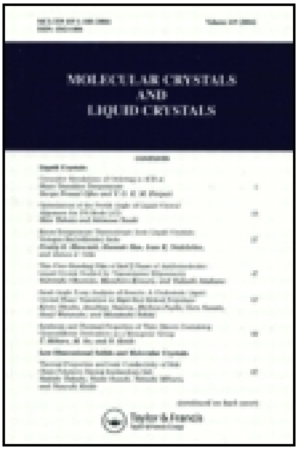

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# Small Angle X-ray Analysis of Orientation Fluctuations in Molecular Fluids

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The absolute small angle X-ray scattering intensity of liquid crystalline phases and of the isotropic fluid state above the clearing temperature contains information both on particle fluctuations as well as on orientation fluctuations. The X-ray scattering is strongly influenced by fluctuations of the direction of the molecular axes and is therefore able to distinguish between parallel and antiparallel orientations. The depolarized light scattering which is sensitive to order parameter fluctuations, on the other hand, does not depend on the sign of the direction of the molecular axes.

We observed that fluctuations of the molecular directions increase with decreasing temperature in the isotropic phase and do not diverge at the nematic or cholesteric transition. They remain short-ranged at these transitions in contrast to the order parameter fluctuations. It is concluded that at temperatures far below these transition temperatures a state is approached, which is characterized by a spontaneous parallel or antiparallel orientation of the molecular axes. This state may be able, in particular cases, to exhibit ferroelectric properties.

## I INTRODUCTION

The structure of an atomic liquid can be represented by a single radial pair correlation function $g(r)$, where $r$ denotes the distance between pairs of atoms. In a molecular liquid, however, one has to account also for the mutual orientations of the molecules. The structure has to be characterized in this case in terms of the angular pair correlation function $g(\mathbf{r}_{12}, w_1, w_2)$, where $\mathbf{r}_{12}$ gives the relative location of a pair of molecules and $w_1$ and $w_2$ the orientation of the molecules relative to some arbitrary laboratory system.[1-3]

It is well documented that macroscopical properties of molecular fluids depend on the local orientational order and are strongly influenced by orientation fluctuations.[4-7] Prominent examples are the liquid crystalline phases.[4-6] Orientation fluctuations are furthermore known to play an important role in the isotropic phase of mesogenic substances at temperatures close to the clearing temperature as well as in the molten state of rigid and semi-flexible chain molecules.[5,6,8] Indications of some orientational order were even reported for melts of *n*-alkanes.[9,10]

Today we do not know of any experimental technique which is able to yield the total angular pair correlation function $g(\mathbf{r}_{12}, w_1, w_2)$.[1,7] X-ray, electron and neutron scattering, for instance, provide information on the pair correlation function of the centers of the molecules $g_0(\mathbf{r}_{12})$.[2] Data on the relative orientation of molecules, independent of the sign of the orientation, are obtainable from studies on the depolarized light scattering or the electric or magnetic birefringence.[1-3,11]

Our present knowledge on orientation fluctuations in molecular fluids is still insufficient. It is thus obvious that additional information on orientation fluctuations is badly needed. It is the purpose of this paper to demonstrate that we might be able to gain additional insights into the orientational order of isotropic and anisotropic molecular fluids by employing small angle X-ray scattering. It is shown that the absolute scattering intensity $I(s)/I_0$ is influenced by fluctuations of the scattering amplitude resulting from orientation fluctuations of molecular axes.

## II THEORETICAL CONSIDERATIONS

The scattering of X-rays by molecular fluids can be represented by:[13]

$$I(s)/I_0 = \rho_N\{\langle F^2(\mathbf{s})\rangle + \rho_N \iiint 4\pi|\mathbf{r}_{12}|^2 dr_{12}dw_1dw_2F(\mathbf{s}, w_1) F(\mathbf{s}, w_2)[g(\mathbf{r}_{12}, w_1, w_2) - 1] \exp(i\mathbf{sr})\} \quad (1)$$

$\rho_N$ is the particle density, **s** the scattering vector the absolute value of which is given by $s = 4\pi \sin \theta/\lambda$, $F(\mathbf{s}, w_i)$ is the scattering amplitude of an individual molecule $i$ having a particular orientation $w_i$ and $\langle F^2\rangle$ is the average scattering of independent molecules. This expression can be considerably simplified for the case of an isotropic liquid exhibiting no orientation correlations:

$$I(s)/I_0 = \rho_N\{\langle F^2\rangle + \rho_N\langle F\rangle^2 \int 4\pi r_{12}^2 dr_{12}[g_0(r_{12}) - 1] \sin(sr_{12})/(sr_{12})\} \quad (2)$$

$g_0(r_{12})$ is the pair correlation function averaged over all orientations and corresponds to the correlation function of the centers of the molecules.[2,12]

