Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Computer simulation of chiral liquid crystal phases VI. A temperature induced helix inversion in a single component cholesteric liquid crystal

R. Memmer; F. Janssen

To cite this Article Memmer, R. and Janssen, F.(1998) 'Computer simulation of chiral liquid crystal phases VI. A temperature induced helix inversion in a single component cholesteric liquid crystal', Liquid Crystals, 24: 6, 805 — 809
To link to this Article: DOI: 10.1080/026782998206614
URL: http://dx.doi.org/10.1080/026782998206614

LIQUID CRYSTALS, 1998, VOL. 24, NO. 6, 805–809

Computer simulation of chiral liquid crystal phases
VI. A temperature induced helix inversion in a single component cholesteric liquid crystal

by R. MEMMER* and F. JANSSEN
Fachbereich Chemie, Universität Kaiserslautern, D-67663 Kaiserslautern, Germany

(*Received 21 October 1997; accepted 8 January 1998*)

A temperature induced helix inversion in a single component system has been observed by investigating a lattice system of chiral molecules using Monte Carlo (MC) computer simulations. The molecules were considered to interact as derived by van der Meer *et al.* taking into account fourth-order terms describing an anharmonic interaction. On cooling from an isotropic system, a cholesteric phase with a temperature dependent pitch was obtained. The cholesteric phase changed its handedness through an infinite-pitch system as a function of temperature. The study of systems with a small chiral energy contribution and a large pitch was enabled using self-determined boundary conditions.

1. Introduction

The cholesteric phase is characterized by its pitch and handedness [1]. It is well known that enantiomers produce cholesteric phases with opposite handedness and that the pitch of a cholesteric phase varies with temperature. The phenomenon of a helix inversion induced by temperature variation has attracted much attention from its discovery up to the present day. It was found more often in binary systems, e.g. in compensated cholesteric phases [2], in mixtures of a nematic and a cholesteric liquid crystal [3] or in induced cholesteric phases formed by chiral dopants dissolved in a nematic phase [4], but also in single component cholesteric liquid crystals [5, 6]. For an explanation of helix inversion in single component cholesteric liquid crystals there is often invoked a conformation mechanism, i.e. a temperature dependent equilibrium between conformers with opposite contributions to the macroscopic twist (see, e.g. [7]) or opposite effects with different temperature dependences for each individual chiral element of a molecule [8].

Theoretical predictions for the temperature dependence of the pitch, in part including the helix inversion, have also been obtained from molecular statistical theories for cholesteric liquid crystals [9, 17]. Based on the electric multipole expansion, van der Meer *et al.* [11] derived an interaction potential between cylindrically symmetric chiral molecules

$$V_{ij} = -J(\hat{\mathbf{u}}_i\ \hat{\mathbf{u}}_j)^2 - K[(\hat{\mathbf{u}}_i \times \hat{\mathbf{u}}_j)\ \hat{\mathbf{r}}_{ij}](\hat{\mathbf{u}}_i\ \hat{\mathbf{u}}_j) - L(\hat{\mathbf{u}}_i\ \hat{\mathbf{u}}_j)^4 - M[(\hat{\mathbf{u}}_i \times \hat{\mathbf{u}}_j)\ \hat{\mathbf{r}}_{ij}](\hat{\mathbf{u}}_i\ \hat{\mathbf{u}}_j)^3 \qquad (1)$$

where $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ are the unit vectors along the symmetry axes of molecules i and j. $\hat{\mathbf{r}}_{ij}$ is a unit vector pointing from the centre of mass of molecule i to the centre of mass of molecule j. The parameters J, K, L, and M depend on the intermolecular separation and can be treated following van der Meer *et al.* [11] as phenomenological parameters in an expansion of V_{ij} in terms of the angles between $\hat{\mathbf{u}}_i$, $\hat{\mathbf{u}}_j$, and $\hat{\mathbf{r}}_{ij}$. For positive values of the scalar quantities J and L the corresponding terms favour the parallel alignment of molecules as preferred in a nematic phase. The terms corresponding to the pseudoscalar quantities K and M, which are zero if the molecules are achiral, favour the twisted orientation of the molecules. In the mean field approximation [11], a temperature dependence of the pitch results as determined by the ratio of the order parameters $\langle P_4 \rangle$ and $\langle P_2 \rangle$. The corresponding wave vector is given by

