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Switching the dipole moment for 5CB on and off

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A Commentary on the paper "A molecular dynamics study of the nematic phase of 4-*n*-pentyl-4′-cyanobiphenyl", by S. J. Picken, W. F. van Gunsteren, P. Th. van Duijnen and W. H. de Jeu. First published in *Liquid Crystals*, **6**, 357-371 (1989).

The start of this whole endeavour was pretty much by pure chance. One of the authors, Stephen Picken, in 1981 learned that Dr.ir. Wim de Jeu, who was heading a group on liquid crystal physics within the Solid State Physics Laboratory of the University of Groningen, was looking for a graduate student. This was to help L.G.P. Dalmolen, one of his Ph.D. students, with Raman depolarisation measurements on the orientational order parameters of cyanobiphenyl (nCB) liquid crystals. After a discussion with Wim de Jeu about liquid crystals and such Stephen started his experimental graduation project.

The Raman depolarisation method had been applied to several nematic systems, as it was one of the few techniques that allowed determination of $<P_4>$ the fourth rank orientational order parameter [1]. The second rank order parameter $<P_2>$ behaviour versus temperature was reasonably well mapped out at the time. $<P_2>$ was accessible via birefringence, NMR, dichroism, and diamagnetic susceptibility measurements. Within reasonable bounds the $<P_2>$ order parameter seemed to comply with predictions resulting from the Maier-Saupe model. Interestingly, work by Miyano [2] had indicated that the $<P_4>$ order parameter from Raman depolarisation could show anomalous behaviour compared to the Maier-Saupe model prediction, with low and even negative values of $<P_4>$ being found in some cases. So this was the puzzle that was to be studied further from an experimental point of view. The results of this experimental work were reported by Dalmolen *et al.* [3].

Already before that publication the Raman results were presented as a poster at the MSC (Materials Science Centre at Groningen University) meeting held in 1983 on the island of Vlieland just of the north coast of the Netherlands [4]. During the poster session Stephen Picken had a discussion with Professor Dr. Jan Kommandeur, Professor of Physical Chemistry at Groningen University. The poster described the hypothesis that the low $<P_4>$ values were due to antiparallel association of the nCB molecules. The idea was that the long axis of the associated dimers was at an angle with respect to the CN dipole that was used as the Raman active bond. Some simple calculations showed that this could indeed lead to low or negative $<P_4>$ values. The hypothesis seemed plausible but hard to explore further by experimental or indeed theoretical means. The number of experimental techniques to determine $<P_4>$ was limited. Theory, then and now, could not deal with the exact calculation of multiple particle interactions without invoking approximations along the line. So Professor Kommandeur's remark came as a minor shock: "Why don't you just calculate this on a computer? We have someone at the Chemistry Department, Wilfred van Gunsteren, who does that sort of thing."

Upon returning to the Solid State Physics Department Stephen Picken and Wim de Jeu made an appointment with Wilfred van Gunsteren to see what this was all about. At the time Wilfred van Gunsteren was simulating surfactant bilayers in water (dodecanol, sodium dodecanoate and water) on the Cyber mainframe computer so in fact he already had some experience on lyotropic liquid crystal systems [5]. The molecular dynamics (MD) simulations were done using the famous GROMOS molecular dynamics simulation package that he had developed with Professor Herman Berendsen. GROMOS is still widely used for MD simulation [6].

The result of the discussion was that Stephen Picken started to do MD simulations under Van Gunsteren's guidance as his theoretical graduation project. The Physics Department at Groningen offered "Gemengde

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Natuurkunde" literally "mixed physics" as a possibility for graduation. This involved two eight month graduation research projects – one experimental and one theoretical. The first minor hurdle was to convince the Theoretical Physics Department that doing an MD simulation could count as a "theoretical physics graduation project". A trick that Wim de Jeu somehow managed to pull off. One should note that from a theoretical physicist's point, an MD simulation was probably not much more than using brute force computation to investigate ill-defined problems and using questionable simplifications of the real problem at hand. There were more hurdles to come.

On starting the graduation project it turned out that the MD simulations used a large FORTRAN program and a whole range of special user settings were required on the mainframe computer. The computer time was measured in SRU's (system resource units) and CPU-seconds and these had to be set to much higher limiting values than for a normal user. Also, there was the optional requirement of having no less that two magnetic tapes loaded simultaneously for storing the massive amounts of data. About 4 Mbytes per MD-run of velocities and co-ordinates had to be stored which nowadays would not cause any major excitement. The Administrator at the Solid State Physics Department, involved with the mainframe use, made the changes to Stephen's settings and we were off.

The first immediate effect of this was that Stephen managed to consume the entire year's mainframe-computing budget of the Solid State Physics Department in just one weekend, and he had only just started. This caused some mild irritation among colleagues and supervisors. Somehow Wim de Jeu managed to convince the Department Administration that an undergraduate student should get additional funds to make all of this possible.

There are several lessons to be learnt from this experience (i) it is ok to improvise, (ii) weird ideas are worth pursuing and (iii) it is useful to have a supervisor who is prepared to deal with all the flack. A remaining question is – would this still be possible today with stricter budgeting, monitoring and assessment of the projects and departmental affairs?

Presentation of the work

The results of the MD simulations were first presented as a poster [7] at the 1984 International Liquid Crystal Conference (ILCC) in York and later that year at the FOM Veldhoven meeting. At the York ILCC there was already considerable interest in this work although it was felt that a larger simulation system would have been preferable. At the time a simulation of 1219 particles (64 5CB molecules of 19 atoms) was relatively large and the limit was about 6000 particles. This would have made the linear dimensions of the box about 1.7 times bigger but at the cost of 8–24 times more computing time depending on the required search scheme. Also, longer simulations would be preferred to prove that the system was in equilibrium. Nevertheless, for a considerable time this work was the only atomistic detail simulation of a liquid crystal that had been reported.

