t})}}\left(e^{-\frac{(u-1)^2}{2\sigma_u^2(\tilde{t})}} + e^{-\frac{(u+1)^2}{2\sigma_u^2(\tilde{t})}}\right), \tag{19}$$

With $\sigma_u^2(\tilde{t}) = 2\widetilde{\omega}_D\tilde{t} = 8/N^2\,\tilde{t}$ characteristic for one-dimensional diffusion processes. The definition range of the tilt variable is $u \in [-1,1]$, so that the Gaussian approximation is only valid for $\sigma_u^2(\tilde{t}) \ll 1$, equivalently $\tilde{t} \ll N^2/8$, since in this case the distribution does not yet extend considerably towards $u = 0$ (no overlap of the positive and negative u branches of the distribution given by relation (19)). For larger $\tilde{t}$, the profile of $w(u,\tilde{t})$ becomes non-Gaussian and the relation $N^2\sigma_u^2(\tilde{t})/(8\tilde{t}) = 1$ is not satisfied anymore.

In the case of Gaussian propagator approximation, the dynamic order parameter can be expressed as

$$Q(\tilde{t}) \approx 1 - 3\sqrt{\frac{2}{\pi}}\sigma_u(\tilde{t}) + \frac{3{\sigma_u}^2(\tilde{t})}{2}. \tag{20}$$

Evidently, condition $\sigma_u^2(\tilde{t}) \ll 1$ that implies Gaussian profile of $w(u,\tilde{t})$ is equivalent to condition $1 - Q(\tilde{t}) \ll 1$.

Motional narrowing of deuteron NMR spectral lines. Deuteron NMR spectrum is calculated as a Fourier transform

$$\mathcal{J}^{\pm}(\nu) \propto \mathrm{Re}\left\{\int_{-\infty}^{\infty}\mathcal{M}^{\pm}(t)\mathrm{e}^{-\mathrm{i}2\pi\nu t}dt\right\} \tag{21}$$

of the time-dependent transversal magnetization $\mathcal{M}^{\pm}(t) = \sum_{k=1}^{N} M_k^{\pm}(t)$. Here $M_k^{\pm}(t)$ are the components of the magnetization vector $\boldsymbol{M}^{\pm}(t)$ (Eq. (10)). Using expressions (9) and (10) and observing that $\boldsymbol{M}(0) = \boldsymbol{P}_{\mathrm{stat}}$ we rewrite

$$\mathcal{M}^{\pm}(t) \propto \boldsymbol{P}_{\mathrm{stat}}^{\mathsf{T}} \cdot \exp\left(\underline{\boldsymbol{\mathcal{K}}}^{\pm}t\right) \cdot \boldsymbol{P}_{\mathrm{stat}} \tag{22}$$

and consequently[1]

$$\mathcal{J}^{\pm}(\nu) \propto \mathrm{Re}\{\boldsymbol{P}_{\mathrm{stat}}^{\mathsf{T}}\left[i2\pi\left(\underline{\mathbf{v}}^{\pm} - \nu\underline{\mathbf{I}}\right) - \widetilde{T}_2^{-1}\underline{\mathbf{I}} + \frac{1}{\tau}\underline{\mathbf{K}}\right]^{-1}\boldsymbol{P}_{\mathrm{stat}}\}\,. \tag{23}$$

We now relate the spectrum to the relaxation dynamics of the order parameter. The nominal exchange time τ, which determines the nematic director reorientational exchange effectiveness, is related to the nominal Q-decay time via

$$\tau(\sigma_u, N, \Delta N) = \frac{\tau_Q}{\tilde{\tau}_Q(\sigma_u, N, \Delta N)}\,. \tag{24}$$

One can regard τ_Q as the nominal time characterizing the loss of correlations among orientational states of the nematic director, without knowing the details on the reorientational processes. With a specific choice of orientational distribution (parameter $\sigma_u = \tan\sigma_\theta$) and exchange topology (matrix $\underline{\mathbf{K}}(N,\Delta N)$), relation (24) provides for scaling of the nominal exchange rate τ^{-1} with respect to σ_u, N, and ΔN to value $\tau(\sigma_u, N, \Delta N)$ that will result in a desirable τ_Q. The dimensionless scaling denominator $\tilde{\tau}_Q(\sigma_u, N, \Delta N)$ is determined by methodology described in previous subsection. τ_Q, measured against the rigid lattice line width, is found to determine to what extent the detected spectrum will be motionally averaged, and thus plays the role of exchange time τ_{exch}. The motional narrowing effectiveness parameter is thus

$$\alpha = (\Delta\omega_{\mathrm{r.l.}}\tau_Q)^{-1}\,, \tag{25}$$

with $\Delta\omega_{\mathrm{r.l.}} = 2\pi\Delta\nu_{\mathrm{r.l.}}$ where $\Delta\nu_{\mathrm{r.l.}} \approx \bar{\nu}_q S$ denotes the rigid lattice line width. $\alpha \ll 1$ represents the rigid lattice regime, $\alpha \approx 1$ the intermediate regime, and $\alpha \gg 1$ the strong motional narrowing regime. $\mathcal{J}^{\pm}(\nu)$ can then be rewritten in terms of α as

$$\mathcal{J}^{\pm}(\nu) \propto \mathrm{Re}\{\boldsymbol{P}_{\mathrm{stat}}^{\mathsf{T}}\left[i2\pi\left(\underline{\mathbf{v}}^{\pm} - \nu\underline{\mathbf{I}}\right) - \widetilde{T}_2^{-1}\underline{\mathbf{I}} + \alpha\tilde{\tau}_Q 2\pi\Delta\nu_{\mathrm{r.l.}}\underline{\mathbf{K}}\right]^{-1}\boldsymbol{P}_{\mathrm{stat}}\}. \tag{26}$$

According to above relation, if one knows the rigid lattice line width $\Delta\nu_{\mathrm{r.l.}}$ as well as $\tilde{\tau}_Q(\sigma_u, N, \Delta N)$ and $\underline{\mathbf{K}}(N,\Delta N)$, motional narrowing effects can be reproduced by varying a single parameter α in the range $[0,\infty]$. The usefulness of the α-parametrization is in particular supported by the fact that the intermediate motional narrowing regime is reached at $\alpha \approx 1$ universally for any exchange type, i.e. independently from σ_u, N, and ΔN. We finally note that the continuous director reorientational exchange case is reproduced in the $N \to \infty$ limit (we used $N = 100$ in our simulations).

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