Computer Simulation of Chiral Liquid Crystal Phases IX. Chiral Induction in Guest-host Systems – Calculation of the Helical Twisting Power

Reiner Memmer and Folkert Janssen

Fachbereich Chemie, Universität Kaiserslautern, D-67663 Kaiserslautern

Reprint requests to Dr. R. M.; E-mail: memmer@rhrk.uni-kl.de.

Z. Naturforsch. **54a,** 747–754 (2000); received October 29, 1999

Presented at the 27th Freiburger Arbeitstagung Flüssigkristalle, 25–27 March 1998, Freiburg, Germany

The chiral induction in liquid crystalline phases was studied by Monte Carlo simulation of the chiral Lebwohl-Lasher model. Binary guest-host systems composed of achiral and chiral molecules as well as of different chiral molecules were investigated in dependence on the composition. A cholesteric phase was induced by dissolving a small fraction of chiral molecules in a nematic phase. For dilute solutions the equilibrium pitch was found to be a linear function of the chiral dopant concentration. Independent of system size effects the application of self-determined boundary conditions enabled the determination of the symmetry adapted quantities for the chiral induction, the helical twisting power (HTP) and the achiral helical twisting power (AHTP). Additionally, a different orientational behaviour of enantiomeric dopants in the chiral surroundings of a cholesteric host phase has been determined.

Key words: Chirality; Liquid Crystals; Computer Simulation; Induced Cholesteric Phases; Helical Twisting Power.

1. Introduction

Chirality plays an important role in many areas of both living and inanimate nature whereas chiral objects occur on different dimensional scales [1]. Considering liquid crystal phases, a state of matter with long range orientational order, molecular chirality of the constituting mesogenic molecules leads to the manifestation of suprastructural chirality [2, 3], in form of characteristic helical superstructures in the arrangement of the molecules as e.g. in the cholesteric and different blue phases [4]. Helical superstructures in liquid crystal phases can also be induced by chiral dopants dissolved in achiral host phases, a process called chiral induction which maps the molecular chirality of the guest molecule to sign and size of the pitch. For instance, dissolving a chiral compound in a nematic phase induces a cholesteric phase, which is characterised by its pitch and handedness. Here, the derivative of the inverse pitch with respect to the mole fraction of the chiral dopant is a suitable pseudoscalar quantity for the tendency of the chiral guest molecule to twist the nematic phase [5]. In order to obtain also symmetry adapted quantitative measures for the chiral induction considering the change of the suprastructural chirality dissolving chiral dopants in a chiral phase, a generalised definition has been introduced [6]: The pseudoscalar helical twisting power

$$(\mathrm{HTP})_\mathrm{e} = \frac{1}{2}\left\{\left(\frac{\partial p^{-1}}{\partial x_\mathrm{e}}\right)_{x_\mathrm{e}=0} - \left(\frac{\partial p^{-1}}{\partial x_{\mathrm{e}^\dagger}}\right)_{x_{\mathrm{e}^\dagger}=0}\right\} \tag{1}$$

and the scalar achiral helical twisting power

$$(\mathrm{AHTP})_\mathrm{e} = \frac{1}{2}\left\{\left(\frac{\partial p^{-1}}{\partial x_\mathrm{e}}\right)_{x_\mathrm{e}=0} + \left(\frac{\partial p^{-1}}{\partial x_{\mathrm{e}^\dagger}}\right)_{x_{\mathrm{e}^\dagger}=0}\right\} \tag{2}$$

are given by difference and sum of derivatives of the inverse pitch, respectively, where $\mathrm{e}^\dagger$ denotes the enantiomer of e and x_e, $x_{\mathrm{e}^\dagger}$ are the corresponding mole fractions. The AHTP is zero for chiral molecules in an achiral host phase, where enantiomers dissolved under the same conditions induce chiral phases with opposite handedness, i.e.

$$\left(\frac{\partial p^{-1}}{\partial x_\mathrm{e}}\right)_{x_\mathrm{e}=0} = -\left(\frac{\partial p^{-1}}{\partial x_{\mathrm{e}^\dagger}}\right)_{x_{\mathrm{e}^\dagger}=0}. \tag{3}$$

In contrast, the AHTP is different from zero for an achiral or a chiral compound dissolved in a chiral phase. The determination and prediction of the helical twisting power of chiral dopants has been subject of many experimental and theoretical investigations already since the dis-

0932-0784 / 1200 / 0747-0001 $ 06.00

covery of the chiral induction. On the one hand, there is an intensive search for chiral dopants with high HTP due to the technological relevance of induced helical superstructures in the display technology [7, 8]. On the other hand, the knowledge of the structure-property relationship between molecular chirality and induced handedness would allow a straightforward determination of the absolute configuration of chiral compounds, which is of general importance, e.g. with regard to many pharmaceutical applications of chiral molecules [9, 10]. Recently, for selected molecules, e.g. helicenes and atropisomers, relations between the absolute configuration of the chiral dopant and the handedness of the induced cholesteric phase have been obtained from the calculation of the HTP by the surface chirality model of Ferrarini et al. [11]. But in general, relatively little is known about the link between chirality at the microscopic and the macroscopic level, i.e. about the connection between the molecular chirality and the suprastructural chirality of the phases, as recently pointed out by Lubensky et al. [12].