Further simplifications arise if the molecules are characterized by a spherical symmetric distribution of the electron density, that is if:

$$\langle F^2\rangle = \langle F\rangle^2 \quad (3)$$

We then obtain for the X-ray scattering intensity:

$$\mathrm{I}(s)/\mathrm{I}_0 = \langle F\rangle^2 \rho_N [1 + \rho_N \int 4\pi r_{12}^2 dr_{12} (g_0(r_{12}) - 1) \sin(sr_{12})/(sr_{12})] \quad (4)$$

This expression predicts that the scattering in the small angle X-ray range for $s \approx 0$ is determined by the mean square particle fluctuations $\overline{\delta N^2}$ and consequently by the absolute temperature $T$ and the isothermal compressibility of the liquid $\kappa(T)$, since according to statistical mechanics:

$$\begin{aligned} \mathrm{I}(s = 0)/\mathrm{I}_0 &= Z^2 \rho_N \{1 + \rho_N \int 4\pi r_{12}^2 dr_{12} (g_0(r_{12}) - 1)\} \\ &= Z^2 \rho_N \overline{\delta N^2}/N \qquad (5) \\ &= Z^2 \rho_N^2 kT\kappa(T) \end{aligned}$$

if the absolute intensity is properly normalized.[14-16] $Z$ is the number of electrons per molecule.

It is usually observed that Eq. (5) does not only predict the correct values of the scattering intensity at $s = 0$ but is able to represent the intensity over an appreciable range of $s$-values in the small angle X-ray region. This was observed for fluids composed of flexible chain molecules or small molecules.[17-19] The reason is that the particle fluctuations are usually not correlated over distances which are large compared with intermolecular distances. Otherwise the scattering intensity would decrease with increasing values of $s$.[14]

Deviations from the simple scattering properties, represented by Eqs. (4) and (5), have of course to be expected if orientation correlations exist in the fluid state provided that the electron density distribution within the molecules is not spherical symmetric. Fluctuations of the scattering amplitude will occur in that case at constant particle density since the number of molecules having a particular orientation relative to the scattering vector **s** will fluctuate. For the sake of simplicity only the case of macroscopically isotropic fluids will be treated.

In order to analyze the relation between orientation fluctuations and the X-ray scattering resulting from them it is advantageous to express the angle dependent quantities in Eq. (1) as a series in a set of orthonormal functions of the molecular orientation angles, the Wigner rotation matrix elements $D^l_{mn}(w)$.[2,3,20,21] The angular pair correlation function is represented by:

$$g(\mathbf{r}_{12}, w_1, w_2) = \sum_{\substack{l_1, l_2, l_{12}, \\ n_1, n_2}} g^{l_1 l_2 l_{12}}_{n_1 n_2}(r_{12}) \sum_{m_1, m_2, m_{12}} C(l_1 l_2 l_{12} m_1 m_2 m_{12}) D^{l_1}_{m_1 n_1}(w_1) D^{l_2}_{m_1 n_2}(w_2) D^{l_{12}}_{m_{12} 0}(w_{12}) \quad (6)$$

where $C(l_1l_2l_{12}m_1m_2m_{12})$ is a numerical factor and $w_{12}$ the polar angle of the center-center vector $\mathbf{r}_{12}$ in the laboratory system. The expansion coefficients $g^{l_1l_2l_{12}}_{n_1n_2}(r_{12})$ are functions only of the intermolecular distance.

The coefficient $g^{000}_{00}(r_{12})$ corresponds to the pair correlation function of the molecular centers and thus to $g_0(r_{12})$ in Eqs. (2), (4) and (5). The scattering amplitude $F(\mathbf{s}, w)$ and the exponential term $\exp(i\mathbf{s}\mathbf{r}_{12})$ are expanded in a similar way, the expansion coefficient of the scattering amplitude $F^l_n(s)$ depends only on the absolute value of the scattering vector.

The X-ray scattering can then be expressed as follows:

$$\begin{aligned} \mathrm{I}(s)/\mathrm{I}_0 = \rho_N|F^0_0(s)|^2[1 + \rho_N\int (g^{000}_{00}(r_{12}) - 1)j_0(sr_{12})4\pi r^2_{12}dr_{12}] \\ + \rho_N\Bigg\{ \sum_{n,l\neq 0} |F^l_n(s)|^2 + \rho_N \sum_{l_1l_2l_{12}} D(l_1l_2l_{12}) \\ \sum_{n_1n_2} (-1)^{n_2} F^{l_1*}_{n_1}(s)F^{l_2}_{n_2}(s) \int g^{l_1l_2l_{12}}_{n_1-n_2}(r_{12})j_{l_{12}}(sr_{12})4\pi r^2_{12}dr_{12}\Bigg\} \end{aligned} \tag{7}$$

$D(l_1l_2l_{12})$ is a numerical factor and $j_l(sr_{12})$ is the spherical Bessel function.