In March, 1985 Stephen Picken graduated and started working at Akzo Nobel Corporate Research Laboratories, working on the study of liquid crystal polymer solutions that are used for aramid fibre spinning. Wilfred van Gunsteren was supposed to repeat the calculation for a larger system, but somewhat later he left Groningen to take a position at the ETH in Zürich. Due to these changes of environment the work on writing the MD simulation paper stagnated until 1988 when Stephen Picken and Wim de Jeu met at the Freiburg ILCC. Via arm-twisting and intimidation Wim de Jeu managed to put sufficient pressure on Stephen to start writing the article. This was sent to *Liquid Crystals* on 2nd November 1988 and was finally accepted on 21 April 1989. The comments of the referees again referred to the system size and whether stable nematic equilibrium had been achieved. By adding the rather suggestive lines showing the various temperature stages in the simulation the referees were convinced that equilibrium had been reached (see figure 6 in the 1989 *Liquid Crystals* paper), at least for the charged system. In retrospect one can still argue whether or not this had been achieved.

The primary point of the publication was however to show that the addition of a dipole moment gives rise to lower $<P_4>$ values by comparing two simulations that were identical except for the presence or absence of atomic charges on the mesogenic molecule (i.e. with and without a dipole moment giving rise to molecular association). This possibility remains one of the unique assets of MD simulation. One can simulate systems that are impossible in real life so that effects from various contributions like charges or mass or flexibility can be separated out. This to us appears to be more important than being able to mimic nature as it allows "what-if" questions to be addressed.

The first reference to the MD simulation results in the paper by Dalmolen *et al.* [3] may also help to provide a clearer picture of the context (from pages 1448–9):

'Though qualitatively several experimental observations seem to fit in nicely with the model described, it is somewhat unsatisfactory that this cannot be made more quantitative. This is due to the fact that the two effects (i) and (ii) (*note*: these are deviations of the long axis and steric dimer monomer interactions) on $<P_4>$ cannot easily be separated, while moreover more realistic models of the semi-flexible molecules are not tractable. In an attempt to obtain a firmer basis for the model molecular dynamics calculations have been carried out for 5CB [27] (reference [7] in this Commentary). The system consisted of 64 molecules, while periodic boundary conditions were applied. The molecules were simulated by combination of the appropriate atoms, and using specific potentials to describe bond angles, dihedral angles, etc. Lennard-Jones and Coulomb forces were used to describe all other interactions, including intermolecular ones. In this way the molecules are treated rather realistically with internal degrees of freedom. In particular two runs have been compared: one without charges on the atoms, and one in which Coulomb interactions were included from charges calculated to give the correct dipole moment. Analysis of the orientational distribution showed that "switching on" the charges (and thus allowing for possible anti-parallel dipole correlation) indeed leads for 5CB to a broadening of the distribution function and to a decrease of $<P_4>$. Though this does not prove any actual mechanism, it gives some support for the basic ingredient of the model given here.'

Developments since the 1989 paper

Considering the limited space available for this Commentary it is worth referring to the review article *Computer simulation of liquid crystals* by Care and Cleaver [8] for a more complete overview of the current state of affairs. Here we will only highlight the development of atomic detail MD simulations of liquid crystals while we fully realise that a lot of beautiful MD work has been done making use of soft-ellipsoids (Gay-Berne potential). Indeed Monte Carlo simulations have also been used successfully on both atomic and idealised model systems.

In 1994 Cleaver and Tildesley [9] described an MD simulation of 8CB monolayers on graphite – which could be compared to results from AFM and STM studies that were just becoming available. Also in that year Yoneya and Berendsen [10] reported results on an MD simulation of a chiral nematic phase of 32 molecules again using GROMOS but with twisted periodic boundary conditions. Glaser *et al.* [11] reported the first atomic detail simulation of a smectic layer consisting of 36 molecules. Finally, in 1994 Komolkin *et al.* [12] described a nematic system of 75 molecules also including explicit hydrogens so that the simulations could be compared to NMR data.

Relatively soon afterwards the size of the simulations started to increase. In 1996 Sandstrom *et al.* [13] reported atomic detail simulation of 110 5CB molecules plus 10 solute benzene molecules and Hauptmann *et al.* [14] gave detailed analysis on long simulations of 144 5OCB molecules using different starting values for the initial $<P_2>$ orientational order parameter. This study showed how difficult it is to obtain unambiguous results for $<P_2>$ versus temperature as the starting configuration had a strong influence throughout the MD runs. In 1998 Yakovenko reported [15] a 200 molecule MD simulation of PCH5 to try to simulate the nematic-isotropic transition temperature, however, this proved to be too computationally expensive. McBride *et al.* [16] reported another attempt at this, describing results from very long MD runs of 64 and 125 bicyclo-octane 5,5′BBCO molecules. Starting from isotropic systems at 300 K a $<P_2>$ of about 0.8 was reached after 12 ns simulation.

Some more recent studies by Zakharov *et al.* [17] describe the simulation of the rotational viscosity of a nematic phase, and Wang *et al.* [18] simulate no less than 944 atomic detail 5CB molecules – about 18.000 atoms – forming a (very) small droplet. Berardi *et al.* [19] have recently described results of large and long, up to 40 ns, simulations that seem to provide a reasonably good values for the nematic-isotropic transition temperatures in several different systems. Cacelli *et al.* [20] describe 5CB simulations based on quantum mechanical force fields and compare computed and measured $<P_2>$ values. Finally Capar *et al.* [21] compare rotational viscosity values obtained from MD simulations of 5CB, 7CB and 8CB.

Some suggestions in retrospect and future developments

These studies suggest that atomic detail MD simulations of nematic liquid crystal phases nowadays is reasonably well-developed. If we look back at our 1989 *Liquid Crystals* paper in retrospect, there are things which should (or could) have been done better, like tracking the actual director of the system rather than hoping that it would not move away from the original z-axis during the simulation. The correct procedure for this is known: compute the Saupe ordering matrix explicitly and then determine its eigenvalues. This gives both the order parameter(s) and the direction of the director. Concerning the size of the simulation a larger number of molecules would clearly have been preferable but the use of a direct comparison of two systems with and without charge still seems to be a valid method to obtain information on the orientational effect of dipole association on the order parameters. One thing we should have done at the time was to multiply the charges, as obtained from the ab-initio calculations by Piet van Duynen, by a constant factor to give a more realistic dipole moment (the dipole moment we used was nearly a factor of two too small from the LCAO calculations compared to experimental data). In that case one might expect a stronger effect on the <P_4> versus <P_2> plots obtained from the MD trajectories. Also, note the exclusion of dipole-induced dipole interactions in our MD simulations i.e. the atomic charge values used do not couple to the local electric fields. If a reasonable agreement between experiments and simulations, e.g. for predicting T_{NI}, is desired clearly the induced dipoles should be included at least for strongly polar LC systems. Once successful MD simulation of the nematic phase becomes established it should be possible to improve further our understanding of the statistical mechanics of the nematic phase. Why do the current approximations work so well and what needs to be added to the models to obtain predictive power without having to resort to simulation?