Investigations by means of computer simulation, e.g. the Monte Carlo (MC) and molecular dynamics (MD) method, allow to deduce a link between microscopic and macroscopic properties starting with model interactions between the particles [13]. A variety of model systems for single-component cholesteric phases has been studied, e.g. the chiral Gay-Berne fluid [14, 15] and systems composed of rigid, chiral Gay-Berne atropisomers [16, 17]. Recently, extensions of the Lebwohl-Lasher model, the lattice version of the Maier-Saupe model [18], to single-component systems of chiral molecules have also been investigated [19–22]. Here, self-determined boundary conditions enabled the determination of the equilibrium pitch of cholesteric phases in dependence on temperature and chirality parameter whereas even a helix inversion has been observed. Chiral induction in liquid crystals has been studied in guest-host systems of rigid chiral Gay-Berne atropisomers and achiral flexible rotamers, where a chirality transfer could be proven by an induced excess of chiral dopant conformers [23], and in a nematic phase in contact with a chiral surface [24]. By means of computer simulation the HTP has been determined only for chiral dimers formed from uniaxial hard ellipsoids measuring the difference in chemical potentials of right- and left-handed dopants in a twisted nematic phase of achiral molecules stabilised by twisted boundary conditions [25]. Due to equilibrium pitch values typically in the order of several hundred molecular diameters the determination of the HTP from a direct simulation of induced cholesteric phases would require far larger than accessible system sizes using periodic boundary conditions, where the pitch must be commensurate with the simulation box length [26]. In the following, binary lattice systems will be studied under self-determined boundary conditions in order to investigate the chiral induction in liquid crystal phases dissolving a small fraction of guest molecules in a host phase. Of central interest are the characterisation of the structural properties of the phases, especially the pitch and the order parameters, in dependence on the concentration of the dopants.

2. Model System and Computational Details

An arbitrary intermolecular interaction potential $V(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij})$ between two cylindrically symmetric molecules i and j, separated by an intermolecular vector $\boldsymbol{R}_{ij}$ and with orientations specified by the unit vectors $\boldsymbol{u}_i$ and $\boldsymbol{u}_j$ along the symmetry axes, can be expanded in rotational invariants $T^{\ell L\lambda}(\boldsymbol{u}_i, \boldsymbol{r}_{ij}, \boldsymbol{u}_j)$, see e.g. [27],

$$V(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij}) = \sum_{\ell, L, \lambda=0}^{\infty} J^{\ell L\lambda}(r_{ij})\, T^{\ell L\lambda}(\boldsymbol{u}_i, \boldsymbol{r}_{ij}, \boldsymbol{u}_j)\,, \quad (4)$$

where the summation runs through all integer ℓ, L and λ with $|\ell-\lambda| \le L \le \ell+\lambda$. Here $\boldsymbol{r}_{ij}$ denotes the unit vector parallel to $\boldsymbol{R}_{ij}$ and $r_{ij}=|\boldsymbol{R}_{ij}|$. The total intermolecular interaction potential $V(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij})$ can be decomposed into two parts,

$$V(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij}) = V_a(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij}) + V_c(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij})\,, \quad (5)$$

the energy of the achiral interaction $V_a(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij})$ including all terms with scalar rotational invariants, i.e. $\ell+L+\lambda$ odd, and the energy of the chiral interaction $V_c(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij})$ including all terms with pseudoscalar rotational invariants, i.e. $\ell+L+\lambda$ even. The potential can be reduced to

$$V(\boldsymbol{u}_i, \boldsymbol{u}_j, \boldsymbol{R}_{ij}) = -J_{ij}(\boldsymbol{u}_i \cdot \boldsymbol{u}_j)^2 - K_{ij}[(\boldsymbol{u}_i \times \boldsymbol{u}_j) \cdot \boldsymbol{r}_{ij}]\,(\boldsymbol{u}_i \cdot \boldsymbol{u}_j)\,, \quad (6)$$

taking into account each first term of the expansion only and the indistinguishability of director states $\boldsymbol{n}$ and $-\boldsymbol{n}$ which discards all terms with ℓ and λ odd. The necessity of a scalar potential requires a scalar coefficient J_{ij} and a pseudoscalar coefficient K_{ij}, respectively, i.e. K_{ij} changes its sign if both interacting molecules are replaced by their mirror images, which yields K_{ij} equal to zero in the case of two interacting achiral or enantiomeric molecules.

Considering the achiral part only, this model potential has been used for the study of nematic phases in form of

the Lebwohl-Lasher lattice model, i.e. with molecular positions fixed to selected sites, where only nearest neighbour interactions are considered, see e.g. [28, 29] for recent investigations. Recently, its chiral extension denoted as chiral Lebwohl-Lasher model has been studied considering additionally the effective chiral potential given above, which has been obtained by van der Meer et al. [30] based on the electric multipole expansion for chiral molecules under the assumption of a cylindrically symmetric behaviour. The parameters J_{ij} and K_{ij} have been treated as phenomenological parameters measuring the strength of the corresponding interaction energies instead of considering particular models of intermolecular interaction necessary for the determination of their explicit form, e.g. the distance dependence. For positive values of the scalar quantity J_{ij} the corresponding term favours the parallel alignment of molecules as preferred in a nematic phase. The term corresponding to the pseudoscalar quantity K_{ij} favours a twisted orientation of molecules discriminating energetically between left- and right-handed arrangements.