The terms containing $l_1 = l_2 = l_{12} = 0$ have been separated from the remaining terms of Eq. (7), since they correspond to the scattering of fluids exhibiting no orientation correlations, they agree with Eq. (4). Equation (7) thus predicts that the scattering in the small angle region is determined totally by particle fluctuations [Eq. (5)] only in those cases, where either the electron density distribution is spherical symmetric—the $F^l_n(s)$ are 0 in this case for $l \neq 0$—or where no orientational order exists in the fluid state—the $g^{l_1l_2l_{12}}_{n_1n_2}$ are 0 in this case for $l_1, l_2, l_{12} \neq 0, 0, 0$.

In the presence of orientation correlations, however, additional contributions to the X-ray scattering have to be expected in the small angle region, the magnitude of which depends on the particular orientational order. By analyzing the small angle X-ray intensity of molecular fluids and by comparing its absolute value with the value resulting from particle fluctuations one should be able to gain information on orientation fluctuations in molecular fluids.

## III EXPERIMENTAL

The small angle X-ray scattering was performed by means of a Kratky small angle X-ray camera with a slit-like primary beam profile. Desmeared scattering curves were obtained by employing the desmearing procedure developed by Strobl.[22] Absolute intensity data were established by using acetone and methanole as well as Lupolen samples, which were kindly provided by Prof.

Kratky, as calibration samples. The temperature of the samples could be controlled within 0.1 K.

The scattering experiments were performed on materials which were commercially available.

MBBA (*p*-methoxybenzylidene *p*-*n*-butylaniline) was obtained from Riedel de Haen. The samples were kindly distilled by the company, sealed in a glass capillary under nitrogen atmosphere and shipped to us. The transition from the nematic to the isotropic phase occurred at 317 K.

PCB (4,4-*n*-pentylcyanobiphenyl) was purchased from Merck/Darmstadt. The transition from the nematic to the isotropic phase was found to take place at 308 K.

CM (cholesteryl myristate) was obtained from Sigma Chemie/München. It was characterized by a smectic-cholesteric transition at 351.6 K and a cholesteric-isotropic fluid transition at 356.8 K.

Hexadecane, having a purity of 99% was purchased from Riedel de Haen.

The scattering data described below were taken on the samples without additional purification. Data on the isothermal compressibility as a function of the temperature are sparse in many cases. In addition we found that they often lack accuracy. For this reason we took data from ultrasound and hypersound velocity studies[6,23] and calculated the isothermal compressibility from these data, using the following Eq.:[24]

$$\kappa(T)_{\text{isothermal}} = \kappa(T)_{\text{adiabatic}} + T\alpha^2/c_p\rho \qquad (8)$$

where $\alpha$ is the thermal expansion coefficient, $c_p$ the specific heat and $\kappa_{\text{adiabatic}}$ the adiabatic compressibility which is directly related to the sound velocity.[24] We are aware, of course, that dispersion effects may lead to deviations between static and dynamic values of the compressibility. In those cases, however, where we were able to get both static and dynamic values we always found a close agreement between these sets of data. Ultrasound absorption and ultrasound velocities are known to change strongly in the neighborhood of nematic transitions.[6,25–27] These pretransitional effects do not influence, however, the isothermal compressibility at zèro frequency,[28,29] in contrast to the statements of Bendler.[25]

## IV RESULTS AND DISCUSSIONS

The small angle X-ray scattering studies were performed for a variety of low molecular weight fluids, which exhibit different kinds of orientational order. Benzene and water were examined as examples for fluids having no orientational order at all—in the case of benzene[30]—or having a nearly spherical symmetric distribution of the electron density of the individual molecules—in the case of water.[13] The structure of water is known to be characterized by orientation correlations.

The small angle X-ray scattering of fluids is usually independent of the scattering vector within a limited range of $s$-values. This is shown in Figure 1 for the particular case of benzene. The absolute value of the scattering intensity in this range is determined by particle fluctuations, as expressed in Eq. (5) and can thus be calculated from the absolute temperature and the isothermal compressibility. The temperature dependence of the scattering is thus strongly governed by the temperature dependence of the compressibility. The experimentally obtained temperature dependence of the scattering, which is displayed in Figure 2, agrees very well with the values calculated from the temperature dependence of the compressibility of benzene. This result is in agreement with data reported previously[19] and with the predictions of Eq. (7) since no orientation correlations exist in benzene. Very similar results were obtained for water, again in agreement with the literature[31] and with the predictions of Eq. (7).