$$|\mathbf{q}| = \frac{1}{R}\left[\frac{7K + 3M + 4M(\langle P_4 \rangle / \langle P_2 \rangle)^2}{4J + 12L + 16L(\langle P_4 \rangle / \langle P_2 \rangle)^2}\right] \qquad (2)$$

where R denotes the mean intermolecular distance.

Computer simulations represent a powerful method for the investigation of model liquid crystals [18]. A restriction to small system sizes can be avoided by studying lattice models, e.g. the nematic–isotropic

---

*Author for correspondence.

transition has often been studied using the Lebwohl–Lasher model [19], which is the lattice version of the Maier–Saupe model [20]. Recently, lattice systems of chiral molecules with interactions given by equation (1) have been studied, having for simplicity orientations confined to two dimensions only. Cholesteric phases with temperature independent pitch have been obtained by Luckhurst *et al.* using only the second order terms [21], whereas a temperature dependent pitch resulted by additionally taking into account fourth-order terms [22].

In the following account a computer simulation study of the phenomenon of a temperature induced helix inversion will be presented for a system of such chiral molecules.

2. Model system

The centres of the molecules are fixed on the sites of a three-dimensional simple cubic lattice with l layers. Molecular orientations are confined to be orthogonal to a selected axis chosen as the z axis, i.e. represented by unit vectors $\hat{\mathbf{u}}_i = (u_{ix}, u_{iy}, 0)$. Only nearest neighbour interactions are taken into account, i.e. each particle interacts with its four horizontal neighbours in the same plane parallel to the xy plane and its two vertical neighbours along the z direction. For this study, a parametrization was chosen which should be favourable for a temperature induced helix inversion according to the qualitative discussion in [13]. The orientational dependence of the potential $V_{ij}^* = V_{ij}/J$ on the angle α_{ij} between the unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ shows a minimum shifted to a finite angle close to the origin and an anharmonicity on the other side as the shift for the chosen values $K/J = 2$, $L/J = 1$ and $M/J = -2{\cdot}5$ of the phenomenological parameters (figure 1).

3. Computational details

We have studied the system for the lattice sizes $8 \times 8 \times 8$ and $16 \times 16 \times 16$ using the standard Metropolis Monte Carlo technique [23, 24]. Self-determined boundary conditions have been applied in order to study the equilibrium pitch: in the x and the y directions periodic boundary conditions have been used, whereas the surrounding images of the central simulation box in the z direction have been obtained by a translation followed by a rotation of all molecular orientations around the z axis with a twist angle Φ. A collective Monte Carlo trial was used to modify this twist angle during the simulation and to enable the system to select a suitable value, i.e. to choose its own boundary conditions along the z axis, as a function of variables such as temperature or chirality parameters. Both the algorithm introduced by Saslow *et al.* [25] and the modified algorithm developed in [22] have been used.

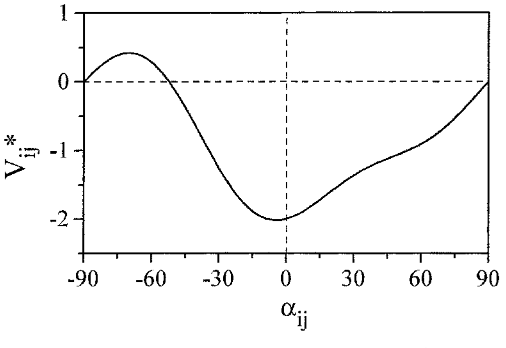

Figure 1. The orientational dependence of V_{ij}^* on the angle α_{ij} between the unit vectors $\hat{\mathbf{u}}_i$ and $\hat{\mathbf{u}}_j$ for $K/J = 2$, $L/J = 1$, $M/J = -2{\cdot}5$.

