Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Molecular Ordering in Liquid Crystals from Incoherent Quasi-Elastic Neutron Scattering

Pier Luigi Nordio [a] & Ulderico Segre [a]

[a] Institute of Physical Chemistry, University of Padua, Italy

Version of record first published: 18 Oct 2010

To cite this article: Pier Luigi Nordio & Ulderico Segre (2003): Molecular Ordering in Liquid Crystals from Incoherent Quasi-Elastic Neutron Scattering, Molecular Crystals and Liquid Crystals, 394:1, 51-58

To link to this article: http://dx.doi.org/10.1080/15421400390226137

Mol. Cryst. Liq. Cryst., Vol. 394, pp. li–lviii, 2003

ISSN 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390226137

MOLECULAR ORDERING IN LIQUID CRYSTALS FROM INCOHERENT QUASI-ELASTIC NEUTRON SCATTERING

Pier Luigi Nordio and Ulderico Segre
Institute of Physical Chemistry, University of Padua, Italy

The Elastic Incoherent Structure Factor (EISF) for neutron scattering in liquid crystals has been interpreted theoretically by evaluating the correlation functions for the molecular reorientation according to the diffusion model for highly ordered fluids. It is shown that the available experimental data are compatible with the orientational distribution function predicted by the Maier–Saupe model for uniaxial mesophases provided that the long time behaviour of the correlation functions within the time scale of the experiment be properly considered.

INTRODUCTION

The dynamics of the molecular diffusion in liquids can be probed by a variety of spectroscopical methods, and among these the scattering techniques have the definite advantage to exhibit both the q-(momentum transfer) and ω-(energy change) dependence of the Fourier transform for the space-time correlation functions of the molecular motions.

In particular, the incoherent quasi-elastic scattering of neutrons has found increasing application in the investigations of liquid crystalline phases, despite of the difficulties in discriminating the contributions from the various kinds of molecular motions (vibrations, translations, internal motions, rotations). These difficulties can be partly overcome by a suitable choice of the experimental energy resolution width $\Delta\omega_{\frac{1}{2}}$ and the q range, as discussed in the papers by Dianoux, Volino and Hervet, who derived detailed expressions for the scattering law for neutrons in liquid crystals,

Received February 21, 1978; in final form April 25, 1978.

The authors acknowledge the organizing committee and the participants to the Advanced Study Institute on the Molecular Physics of Liquids Crystals (Cambridge, August, 1977), for the discussions which have stimulated this research. The work has been supported by the Italian National Research Council, through its Centro Studi sugli Stati Molecolari Redicalicied Eccitati.

and performed a series of experiments in the smectic phases of TBBA [1–3]. Under the conditions $D_R > D_T q^2$ and $D_T q^2 \simeq \Delta\omega_{\frac{1}{2}}$, where D_R and D_T are typical diffusion coefficients for the rotational and translation motions, the spectra appear as a relatively sharp peak (elastic component) superimposed on a very broad line (quasi-elastic component) [1–4]. The fraction of the total intensity contained in the purely elastic term is called the Elastic Incoherent Structure Factor (EISF), whose q-dependence provides information on the angular distribution function for the molecular orientation in the mesophase.

It has been argued [2, 3] that the experimental EISF in a liquid crystal phase can be interpreted only if the distribution function for the fluctuations of the long axis of the mesogen molecules about the local director is given as $\exp(\mu \cos\beta), \beta$ being the instantaneous angular displacement. Even if this assumption has been justified by the consideration that π-jumps should be excluded in the time scale determined by the instrumental resolution, it appears surprising on the basis of the general acceptance of the non-polar character of the mesophases, [5, 6] which requires the angular distribution function to be expressed in terms of even powers of $\cos\beta$. In fact we shall prove that the previous assumption is quite unnecessary if the details of the anisotropic motions in oriented phases are properly taken into account.

