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Short Communication

Behaviour of mesomorphic systems of conformationally rigid and flexible molecules in external orienting fields

Vl.K. Pershin and V.A. Konoplev

Ural Polytechnical Institute, 620002 Sverdlovsk-2, U.S.S.R.

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Abstract. — A comparative analysis of the influence of external orienting quadrupolar symmetry fields on mesophases formed by conformationally rigid and flexible particles with positive susceptibility anisotropy for which weak and strong first order transitions to the isotropic liquid state are, respectively, realized (in the absence of fields) is fulfilled theoretically. Peculiarities allowing to distinguish experimentally mesomorphic systems described adequately by the approximations of rigid and flexible molecules are noted.

Investigation of liquid crystals (LC) in electric and magnetic fields is of fundamental and practical importance. To date a large number of papers (see, for example, review articles [1,2]) have been devoted to this question. The main part of experimental and theoretical data relates to mesophases formed by conformationally rigid particles. Great efforts have been done for an account of molecular flexibility in orientationally ordered systems [3-13]. The first attempt for a theoretical description of the orienting fields action on the nematic phase of thermotropic LC polymers in terms of the Worm-like chain model based on the Maier-Saupe theory [14] has been carried out in [15]. However, essential distinctions from the conclusions of earlier papers [16-20] in which LC mesophases formed by rigid particles had been studied and a description had also been fulfilled in terms of the Maier-Saupe model were not found in [15]. Apparently, the results of [15] reflect well enough a behaviour of systems of flexible chain molecules in magnetic and electric fields which, in the absence of the latter, behave like monomeric LC, in particular, they undergo first order phase transitions close to the second order ones exhibiting insignificant orientational order parameter $\langle P_2 \rangle$ jumps ($\Delta S \sim 0.3 \pm 0.4$) in points of nematic (N) - isotropic liquid (IL) transformations (compare curves 1 and 2 in Fig. 1a). Such structures include, for instance, comb-like LC polymers of the polysiloxane type in which rigid mesogeneous groups connected with the main chains by flexible sewings are responsible for orientational ordering [21]. However, there is a large number of mesomorphic systems of flexible molecules (soaps [22], lecithins [23], aromatic polyesters [24,25], cynamates [26], cyanobiphenyls [27], etc.) with an essentially different behaviour: a weak $\langle P_2 \rangle$ change with the temperature rise and large jumps ($\Delta S \sim 0.7 \pm 0.9$) in points of transitions into IL are characteristic for them (see, for instance, Fig. 1b). Obviously,
peculiarities of the behaviour in external fields are to be observed in such structures which distinguish them fundamentally from low molecular LC described adequately by the approximation of rigid particles. The present paper is devoted to the comparative analysis of field effects on systems of conformationally rigid and flexible molecules.

![Graphs](image)

**Fig. 1.** — Experimental dependences of the orientational order parameter \( \langle P_2 \rangle \) on the temperature \( t' = T/T_{or} (T_{or} \text{ is the temperature of the nematic-isotropic liquid phase transition}) \) of monomeric azocompounds (curve 1 in Fig. 1a), their comb-like polymer analogs on the basis of siloxanes (curve 2 in Fig. 1a) [21], linear liquid crystalline polymers of the aromatic polyester type (Fig. 1b) [25], and corresponding theoretical dependences calculated by means of formulae (3) at \( \varepsilon = 6 \) in the approximation of conformationally rigid (Fig. 1c, \( \gamma = 0.9 \)) and conformationally flexible (Fig. 1d, \( \gamma = 0.2 \)) molecules in the absence of external fields.

We consider a model of mesophase with inner degrees of freedom in the quadrupolar symmetry magnetic field \( \mathcal{H} \) allowing to reproduce both types of dependences of \( \langle P_2 \rangle \) on temperature in figure 1a,b with weak and strong first order N-IL transitions at \( \mathcal{H} = 0 \) (compare Fig. 1a,b and Fig. 1c,d). This model is described by the Hamiltonian

\[
H = -\frac{1}{2} \sum_{i,j=1}^{N} \sum_{\alpha,\beta=1}^{2} V_{\alpha\beta}(ij) P_2(\cos \theta_{ij}) n_{\alpha}(i) n_{\beta}(j) + \sum_{i=1}^{N} E_{i} - \frac{1}{3} \Delta \chi \ H^2 \sum_{i=1}^{N} P_2(\cos \theta_{i}),
\]