For each system size all runs were started from an initial configuration with orientations randomly distributed parallel to the xy plane using an initial twist angle $\Phi = 0°$, i.e. periodic boundary conditions. The system size $8 \times 8 \times 8$ was studied using the spiralling algorithm. An equilibration run of 80 000 cycles was followed by a production run of the same length. Additionally, the larger lattice size $16 \times 16 \times 16$ was studied using the modified algorithm [22] in order to check the results. Both the equilibration and the production run were made over a period of 40 000 cycles. For the calculation of the errors in the calculated observables the simulations were divided into trajectory segments of 1000 cycles.

The scaled temperature $T^* = k_B T/J$ and scaled energy per particle

$$\langle U^*\rangle = \langle U\rangle/(NJ) = \langle U_J^*\rangle + \langle U_K^*\rangle + \langle U_L^*\rangle + \langle U_M^*\rangle \tag{3}$$

are used, where N denotes the number of particles. For the interaction between particles with orientations confined to two dimensions the contributions are defined by

$$\langle U_J^*\rangle = -J/(NJ)\langle \cos^2 \alpha_{ij}\rangle \tag{4}$$

$$\langle U_K^*\rangle = -K/(NJ)\langle r_{ijz} \cos \alpha_{ij} \sin \alpha_{ij}\rangle \tag{5}$$

$$\langle U_L^*\rangle = -L/(NJ)\langle \cos^4 \alpha_{ij}\rangle \tag{6}$$

and

$$\langle U_M^*\rangle = -M/(NJ)\langle r_{ijz} \cos^3 \alpha_{ij} \sin \alpha_{ij}\rangle \tag{7}$$

where r_{ijz} denotes the z coordinate of $\hat{\mathbf{r}}_{ij}$. The scaled heat capacity at constant volume $C_V^* = C_V/k_B$, where k_B denotes the Boltzmann constant, was calculated from fluctuations in the energy. Additionally, for each layer l along the z axis the second and fourth rank orientational order parameters

$$\langle P_m\rangle_l = \langle P_m(\hat{\mathbf{u}}_i\, \hat{\mathbf{n}}_l)\rangle, \qquad m = 2, 4 \tag{8}$$

were calculated, where P_m is the Legendre polynomial of rank m. $\hat{\mathbf{n}}_l$ denotes the director of the layer l, defined as the eigenvector corresponding to the largest eigenvalue of the second rank ordering tensor with coordinates

$$Q^{(l)}_{\alpha\beta} = \frac{1}{N_l}\sum u_{i\alpha}u_{i\beta} \tag{9}$$

where $\alpha, \beta = x, y, z$ and the summation is restricted to all N_l molecules of layer l. The order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ of the system are defined as averages over all layers of the corresponding quantities $\langle P_m\rangle_l$. The average $\langle \Delta\alpha\rangle$ of the angles $\Delta\alpha_{l,l+1} = \angle \hat{\mathbf{n}}_l, \hat{\mathbf{n}}_{l+1}$ between the local directors of two neighbouring layers l and $l+1$ defines the helical wave vector $|\mathbf{q}|$. The pitch p of the cholesteric phase is given by $p = 2\pi/\langle \Delta\alpha\rangle$ in numbers of layers necessary for a rotation of 2π of the local director around the helical axis.