THEORY

In the following, we shall consider a liquid crystalline phase composed of axially symmetric rod-like molecules, in the absence of orienting fields so that the director is isotropically distributed over the sample. If it is further assumed that the mesophase has an uniaxial local symmetry, the intermediated scattering function for the rotational diffusion of the N protons rigidly held to the mesogen molecule is defined as [2, 7]:

$$F_R(q,t) = \frac{4\pi}{N} \sum_{i=1}^{N} \sum_{kmn} j_k^2(qR_i) |Y_{kn}(\vartheta_i \varphi_i)|^2 \langle D_{mn}^k(0) D_{mn}^{k^*}(t) \rangle \tag{1}$$

where $(R_i \vartheta_i \varphi_i)$ define the position of the ith nucleus relative to a molecular frame centered at the c.o.m. and with the z-axis coincident with the symmetry axis, $j_k(x)$ is a spherical Bessel function of the first kind, $D_{mn}^k(\alpha\beta\gamma)$ is a Wigner rotation matrix component specifying the instantaneous orientation of the molecule with respect to the local director, and

$$\langle D_{mn}^k(0) D_{mn}^{k^*}(t) \rangle \equiv f_{mn}^k(t) \tag{2}$$

is a correlation function for the molecular reorientation. It is useful to remember here that the correlation function $\langle f(0) f^*(t) \rangle$ assumes the

limiting values $\langle |f|^2 \rangle$ at time $t = 0$, and $|\langle f \rangle|^2$ at $t \to \infty$, the angular brackets indicating an equilibrium ensemble average. Under the above symmetry assumptions:

$$f_{mn}^{k}(t \to \infty) = \delta_{m0}\delta_{n0}\langle P_k \rangle^2 \tag{3}$$

where $P_k(\cos\beta)$ is a Legendre polynomial.

The scattering function $F_R(q,t)$ can then be splitted into a time-dependent part $F'_R(q,t)$, which is general given as a sum of decreasing exponentials, and a time-independent term $F_R(q,\infty)$ given by

$$F_R(q,\infty) = \frac{1}{N}\sum_{i=1}^{N}\sum_{k=0}^{\infty}(2k+1)j_k^2(qR_i)P_k^2(\cos\vartheta_i)\langle P_k \rangle^2 \tag{4}$$

If the correlation functions for *all* the Wigner components decay to their long time limit within the time scale of the experiment, then the Fourier transformation of $F_R(q,t)$ provides the scattering law

$$S_R(q,\omega) = A_0(q)\delta(\omega) + S_R^{qe}(q,\omega) \tag{5}$$

where $A_0(q)$ is just $F_R(q,\infty)$. Therefore $S_R(q,\omega)$ is expected to contain a purely elastic component $A_0(q)\delta(\omega)$–the EISF–superimposed to a quasi-elastic component given as a sum of Lorentzians. It has been already pointed out that the fitting of the experimental EISF in a liquid crystalline sample apparently requires, for the calculation of the average values $\langle P_k \rangle$, the use of an angular distribution function of the form

$$f_1(\beta) = Z_1^{-1}\exp(\mu\cos\beta) \tag{6}$$

where μ is an adjustable parameter and Z_1 a normalization constant. The average values of the Legendre polynomials, or order parameters, are given by the recursion relations

$$\begin{aligned} \langle P_0 \rangle &= 1, \langle P_1 \rangle = \coth\mu - \frac{1}{\mu} \\ \langle P_{k+1} \rangle &= -\frac{2k+1}{\mu}\langle P_k \rangle + \langle P_{k-1} \rangle \end{aligned} \tag{7}$$

On the other hand, the distribution function corresponding to symmetric maxima at $\beta = 0$ and π

$$f_2(\beta) = Z_2^{-1}\exp(\lambda\cos^2\beta) \tag{8}$$

appears to be inadequate to interpret the q-dependence of $A_0(q)$, as shown in the Figure. The shaded area (I) encloses the experimental points for partially deuterated TBBA in the smectic A phase, taken from Ref. 3. These points can be fitted by the Eq. (4) in connection with the distribution function $f_1(\beta)$, when μ values corresponding to order parameters $\langle P_2 \rangle$ in