The extension of these model systems to binary mixtures of achiral and chiral molecules necessitates the introduction of potentials between an achiral and a chiral molecule. As pointed out e.g. by Issaenko et al. [31] an effective chiral potential proportional to $[(\boldsymbol{u}_i \times \boldsymbol{u}_j) \cdot \boldsymbol{r}_{ij}]$ arises between two chiral molecules as well as between a chiral molecule and an achiral one, i.e. in binary systems the interactions between all pairs of molecules can be described by (6). In order to relate the phenomenological parameters for the interactions between molecules of different kind to those of the pure components, the corresponding mean value has been taken, which corresponds to the absence of chiral interactions between a pair of enantiomeric molecules e and e†, i.e. $K_{ee^\dagger} = 1/2\,(K_{ee} + K_{e^\dagger e^\dagger}) = 0$ using $K_{ee} = -K_{e^\dagger e^\dagger}$. For the study of the chiral induction, the binary guest-host systems summarised in Table 1 have been investigated, considering mixtures of achiral and chiral molecules as well as of different chiral molecules.

Systems of $N = l^3$ molecules with centres fixed on the sites of a three-dimensional simple cubic lattice with $l = 8$, 16, and 24 layers were studied using the standard Metropolis Monte Carlo technique. The molecular orientations are confined orthogonal to a selected axis chosen to be the z axis, i.e. represented by unit vectors $\boldsymbol{u}_i = (u_{ix}, u_{iy}, 0)$. Self-determined boundary conditions (see [21] for further details) have been applied in order to study the equilibrium properties in systems with periodic structures incommensurable to the system size: In the x and

Table 1. Investigated guest-host systems.

System	Host molecules	Guest molecules
I	achiral: A ($J_{AA} = +1$, $K_{AA} = 0$)	chiral: B ($J_{BB} = +1$, $K_{BB} = +1$)
I′	achiral: A ($J_{AA} = +1$, $K_{AA} = 0$)	chiral: B† ($J_{B'B'} = +1$, $K_{B'B'} = -1$)
II	chiral: B ($J_{BB} = +1$, $K_{BB} = +1$)	chiral: C ($J_{CC} = +1$, $K_{CC} = +0.5$)
II′	chiral: B ($J_{BB} = +1$, $K_{BB} = +1$)	chiral: C† ($J_{C'C'} = +1$, $K_{C'C'} = -0.5$)

the y direction 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 cycle consists of $N = l^3$ single molecule MC steps with a random rotation of an arbitrarily chosen molecule about the z axis followed by a collective MC trial where it was attempted to modify the twist angle Φ using the local twist algorithm introduced in [21].

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. For each composition, equilibration runs of 160 kc ($l = 8$), 80 kc ($l = 16$), and 40 kc ($l = 16$), respectively, were followed by production runs of the same length, where kc denotes 1000 cycles. All systems were studied at scaled temperature $T^* = k_B T / J_{AA} = 0.5$, i.e. as well in the nematic temperature range as in the cholesteric temperature range of single-component systems of achiral molecules A and chiral molecules B, respectively [21]. The scaled energy per particle is given by

$$\langle U^* \rangle = \langle U \rangle / (N J_{AA}) = \langle U_J^* \rangle + \langle U_K^* \rangle \tag{7}$$

with contributions considering orientations confined to two dimensions given by

$$\langle U_J^* \rangle = -\langle J_{ij} \cos^2 \alpha_{ij} \rangle / (N J_{AA}) \tag{8}$$

and

$$\langle U_K^* \rangle = -\langle K_{ij}\, r_{ijz} \cos \alpha_{ij} \sin \alpha_{ij} \rangle / (N J_{AA}) , \tag{9}$$

where r_{ijz} denotes the z coordinate of $\boldsymbol{r}_{ij}$ and α_{ij} the angle between the unit vectors $\boldsymbol{u}_i$ and $\boldsymbol{u}_j$. In order to characterise the long range orientational order, for each layer l along the z axis the local director $\boldsymbol{n}_l$ has been calculated, defined as the eigenvector corresponding to the largest eigenvalue of the total second rank ordering tensor with coordinates

$$Q_{\alpha\beta}^{(l)} = \frac{1}{N_l} \sum u_{i\alpha}\, u_{i\beta} , \tag{10}$$

whereas the summation is restricted to all N_l molecules of layer l and α, $\beta = x, y, z$, i.e. as in a study of binary mixtures of nematic liquid crystals [32] the director is taken as a common property of the guest-host system. The second rank orientational order parameters $\langle P_2 \rangle^\alpha$, α=G for guest and α=H for host molecules, respectively, have been obtained according to

$$\langle P_2 \rangle^\alpha = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} P_2 (\boldsymbol{u}_i \cdot \boldsymbol{n}_l), \tag{11}$$

i.e. calculating the average of the Legendre polynomial P_2 by a summation restricted to all N_α molecules of type α, taking into account for each molecule the appropriate local director $\boldsymbol{n}_l$. The pitch p of a 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, where $\langle \Delta\alpha \rangle$ denotes the average of the angles $\Delta\alpha_{l,l+1} = \angle \boldsymbol{n}_l, \boldsymbol{n}_{l+1}$ between the local directors of two neighboured layers l and $l+1$. The HTP and AHTP, as defined in (1) and (2), have been calculated in dilute solutions by least square fits to a straight line of the inverse pitch p^{-1} versus the mole fraction of dopant molecules.