4. Results

The scaled energy $\langle U^*\rangle$ varies continuously with temperature (figure 2) and has a changing curvature indicating a phase transition. It is remarkable that the energy contributions $\langle U^*_K\rangle$ and $\langle U^*_M\rangle$, which are zero for achiral molecules, are very small compared with $\langle U^*_J\rangle$ and $\langle U^*_L\rangle$. The signs of $\langle U^*_K\rangle$ and $\langle U^*_M\rangle$ are different and change as a function of temperature. An approximate value for the phase transition temperature $T^* \approx 2{\cdot}20$ is obtained from the maximum of the heat capacity C^*_V for the smaller system (figure 3). An asymmetric heat capacity peak which is much steeper for temperatures above the phase transition and a size dependent effect with higher values of C^*_V in the larger system are obvious. On cooling, the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ increase rapidly in the phase transition region indicating a phase transition from a disordered to an ordered phase (figure 4). Both parameters vary continuously over the whole temperature range. Especially in the temperature range of the disordered phase, a strong size dependence is obvious. In the larger sample $\langle P_2\rangle$ and $\langle P_4\rangle$ become closer to their minimum values in a system with orientations randomly distributed parallel to a plane.

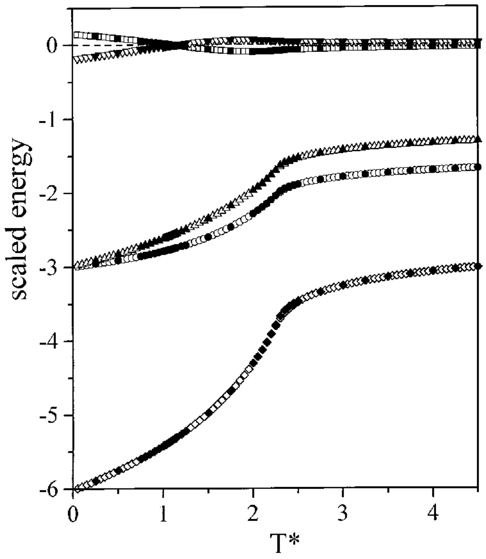

Figure 2. The scaled energy $\langle U^*\rangle$ (diamonds) and its contributions $\langle U^*_J\rangle$ (circles), $\langle U^*_K\rangle$ (squares), $\langle U^*_L\rangle$ (triangles) and $\langle U^*_M\rangle$ (inverted triangles) as a function of the temperature T^* for lattice sizes $8\times8\times8$ (open symbols) and $16\times16\times16$ (full symbols).

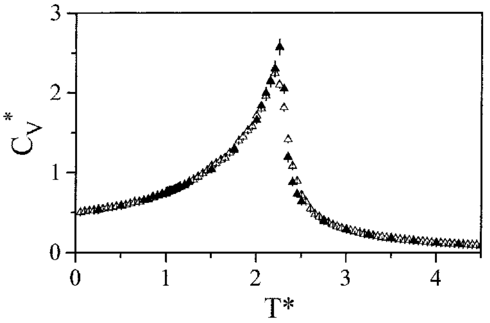

Figure 3. The heat capacity C^*_V as a function of the temperature T^* for lattice sizes $8\times8\times8$ (open symbols) and $16\times16\times16$ (full symbols).

For the temperature range below the phase transition, the average angle $\langle \Delta\alpha\rangle$ between the local directors of two neighbouring layers l and $l+1$ was calculated to give further insight into the characteristics of the ordered state. The values of $\langle \Delta\alpha\rangle$, i.e. the inverse pitch, obtained were in good agreement for both system sizes, showing that the self-determined boundary conditions enabled the determination of the equilibrium pitch independent of the system size (figure 5). At the phase transition temperature, $\langle \Delta\alpha\rangle$ has its maximum value and on cooling it decreases continuously to zero and even changes its sign at a temperature estimated to be $T^* \approx 1{\cdot}055$. Only a first crude comparison with the mean-field result [11]

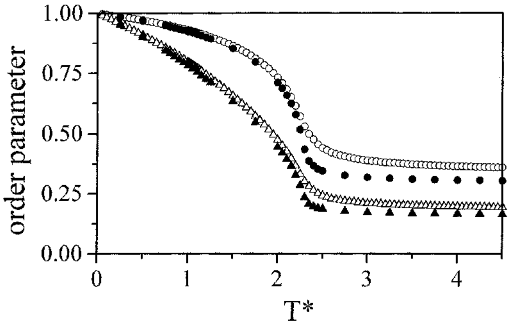

Figure 4. The second and fourth rank order parameters $\langle P_2\rangle$ (circles) and $\langle P_4\rangle$ (triangles) as a function of the temperature T^* for lattice sizes $8\times8\times8$ (open symbols) and $16\times16\times16$ (full symbols).