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A molecular dynamics study of the nematic phase of 4-*n*-pentyl-4′-cyanobiphenyl

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Preliminary molecular dynamics simulations of the nematic phase of 4-*n*-pentyl-4′-cyanobiphenyl are described. The simulations include all molecular degrees of freedom. The influence of the molecular dipole moment is investigated by comparing simulations with and without a charge distribution on the molecules. Inclusion of the charge distribution is found to lead to a slight broadening of the orientational distribution function, in qualitative agreement with Raman measurements of the orientational order parameters.

1. Introduction

Liquid crystals [1] are characterized by the presence of orientational order of the anisotropic molecules, while positional order is either completely absent (nematic phase) or strongly reduced (for example in smectic phases). In the case of elongated molecules, the orientational order leads to a unique macroscopic axis, the director, which gives the average orientation of the long molecular axes. The smectic phases are characterized by an additional density wave in one direction, in the smectic A phase along the director. Molecular dynamics studies of liquid crystals [2, 3] have so far usually been restricted to model bodies to represent the real molecules (spherocylinders, ellipsoids, etc.) In this paper preliminary results are given for simulations on a set of realistic mesogenic molecules. It should be emphasized, however, that the purpose of the present study was not to investigate the phase behaviour in any detail. The simulations that are described are intended to show the possiblities and difficulties of such detailed molecular dynamics simulations, and could be a starting point for a more complete treatment of larger systems. Within this limited framework calculations have been done in the nematic phase region to study the influence of the molecular charges on the orientational distribution. For that reason 4-*n*-pentyl-4′-cyanobiphyl (5CB) was chosen.

The degree of orientational order in the nematic phase can be described by the orientational distribution function $f(\beta)$

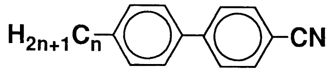
$$N(\beta)d\beta = f(\beta)\sin\beta\, d\beta, \qquad (1)$$

where $N(\beta)\ d\beta$ is the fraction of molecules with their long axis oriented at an angle between β and $\beta+d\beta$ with the director. The function $f(\beta)$ can be expanded in terms of the Legendre polynomials of even order

$$f(\beta) = \sum_{l=0}^{\infty} \frac{1}{2}(4l+1)\langle P_{2l}(\cos\beta)\rangle P_{2l}(\cos\beta). \qquad (2)$$

The expectation value $<P_2(\cos\beta)>$ is usually called the order parameter, and can be related to the anisotropy of second rank properties such as the birefringence or the anisotropy of the magnetic susceptibility [1]. In the isotropic phase all $<P_{2l}(\cos\beta)>$ values are zero, while for perfect orientational order all $(P_{2l}(\cos\beta)>$ are one. Using depolarized Raman scattering not only $<P_2(\cos\beta)>$ but also $<P_4(\cos\beta)>$ can be determined [1, 4].

The choice of 5CB was motivated by the observation that the values found for $<P_4(\cos\beta)>$ of the *n*CB series



showed an anomalous trend giving very low values for the lower members [5]. This was attributed to the effect

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of antiparallel association of the molecules due to the strong terminal dipole moment. If this association is imagined to take place mainly in the form of dimers, it is easy to visualize that the long axis of a constituent molecule (taken as the para axis) will not coincide with what is expected to be the long axis of the dimer. Assuming the angle between the two axes to be β_0 this influences the order parameters via

$$\langle P_{2l}(\cos\beta)\rangle_{\text{eff}} = \langle P_{2l}(\cos\beta)\rangle_{\text{mon}} P_{2l}(\cos\beta_0). \qquad (3)$$

Here the index mon refers to the value to be expected for non-associating molecules (monomers). In this view the higher homologues are expected to have a low value of β_0, leading to normal values for the effective $<P_4(\cos\beta)>$. while the larger values of β_0 obtained for the lower homologues give rise to the anomalous low values of $<P_4(\cos\beta)>$. This effect is illustrated in figure 1 for various values of β_0 [5].

The molecular dynamics method allows us to compare the results of two simulations, one without charges and one including a point charge representation of the molecular charge distribution, keeping other molecular properties the same. Obviously, such a comparison is impossible in a real experimental situation. To obtain the charge distribution within the molecules, *ab initio* LCAO calculations were performed. The results were used as input for the simulations. Inclusion of the charges indeed gives some broadening of the orientational distribution, thus providing support to the interpretation of the order parameters given here. Though the limited simulation time adds some uncertainty to any conclusion, we feel neverthless that by comparing two systems, with and without a molecular charge distribution, it is possible to predict qualitatively the influence of the dipole moment on the order parameters of 5CB.

The plan of the paper is as follows. In the § 2 the system to be simulated is described in more detail. Then in § 3 the molecular dynamics method is discussed further. In the last section the method of analysis and the results are presented.

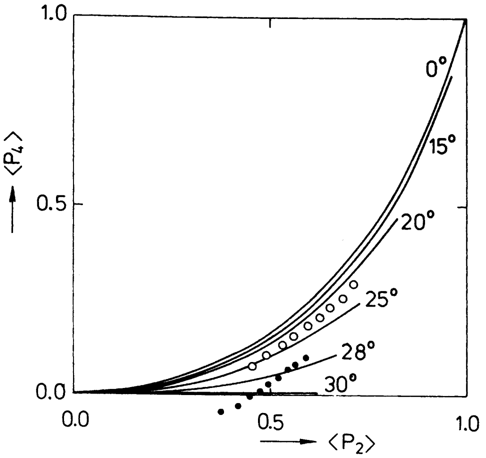


Figure 1. Experimental (circles) and calculated (solid lines) values of $<P_2(\cos\beta)>$ versus $<P_4(\cos\beta)>$ for various values of β_0; The latter are calculated using the model described in the Introduction. Open circles are experimental data for 7CB, closed circles for 5CB ([5]).

