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Computer simulation of chiral liquid crystal phases IV. Intermolecular chirality transfer to rotamers in a cholesteric phase†

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Intermolecular chirality transfer was studied by investigating the conformational distribution of rotamers in a cholesteric guest-host phase using Monte Carlo (MC) simulations in the NVT ensemble. The guest-host system under investigation was given by $N_c = 238$ rigid, chiral Gay-Berne atropisomers as host molecules and $N_g = 18$ flexible Gay-Berne rotamers as guest molecules. The rigid, chiral Gay-Berne atropisomers of point symmetry group D_2 were defined by joining two Gay-Berne particles through a bond with a suitable fixed dihedral angle. The possibility of internal rotation about the bond axis without a rotational barrier was introduced as an internal degree of freedom for the guest molecules, for convenience denoted as Gay-Berne rotamers. Starting from an isotropic configuration, cholesteric phases were obtained on equilibrating the guest-host systems, whereby left-handed and right-handed cholesterics were formed depending on the M- and P-helicity of the atropisomers, respectively. Analysing the conformational distribution of the guest molecules in the cholesteric phase, we found an enantiomeric excess of rotamers of the guest molecules with the same helicity as the host molecules which is favoured on account of the intermolecular interactions in the cholesteric phase.

1. Introduction

Chiral compounds dissolved in nematic solvents are able to induce cholesteric phases. This chiral induction is a subject of wide interest and has been studied intensively, for example, by measuring the helical twisting power (HTP) of many compounds [1-7]. A different intermolecular chirality transfer has to be discussed for each conformer of a compound [6, 7]. For axially chiral biaryls dissolved in nematics of the biphenyl type, Gottarelli *et al.*, deduced the rule that left-handed cholesterics (M) are correlated to M-helicity, and right-handed cholesterics (P) to P-helicity of the chiral biaryl inducer [1]. It was proposed that the high values of the HTP of the chiral biaryls obtained in such systems can be explained by an induced excess of a conformation of the solvent molecules with the helicity of the chiral solute. The solvent dependence of the optical rotation $[\alpha_D]$ of axially chiral biaryls dissolved in the isotropic phase of biphenyl-type solvents seems to be consistent with this explanation [8]. An induced enantiomeric excess of chiral conformers of

an achiral compound dissolved in an induced cholesteric phase was also proposed by Labes *et al.*, on the basis of fingerprint measurements [9, 10]. By this mechanism the pitch of the phase should be increased or decreased strongly, a concept which could not be proved until now by reinvestigating pitch measurements by the Cano wedge, droplet and fingerprint methods [11, 12].

A powerful tool for a study of the behaviour of many-body systems is given by the computer simulation of suitable model systems. Here the molecular dynamics technique (MD) and the Monte Carlo technique (MC) have a wide field of applications [13-15]. A suitable model system for the computer simulation of achiral liquid crystalline phases is given by the Gay-Berne fluid [16] which exhibits a variety of mesophases by variation of temperature, identified as isotropic, nematic, smectic A, smectic B, and crystal phases by Luckhurst *et al.*, using MD calculations [17]. As a model system for the simulation of chiral phases, we introduced the chiral Gay-Berne fluid by adding a chirality producing term to the Gay-Berne potential [18, 19]. This model shows a rich polymorphism. Cholesteric, blue, and helical smectic phases have been located in the chirality-temperature

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phase diagram by performing MC calculations using periodic boundary conditions. It was shown that the limitations caused by these periodic boundary conditions can be reduced by application of twisted boundary conditions which enables the formation of helical phases with lower total potential energy, decreased chiral energy contribution, and larger pitch [19, 20]. They have been applied also for the calculation of twist elastic constants [21] and the helical twisting power [22] in systems composed of non-spherical hard particles.

Recently, we introduced a new model system for the simulation of cholesteric phases which allows a study of a more realistic correlation between molecular structure and helicity of the cholesteric phase [23]. Its molecules were related to the flexible Gay–Berne dimer which has been studied by Luckhurst *et al.*, in isotropic, nematic, and smectic phases [24]. Now a rigid, chiral Gay–Berne atropisomer of point symmetry group D_2 was defined by joining the centres of two Gay–Berne particles through a bond with a fixed dihedral angle between the axes of rotational symmetry of the two joined Gay–Berne particles. Pure systems of such chiral atropisomers with M-helicity and P-helicity, respectively, have been investigated. Starting from an isotropic configuration, cholesteric phases were obtained on equilibrating the systems whereby left-handed and right-handed cholesterics were formed corresponding to the helicity of the atropisomers [23].