3. Results and Discussion

3.1. Binary Systems of Achiral and Chiral Molecules

Binary guest-host systems composed of achiral and chiral molecules were studied in dependence on the composition in order to investigate the chiral induction in nematic liquid crystal phases. The guest-host system I composed of achiral molecules A ($J_{AA} = +1$, $K_{AA} = 0$) and chiral molecules B ($J_{BB} = +1$, $K_{BB} = +1$) was studied in a system of size $l = 8$ considering the whole composition range from $x_B^* = 0$ up to $x_B^* = 1$. Starting from an initial configuration with molecular orientations randomly distributed parallel to the xy plane a single-component system of achiral molecules A has been equilibrated at $T^* = 0.5$. Along this isotherm the mole fraction x_B^* of the chiral guest molecules B was increased step by step with a step size of $\Delta x_B^* = 0.0625$ replacing an appropriate number of arbitrarily chosen achiral host molecules A by guest molecules until a single-component system of chiral molecules B was obtained. In order to check the simulation, additionally a run starting with $x_B^* = 1$ decreasing the mole fraction of chiral guest molecules has been performed. The inverse pitch p^{-1} increases monotonously as a function of the mole fraction x_B^* whereas it shows a non-ideal behaviour (Figure 1). At $x_B^* = 0$ the inverse pitch is equal to zero within the statistical errors. Here, in the single-component system of achiral molecules, a nematic phase with an order parameter $\langle P_2 \rangle^H \approx 0.906$ has been formed. At $x_B^* = 1$, i.e. in the single-component system of chiral molecules, a cholesteric phase with an inverse pitch $p^{-1} = 0.0624 \pm 0.0001$, which is in good agreement with the theoretical value of $p^{-1} = 0.0625$ according to the relation

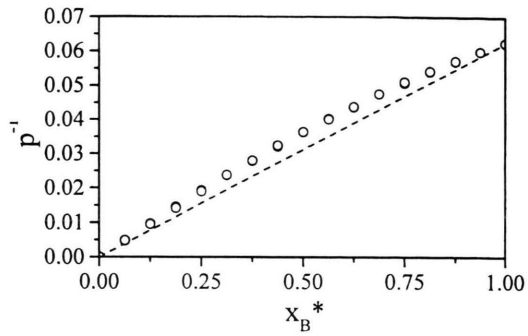

Fig. 1. The inverse pitch p^{-1} in the binary guest-host system I composed of achiral molecules A ($J_{AA} = +1$, $K_{AA} = 0$) and chiral molecules B ($J_{BB} = +1$, $K_{BB} = +1$) as a function of the mole fraction x_B^* for lattice size $l = 8$. The inverse pitch values in the single-component systems, a nematic phase at $x_B^* = 0$ and a cholesteric phase at $x_B^* = 1$, are connected by a dashed line. Results from simulation runs with increasing (○) and decreasing (●) mole fraction x_B^* are shown.

$$p^{-1} = \frac{1}{4\pi} \arctan \frac{K}{J} \tag{12}$$

recently given by Luckhurst et al. [19], has been formed as characterised previously in detail [21].

Already at $x_B^* = 0.0625$, the lowest concentration of chiral dopant molecules studied, a cholesteric phase was induced, which is obvious from the significant non-zero value of the inverse pitch and the visualisation of two selected layers chosen along the z axis of a configuration (Figure 2). Each molecule is represented by a cylinder along its molecular symmetry axis $\boldsymbol{u}_i$ whereas achiral host molecules and chiral guest molecules are coded black and white, respectively. In each layer l a preferred orientation of the molecular symmetry axes $\boldsymbol{u}_i$ parallel to the local director $\boldsymbol{n}_l$ is obvious. Small but significant is the right-handed rotation of the local director propagating along the helical axis. The application of self-determined boundary conditions enabled the formation of an induced cholesteric phase with a helical superstructure where about 200 layers of molecules are necessary for the formation of a segment of length p, a pitch value which would require an enormous system size using periodic

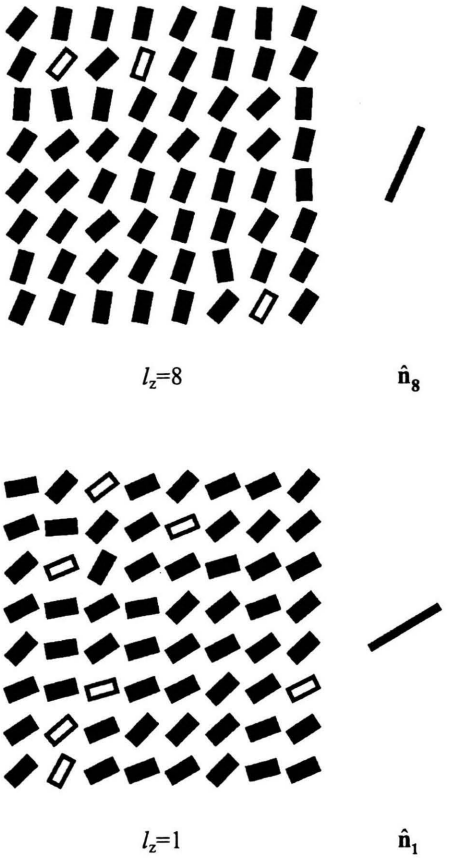

Fig. 2. Visualisation of the layers $l_z=1$ (below) and $l_z=8$ (above) of the induced cholesteric phase in the binary guest-host system I composed of achiral molecules A ($J_{AA}=+1$, $K_{AA}=0$, black) and chiral molecules B ($J_{BB}=+1$, $K_{BB}=+1$, white) at $x_B^*=0.0625$ for lattice size $l=8$.

boundary conditions in order to commensurate with the box size [26].