2. Molecular model and force field

The molecular dynamics simulations were performed on systems containing 64 5CB molecules, using rectangular periodic boundary conditions. Each molecule contains 19 atoms of types N, C, CH, CH_2 and CH_3. This means that 1216 ($=64\times19$) particles were used in the simulations. In table 1 the various terms in the interatomic potential which is used are listed; table 2 shows the numerical values for the parameters. These are average values obtained from diverse experimental methods, such as Raman scattering, FT IR, NMR, compressibility measurements, etc. The bond lengths of the molecules are kept fixed using the method SHAKE [6]. The Lennard-Jones interaction is used for all non-bonded interactions and for intramolecular interactions beyond the 1–2 and 1–3 pairs (first and second covalently bonded neighbours). For the 1–4 intramolecular interaction special values of the constants A and B are used to obtain a realistic description of the conformer statistics (e.g. in the alkyl chain). Also the Coulomb interaction is calculated over all pairs excluding the 1–2 and 1–3 pairs [7]. As yet no succesful method for including molecular polarizability has been found.

Table 1. The potential U that was used. The angle θ_{ijk} is the angle between bonds ij and jk. The angles ϕ_{ijkl} and ψ_{ijkl} are the dihedral angles between the planes through atoms i, j and k, and the planes through atoms j, k and l. The summations are performed over all relevant ij pairs, ijk triplets, or $ijkl$ quadruplets as the case may be.

Potential	Description
$U=\sum_{ij}\frac{A_{ij}}{r_{ij}^{12}}-\frac{B_{ij}}{r_{ij}^{6}}$	Lennard-Jones terms
$+\sum_{ij}\frac{1}{4\pi\varepsilon_0}\frac{Q_iQ_i}{r_{ij}}$	Coulomb term
$+\sum_{ijk}\frac{1}{2}(K_\theta)_{ijk}(\theta-\theta_0)_{ijk}^2$	Bond angle bending term
$+\sum_{ijkl}(K_\phi)_{ijkl}\left(1+\cos(n\phi-\delta)_{ijkl}\right)$	Torsional angle term
$+\sum_{ijkl}\frac{1}{2}(K_\psi)_{ijkl}(\psi-\psi_0)_{ijkl}^2$	Improper dihedral angle term

Table 2.1. Lennard-Jones parameters A and B for atoms of the same type. Interactions for unlike atoms are taken to be the square root of the product of the respective entries in this table, e.g.

$$A_{N-CH_3} = (3.39 \times 26.15)^{1/2} \times 10^9 = 9.415 \times 10^9.$$

Bond type	A and A_{14}/ J mol^{-1} Å^{12}	B and B_{14}/ J mol^{-1} Å^{9}
N–N	3.389×10^9	2.436×10^6
	3.389×10^9	2.436×10^6
C–C (cyano)	3.374×10^9	2.340×10^6
	3.374×10^9	2.340×10^6
C_b–C_b (phenyl)	3.374×10^9	2.340×10^6
	3.374×10^9	2.340×10^6
CH–CH	1.512×10^{10}	0.551×10^7
	0.833×10^{10}	0.551×10^7
CH_2–CH_2	3.533×10^{10}	0.910×10^7
	0.711×10^{10}	0.472×10^7
CH_3–CH_3	2.615×10^{10}	0.888×10^7
	0.955×10^{10}	0.685×10^7

Table 2.2. Atomic masses.

Type	Mass/AMU
N	14.007
C	12.011
C_b	12.011
CH	13.019
CH_2	14.027
CH_3	15.035

This enhances the qualitative nature of any agreement with experimental values.

The partial atomic charges were obtained from *ab initio* LCAO calculations performed by one of us (P.Th. van Duijnen). The molecular wave function was calculated using the Hartree-Fock method, taking all electronic orbitals into account. The atomic charges which were used were not the usual Mulliken charges. Instead the partial atomic charges were calculated under preservation of the total charge and the overall dipole moment of the molecule [8]. The results of this calculation are shown in Figure 2. The calculated dipole moment is 2.49 D; experimental values are 4.34 D for cyanobiphenyl in benzene and 3.5 D for a cyanide group in a non-polarizable medium [9].

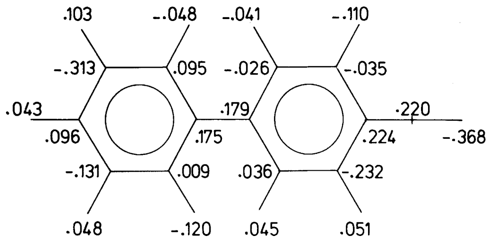
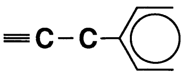
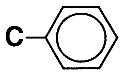
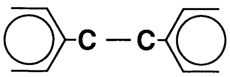
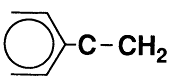


Figure 2. Partial atomic charges (in electronic units) for the cyanobiphenyl group from *ab initio* LCAO calculations. No partial charges were used for the alkyl chain.

Table 2.3. Bond lengths.

Bond type	Length/Å
N≡C	1.125
	1.420
CH and 	1.390
	1.495
 CH_2-CH_2 CH_2-CH_3	1.530

3. Computational procedure

To obtain an initial configuration for the simulations we placed the 64 molecules, at random positions and with a random orientation around the biphenyl axis, in a rectangular box. The molecules were alternately placed with an up or a down orientation to prevent a net dipole moment for the initial configuration. Molecular overlap was avoided by assigning an excluded volume to each particle. The starting configuration obtained by this method is shown in figure 3. Of course the density of the starting configuration is much too small due to inefficient filling of the available space.

Before starting the simulation the initial configuration was treated by an energy minimization routine that reduces the potential energy. This is required to prevent initial bad contacts or strained bonds leading to high initial velocities of the particles. The energy minimization was performed by using a steepest gradient method which changes the conformation along the steepest path down the potential energy surface [7]. After the energy minimization the particles are assigned with a velocity taken from a maxwellian distribution. Using the method SHAKE [6] constraints are incorporated to remove the velocity components in the direction of the bonds. Also, any centre of mass velocity and angular momentum of the whole system is removed. Having obtained both coordinates and velocities for the initial conformation in this way the simulation can be started.