Meantime, achiral guest–host systems with Gay–Berne particles as host molecules and guest molecules described by site–site potentials have been investigated [25, 26]. Now we extend our model to the study of chiral guest–host systems. The aim of our paper is to study a mechanism of intermolecular chirality transfer with the help of a suitable model for a guest–host system using MC simulations in order to contribute to the discussion about an induced enantiomeric excess of chiral solvent conformers. In the following, we investigate a guest–host system with rigid, chiral Gay–Berne atropisomers as host molecules and flexible Gay–Berne rotamers as guest molecules for which the possibility of internal rotation about the bond axis without a rotational barrier is introduced as an internal degree of freedom.

2. Model system

A Gay–Berne molecule is defined by joining the centres of two equivalent Gay–Berne particles a and b through a bond as shown in figure 1. The position of a molecule i can be described using the vectors $\mathbf{r}_a^{(i)}$ and $\mathbf{r}_b^{(i)}$ to the centres of the Gay–Berne particles a and b. The orientation of the two rotationally symmetric particles is given by the unit vectors $\hat{\mathbf{u}}_a^{(i)}$ and $\hat{\mathbf{u}}_b^{(i)}$ along their symmetry axes.

The geometry of a Gay–Berne molecule i is given by four internal coordinates: the bond length $r_{ab}^{(i)}$, the bond

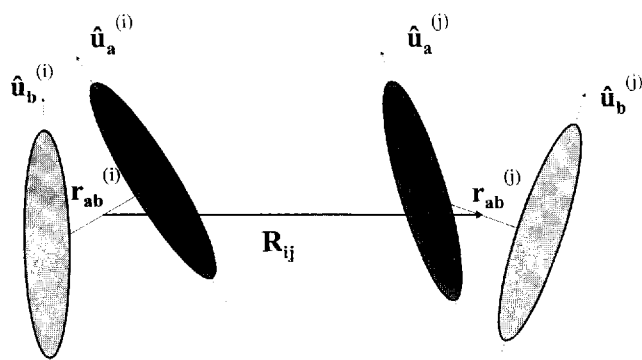


Figure 1. The geometry of Gay–Berne molecules defined by joining the centres of two equivalent Gay–Berne particles.

angles $\theta_a^{(i)}$ and $\theta_b^{(i)}$, and the dihedral angle $\phi^{(i)}$. The bond length is $r_{ab}^{(i)} = |\mathbf{r}_{ab}^{(i)}|$, the absolute value of the intramolecular vector $\mathbf{r}_{ab}^{(i)} = \mathbf{r}_b^{(i)} - \mathbf{r}_a^{(i)}$. The bond angles $\theta_a^{(i)}$ and $\theta_b^{(i)}$ denote the angles between the vectors $\hat{\mathbf{u}}_a^{(i)}$, $\mathbf{r}_{ab}^{(i)}$ and $\hat{\mathbf{u}}_b^{(i)}$, $\mathbf{r}_{ab}^{(i)}$, respectively. The dihedral angle $\phi^{(i)}$ is the angle between the planes defined by the vectors $\hat{\mathbf{u}}_a^{(i)}$, $\mathbf{r}_{ab}^{(i)}$ and $\hat{\mathbf{u}}_b^{(i)}$, $\mathbf{r}_{ab}^{(i)}$, respectively.

Selected values for the bond angles are chosen: $\theta_a^{(i)} = 90^\circ$ and $\theta_b^{(i)} = 90^\circ$, i.e. the constraints $\mathbf{u}_a^{(i)} \perp \mathbf{r}_{ab}^{(i)}$, $\mathbf{u}_b^{(i)} \perp \mathbf{r}_{ab}^{(i)}$. The Gay–Berne molecule thus defined is achiral for a dihedral angle $\phi^{(i)} = 0^\circ$ (point symmetry group D_{2h}) or $\phi^{(i)} = 90^\circ$ (point symmetry group D_{2d}). For all other values of $\phi^{(i)}$, a rigid, chiral Gay–Berne molecule of point symmetry group D_2 is obtained. The three C_2 axes are denoted by $C_2^{(1)}$ (parallel to $\mathbf{r}_{ab}^{(i)}$), $C_2^{(2)}$, and $C_2^{(3)}$ as shown in