For the binary systems, the scaled energy per particle $\langle U^* \rangle$ and its achiral and chiral contributions $\langle U_J^* \rangle$ and $\langle U_K^* \rangle$ are shown in Fig. 3 as function of the mole fraction x_B^*. In a study of single-component systems of chiral Gay-Berne molecules under periodic boundary conditions a discontinuous behaviour of the chiral energy contribution indicated a threshold value of the chirality parameter necessary for the formation of a cholesteric phase [33]. Now, under self-determined boundary conditions already a small chiral energy contribution $\langle U_K^* \rangle$, which goes continuously to zero with decreasing mole fraction of chiral dopants, was sufficient for the induction of cholesteric phases. In agreement with experimental results where even mole fractions of the chiral dopant below 10^{-4} are

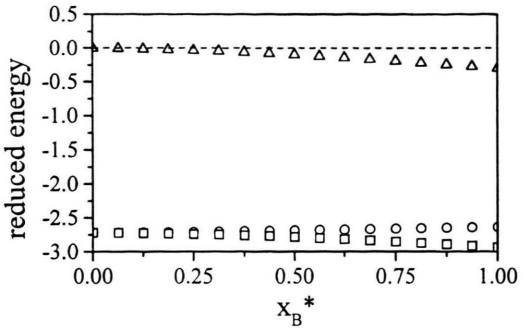

Fig. 3. The scaled energy per particle $\langle U^* \rangle$ (❑), the achiral contribution $\langle U_J^* \rangle$ (○) and the chiral contribution $\langle U_K^* \rangle$ (△) in the binary guest-host system I composed of achiral molecules A ($J_{AA}=+1$, $K_{AA}=0$) and chiral molecules B ($J_{BB}=+1$, $K_{BB}=+1$) as a function of the mole fraction x_B^* for lattice size $l=8$.

sufficient for the induction of macroscopically helical superstructures in nematic host phases [7], no hints for the existence of a threshold concentration are obvious, as experimentally proven e.g. for the induction of S_C^* phases [34].

For the determination of the HTP in the guest-host system I, dilute solutions given by a small amount of chiral dopants dissolved in an achiral host phase were studied in detail in the concentration range $0 \leq x_B^* \leq 0.125$. Different system sizes have been taken into account in order to prove the determination of the equilibrium pitch. Additionally, the corresponding guest-host system I′ composed of the same achiral molecules but enantiomeric chiral molecules was studied. In the diluted concentration range investigated, the inverse pitch was found in a very good approximation as linear function of the mole fraction (Fig. 4) as experimentally observed for many dilute solutions of chiral dopants in nematic phases, see e.g. [5]. No significant system size effects appear, which rather could be assigned to the usual findings of higher order parameters in simulations of smaller systems than to effects of the applied boundary conditions which in fact allow the determination of the equilibrium properties of systems with periodic superstructures incommensurable to the comparably small system sizes studied.

From the slope of the corresponding straight line fits, the determination of the HTP of the chiral guest molecules in the achiral host phase, defined as limiting value via (1), was enabled, which yields $(HTP)_B$ values in good agreement for the system sizes studied (Table 2). The consistency of the results obtained is additionally proofed by values for the AHTP of the chiral guest molecules in the nematic host phase equal to zero within the statisti-

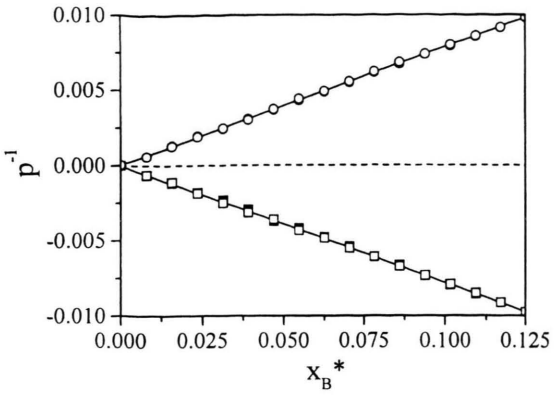

Fig. 4. The inverse pitch p^{-1} in the binary guest-host systems I (○) and I′ (❑) composed of achiral host molecules A ($J_{AA}=+1$, $K_{AA}=0$) and chiral guest molecules B ($J_{BB}=+1$, $K_{BB}=+1$) and the enantiomer $B^{\dagger}$ ($J_{BB}=+1$, $K_{BB}=-1$), respectively, as a function of the mole fraction x_B^* of the guest molecules for lattice sizes $l=16$ (full symbols) and $l=24$ (open symbols) in the concentration range $0\leq x_B^*\leq 0.125$. The solid lines correspond to linear fits for lattice size $l=24$.

Table 2. $(HTP)_B$ and $(AHTP)_A$ in guest-host system I of lattice size l.

l	$(HTP)_B$	$(AHTP)_A$
16	0.0783 ± 0.0003	-0.0439 ± 0.0003
24	0.0782 ± 0.0003	-0.0439 ± 0.0003

cal errors, as required by the induction of chiral phases with opposite handedness but identical size of the pitch by enantiomers dissolved under the same conditions in achiral host phases.