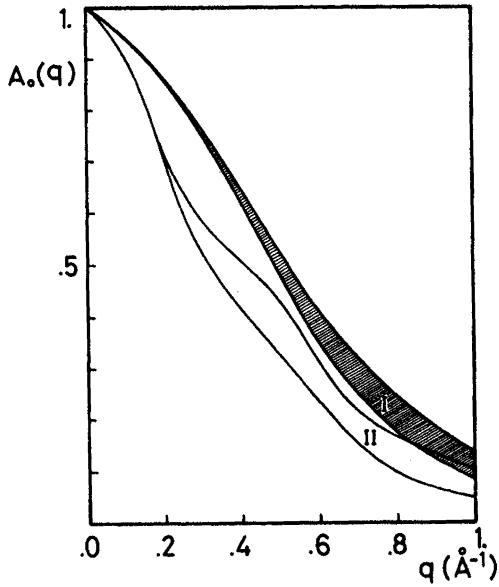

FIGURE EISF for partially deuterated TBBA in the smectic A phase. The shaded area encloses the experimental points (from Ref. 3) Area II encloses the theoretical curves calculated from Eq. (4) and the distribution function $\exp(\lambda \cos^2 \beta)$, with λ values corresponding to $\langle P_2 \rangle$ in the range 0.4 (lower curve) to 0.9 (upper curve). A good fit requires the initial values of the odd-rank correlation functions to be taken into account, as discussed in the text.

the range 0.4–0.7 are used. In particular, the curve calculated in correspondence to $\langle P_2 \rangle = 0.7$ reproduces quite nicely the upper limit of the shaded area.

On the other hand, the area II is delimited by the curves calculated from Eq. (4) and the distribution function $f_2(\beta)$, with λ values corresponding to $\langle P_2 \rangle = 0.4$ (lower curve) and 0.9 (upper curve). One should then conclude that all the curves calculated by means of the distribution function $f_2(\beta)$ for reasonable values of the ordering parameters lie sensibly outside the zone of the experimental points. The reason for the discrepancy appears to be essentially bound to the vanishing average of the odd-rank Legendre polynomials, when calculated by means of Eq. (8).

However, the assumption that *all* the correlation functions reach their limiting value within the time scale of the experiment is likely to be incorrect. In fact, if the correlation functions of the Wigner components are calculated by solving a diffusion equation modified by the introduction of a Maier–Saupe type orientational potential [8, 9].

$$V(\beta) = -kT \ln f_2(\beta) \tag{9}$$

one finds that the calculation predicts a large slowing down of the decay for the odd-rank components with $m = n = 0$, when the degree of order increases. Investigation particular, this effect is responsible for the low-frequency shift of the dielectric dispersion in nematics [9]. On the contrary, the correlation functions for the even-rank components with $m = n = 0$ decay in an oriented phase to the long time value faster than in the isotropic phase. According to this result of the diffusion model, if the rotational correlation times are comparable with $1/\Delta\omega_{\frac{1}{2}}$ in an isotropic melt, one could assume as a first approximation that in phases with relatively high orientational order, such as the smectic phases, the even-rank correlation functions decay to their non-zero limiting value $\langle P_k \rangle^2$ within the observation time, whereas the odd-rank terms remain essentially at their initial value $\langle P_k^2 \rangle$ in the same time interval.