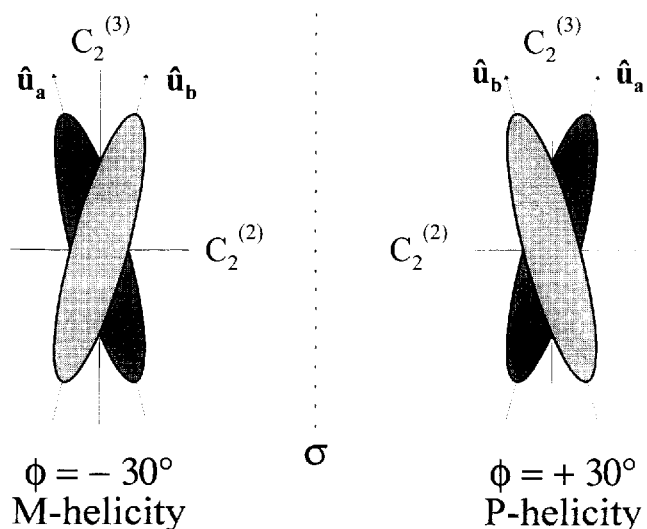


Figure 2. A rigid, chiral Gay–Berne molecule and its mirror image: (left) the atropisomer with M-helicity along the $C_2^{(1)}$ axis ($\phi = -30^\circ$); (right) the atropisomer with P-helicity along the $C_2^{(1)}$ axis ($\phi = +30^\circ$). The brighter ellipsoid indicates the Gay–Berne particle closer to the observer.

figure 2 for the two atropisomers with M-helicity ($\phi^{(i)} = -30^\circ$) and P-helicity ($\phi^{(i)} = +30^\circ$) along $C_2^{(i)}$ [27]. Chiral Gay–Berne molecules with these selected values for the dihedral angle are used as host molecules. The guest molecules are given by Gay–Berne rotamers with the dihedral angle $\phi^{(i)}$ as a free variable.

The intermolecular interactions between two Gay–Berne molecules i and j separated by an intermolecular vector \mathbf{R}_{ij} with orientations denoted by Ω_i and Ω_j , respectively, are described by the sum of pair potentials between the Gay–Berne particles of the two molecules

$$\begin{aligned} U(\Omega_i, \Omega_j, \mathbf{R}_{ij}) &= \sum_{\alpha=a,b} \sum_{\beta=a,b} U_a(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \mathbf{r}_{\alpha\beta}^{(i,j)}) \\ &= U_a(\hat{\mathbf{u}}_a^{(i)}, \hat{\mathbf{u}}_a^{(j)}, \mathbf{r}_{aa}^{(i,j)}) + U_a(\hat{\mathbf{u}}_a^{(i)}, \hat{\mathbf{u}}_b^{(j)}, \mathbf{r}_{ab}^{(i,j)}) \\ &\quad + U_a(\hat{\mathbf{u}}_b^{(i)}, \hat{\mathbf{u}}_a^{(j)}, \mathbf{r}_{ba}^{(i,j)}) + U_a(\hat{\mathbf{u}}_b^{(i)}, \hat{\mathbf{u}}_b^{(j)}, \mathbf{r}_{bb}^{(i,j)}) \quad (1) \end{aligned}$$

where $\mathbf{r}_{\alpha\beta}^{(i,j)} = \mathbf{r}_\beta^{(j)} - \mathbf{r}_\alpha^{(i)}$ denotes the intermolecular vector between the centre of the particle $\alpha = a, b$ of molecule i and the centre of the particle $\beta = a, b$ of molecule j . No intramolecular interaction is taken into account, neither for the chiral Gay–Berne host molecules nor the Gay–Berne guest rotamers. For the guest molecules a rotation of the Gay–Berne particles about the bond axis without a rotational barrier is thereby enabled, whereas for the host molecules only a constant energy contribution is omitted. The achiral interaction potential U_a is the Gay–Berne potential [16]

