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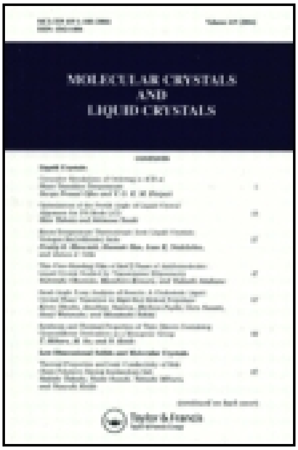

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Low Frequency Mode in Liquid Crystals

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Version of record first published: 28 Mar 2007.

To cite this article: V. Dimic & M. Osredkar (1973): The Low Frequency Mode in Liquid Crystals, Molecular Crystals and Liquid Crystals, 19:3-4, 189-194

To link to this article: http://dx.doi.org/10.1080/15421407308084649

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Molecular Crystals and Liquid Crystals. 1973. Vol. 19, pp. 189–194
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The Low Frequency Mode in Liquid Crystals

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Received November 5, 1971; *in revised form February* 19, 1972

Abstract—In various liquid crystals an inelastic neutron peak under the elastic or quasi-elastic distribution of scattered neutrons has been found. This inelastic peak with the frequency of about 15 cm^{-1} is attributed to strongly damped torsional oscillations of the molecule. It is concluded that the dispersion curve of this mode is essentially flat.

1. Introduction

Many scattered neutron spectra in the near elastic region obtained from molecular hydrogeneous liquids have shown that the effect of molecular reorientations and librational motions play an important role in the time domain of neutron observations ($10^{-13} - 10^{-11}$ sec).(1) This is particularly important for molecules containing heavier atoms like carbon, oxygen, etc. which may take part in rotational reorientations. If the librational mass is large, the rotational part of the measured neutron spectrum may be concentrated near the ingoing energy because classically the rotational frequency is $\Omega = (kT/I)^{1/2}$, i.e. is small for a large moment of inertia, I, of the molecule. When protons are performing rotational motions (or part of a molecule like a CH_3 group) I is small and the rotational contribution to the observed neutron spectrum is extended to large energy transfer $\hbar\Omega$.

Using these experimental arguments and following the ideas outlined by Sears(2,3,4) and Agrawal and Yip(5) a model for the combined rotational and translational motion was formulated by Larsson.(6) The principle of the model is the following: the strongly hindered rotational motion is divided into two phases: for a time T_0 a proton (in a rigid molecule) vibrates around a quasi-equilibrium

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position, which in itself performs simple diffusion motion by small steps. After time T_0 the molecular direction in space changes abruptly. This is diffusive motion in large jump-like steps, rotational jump. These rotational motions (small and large jumps) are superimposed on the centre of mass motion.

On the basis of this model, the experimental results from various hydrogeneous solids and liquids were analysed(6,7) and many discrepancies between theory and experiments were removed. In this connection it is interesting to mention the high-resolution study on pentane and pentanol(8) where it has been found that the quasi-elastic peak is divided into a narrow central component and a broader one. A closer investigation has shown that the high central peak originates from the diffusive motions of the centre-of-mass. The broader one comes from strongly damped torsional oscillations of the molecule causing large jumps which contribute to the rotational part of the diffusion. Gordon(9) has shown, that large jump diffusion is equivalent to free rotation over a limited angle. The width of the broader peak is, however, almost independent of the momentum transfer; therefore it could be considered as inelastic scattering due to energy transfers in a torsion spectrum.

2. Experimental Method

The quasi-elastic broadening of the Be-filtered neutron beam has been measured at four different angles $\theta = 27°$, $54°$, $75°$ and $110°$ with the time of flight method. The spectrometer is controlled by a CDC 1700 on line computer. A liquid methane cold neutron source in the tangential beam tube has been used. The thickness of the sample placed into a cylindrical container was such that the transmission was about 90%. The temperature was varied between—150° C and 240 °C. The instrumental energy resolution at the beryllium cut-off was 0.17 meV.

3. Data and Results

Very little is known on the dynamics of anisotropic liquid crystals where the flow of such a liquid influences the orientation of the molecule. Therefore, extensive studies of the broadening of the

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incoherent quasi-elastic neutron scattering peaks as a function of momentum transfer observed at different temperatures for various liquid crystals have been undertaken.(10,11) The liquid crystals studied were: P-azoxyanisole (PAA), anisalazine, 4,4'-diheptyloxyazoxybenzene, 4,4'-dihexyloxyazoxybenzene, anhydrous Na-palmitate and Na-stearate. The scattered cold neutron spectra were obtained in solid, nematic or smectic and liquid phases. One of the results of the above mentioned experiment is that a quite distinct neutron peak appears under the elastic distribution of scattered neutrons, as can be clearly seen in Fig. 1. This peak appears in all