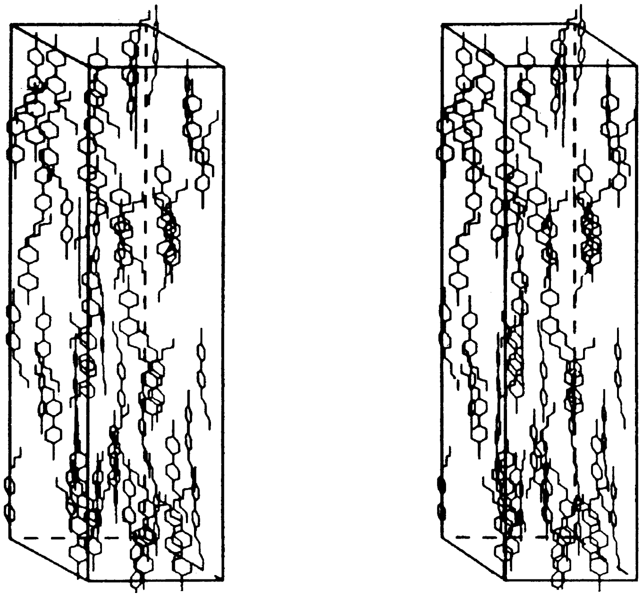


Figure 3. The initial configuration for the molecular dynamics simulations (stereoscopic pair).

Table 2.4. Bond-angle interaction parameters.

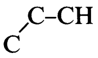
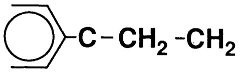
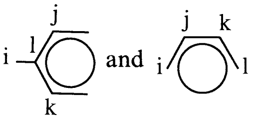
Bond type	Angle θ_0	K_θ/J mol^{-1} rad^{-2}
N≡C−C	180°	0.50×10^6
 etc.	120°	0.42×10^6
 CH_2-CH_2-CH_2 CH_2-CH_2-CH_3	111°	0.46×10^6

Table 2.5. Improper dihedral interaction parameters.

On all combinations

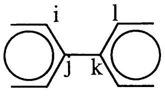
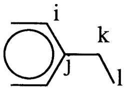
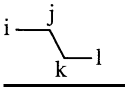


the phenyl rings are kept flat using:
$K_\psi=0.17\times10^6$ J mol^{-1} rad^{-2}, $\psi_0=0°$

The molecular dynamics algorithm used is the so-called leap-frog algorithm [10]

$$\begin{aligned}\mathbf{r}_i(t+\Delta t)&=\mathbf{r}_i(t)+\mathbf{v}_i\left(t+\frac{1}{2}\Delta t\right)\Delta t\\ \mathbf{v}_i\left(t+\frac{1}{2}\Delta t\right)&=\mathbf{v}_i\left(t-\frac{1}{2}\Delta t\right)+\frac{\mathbf{F}_i(t)\Delta t}{m_i},\end{aligned}\tag{4}$$

Table 2.6. Dihedral interaction parameters.

Type	K_ϕ/J mol^{-1}	n	ϕ_0	Description
	0.50×10^6	4	23°	Diphenyl [16]
	0.4×10^3	6	0°	Phenyl-alkane
	5.9×10^3	3	0°	Alkane

where Δt is the length of the time step used. In our case Δt was 0.004 ps as no very rapid motions are to be expected in this system. The force F on each particle is derived from the potential

$$\mathbf{F}_i=m_i\mathbf{a}_i=-\frac{\partial U(\{\mathbf{r}\})}{\partial \mathbf{r}_i}.\tag{5}$$

The advantage of using the leap-frog algorithm is that the particle velocities are explicitly used in the calculation of the new configuration. These velocities are required anyway to perform temperature and pressure scaling. Temperature scaling is used to keep the temperature of the system, on average, constant and to allow a smooth transition from one temperature to another [11]. It is performed by the algorithm [12]

$$\mathbf{v}(t):=\mathbf{v}(t)\left(1+\frac{\Delta t}{\tau_T}\left(\frac{T_{\text{ref}}}{T(t)}-1\right)\right)^{1/2}.\tag{6}$$

This is equivalent to a coupling of the system (with temperature $T(t)$) to a heat bath of temperature T^{ref}. The coupling time constant is τ_T and is usually taken to be 0.1 ps. Analogously, the pressure is kept, on average, at P_{ref} by using a scaling factor [12]

$$S_i(t)=\left(1-\beta\frac{\Delta t}{\tau_P}[P_{\text{ref}}-P_i(t)]\right)^{1/3},\quad i=x,y,z,\tag{7}$$

where β is the isothermal compressibility of the system, τ_P is the coupling time constant (again taken as 0.1 ps) and P_i is the pressure along direction i. We used $P_{\text{ref}}=9.8\times10^4$ Pa and $\beta=5.9\times10^{-10}$ Pa^{-1}. The size of the entire system is scaled by a factor S_i in the corresponding x, y or z direction. The pressure P_i is obtained from the virial theorem and is given by

$$P_iV=\sum_j m_j v_i^2(j)+\sum_j r_i(j)F_i(j),\tag{8}$$

where V is the volume of the system, and the index j denotes particles.

As we have mentioned the density of the initial configuration was too low. Performing a molecular dynamics simulation using pressure scaling (equations (7) and (8)) led to the formation of holes in the configuration. This is probably caused by the fact that the virial theorem, which is used to evaluate the pressure, is not applicable to systems that are not in equilibrium. The correct (non-equilibrium) equation to calculate the pressure would be

$$P_i V = \sum_j \left[m_j v_i^2(j) + r_i(j) F_i(j) - \frac{\partial}{\partial t}\{r_i(j)\boldsymbol{p}_i(j)\}\right], \tag{9}$$

where $\mathbf{p}_i(j)$ is the momentum of particle j in the direction i. The last term is usually taken to be zero on average (in equilibrium). However for a system that is systematically shrinking it leads to a decrease of the calculated pressure. This in turn leads to a faster scaling down of the dimensions of the system than with the normally used equation (8), thus hopefully preventing the formation of holes. Unfortunately, when using periodic boundary conditions, equation (9) leads to ambiguous results for the evaluation of $\Sigma_j\ \mathbf{r}_i(j)\cdot\mathbf{p}_i(j)$. This means that this equation cannot be used sensibly in molecular dynamics simulations with periodic boundary conditions, as described here. To prevent the formation of holes we have used instead a method where the density of the system was increased to the required value by reducing the size of the system during the first 1000 time steps without applying pressure scaling. After this forced adaptation of the density, the pressure scaling (equations (7) and (8)) was switched on and kept the system near the required density.