$$\begin{aligned} U_a(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \mathbf{r}_{\alpha\beta}^{(i,j)}) &= 4\varepsilon(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)}) \left\{ \left(\frac{\sigma_0}{r_{\alpha\beta}^{(i,j)} - \sigma(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)}) + \sigma_0} \right)^{12} \right. \\ &\quad \left. - \left(\frac{\sigma_0}{r_{\alpha\beta}^{(i,j)} - \sigma(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)}) + \sigma_0} \right)^6 \right\} \quad (2) \end{aligned}$$

where $\hat{\mathbf{r}}_{\alpha\beta}^{(i,j)}$ denotes the unit vector parallel to $\mathbf{r}_{\alpha\beta}^{(i,j)}$ and $r_{\alpha\beta}^{(i,j)} = |\mathbf{r}_{\alpha\beta}^{(i,j)}|$. The explicit expressions for the orientation-dependent parameters $\sigma(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)})$ and $\varepsilon(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)})$ are given in [18]. The guest–host model systems under investigation consist of $N_c = 238$ rigid, chiral Gay–Berne molecules with $\phi^{(i)} = -30^\circ$ (M-helicity) and $\phi^{(i)} = +30^\circ$ (P-helicity), respectively, and $N_a = 18$ flexible Gay–Berne rotamers. In the following, these systems are denoted for convenience as M-system and P-system, respectively.

3. Computational details

We studied the conformational distribution of the guest molecules in the guest–host systems M and P in a cubic simulation box using normal Metropolis Monte Carlo technique in the NVT ensemble [13–15]. Cubic periodic boundary conditions and nearest image summation were applied. In the following, scaled units will be used: scaled temperature $T^* = k_B T / \varepsilon_0$, scaled density $\rho^* = N\sigma_0^3 / V$ with

$N = N_c + N_a$, scaled energy $U^* = U / \varepsilon_0$, and scaled distances $r^* = r / \sigma_0$. A spherical cut-off at $r^* = 3.80$ was applied. The parameter values $\sigma_d / \sigma_s = 3$, $\varepsilon_d / \varepsilon_s = 1/5$, $\mu = 1$, $\nu = 2$, as given in [18] and necessary for the determination of the functions $\sigma(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)})$ and $\varepsilon(\hat{\mathbf{u}}_\alpha^{(i)}, \hat{\mathbf{u}}_\beta^{(j)}, \hat{\mathbf{r}}_{\alpha\beta}^{(i,j)})$, were used for the Gay–Berne particles of both the host molecules and the guest molecules. All simulations were done at a reduced density $\rho^* = 0.15$ and a reduced temperature $T^* = 2.25$. A trial configuration was generated by a random translation of the molecule followed by a random rotation about one of the randomly chosen space-fixed axes. The situation for the non-rigid guest molecules is more complicated and similar to that of *n*-butane [28–30]. For the Gay–Berne molecule, ten generalized coordinates are necessary. These can be divided into two categories: seven soft variables, namely the three coordinates describing its position, three Eulerian angles describing its orientation and the dihedral angle $\phi^{(i)}$, and three hard variables comprising the two bond angles θ_a , θ_b , and the bond length r_{ab} . We used a simplification, and constrained the three hard variables to selected values. A reduced bond length $r_{ab}^* = 1.1$ close to the value with minimal potential energy between two Gay–Berne particles in the side-by-side configuration [17] and the bond angles $\theta_a = 90^\circ$, $\theta_b = 90^\circ$ were kept constant during the simulation. Thus we investigated the flexible constrained model in the limit when bond-length and bond-angle forces become infinite [28–30]. For each flexible guest molecule the translation and rotation were followed by a change in the dihedral angle $\phi^{(i)}$, and as usual the trial configuration was accepted with a probability depending on the change in the intermolecular potential energy. In the initial configurations for the MC runs, the positions, orientations, and conformations were distributed randomly. A very long equilibration run of about 2000 kc (1 kc denotes 1000 cycles, i.e. attempted moves per particle) was followed by a production run of 1000 kc. During the production run the configuration after each tenth cycle was used for the calculation of the functions of interest.