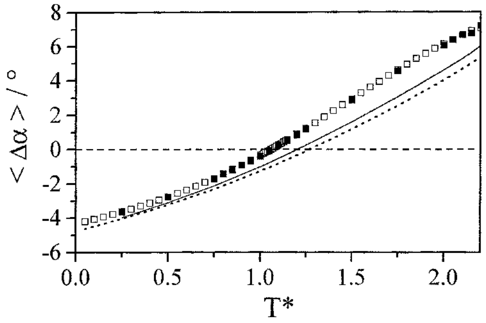

Figure 5. $\langle\Delta\alpha\rangle$ in the temperature range of the cholesteric phase for lattice sizes $8\times8\times8$ (open symbols) and $16\times16\times16$ (full symbols). The lines correspond to equation (2), calculated with $R=1$ and the order parameters obtained in the simulation for lattice sizes $8\times8\times8$ (dotted) and $16\times16\times16$ (solid).

is possible, since in the simulation only orientations confined to two dimensions were used. A similar qualitative behaviour, but a higher inversion temperature, is obtained using equation (2), in spite of the differences (figure 5). The corresponding pitch has its smallest value close to the phase transition temperature and increases on further cooling until a divergence appears (figure 6). At the inversion temperature the helical structure changes its handedness from right-handed to left-handed, and below the inversion temperature the pitch decreases.

5. Conclusions

A three-dimensional lattice system of chiral molecules with orientations confined to two dimensions was investigated as a function of temperature. The anisotropic interactions between the chiral molecules were described in the form derived by van der Meet *et al.* [11] taking into account fourth-order terms. The MC studies of this model system show a phase transition from a disordered to a cholesteric phase with a temperature dependent pitch. The pitch was found not to be influenced by sample size effects, i.e. the chosen self-determined boundary conditions [22, 25] enabled the formation of equilibrium helical structures even for small incommensurate systems. A system with a very large pitch could be studied. Even a small chiral energy contribution was sufficient for the formation of a cholesteric phase, e.g. in comparison with the cholesteric phases investigated in [21, 22, 26]. This has also been used for the study of an induced cholesteric phase and the determination of the helical twisting power [27]. For the parameters of the interaction potential studied, the pitch was found to increase on lowering the temperature until a divergence, i.e. an infinite-pitch system, occurred. It has been shown that, by taking into account the fourth-order terms in the interaction potential, anharmonic interactions between rigid chiral molecules as specified here are sufficient to obtain a helix inversion in a single component cholesteric phase at a certain temperature, a behaviour in agreement with the predictions in the mean-field approximation [11]. At this inversion temperature there is no suggestion of a first-order phase transition between cholesterics of opposite handedness as discussed by Zakhlevnykh and Shliomis [16]. A further study involving unconfined orientations is being conducted to investigate the influence of local phase biaxiality with respect to this behaviour.

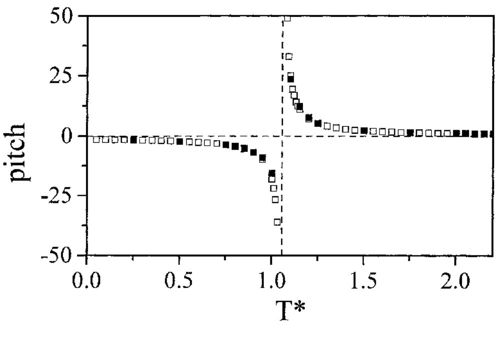

Figure 6. The pitch p in the temperature range of the cholesteric phase for lattice sizes $8\times8\times8$ (open symbols) and $16\times16\times16$ (full symbols).