A final subtlety worth mentioning is the searching scheme that is used to calculate the non-bonded interactions. The non-bonded interactions were taken into account while using cut-off radii to limit the number of interacting pairs to be considered. The non-bonded interactions were completely included within a radius of 0.7 nm. The interacting pairs are stored in a pair list which is updated every 10 molecular dynamics steps. In addition, once every 10 steps the interactions from pairs within a cut-off radius between 0.7 and 1.0nm were calculated. This long range part of the non-bonded interactions can then be used for the next 10 molecular dynamics steps without further change [13]. The computation times for one molecular dynamics step using a Control-Data Cyber 170/760 computer are shown in table 3. The grid searching scheme which, in principle, is more efficient for larger systems is shown for comparison. Using the long range pair list method quite fast simulations are possible i.e. the system was simulated over 60 ps which required about 11.5 hours computation time. Although certain properties, like temperature and density, were well equilibrated within that time, others, like the molecular orientation, were still changing slightly during the last 40–60 ps of the runs. This means that the system is not fully equilibrated. However, since both runs are performed under identical conditions, tentative conclusions about the effects of inclusion of a molecular charge distribution may still be drawn.

Table 3. Computation time for one molecular dynamics step on a Control-Data Cyber 170/760 computer for a grid searching scheme, a simple pair list searching scheme and a pair list scheme where the long range interactions are included every 10 steps.

	Cut off radius/nm	Long range radius/nm	Average CP time per molecular dynamics step/s
Grid scheme	0.8	—	10
Pair list	0.8	—	3.6
Long range pair list	0.7	1.0	2.7

4. Results and discussion

In figure 4 the configuration is shown after 60 ps simulation time. We note that there seems to be a collective tilt occurring in the systems. Such an effect has been found before in simulations of ordered lamellar phases [14]. The tilt varies as a function of time, so that on average the molecules are still aligned along the director. There is no immediately visible difference between the configurations for the charged and uncharged simulations. To make a more accurate analysis possible various properties have to be determined, such as order parameters and diffusion constants. This will now be described in more detail.

The orientational distribution function $f(\beta)$ is obtained by counting the number of molecules with a deviation angle between β and $\beta + d\beta$. The normal expression for $f(\beta)$ (see equation 1) in the discrete case yields

$$f(\beta) = \frac{N(\beta)\Delta\beta}{\sin(\beta + \frac{1}{2}\Delta\beta)\Delta\beta} = \frac{\zeta_{\Delta\beta}(\beta)}{\sin(\beta + \frac{1}{2}\Delta\beta)\Delta\beta}, \tag{10}$$

where

$$\zeta_{\Delta\beta}(\beta) = N(\beta)\Delta\beta$$

is the fraction of molecules between β and $\beta + \Delta\beta$. The order parameters $\langle P_{2l}(\cos\beta)\rangle$ are now found by

$$\langle P_{2l}(\cos\beta)\rangle = 2\sum_{\beta=0}^{\pi/2} \zeta_{\Delta\beta}(\beta) P_{2l}\left(\cos\left(\beta + \frac{1}{2}\Delta\beta\right)\right), \tag{11}$$

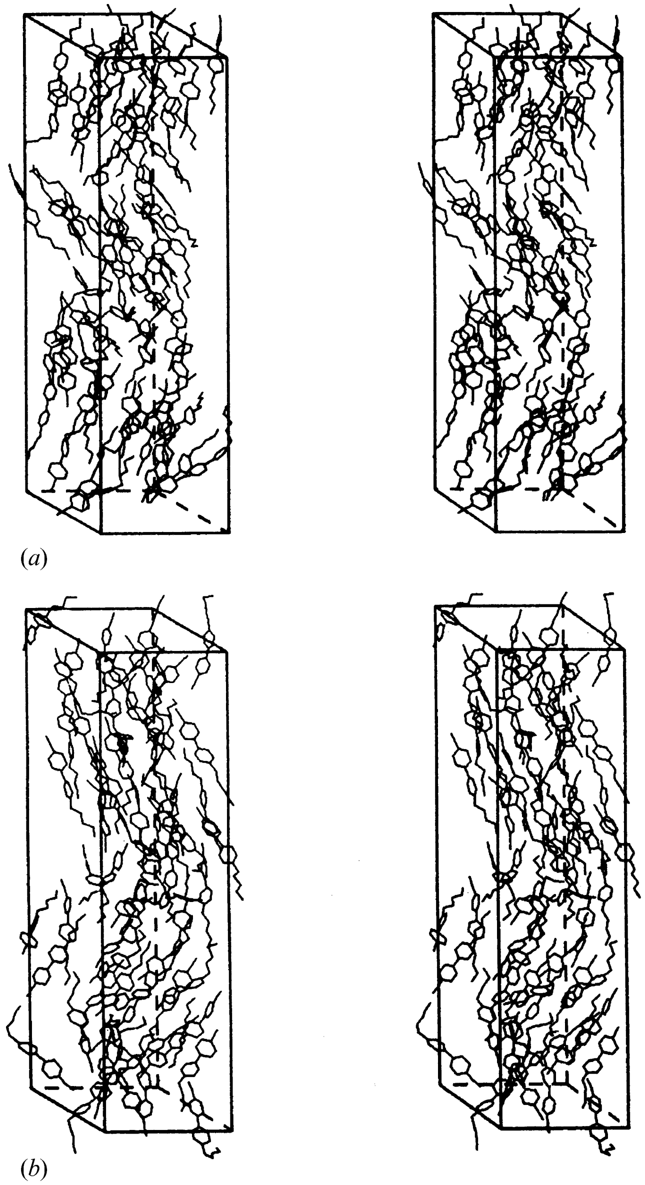


Figure 4. The configurations after 60 ps simulation for the uncharged (*a*) and the charged (*b*) system (stereoscopic pairs).