The small angle scattering curves of fluids exhibiting nematic or cholesteric phases were found to be similar to those of nonmesogenic substances in the fluid state. This holds for the isotropic phase as well as for the anisotropic phases. This is shown for the particular case of MBBA at two different temperatures in the isotropic and nematic phase in Figure 3. The scattering

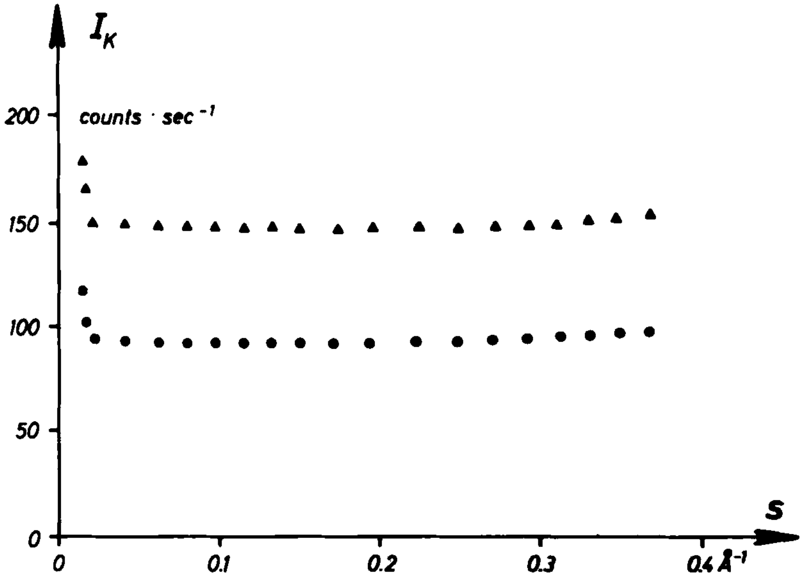

FIGURE 1 Small angle X-ray scattering curves of benzene (● 293 K, ▲ 343 K).

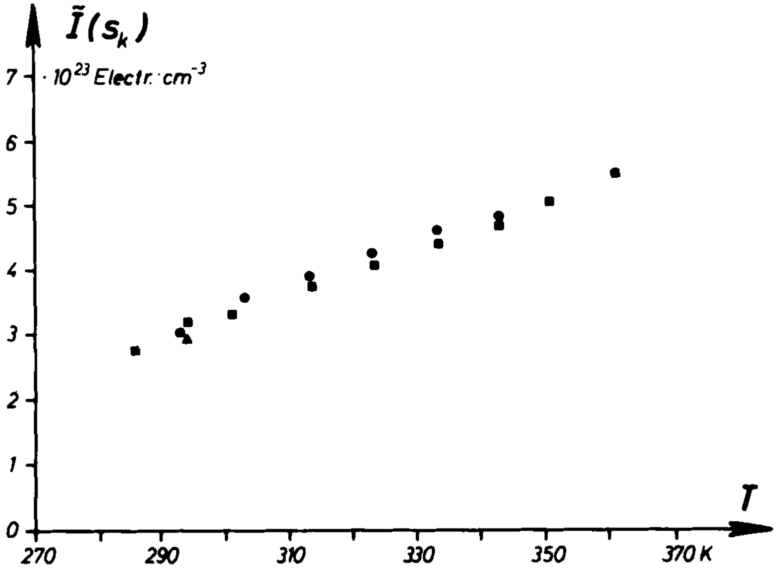

FIGURE 2 Temperature dependence of small angle X-ray scattering of benzene (● experimental data, ■, ▲ theoretical values from static data ■, from ultrasound data ▲).

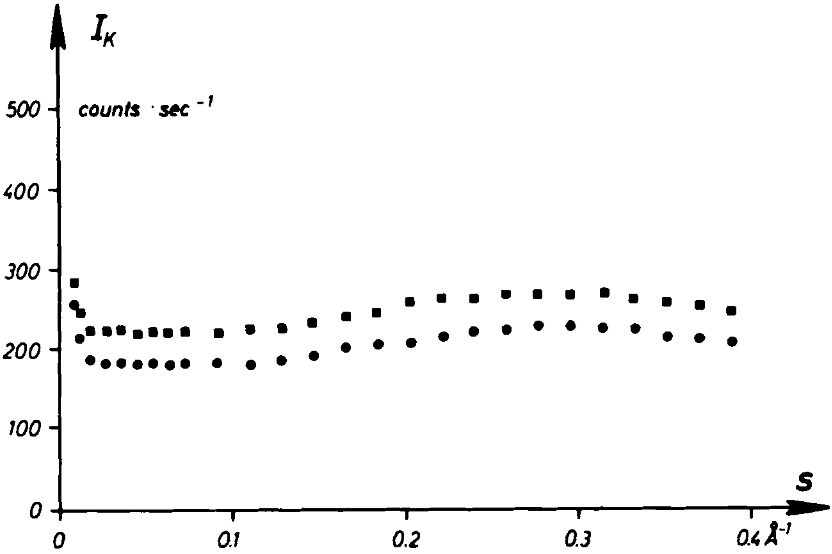

FIGURE 3 Small angle X-ray scattering curves of MBBA (● 293 K, nematic phase, ■ 323 K, isotropic melt).