The suprastructural chirality can also be changed dissolving achiral dopants in a chiral host phase, see e.g. [35] for experimental results. For the determination of the corresponding quantitative measure, the AHTP, guest-host system I was additionally studied in the concentration range $0\leq x_A\leq 0.125$, i.e. with a small amount of achiral molecules A dissolved in a host phase of chiral molecules B. A linear decrease of the corresponding inverse pitch was discovered (Fig. 5) which yielded the $(AHTP)_A$ values of the achiral guest molecules A in the chiral host phase of molecules B given in Table 2, which were again not significantly dependent on the system size.

3.2. Binary Systems of Different Chiral Molecules

In order to investigate the change of the helical superstructure by chiral dopants in chiral surroundings, binary

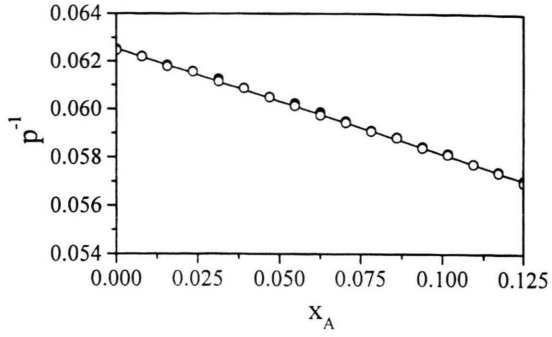

Fig. 5. The inverse pitch p^{-1} in the binary guest-host systems I composed of chiral host molecules B ($J_{BB}=+1$, $K_{BB}=+1$) and achiral guest molecules A ($J_{AA}=+1$, $K_{AA}=0$) as a function of the mole fraction x_A for lattice sizes $l=16$ (●) and $l=24$ (○) in the concentration range $0\leq x_A\leq 0.125$. The solid line corresponds to a linear fit for lattice size $l=24$.

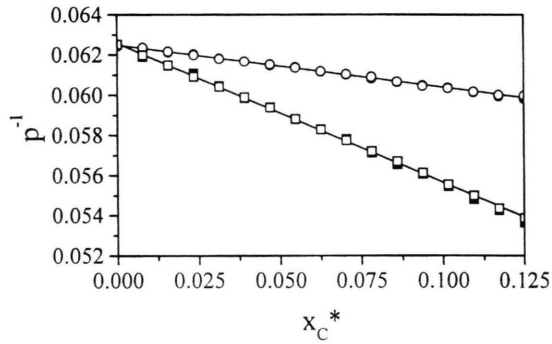

Fig. 6. The inverse pitch p^{-1} in the binary guest-host systems II (○) and II′ (❑) composed of chiral host molecules B ($J_{BB}=+1$, $K_{BB}=+1$) and chiral guest molecules C ($J_{CC}=+1$, $K_{CC}=+0.5$) and the enantiomer $C^{\dagger}$ ($J_{C^{\dagger}C^{\dagger}}=+1$, $K_{C^{\dagger}C^{\dagger}}=-0.5$), respectively, as a function of the mole fraction x_C^* of the guest molecules for lattice sizes $l=16$ (full symbols) and $l=24$ (open symbols) in the concentration range $0\leq x_C^*\leq 0.125$. The solid lines correspond to linear fits for lattice size $l=24$.

guest-host systems composed of different chiral molecules were studied in dependence on the composition. The cholesteric phase obtained in a single-component system of molecules B ($J_{BB}=+1$, $K_{BB}=+1$) described in the previous section was doped with chiral molecules C ($J_{CC}=+1$, $K_{CC}=+0.5$) and the corresponding enantiomers $C^{\dagger}$ ($J_{C^{\dagger}C^{\dagger}}=+1$, $K_{C^{\dagger}C^{\dagger}}=-0.5$), respectively. The behaviour of the inverse pitch, given in Fig. 6 for dilute solutions in the concentration range $0\leq x_C^*\leq 0.125$ as function of the corresponding mole fraction x_C^* of chiral guest molecules, unveils pronounced non-symmetrical effects of the enantiomers in the chiral surroundings as recently discovered experimentally by Yarovoy and

Table 3. $(HTP)_C$ and $(AHTP)_C$ in guest-host system II of lattice size l.

l	$(HTP)_C$	$(AHTP)_C$
16	0.0248 ± 0.0004	-0.0459 ± 0.0004
24	0.0242 ± 0.0003	-0.0450 ± 0.0003

Labes measuring different pitch values for guest-host systems of enantiomeric molecules dissolved in steroidal cholesteric media [35].

Both chiral dopants yield a significant decrease of the inverse pitch in linear dependence on the mole fraction. The inverse pitch decreases faster in the binary system with chiral host and guest molecules described by interactions according to (6) with pseudoscalar parameters K_{ii} of opposite sign. The two symmetry adapted quantitative measures characterising the chiral induction by the chiral guest molecules C in a cholesteric host phase of chiral molecules B, the pseudoscalar HTP and the scalar AHTP, are summarised in Table 3. The AHTP values of chiral molecules C and achiral molecules A (Table 2), both described by interactions with identical scalar parameters J_{ii}, dissolved in the same cholesteric host phase of chiral molecules B are close to each other. Here, further systematic investigations in dependence on the potential parameters are needed in order to clarify this behaviour.