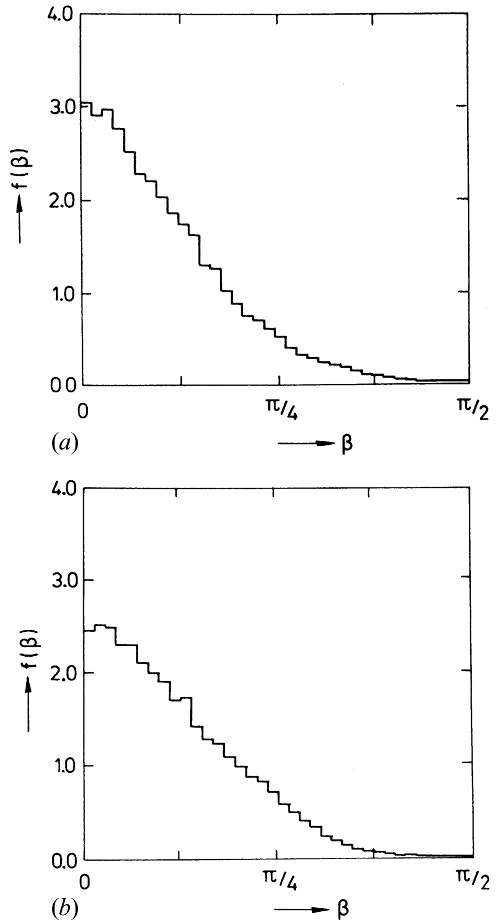


Figure 5. The calculated orientational distribution functions for the uncharged (*a*) and the charged (*b*) systems.

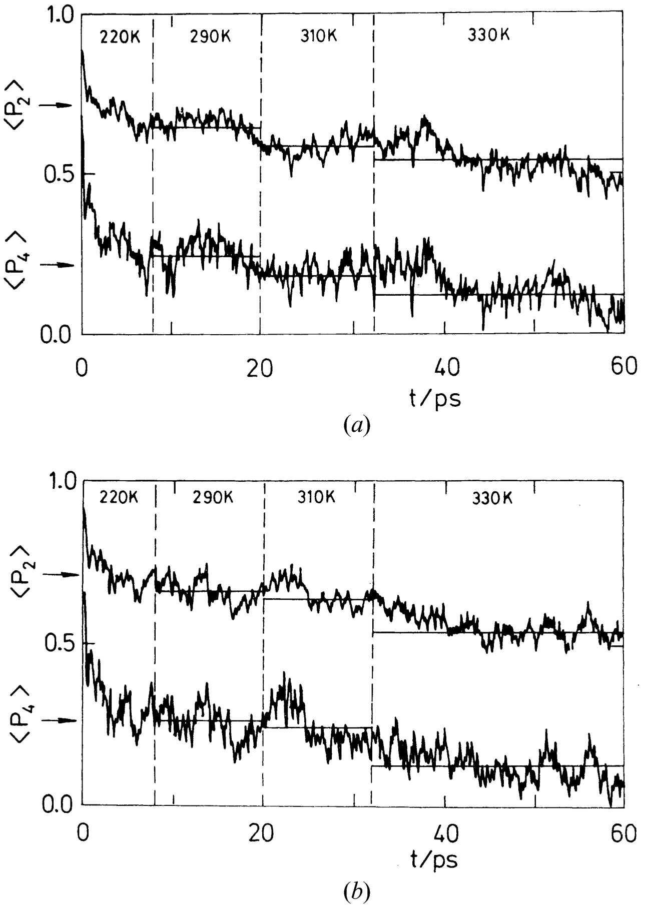
where the summation is performed by dividing the interval [0, $\pi/2$] into segments of width $\Delta\beta$, and use is made of the axial symmetry of the nematic phase;

$$\zeta_{\Delta\beta}(\pi-\beta)=\zeta_{\Delta\beta}(\beta).$$

In figure 5 the orientational distribution functions are shown averaged over 32–56 ps and in figure 6 the order parameters $<P_2(\cos\beta)>$ and $<P_4(\cos\beta)>$ are given as a function of time. During the simulations the reference temperature T_{ref} was increased at the indicated intervals (see figure 6). The orientational distribution function for the charged system is clearly slightly broader compared to that of the uncharged system. However no large differences in $<P_2(\cos\beta)>$ and $<P_4(\cos\beta)>$ are apparent from figure 6 comparing the two simulations. To test if $<P_4(\cos\beta)>$ is affected by the presence of a molecular charge distribution we also show $<P_4(\cos\beta)>$ versus $<P_2(\cos\beta)>$ in figure 7. The black cloud of the simulated results for $<P_4(\cos\beta)>$ versus $<P_2(\cos\beta)>$ for the charged system is steeper than for the uncharged system. This indicates that the inclusion of a molecular charge distribution tends to decrease the value of $<P_4(\cos\beta)>$ for a given value of $<P_4(\cos\beta)>$. From figure 7 we also find that the agreement with the experimental values [5] is improved if the molecular charge distribution is included in the calculation.

To be certain that the simulated systems are nematic it is necessary to calculate smectic order parameters. The smectic order parameter τ_k is defined by

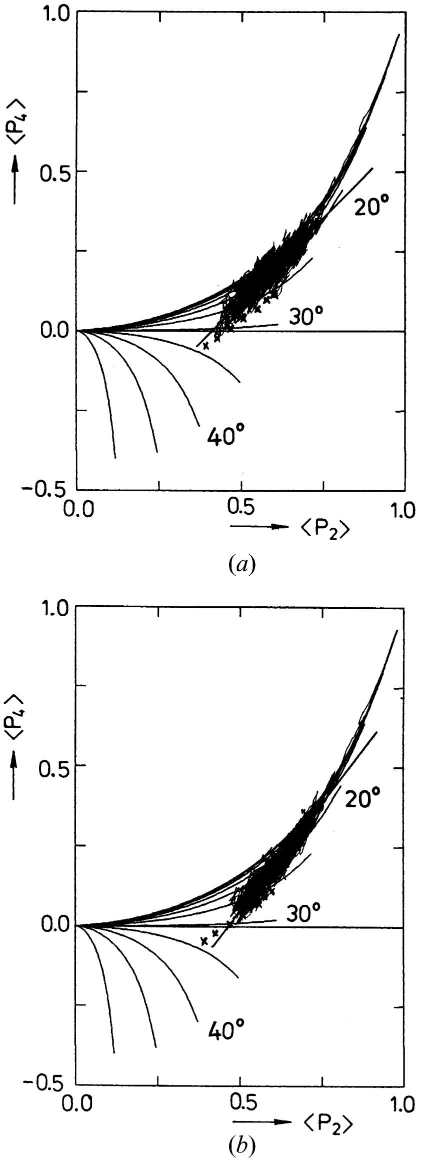
$$\tau_k=\langle\cos(\mathbf{k}\cdot\mathbf{r})\rangle, \qquad (12)$$



(a)

(b)

Figure 6. The calculated results for $<P_2(\cos\beta)>$ and $<P_4(\cos\beta)>$ as a function of time for the uncharged (a) and the charged (b) system. The temperature is increased at the boundaries of the intervals, as indicated.



