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Elastic incoherent neutron scattering of rotational and translational dynamics in liquid crystals

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Abstract

New theoretical approaches for the translational and rotational contributions to the elastic incoherent structure factor (EISF) of neutron scattering in mesomorphic systems are proposed. The influence of the molecular biaxiality and steric hindrance on the reorientational processes is considered. The numerical data for EISF are presented and discussed.

Keywords: Molecular dynamics; Liquid crystals; Elastic incoherent neutron scattering

1. Introduction

The neutron scattering spectroscopy is an important tool for investigation of the molecular dynamics in systems with partial rotational and translational order, e.g. liquid crystals, polymers, membranes, etc. The incoherent scattering function $S_{inc}(\mathbf{Q}, \omega)$ where $\mathbf{Q}$ is the scattering wavevector and $\hbar\omega$ the energy transfer, contains rich information about individual motions (both translational and rotational) of the molecules. The separation of the different contributions to $S_{inc}(\mathbf{Q}, \omega)$ is a difficult task. That's why, a very important characteristics of the neutron scattering spectra is the elastic incoherent structure factor (EISF), defined as the relative intensity of the purely elastic part of $S_{inc}(\mathbf{Q}, \omega)$ [1–6]. The EISF does not depend on the mechanism of the different molecular motions but only on their geometry and time scale, and provides an easy way of separation of the translational and rotational parts of the spectra. In fact, any motion which is not restricted in the space leads only to small broadening of both the elastic and the quasielastic parts of the neutron scattering spectra and thus, does not change the EISF. On the contrary, in the process of the molecular reorientation, the proton never quits some limited volume around its initial position and the EISF becomes very sensitive to the time scale and the geometry of the molecular dynamics.

A few theoretical approaches for calculation of the EISF in liquid crystals are proposed [3,4,7–9]. These approaches, in general, are in good agreement with the experimental data obtained in powder or oriented smectic samples [4,7,8,10,11]. However, the existing theoretical models are less successful in explaining the EISF measured in aligned nematics [3]. In fact, the structure factors obtained with scattering vector $\mathbf{Q}$ parallel or perpendicular to nematic director $\mathbf{n}$ are close to each other [3,4,7–11] which cannot be explained in the frames of the existing theoretical approaches. Similar EISF data for the smectic phases [10,11] have been successfully interpreted taking into account the restricted translational motion of the molecules normal to the smectic planes.

In this paper we present new theoretical models and numerical calculations of the rotational and translational contribution to the EISF of neutron scattering on mesomorphic systems. To ascertain the validity of the proposed models for the influence of molecular dynamics on neutron scattering we selected aligned liquid crystals and, for simplicity, that the mesomorphic phases is uniaxial (e.g. nematic or smectic A phase). Our approach can be easily generalized for other anisotropic phases with rotational and translational degree of freedom.

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2. Theoretical models for rotational and translational contribution to EISF

The time-dependent intermediate scattering function (i.e. the Fourier transform of rotational contribution to the scattering function $S^R_{\rm inc}(\mathbf{Q},\omega)$ is [9–11]:

$$I(\mathbf{Q},t)=\int \mathrm{d}\Omega_0 \int \mathrm{d}\Omega P(\Omega_0,\Omega,t)\exp\{i\mathbf{Q}\cdot[\mathbf{R}(t)-\mathbf{R}(t=0)]\} \tag{1}$$

where $\mathbf{Q}$ is the scattering vector, $\mathbf{R}$ the radius-vector of the proton in the center of mass reference frame, $\Omega_{\rm o}$ and Ω the sets of Euler angles defining the molecular orientation in the laboratory frame at time $t=0$ and t, respectively, and $P(\Omega_{\rm o},\Omega,t)$ is the joint probability density for molecular orientation at $\Omega_{\rm o}$ and Ω. Expanding the exponential in spherical harmonics series, we have:

$$\exp(i\mathbf{Q}\cdot\mathbf{R})=\sum_{\lambda,m,n}(2\lambda+1)\times(i)^{\lambda}j_{\lambda}(QR)D^{\lambda}_{-m0}\left(\Omega^L_Q\right)D^{\lambda}_{0-n}\left(\Omega^M_R\right)D^{\lambda*}_{mn}(\Omega) \tag{2}$$

where $Q=|\mathbf{Q}|$; $R=|\mathbf{R}|$; Ω^L_Q and Ω^L_R are the sets of polar angles of $\mathbf{Q}$ and $\mathbf{R}$ in the laboratory frame; Ω^M_R are the polar angles of $\mathbf{R}$ in the molecular frame; j_λ(QR) are the Bessel's spherical functions; $D^{\lambda}_{mn}(\Omega)$ are the Wigner's matrices.