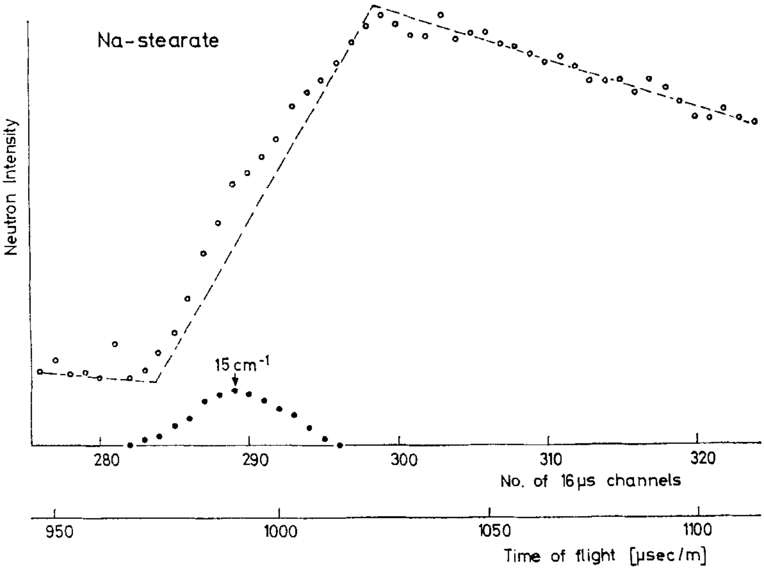

Figure 1. Time of flight spectrum of elastically scattered neutrons at an angle of 110° by Na-stearate with the inelastic peak. The broken curve represents the spectrum of elastically scattered neutrons by vanadium.

phases at the measured momentum transfer of $Q = 0.67\,\text{Å}^{-1}$, $1.38\,\text{Å}^{-1}$, $1.95\,\text{Å}^{-1}$ and $2.60\,\text{Å}^{-1}$ with a frequency of about 15 cm^{-1} and a corresponding energy of about 1.8 meV. This frequency shift was determined with the assumption that the centre of impinging cold neutrons on the sample is at 30 cm^{-1} ($\lambda = 4.7\text{Å}$).

The height of the peak increases with increasing momentum transfer but no variation of the width of the peak as a function of Q

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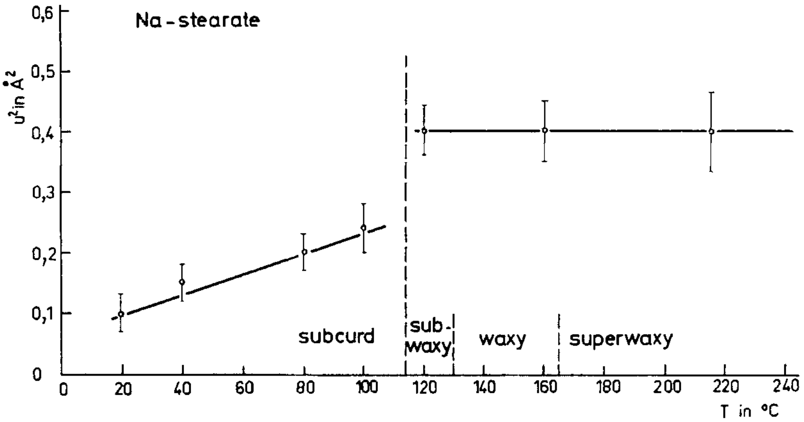

Figure 2. Values of u^2 for Na-stearate.

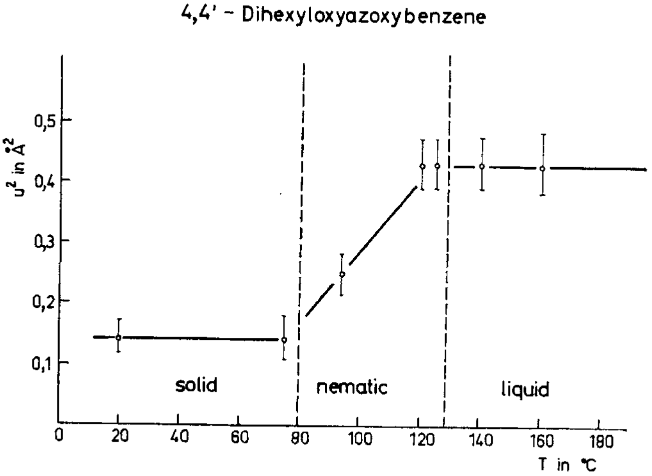

Figure 3. Values of u^2 for 4,4′ dihexyloxyazoxybenzene.

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has been found. The conclusion is that this peak is of inelastic origin. According to the ideas outlined in Introduction, this inelastic neutron peak might be caused by strongly damped torsional oscillations of the whole molecule.

Further information can be obtained by considering the intensity variation I of the quasi-elastic scattered neutrons. The intensity is governed by a single exponential, which can be called the Debye–Waller factor:

$$I(Q) = e^{-u2Q2} \tag{1}$$

Figures 2 and 3 show the values of u^2 for Na-stearate and 4,4′-dihexyloxyazoxy-benzene at different temperatures. If one identifies $u^2 = <r^2>/6$, then the value of the corresponding root mean square radius varies from 0.9 Å at room temperature to 1.6 Å at temperatures higher than 120 °C. Such a large value of the rms radius is probably not associated with true vibrational motions but with rotational motions or torsional oscillations.

Recently the low frequency Stokes Raman spectra of various liquid crystals have been reported.(12) The observed peak corresponded to a frequency of 18 cm^{-1} which is, within experimental error, the same value as was found in our experiment. The fact that the light scattering measurements which correspond to essentially zero momentum transfer yield the same result as the neutron scattering measurements, where the momentum transfer is relatively large, demonstrates that the dispersion curve of the mode in question is essentially flat.

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