Generous allocation of computer time by the Regionales Hochschulrechenzentrum Kaiserslautern and the Höchstleistungsrechenzentrum Jülich, and financial support from the Deutsche Forschungsgemeinschaft are gratefully acknowledged.

References

[1] Friedel, G., 1922, *Ann. Phys. (Paris)*, **18,** 273.
[2] Sackmann, E., Meiboom, S., and Snyder, L. C., 1967, *J. Am. chem. Soc.*, **89,** 5981.
[3] Finkelmann, H., and Stegemeyer, H., 1973, *Z. Naturforsch.*, **28a,** 799.
[4] Heppke, G., Lötzsch, D., and Oestreicher, F., 1987, *Z. Naturforsch.*, **42a,** 279.
[5] Slaney, A. J., Nishiyama, I., Styring, P., and Goodby, J. W., 1992, *J. mater. Chem.*, **2,** 805.
[6] Dierking, I., Gießelmann, F., Zugenmaier, P., Mohr, K., Zaschke, H., and Kuczynski, W., 1994, *Z. Naturforsch.*, **49a,** 1081.
[7] Lisetskii, L. N., and Gerasimov, A. A., 1987, *Zh. fiz. Khim.*, **61,** 2832 (1987, *Russ. J. phys. Chem.*, **61,** 1491).
[8] Stegemeyer, H., Siemensmeyer, K., Sucrow, W., and Appel, L., 1989, *Z. Naturforsch.*, **44a,** 1127.
[9] Keating, P. N., 1969, *Mol. Cryst. liq. Cryst.*, **8,** 315.
[10] Goossens, W. J. A., 1970, *Phys. Lett.*, **31A,** 413.
[11] Van der Meer, B. W., Vertogen, G., Dekker, A. J., and Ypma, J. G. J., 1976, *J. chem. Phys.*, **65,** 3935.
[12] Van der Meer, B. W., and Vertogen, G., 1976, *Phys. Lett.*, **59A,** 279.
[13] Lin-Liu, Y. R., Shih, Y. M., Woo, C.-W., and Tan, H. T., 1976, *Phys. Rev. A*, **14,** 445.
[14] Lin-Liu, Y. R., Shih, Y. M., and Woo, C.-W., 1977, *Phys. Rev. A*, **15,** 2550.

[15] Kimura, H., Hosino, M., and Nakano, H., 1979, *J. Phys. C3*, **4,** 174.

[16] Zakhlevnykh, A. N., and Shliomis, M. I., 1984, *Zh. eksp. teor. Fiz.*, **86,** 1309 (1984, *Sov. Phys. JETP*, **59,** 764).

[17] Varichon, L., Ten Bosch, A., and Sixou, P., 1991, *Liq. Cryst.*, **9,** 701.

[18] Pelcovits, R. A., 1997, *Handbook of Liquid Crystal Research*, edited by P. J. Collings and J. S. Patel (Oxford: Oxford University Press), Chap. 3, pp. 71–98.

[19] Lebwohl, P. A., and Lasher, G., 1972, *Phys. Rev. A*, **6,** 426.

[20] Maier, W., and Saupe, A., 1958, *Z. Naturforsch.*, **13A,** 564.

[21] Luckhurst, G. R., Romano, S., and Zewdie, H. B., 1996, *J. chem. Soc., Faraday Trans.*, **92,** 1781.

[22] Memmer, R., and Janssen, F., 1998, *J. chem. Soc., Faraday Trans.*, **94,** 267.

[23] Allen, M. P., and Tildesley, D. J., 1987, *Computer Simulation of Liquids* (Oxford: Clarendon Press).

[24] Frenkel, D., and Smit, B., 1996, *Understanding Molecular Simulation* (San Diego: Academic Press).

[25] Saslow, W. M., Gabay, M., and Zhang, W.-M., 1992, *Phys. Rev. Lett.*, **68,** 3627.

[26] Memmer, R., Kuball, H.-G., and Schönhofer, A., 1993, *Liq. Cryst.*, **15,** 345.

[27] Memmer, R., and Janssen, F., 1998 (to be published).