4. Results

In order to elucidate the structural features of the phases obtained, the longitudinal orientational pair correlation functions of rank two

$$g_2^{(3)}(r_{ij}^*) = \langle P_2(\cos \delta_{ij}(r_{ij}^*)) \rangle \quad (3)$$

and

$$g_2'^{(3)}(r_{ij}^*) = \langle P_2(\cos \delta'_{ij}(r_{ij}^*)) \rangle \quad (4)$$

as defined in [18, 23] were calculated for the host molecules. Here P_2 is the second Legendre polynomial. $\delta_{ij}(r_{ij}^*)$ denotes the angle between the $C_2^{(3)}$ axes of two selected molecules separated by a scaled distance r_{ij}^* in the

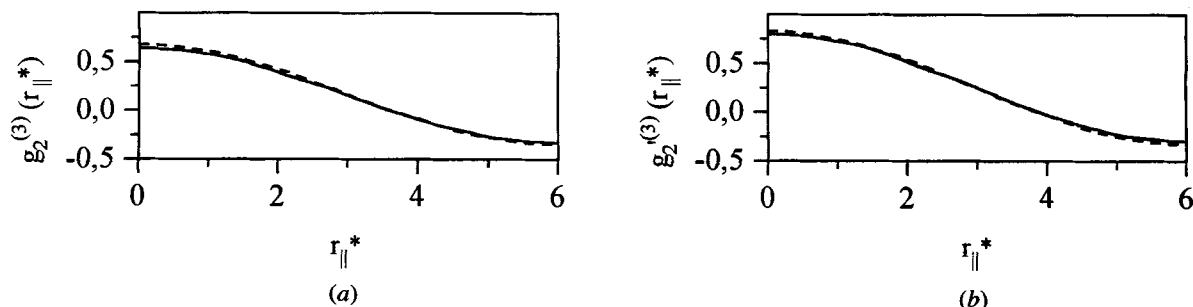


Figure 3. Longitudinal orientational pair correlation functions for the host molecules in the guest–host systems M (solid lines) and P (dashed lines): (a) $g_2^{(3)}(r_{||}^*)$; (b) $g_2'^{(3)}(r_{||}^*)$.

direction parallel to the helical axis identified according to the algorithm given in [18,23]. $\delta_{ij}'(r_{||}^*)$ is defined as the angle between the projections of the $C_2^{(3)}$ axes into the plane perpendicular to the helical axis. As can be seen from figure 3, both functions show the dependencies expected for a cholesteric phase where a part of the helix with a length of a half pitch has been formed inside the simulation cell as discussed in detail in [18,19,23].

In order to analyse the handedness of the cholesteric phases formed, the simulation box was divided into volume segments perpendicular to the helical axis. For each volume segment, a local director has been calculated. In figure 4 the angle of rotation of the local director around the helical axis is shown as a function of the volume segment number for the final configurations of the M- and P-systems. A left-handed cholesteric phase was found in the M-system, and a right-handed cholesteric phase in the P-system.

The conformational distribution functions $p(\phi)$ for the flexible guest molecules in the M- and P-systems are shown in figure 5. The maximum of $p(\phi)$ for $\phi \neq 0$ shows an induced enantiomeric excess where rotamers with the same helicity as the host molecules are favoured.

In order to illustrate the excess of M- or P-rotamers, we show the difference $p(\phi) - p(-\phi)$ in the M- and P-system in figure 6. In both systems the excess of rotamers has its

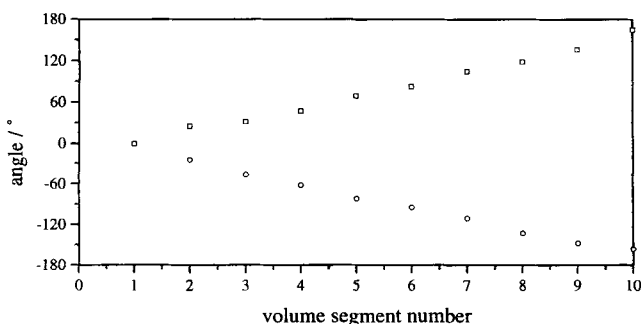


Figure 4. The angle of rotation of the volume segment director around the helical axis as a function of the volume segment number: in the M-system (circles); in the P-system (squares).

maximum value at a dihedral angle close to the selected dihedral angle of the chiral inducer.