intensity is independent of $s$ for $s \leq 0.13 Å^{-1}$. The temperature dependence of the scattering in this range is shown in Figures 4–6 for MBBA, PCB and cholesteryl myristate, both for the isotropic state as well as for the nematic and cholesteric phase respectively. It is observed that the scattering intensity decreases quite strongly with decreasing temperature at high temperatures and becomes approximately temperature independent at lower temperature in the neighborhood of the clearing temperature. Figures 4–6 show that the intensity-temperature curves are continuous at the phase transition temperature.

Figures 4–6 also contain the scattering values calculated on the basis of Eq. (5), that is the scattering expected for the case that only particle fluctuations give rise to the scattering. It is obvious that the two sets of values agree only at high temperatures whereas large deviations occur at lower temperatures, in contrast to the case of benzene and water discussed above.

It is apparent that additional contributions to the small angle X-ray scattering occur in MBBA, PCB and CM both in the isotropic fluid as well as in the mesophases, which vanish in the isotropic phase at elevated temperatures. The additional contributions must arise, as predicted by Eq. (7), from the presence of orientation correlations. These correlations thus do not only exist in the

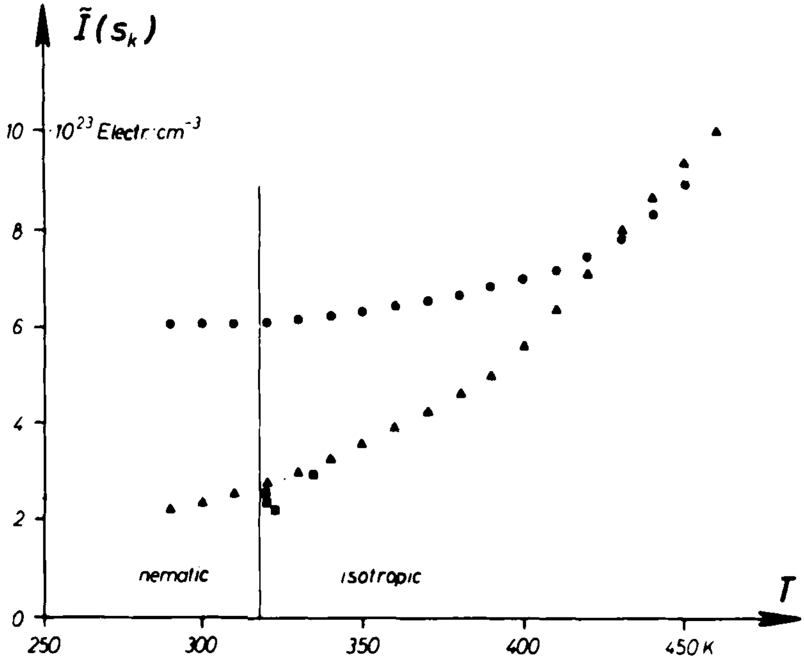

FIGURE 4 Temperature dependence of small angle X-ray scattering of MBBA (● SAXS, ▲, ■, calculated values based on the compressibility equation, static data ■, ultrasound data ▲).

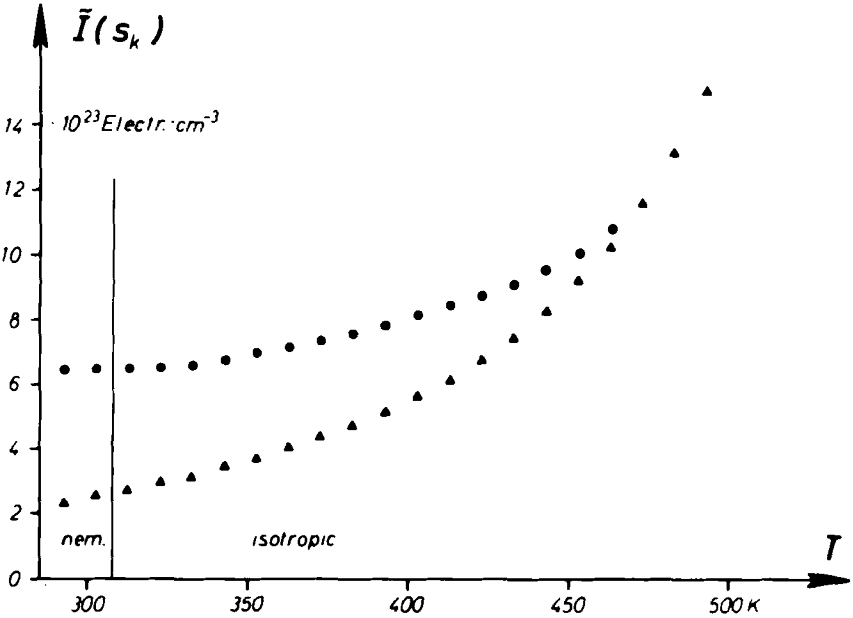

FIGURE 5 Temperature dependence of small angle X-ray scattering of PCB (● SAXS, ▲ calculated values, based on the compressibility equation).