Let $\Omega\{(t)(\equiv\alpha(t)),\ \beta(t),\ \mu(t))\}$ be the set of Euler angles describing the time dependent orientation of the molecule in the reference laboratory frame. At any time the molecule undergoes an orienting action by the molecular field of all the other molecules, represented by the potential of mean torque $U(\Omega)$. Assuming that both the molecules and the phase are cylindrically symmetric (e.g. a nematic or a smectic A phase) we obtain $U(\Omega)=U(\beta)$. The equilibrium orientational distribution function is

$$F(\Omega)=F(\beta)=\frac{1}{4\pi^2}\frac{\exp(-U(\beta)/kT)}{\int\exp(-U(\beta)/kT)d\cos\beta} \tag{3}$$

and

$$F(\Omega)=\frac{1}{8\pi^2}\sum_{\mathrm{even}^s}(2s+1)\langle P_s\rangle D^s_{00}(\Omega) \tag{4}$$

where

$$\langle P_s\rangle=\langle D^s_{00}\rangle=\int F(\Omega)D^s_{00}(\Omega)\mathrm{d}\Omega \tag{5}$$

are the usual orientational order parameters of rank s [12].

The dynamical information is contained in the orientational correlation functions [13]

$$G^{\lambda k}_{mnpq}(t)=\int \mathrm{d}\Omega_0\int \mathrm{d}\Omega D^{\lambda}_{mn}(\Omega_0)D^{k*}_{pq}(\Omega)P(\Omega_0,\Omega,t) \tag{6}$$

and for molecule with cylindrical symmetry we have [13]

$$G^{\lambda k}_{mnpq}(t)=\delta_{mp}\delta_{nq}G^{\lambda k}_{mnmn}(t) \tag{7}$$

The initial values of the correlation functions do not depend on reorientation model and are given by [14]:

$$G^{\lambda k}_{mnmn}(0)=\int \mathrm{d}\Omega D^{\lambda}_{mn}(\Omega_0)D^{k*}_{mn}(\Omega)f(\Omega)=\sum_s(2s+1)\times\langle P_s\rangle(-1)^{m+n}\begin{pmatrix}\lambda & s & k\\ m & 0 & -m\end{pmatrix}\begin{pmatrix}\lambda & s & k\\ n & 0 & -n\end{pmatrix} \tag{8}$$

where $\begin{pmatrix}\lambda & s & k\\ n & 0 & -n\end{pmatrix}$ are the Wigner's 3j-coefficients. The equilibrium values are [13,14]:

$$G^{\lambda k}_{mnmn}(\infty)=D^{\lambda}_{00}D^{k}_{00}\delta_{m0}\delta_{n0} \tag{9}$$

and they are also model-independent.

To develop further the influence of molecular dynamics to EISF we substitute Eq. (2) into Eq. (1), thus

$$I(Q,t)=\sum_{\substack{\lambda=0\\(\lambda+k)\\ \mathrm{even}}}^{\infty}\sum_{k=\lambda}^{\infty}\sum_{n=0}^{\lambda}\sum_{m=0}^{\lambda}F^{\lambda k}_{mn}(\theta_Q,\theta_R,QR)G^{\lambda k}_{mnmn}(t) \tag{10}$$

with

$$F^{\lambda k}_{mn}(\theta_Q,\theta_R,QR)=(2-\delta_{\lambda k})(2-\delta_{n0})(2-\delta_{m0})(-1)^{\lambda/2-k/2}(2\lambda+1)\times(2k+1)j_\lambda(QR)j_k(QR)d^{\lambda}_{n0}(\theta_R)d^{k}_{n0}(\theta_R)d^{\lambda}_{m0}(\theta_Q)d^{k}_{m0}(\theta_Q) \tag{11}$$

where θ_Q is the angle between $\mathbf{Q}$ and the symmetry axis (the director) of the phase, θ_R is the angle between $\mathbf{R}$ and the symmetry axis (the long axis) of the molecule and $d^k_{n0}(\theta)$ are the reduced Wigner's matrices.

The structure factor is [9]:

$$\mathrm{EISF}=\lim_{t\to\tau_\infty} I(Q,t) \tag{12}$$

where τ_∞ depends on the resolution of the experiment and it is the longest time for which the quasielastic component can be still distinguished from the elastic one. In very high-resolution backscattering experiments [15–17] the halfwidth $\Delta\Gamma$ of the resolution function is about 1 μeV and τ_∞ is of the order of 10^{-8} s [9]. In these experiments, however, the available Q-range is very small and there is no quasielastic contribution to the spectra but only small broadening of the elastic part due to the translational diffusion [9]. In the rest of the existing experiments $\Delta\Gamma\sim$20–30 μeV and $\tau_\infty\sim10^{-9}$–10^{-10} s.

The reorientation of the highly anisotropic molecules is a very complicated process. There are at least two different rotational motions with a different time scale. In fact, the reorientation around the long molecular axis (spinning motion) is fast since both the moment of inertia and steric hindrances are small. Several experimental techniques give for the spinning correlation time $\tau_{\rm s}$ values of the order of 10^{-11} s