(a)

(b)

Figure 7. The calculated $<P_4(\cos\beta)>$ versus $<P_2(\cos\beta)>$ curves (the black clouds) for the two simulations without (a) and with (b) a molecular charge distribution. The straight lines indicate the average slope of $<P_4(\cos\beta)>$ versus $<P_2(\cos\beta)>$. The curves are from the model described in the Introduction. The measured values for 5CB are indicated by the crosses.

where **k** is the reciprocal lattice vector along the director **n**

$$\mathbf{k} = \frac{2\pi}{\mathbf{r}_s} \tag{13}$$

and where $\mathbf{r}_s$ is the layer spacing to be considered. In a system of molecules of length l, smectic order parameters corresponding to lengths l, $1.4l$ and $2l$ appear to be relevant. These are associated with the various types of smectic A phase: S_A, S_{Ad}, and S_{A2}. The length of $1.4l$ corresponds to the length of a dimer compared to the length of an individual molecule in the case of 5CB. This was estimated using space filling molecular models and assuming complete overlap of the aromatic cyanobiphenyl groups. The evaluation of τ_k using this equation gives rise to a rather fundamental problem in that the origin of the layer coordinates is not known. Thus an unknown phase factor in $\mathbf{k}\cdot\mathbf{r}$ has to be dealt with. This is readily done by evaluating the average

$$\tau_k = \|\langle \exp(i\mathbf{k}\cdot\mathbf{r})\rangle\|, \tag{14}$$

where $\|$ indicates the norm of a complex number. If the origin of **r** is centred on a layer, expressions (12) and (14) for τ_k yield the same result. The latter expression however is independent of an overall translation of **r**. The various smectic order parameters for the charged and uncharged systems are all found to be very small ($\leqslant 0.1$) and show an erratic behaviour as a function of time. In the simulations the axial ratio of the box is the same as that of the individual molecules; the box is approximately four molecules long. The effect of the periodic boundary conditions could be to increase the smectic order parameters (at least for l and $2l$). The observation that the smectic order parameters are small then gives confidence that the simulated systems are indeed nematic,

Diffusion constants $D_i(i=x,\ y,\ z)$ can be obtained from the Einstein relation

$$D_i=\lim_{t\to\infty}\frac{1}{2t}\langle(r_i(t)-r_i(0))^2\rangle. \qquad (15)$$

The slope of a graph of $<(r_i(t)-r_i(0))^2>$ versus t is then approximately $2D_i$. Any jumps in the position of a particle due to the periodic boundary conditions were accounted for in the evaluation of $<(r_i(t)-r_i(0))^2>$. The diffusion constants are shown in table 4; the values in the perpendicular direction are averages over x and y, as in the simulation no cylindrical symmetry is reached. These results can be compared to the values from a molecular dynamics simulation of simple Lennard-Jones ellipsoids as described in ref [2] and to the experimental values from NMR spectroscopy [15]. It is observed that the agreement with experiment is not very impressive; ellipsoidal particles diffuse too fast. This situation is slightly improved by the inclusion of atomic details in the particles. We also observe that the inclusion of the molecular charge distribution tends to reduce the anisotropy of the calculated diffusion constants. It should be noted that the accuracy of the diffusion constants is very poor (errors of at least 50 per cent). The results shown in table 4 should be considered as only estimates. Even if much longer simulations on larger and better equilibrated systems are performed, the results are still expected to be unsatisfactory. The anomalous temperature dependence of $D_{\|}$ is probably caused by the decrease of $<P_2(\cos\beta)>$ with increasing temperature. In conclusion we have shown that it is possible to use molecular dynamics for the simulation of real liquid crystals where all molecular degrees of freedom are included. This allows a detailed study of the influence of the molecular structure on the physical properties of these materials. The molecular dynamics method provides the unique possibility to evaluate various aspects of a molecular model by switching specific interactions on or off. The simulations described here tentatively show that the presence of a molecular charge distribution indeed reduces the value of the order parameter $<P_4(\cos\beta)>$, for a given value of $<P_2(\cos\beta)>$. This is in agreement with experimental results.

The main limitation for the use of the molecular dynamics method is the rather large computational effort required for even a relatively small number of particles. In this respect we feel that the present results should be treated with some caution until a similar simulation with a larger number of molecules has been done. Moreover, to obtain quantitative results on order parameters, much longer simulations should be performed than was possible at the time this work was carried out. Of course the ever increasing power of super-computers and the planned construction of dedicated molecular dynamics machines is steadily reducing the computation time. We feel that the method is not (yet) suitable as a standard tool for the investigation of liquid crystals, but should be used to study specific problems that have not yielded to more traditional methods of research. Future molecular dynamics simulations could address a variety of interesting problems such as the structure of disc-like liquid crystal phases and of polymer liquid crystals. Also the influence of the flexible alkyl chains on the type(s) of phase(s) could be studied at a molecular level.

Acknowledgement

This work was performed while the first and last author were at the Solid State Physics Laboratory of the University of Groningen. The authors would like to thank Professor J. Kommandeur for suggesting the use of the molecular dynamics method for the study

Table 4. The experimental and calculated diffusion constants along (‖) and perpendicular (⊥) to the director **n**.

	$D_{\|}$/cm^2 s^{-1}		$D_{\perp}$/cm^2 s^{-1}	
T/K	Uncharged	Charged	Uncharged	Charged
220	4.3×10^{-5}	4.0×10^{-5}	1.9×10^{-5}	1.3×10^{-5}
290	3.3×10^{-5}	2.5×10^{-5}	1.8×10^{-5}	1.4×10^{-5}
310	1.8×10^{-5}	2.1×10^{-5}	0.9×10^{-5}	2.4×10^{-5}
330	2.6×10^{-5}	1.1×10^{-5}	1.9×10^{-5}	1.0×10^{-5}
MD ellipsoidal Lennard-Jones [2] T=300 K	18×10^{-5}		4.5×10^{-5}	
Experimental value N.M.R. [15] T=296.5 K	5.3×10^{-7}		4.1×10^{-7}	

of liquid crystals. This work is part of the research program of the Stitchting voor Fundamentel Onderzoek der Materie (Foundation for the Fundamental Research on Matter, FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research, NWO).

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