mesophases and in the isotropic phase in the neighborhood of the clearing temperature but seem to occur at temperatures as far as about 150 K above the nematic or cholesteric transition temperature.

Strongly correlated orientation fluctuations are known to exist in the isotropic phase of mesogenic substances. This phenomenon was treated theoretically by De Gennes[5] who took into account that the free energy of the condensed state depends on the order parameter $S$. He assumed an analytical function for the dependence of the free energy on the order parameter and was able to predict that the fluctuations of the orientational order and their spatial extension should increase strongly with decreasing temperature in the isotropic state, as a pseudocritical temperature $T^*$ is approached. This particular temperature is usually slightly lower than the actual transition temperature. Results on the electric or magnetic birefringence as well as on depolarized light scattering are in agreement with his predictions on the temperature dependence of the mean square of the order parameter fluctuations $\overline{\delta S^2}$ and the spatial extension of the fluctuations $\xi$, expressed in Eqs. (9) and (10):[5,6]

$$\overline{\delta S^2} \sim T/(T - T^*) \tag{9}$$

$$\xi \sim \xi_0/(T - T^*)^{0.5} \tag{10}$$

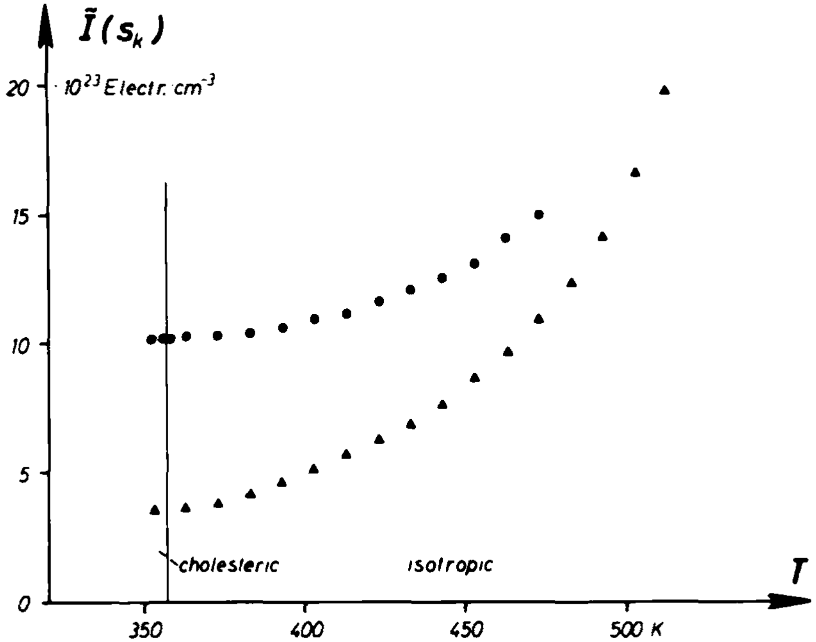

FIGURE 6 Temperature dependence of small angle X-ray scattering of cholesteryl myristate (● SAXS, ▲ calculated values, based on the compressibility equation).

We thus know that orientation fluctuations exist in the isotropic fluid of mesogenic substances, which, according to Eq. (7), contribute to the total small angle X-ray scattering.

Our experimental results, displayed in Figures 4–6, reveal, however, that the orientation fluctuations influence light scattering (or electric or magnetic birefringence) and X-ray scattering in a different way. The X-ray scattering intensity does not diverge in the neighborhood of the nematic transition but remains nearly constant in this range. In addition the small angle X-ray curve remains independent of $s$ in the range of $s$-values considered here even close to the nematic transition, in contrast to light scattering which becomes strongly dependent on $s$, due to long range correlations of the fluctuations.[5] These results have to be taken as an indication that light scattering and X-ray scattering sample different aspects of the total orientational order and its fluctuations.

The depolarized light scattering of linear molecules is known to be determined predominantly by the coefficient $g_{00}^{220}(r_{12})$ of the expansion, given in Eq. (6).[1,3,32,33] This also holds for the electric and magnetic birefringence. These methods therefore are sensitive to the relative orientation of molecular axes independent of the sign of the orientation. Parallel and antiparallel orientations of the molecules cannot be distinguished.