This result is especially transparent if one considers the asymptotic solutions of the diffusion equations, valid for relatively high degree of ordering [10]. Under these conditions one obtains:

$$\langle D^k_{mn}(0) D^{k*}_{mn}(t) \rangle = \frac{1}{2} \sum_j [\langle 00|d^k_{mn}|j\alpha_-\rangle^2 \exp(-E_{jmn}t) + \langle 00|d^k_{m-n}|j\alpha_+\rangle^2 \exp(-E_{jm-n}t)] \tag{10}$$

$$E_{jmn} = [2(2j + \alpha_-) + n(m - n)]D_\perp + n^2 D_\parallel \tag{11}$$

where $\alpha_\pm = |m \pm n|$, $D_\parallel$ and $D_\perp$ are the principal components of the rotational diffusion tensor, $d^k_{mn}(\beta)$ is a reduced Wigner function [11] and $\langle pq|d^k_{mn}|p'q'\rangle$ stands for an integral over the eigenfunctions of the asymptotic form of the diffusion operator.

From Eq. (11) it follows that time-independent terms appear only for $m = n = 0$ and $j = 0$ and so the expression for the EISF becomes

$$A_0(q) = \frac{1}{N} \sum_{i=1}^{N} \sum_{k=0}^{\infty} (2k + 1) j_k^2(qR_i) P_k^2(\cos \vartheta_i) F_k^2 \tag{12}$$

where $F_k = \langle 00|d^k_{00}|00\rangle$. This coefficient is then calculated to be

$$\langle 00|d^k_{00}|00\rangle = 1 - \frac{k(k+1)}{4\lambda} \tag{13}$$

and it is interesting to verify that it is the same as $\langle P_k \rangle$ given in Eq. (7), up to order of $(1/\mu)^2$, when μ is taken as 2λ. This means that the present treatment gives formally and numerically the same results for the EISF of that proposed by Volino et al. (at least for relatively high degrees of ordering), but the physical meaning of the F_k is different. In fact F_k^2 is equal

to $\langle P_k \rangle^2$ for k even, and to $\langle P_k^2 \rangle$ for k odd, the average being intended to be performed with the distribution function given in Eq. (8). This is readily verified by using the asymptotic form of the Legendre polynomials as shown in the Appendix.

CONCLUSIONS

The key for the interpretation of the neutron EISF presented here, is to realize that the correlation functions of Legendre polynomials of even or odd rank show very different relaxation behaviour.

In isotropic phase, the correlation functions $\langle P_k(0)P_k(t)\rangle$ are described by a single exponential decay, with rate constant $\alpha_k D_\perp$ and $\alpha_k = k(k+1)$. At relatively high degrees of ordering, the correlation functions are again expressed as a single exponential, where α_k is now strongly dependent upon the orientational order, tending rapidly to a vanishing value only in the case of k odd. Experimental evidence for this is provided by the dielectric relaxation measurements, which give information on the correlation function of $P_1(\cos\beta)$, when the internal field effects are taken into account [7]. They show that the dispersion frequency related to reorientations of the long molecular axis may decrease of two orders of magnitude going from the isotropic to the nematic phase [12]. Since for most mesogens $D_\perp$ is of the order of 10^8–10^{10}, which corresponds to the typical range of the resolution widths, it follows that the condition $\alpha_k D_\perp \ll \Delta\omega_{\frac{1}{2}}$ for k odd is likely to be verified in the oriented phase. Under this condition, the correlation function remains practically constant during the observation time. In conclusion, the theoretical fit of the experimental EISF can be done by using the Maier–Saupe distribution function, whose general form is dictated by the accepted $D_{\infty h}$ symmetry of the nematic and smectic-A mesophases.

APPENDIX

By using the Maier–Saupe orientational potential

$$-\frac{V(\beta)}{kT} = \lambda_2 P_2(\cos\beta) \tag{A.1}$$

the orientational distribution function is

$$\begin{aligned} f_2(\beta) &= Z_2^{-1}\exp[-V(\beta)/kT] \\ &= \exp(-\lambda\sin^2\beta)/\int_0^\pi \exp(-\lambda\sin^2\beta)\sin\beta d\beta \end{aligned} \tag{A.2}$$

where $\lambda = 3\lambda_2/2$. By expanding $f_2(\beta)$ about $\beta = 0$ and π, and making use of the relation 11