In order to figure out the orientational properties the second rank order parameters $\langle P_2 \rangle^H$ of the host molecules and $\langle P_2 \rangle^G$ of the guest molecules have been calculated (Fig. 7), both with respect to the local director defined as a common property of all molecules of the corresponding layer analogously to the method introduced in [32]. Considering Fig. 7 a and Fig. 7 b, which show the results for system sizes $l = 16$ and $l = 24$, respectively, the well known system size effects with higher order parameters in smaller systems, see e.g. the study of the planar Lebwohl-Lasher lattice model [36], are obvious. A common feature of the guest-host systems studied are $\langle P_2 \rangle^G$ values of the guest molecules below the order parameter $\langle P_2 \rangle^H$ of the corresponding host molecules. Small but significant non-symmetric effects of the enantiomers in the chiral surroundings are obvious. By dissolving chiral guest molecules C and $C^\dagger$, respectively, in the cholesteric host phase of molecules B, the host order parameter $\langle P_2 \rangle^H$ is decreased, again with larger effects if the chiral host and guest molecules are described by interactions with pseudoscalar parameters K_{ii} of opposite sign. Additionally, the enantiomers themselves show a different orientational behaviour in chiral surroundings with

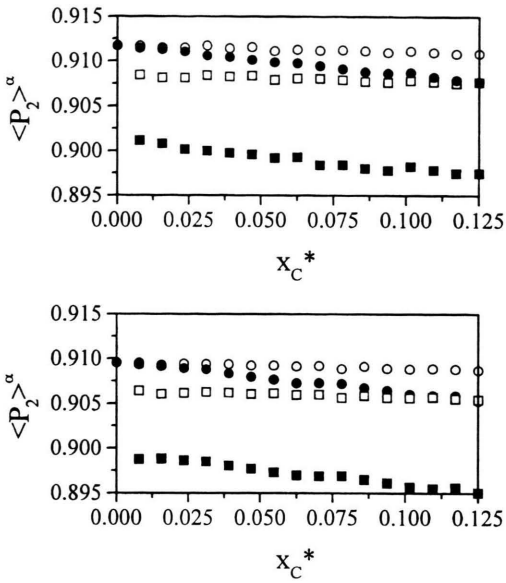

Fig. 7. The local host order parameters $\langle P_2 \rangle^H$ (○) and the local guest order parameters $\langle P_2 \rangle^G$ (□) in the binary guest-host systems II (open symbols) and II′ (full symbols) composed of chiral host molecules B ($J_{BB} = +1$, $K_{BB} = +1$) and chiral guest molecules C ($J_{CC} = +1$, $K_{CC} = +0.5$) and the enantiomer $C^\dagger$ ($J_{C^\dagger C^\dagger} = +1$, $K_{C^\dagger C^\dagger} = -0.5$), respectively, as a function of the mole fraction x_C^* of the guest molecules in the concentration range $0 \le x_C^* \le 0.125$: (a) lattice size $l = 16$, (b) lattice size $l = 24$.

higher order parameters $\langle P_2 \rangle^G$ if the chiral host and guest molecules are described by interactions with pseudoscalar parameters K_{ii} of the same sign. Recently, such a non-symmetric behaviour has been quantified for the first time studying systems of a rigid chiral compound dissolved in a lyotropic cholesteric liquid crystal [37], where it was also concluded that the principal axis systems of the order tensors of the enantiomers, which is fixed by the effective symmetry of the interactions taken into account in the current computer simulation study, are not images of each other.

4. Conclusions

The chiral induction in liquid crystalline phases was studied by Monte Carlo simulation of three-dimensional binary lattice systems of molecules with orientations confined to two dimensions. The anisotropic interactions were taken in the form derived by van der Meer et al. [30] suitable for the description of the pair potential between two chiral molecules as well as between a chiral and an achiral molecule. Binary guest-host systems composed

of achiral and chiral molecules as well as composed of different chiral molecules were investigated in dependence on the composition in order to study the influence of chiral guest molecules with respect to the induction and perturbation of helical superstructures in achiral and chiral host phases. For the first time by computer simulation of a many-particle system, a cholesteric phase was induced dissolving a small fraction of chiral molecules in a nematic phase which was caused by intermolecular interactions perturbing the parallel orientation of the achiral host molecules along the helical axis. In agreement with experimental results, no hints for the existence of a threshold concentration necessary for the induction have been obtained. In dilute solutions, the inverse pitch was found to be a linear function of the mole fraction of the chiral dopants. The formation of cholesteric phases with large pitch values incommensurable to the small system sizes studied, and the determination of their equilibrium properties, especially the quantitative measures for the chiral induction, the HTP and the AHTP, was enabled independent of sample size effects by the application of self-determined boundary conditions. Pronounced nonsymmetric effects have been discovered dissolving enantiomeric dopants in chiral surroundings, given here by a cholesteric host phase, both with respect to the order parameters of the chiral host and guest molecules and with respect to the change of the helical superstructures expressed by the determined values of the HTP and AHTP. A future task is the extension to studies in dependence on temperature of guest-host systems with unconfined molecular orientations in order to figure out especially the dependence of the helical twisting power on order parameters considering also the local phase biaxiality of cholesteric phases.