The X-ray scattering, on the other hand, is determined by a large number of expansion coefficients, as is evident from Eq. (7). The number is only limited by the symmetry requirements of the individual molecules.[12] This shows that X-ray scattering is able to yield data on the orientational order which cannot be extracted from light scattering data.

Presently we do not know exactly how important the individual terms of the expansion are in determining small angle X-ray scattering. It is safe to assume, however, that in the case of molecules which do not have a plane of symmetry perpendicular to their longitudinal axes—this is the case for the substances studied here—the prominent term will be the one with $l_i = 1$ and the most important one for small values of $s$ the term with $l_{12} = 0$, containing the Bessel function $j_0(sr_{12})$ [Eq. (7)] since higher order Bessel functions are very small at small values of $(sr_{12})$. We thus may express the X-ray scattering in the small angle range to a first approximation by:

$$\Delta \mathrm{I}(s)/\mathrm{I}_0 = \rho_N |F_0^1|^2 \left[ 1 + \rho_N D(1\ 1\ 0) \int g_{00}^{110}(r_{12}) j_0(sr_{12}) 4\pi r_{12}^2 dr_{12} \right] \quad (11)$$

($\Delta \mathrm{I}(s)/\mathrm{I}_0$: scattering due to orientation correlations) for the particular case of linear molecules. In the term $g_{00}^{110}(r_{12})$ the orientation of both molecular axes are important, parallel and antiparallel orientations contribute differently to this coefficient. Small angle X-ray scattering is thus sensitive to this particular aspect of the orientation order. A statistical distribution of parallel and antiparallel orientations of molecular axes will result in a vanishing $g_{00}^{110}(r_{12})$ at all $r_{12}$ and thus in negligible small angle X-ray scattering $\Delta \mathrm{I}(s)$, even if the molecular axes are parallel to each other as in the nematic phase.

The data on small angle X-ray scattering in mesogenic substances reported above indicate that deviations from a random distribution of parallel and antiparallel orientations of molecular axes do not exist in the isotropic phase at elevated temperatures. Deviations from a random distribution occur, however, at lower temperatures. These deviations are apparently not directly related to order parameter fluctuations as detected for instance by depolarized light scattering, for the following reasons: The correlation length of the fluctuations, detected by small angle X-ray scattering, remains short ranged, that is of the order of intermolecular distances, in the neighborhood of the nematic transition and even in the nematic (or cholesteric) phase, in contrast to the order parameter fluctuations. In addition the mean square value of the fluctuations does not diverge at the transition, again in contrast to the corresponding value of the order parameter fluctuations. These conclusions are based on the observation that the small angle scattering curve remains independent of $s$ and that the scattering intensity does not diverge in the neighborhood of the phase transition temperature. It is obvious that the fluctuations analyzed by small angle X-ray scattering do not couple to the order parameter fluctuations nor to the average order parameter.

The observation that deviations from a random distribution of parallel and antiparallel orientations occur and grow with decreasing temperature leads to the conclusion, that the orientation dependent interaction energy $U$ of the molecules does not only depend on the mutual orientation independent of the sign of the orientation, as assumed in most theories of liquid crystals,[5,6,34,35] but depends also on the sign of orientation:

$$U_{\text{anisotropic}} = A\, U_1(\cos^2 \theta) + B\, U_2(\cos \theta) \tag{12}$$

where $U$ is the interaction energy, $\theta$ the angle between the particular pairs of molecules and $A$ and $B$ are constants. The free energy $F$ of the isotropic and anisotropic fluid states will therefore depend not only on $\cos^2 \theta$, as taken into account by De Gennes, but also on $\cos \theta$.

Thermal fluctuations usually increase with increasing temperature.[14,15] The temperature dependence can be calculated from that of the second derivative of the free energy with respect to the fluctuating quantity, since the mean square fluctuations are given by the reciprocal of this derivative.[14,15] This value usually increases with increasing temperature. We observe, however, that the small angle X-ray scattering, which we have attributed to orientation fluctuations, increase with decreasing temperature. It displays thus a temperature dependence which resembles that of the order parameter fluctuations which was interpreted by De Gennes in terms of a hypothetical phase transition at a temperature $T^*$, as discussed above. We therefore conclude that such a hypothetical transition also exists for the orientation fluctuations, detected by small angle X-ray scattering. This transition has to occur at a temperature which is far below the nematic phase transition or cholesteric phase transition, since neither a divergence of the scattered intensity nor a change of the shape of the scattering curve is observed in the temperature range studied so far. In the systems studied up to now the transition is expected to occur at temperatures at which the solid crystalline state is the stable state.