$$d^k_{mn}(\pi - \beta) = (-1)^{k+m} d^k_{m,-n}(\beta) \tag{A.3}$$

one obtains as the asymptotic form of $f_2(\beta)$:

$$f_2(\beta) \simeq \lambda[e^{-\lambda\beta^2} + e^{-\lambda(\pi-\beta)^2}] \tag{A.4}$$

$$\langle d^k_{mn} \rangle \simeq \int_0^\infty [d^k_{mn}(\beta) + (-1)^{k+m} d^k_{m,-n}(\beta)]_{\beta\to 0} e^{-\lambda\beta^2} \beta d\beta \tag{A.5}$$

$$\langle (d^k_{mn})^2 \rangle \simeq \int_0^\infty [(d^k_{mn}(\beta))^2 + (d^k_{m,-n}(\beta))^2]_{\beta\to 0} e^{-\lambda\beta^2} \beta d\beta \tag{A.6}$$

In the particular case $m = n = 0$ the reduced Wigner functions reduce to Legendre polynomials, whose limiting form for $\beta \to 0$ is

$$P_k(\cos\beta) \simeq 1 - \frac{k(k+1)\beta^2}{4} \tag{A.7}$$

$$\langle P_k \rangle \simeq 1 - \frac{k(k+1)}{4\lambda} \tag{A.8}$$

for k even and zero otherwise, and

$$\langle P_k^2 \rangle \simeq 1 - \frac{k(k+1)}{2\lambda} \tag{A.9}$$

Thus $F_k^2 = 1 - k(k+1)/2\lambda$ to the order of $1/\lambda^2$ for both even and odd values of k. These results are valid only under the condition $k(k+1)/2 < \lambda$, but the sum over k in Eq. (12) converges very rapidly, so that the k values can be always restricted with good approximation to 0, 1 and 2.

REFERENCES

[1] Dianoux, A. J., Volino, F., & Hervet, H. (1975). *Mol. Phys.*, *30*, 1181.
[2] Volino, F., Dianoux, A. J., & Hervet, H. (1976). *J. Physique Colloq.*, *37*, C3–55.
[3] Volino, F., Dianoux, A. J., & Hervet, H. (1977). *Mol. Cryst. Liq. Cryst.*, *38*, 125.
[4] Leadbetter, A. J. & Richardson, R. M. Incoherent quasi-elastic neutron scattering. In: *The Molecular Physics of Liquid Crystals*, Luckhurst, G. R. & Gray, G. W. (eds.). In press.
[5] Maier, W. & Saupe, A. (1958). *Z. Naturforsch. A*, *13*, 564; (1959). *Z. Naturforsch. A*, *14*, 882; (1960). *Z. Naturforsch. A*, *15*, 287.
[6] Luckhurst, G. R. (1974). Magnetic resonance spectroscopy in Liquid crystals. In: *Liquid Crystals and Plastic Crystals*, Gray, G. W. & Winsor, P. A. (eds.). Ellis Horwood Ltd., Chichester, vol. 2, 144.
[7] Berne, B. J. (1971). Time-dependent properties of condensed media. In: *Physical Chemistry*, Eyring, H., Henderson, D., & Jost, W. (eds.). Vol. VIII B, 539.

[8] Nordio, P. L., Rigatti, G., & Segre, U. (1972). ***J. Chem. Phys.***, ***56***, 2117.
[9] Nordio, P. L., Rigatti, G., & Segre, U. (1973). ***Mol. Phys.***, ***25***, 129.
[10] Nordio, P. L. & Segre, U. (1977). ***J. Magn. Res.***, ***27***, 465.
[11] Brink, P. M. & Satchler, G. R. (1968). ***Angular Momentum***, Clarendon Press, Oxford.
[12] Martin, A. J., Meier, G., & Saupe, A. (1971). ***Symp. Faraday Soc.***, ***5***, 119.