Generous allocation of computer time by the Regionales Hochschulrechenzentrum Kaiserslautern and the John von Neumann-Institut für Computing, Jülich and funding by Fonds der Chemischen Industrie and by Deutsche Forschungsgemeinschaft (Grants Ku 216/26-1 and Me 1011/3-1) are gratefully acknowledged. We would like to thank Prof. Dr. H.-G. Kuball for many helpful discussions and critical comments.

[1] Chirality – From Weak Bosons to the α-Helix, R. Janoschek (ed.), Springer, Berlin 1991.
[2] H.-G. Kuball, R. Memmer, and O. Türk, Comments on Chirality, in: Chiral Liquid Crystals, L. Komitov (ed.), World Scientific Press, Singapore 2000, in press.
[3] H.-G. Kuball, Liquid Crystals Today **9,** 1 (1999).
[4] J. W. Goodby, Symmetry and Chirality in Liquid Crystals, in: Handbook of Liquid Crystals, D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill (eds.), Wiley-VCH, Weinheim 1998, pp. 115–132.
[5] H. Finkelmann and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. **82,** 1302 (1978).
[6] H.-G. Kuball, H. Brüning, T. Müller, O. Türk, and A. Schönhofer, J. Mater. Chem. **5,** 2176 (1995).
[7] H.-G. Kuball, B. Weiß, A. K. Beck, and D. Seebach, Helv. Chim. Acta **80,** 2507 (1997).
[8] D. Pauluth and A. E. F. Wächtler, Synthesis and Application of Chiral Liquid Crystals, in: Chirality in Industry II, A. N. Collins, G. N. Sheldrake, and J. Crosby (eds), Wiley, Chichester 1997, pp. 263–286.
[9] H.-G. Kuball and H. Brüning, Chirality **9,** 407 (1997).
[10] G. P. Spada and G. Proni, Enantiomer **3,** 301 (1998).
[11] A. Ferrarini, G. Gottarelli, P. L. Nordio, and G. P. Spada, J. Chem. Soc., Perkin Trans. **2,** 411 (1999).
[12] T. C Lubensky, A. B. Harris, R. D. Kamien, and G. Yan, Ferroelectrics **212,** 1 (1998).
[13] Observation, Prediction and Simulation of Phase Transitions in Complex Fluids, M. Baus, L. F. Rull, and J.-P. Ryckaert (eds.), Kluwer Academic Publishers, Dordrecht 1995.
[14] R. Memmer, Ber. Bunsenges. Phys. Chem. **102,** 1002 (1998).
[15] R. Memmer, Liq. Crystals, (2000) in press.
[16] R. Memmer, H.-G. Kuball, and A. Schönhofer, Mol. Phys. **89,** 1633 (1996).
[17] S. Sarman, J. Chem. Phys. **110,** 12218 (1999).
[18] W. Maier and A. Saupe, Z. Naturforsch. **13a,** 564 (1958).
[19] G. R. Luckhurst, S. Romano, and H. B. Zewdie, J. Chem. Soc., Faraday Trans. **92,** 1781 (1996).
[20] J. Saha and M. Saha, Mol. Sim. **19,** 227 (1997).
[21] R. Memmer and F. Janssen, J. Chem. Soc., Faraday Trans. **94,** 267 (1998).
[22] R. Memmer and F. Janssen, Liq. Crystals **24,** 805 (1998).
[23] R. Memmer, H.-G. Kuball, and A. Schönhofer, Liq. Crystals **19,** 749 (1995).
[24] R. Berardi, H.-G. Kuball, R. Memmer, and C. Zannoni, J. Chem. Soc., Faraday Trans. **94,** 1229 (1998).
[25] M. P. Allen, Phys. Rev. E **47,** 4611 (1993).
[26] M. P. Allen, Simulations and Phase Behaviour of Liquid Crystals, in: [13], pp. 557–591.
[27] M. A. Osipov, Molecular Theory of Cholesteric Polymers, in: Liquid Crystalline and Mesomorphic Polymers, V. B. Shibaev and L. Lam (eds.), Springer, New York 1993, pp. 1–25.
[28] D. Gonin and A. Windle, Liq. Crystals **23,** 489 (1997).
[29] A. M. Smondyrev and R. A. Pelcovits, Liq. Crystals **26,** 235 (1999).
[30] B. W. van der Meer, G. Vertogen, A. J. Dekker, and J. G. J. Ypma, J. Chem. Phys. **65,** 3935 (1976).
[31] S. A. Issaenko, A. B. Harris, and T. C. Lubensky, Phys. Rev. E **60,** 578 (1999).
[32] R. Hashim, G. R. Luckhurst, and S. Romano, Liq. Crystals **1,** 133 (1986).
[33] R. Memmer, H.-G. Kuball, and A. Schönhofer, Liq. Crystals **15,** 345 (1993).
[34] H. Stegemeyer, H.-J. Kersting, and W. Kuczynski, Ber. Bunsenges. Phys. Chem. **91,** 3 (1987).
[35] Y. K. Yarovoy and M. M. Labes, Mol. Cryst. Liq. Cryst. **270,** 101 (1995).
[36] C. Chiccoli, P. Pasini, and C. Zannoni, Physica **148 A,** 298 (1988).
[37] P. Lesot, Y. Gounelle, D. Merlet, A. Loewenstein, and J. Courtieu, J. Phys. Chem. **99,** 14871 (1995).