The hypothetical state at low temperatures is characterized by a spontaneous parallel or antiparallel orientation of the molecular axes. This state may thus be able to exhibit ferroelectric properties, provided that the parallel orientation is favored and that the dipoles of the molecules are parallel to the molecular axes.

In order to find out whether the dipolar structure of the molecules influences the orientation fluctuations considered here, one has to compare the small angle scattering of substances having different dipolar structures. MBBA has a dipole moment which is approximately perpendicular to the long axis of the molecule. It therefore exhibits a negative dielectric anisotropy and a negative electric birefringence.[5,6,36] PCB, on the other hand, has a strong dipole moment which is oriented in the direction of the molecular axis.[6] It is therefore characterized by a positive dielectric anisotropy. Cholesteryl myristate has a dipole moment, which is oriented approximately at 60° relative to the long axis of the molecule. The molecules contain furthermore chiral groups which are responsible for the cholesteric phase. Figures 4–6 show, that the scattering is very similar for all three substances, despite strong differences in the dipolar structure. We therefore conclude that the interactions, depending on $\cos \theta$ do not originate from dipolar forces but arise from dispersion forces in the same way as the interactions, depending on $\cos^2 \theta$.[34,35]

Presently studies are performed in order to determine orientation fluctuations in smectic phases and the anisotropy of these fluctuations in the nematic and smectic phases.

A particular kind of molecular fluids which we have studied in addition to the fluids, described so far, were melts of $n$-alkanes. It has been reported in the literature that these melts exhibit pretransitional phenomena similar to those of isotropic phases of mesogenic substances.[9,10] The depolarized light scattering, the electric as well as the magnetic birefringence could be interpreted either on the basis of the De Gennes theory or of the theory of heterophase fluctuations proposed by Frenkel.[37]

We found that the small angle X-ray scattering of the melts of $n$-alkanes is characterized by a scattering curve which is independent of the absolute value of the scattering vector over a limited range of $s$-values, in agreement with the scattering curves found for mesogenic and nonmesogenic fluids. The absolute scattering intensity in this range of $s$-values was found to agree exactly with the values calculated on the basis of Eq. (5), that is the scattering is totally determined by thermal particle fluctuations. This is shown in Figure 7, which displays the experimental values as well as the theoretical values for the particular case of hexadecane. We thus did not get any indications of orientation fluctuations. This is not very surprising, since these fluctuations will be very small in any case and since the electron density distribution of nonextended alkane molecules does not differ very much from that of a spherical symmetric distribution.

The conclusions to be drawn from the results presented in this paper are that we are able to get information on orientation fluctuations in molecular fluids by means of small angle X-ray scattering and that the information differs from that which can be extracted from light scattering data. The fluctuations of the direction of the molecular axes increase with decreasing temperature in the isotropic and nematic (or cholesteric) phase and are continuous at the nematic transition. A state is apparently approached at low temperatures which is characterized by a spontaneous parallel or antiparallel orientation of the molecular axes.

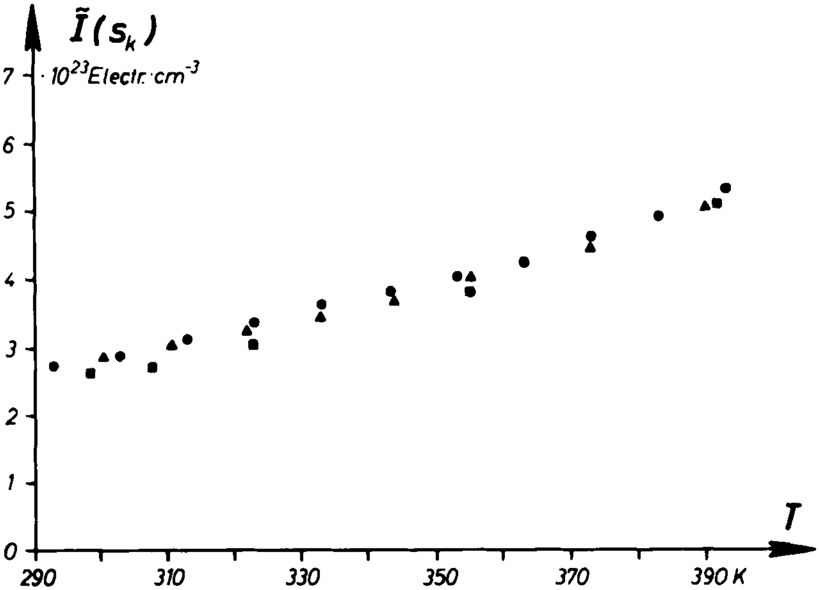

FIGURE 7 Temperature dependence of small angle X-ray scattering of hexadecane (● SAXS, ■, ▲ calculated values, based on the compressibility equation, static data ■, ultrasound data ▲).

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