5. Conclusions

The MC studies of rotamers dissolved in a host system of chiral atropisomers show cholesteric phases where right-handed and left-handed helices have been formed depending on the helicity of the host molecules. In addition, an intermolecular chirality transfer to the guest molecules was found, as identified by an excess of guest conformers with a helicity corresponding to the helicity of the host molecules. This is in analogy to the mechanism proposed by Gottarelli *et al.* [1], for the intermolecular chirality

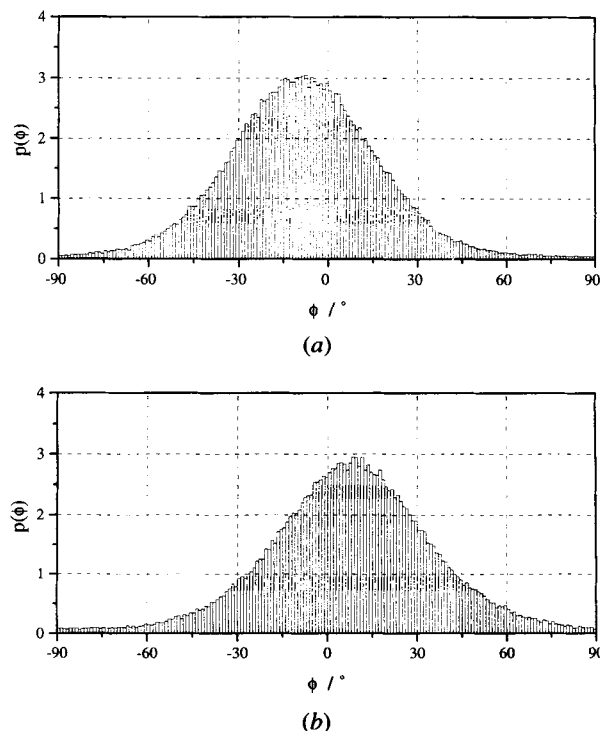


Figure 5. Conformational distribution functions $p(\phi)$ for the flexible guest molecules at $T^* = 2.25$: (a) $p(\phi)$ in the M-system; (b) $p(\phi)$ in the P-system. For both functions, histograms with the width $\Delta\phi = 1^\circ$ have been constructed.

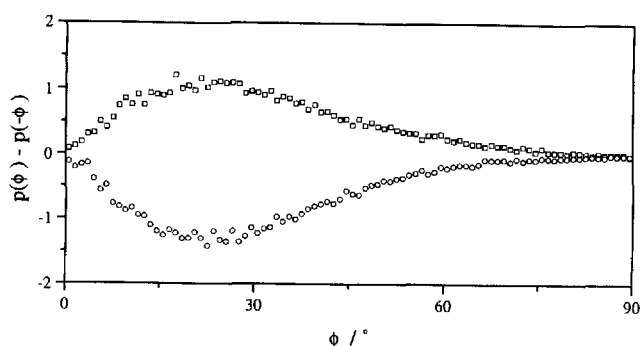


Figure 6. Differences $p(\phi) - p(-\phi)$ of the conformational distribution functions of the guest molecules: in the M-system (circles); in the P-system (squares).

transfer from axially chiral biaryls as guest molecules to biphenyl-type solvents. It must be pointed out that in the situation investigated experimentally, a chiral solute molecule is surrounded by an excess of achiral solvent molecules, in contrast to the guest–host model system under investigation here, where an achiral solute molecule is surrounded by an excess of chiral solvent molecules. Such surroundings surely will enlarge or even enable the intermolecular chirality transfer. Therefore, further simulations should be done with different concentration ratios of chiral and achiral molecules. The model system introduced should further allow an investigation of the dependence of the intermolecular chirality transfer on variables such as temperature and density. Of course, for all simulations the restrictions caused by the small system size and the periodic boundary conditions have to be kept in mind. It might be helpful for a better understanding to quantify the intermolecular chirality transfer by averaging a measure of the molecular chirality of each conformer as given, for example, by the pseudoscalar quantity $\Delta_i = (\hat{\mathbf{u}}_a^{(i)} \cdot \hat{\mathbf{u}}_b^{(i)}) [(\hat{\mathbf{u}}_a^{(i)} \times \hat{\mathbf{u}}_b^{(i)}) \cdot \mathbf{r}_{ab}^{(i)}]$ [31], using the conformational distribution function. Furthermore, investigation of the order parameters of the different rotamers in the cholesteric phase is of interest, especially the question as to whether or not rotamers with different helicity behave differently in this respect.

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