(1)

in which intra- and intermolecular interactions are taken in the pseudo-spin approximation [4-6, 11] and in the Maier-Saupe one [14], respectively. We note that, from the mathematical point of view, additional contributions to the system's energy are qualitatively identical at the effect of both the magnetic and electric fields [28-30]. In (1): \( N \) is a number of particles; \( P_2 \) is the second order Legendre polynomial; \( \theta_{ij} \) is an angle between the long axes of the \( i \) and \( j \) particles; values
Fig. 2. — (a,b) Temperature dependences of the orientational order \( P_2 \) (a) and conformational disorder \( x(b) \) parameters of the mesomorphic system of conformationally rigid molecules (\( \gamma = 0.9 \)) in the magnetic field \( \mu = 0 \) (1), 0.004 (2), 0.008 (3), 0.012 (4), 0.016 (5). (c,d) Temperature dependences of the orientational order \( P_2 \) (c) and conformational disorder \( x(d) \) parameters of the mesomorphic system of conformationally flexible molecules (\( \gamma = 0.2 \)) in the magnetic field \( \mu = 0 \) (1), 1.2 (2), 2.4 (3), 3.6 (4), 4.8 (5). \( \tau = t/t_0 \), where \( t_0 \) is the orientational phase transition temperature at \( \mu = 0 \). Points "A" and "B" in the curve 4 indicate states of systems of conformationally rigid (a,b) and flexible (c,d) molecules in magnetic fields at whose reaching differences between nematic and paranematic phases disappear.

\( n_\beta (l_i) \) equal to 1 or zero describe the presence or absence of the \( i \) particle in the conformational state \( \beta \); \( \Delta \chi \) is a positive anisotropy of the diamagnetic susceptibility; \( \theta_i \) is the angle between the long axis of the particle and the magnetic field direction at coincidence with the system's director. Formula (1) is written in the approximation of two conformational states [4-6] in which all the possible configurations \( \{l_i\} \) of particles with configurational energies \( E(l_i) \) are conventionally divided into two subsets corresponding to "unfold" \( (n_2 = 1) \) and "fold" \( (n_1 = 1) \) conformations with keeping the molecular geometric anisotropy.

To calculate the system's thermodynamic potential \( \Psi \), we use a variational principle [31] \( \Psi \leq \Psi_v = -kT \ln S_p [\exp \left( -H_0/kT \right)] + \langle H - H_0 \rangle \) where \( k \) is the Boltzman constant, \( T \) is the temperature, the brackets \( \langle \ldots \rangle \) indicate a thermodynamic average with the Hamiltonian \( H_0 = -p \sum_{i=1}^{N} P_2 (\cos \theta_i) + h \sum_{i=1}^{N} n_1 (l_i) + \sum_{i=1}^{N} E(l_i) \), \( p, h \) are variational parameters. Taking into account the formulae introduced above we write a variational thermodynamic potential in the sizeless form

\[
\Psi = \Psi_v / (N \kappa V_2) = -t \ln J_0(a) + ta (2 \langle P_2 \rangle + 1) / 3 + t \ln(1 - x) + t x R(x, \varepsilon) - \langle P_2 \rangle \cdot Q^2(x, \gamma) / 2 - \mu \langle P_2 \rangle
\]  \( \text{Eq. (2)} \)

and equations \( \nabla \Psi = 0 \) of state

\[
\mu = 2at / 3 - \langle P_2 \rangle Q^2(x, \gamma), \quad tR(x, \varepsilon) = (1 - \gamma) \langle P_2 \rangle ^2 Q(x, \gamma)
\]  \( \text{Eq. (3)} \)
of the mesophase in the magnetic field. In (2, 3): \( \langle P_2 \rangle = 3J_1(a) [2J_0(a)]^{-1} - 1/2 \) where \( a = 3p/2kT \), \( J_m(a) = \int_0^1 u^{2m} \exp \left( au^2 \right) du \) are the Maier-Saupe integrals, \( x = \langle n_1(l_i) \rangle = [Z_1 + Z_2 \exp (\hbar/kT)]^{-1} \) \( Z_1 \) is a conformational disorder parameter reflecting a portion of molecules in the “fold” conformation; \( Z_m = \sum_{l_i} \exp [-E(l_i)kT], (m = 1, 2), \) \( \epsilon = \ln (Z_1/Z_2) \) are energetic parameters; \( R(x, \epsilon) = \ln [x/(1 - x)] - \epsilon, Q(x, \gamma) = (1 - \gamma) x - 1, t = kT/(\kappa V_{22}) \), \( \mu = \Delta x \cdot H^2/(3\kappa V_{22}) \) are a sizeless temperature and field, respectively, \( \kappa \) is the number of nearest neighbours; \( V_{0\beta} \equiv V_{0\beta}(ii + 1); \gamma \) is the effective molecular rigidity parameter set by the equality \( V_{22,11} = 1 - \gamma : \gamma^2, (0 < \gamma < 1) [11,12] \).

Figure 1c,d shows temperature dependences of the parameter \( \langle P_2 \rangle \) calculated by means of formulae (3) at \( \epsilon = 6, \mu = 0 \) for rigid \( (\gamma = 0.9) \) and flexible \( (\gamma = 0.2) \) particles. It is seen from figure 2 how these dependences (Fig. 2a,c) and those of the conformational disorder parameters (Fig. 2b,d) change in the magnetic field. Calculations fulfilled by means of formulae (2, 3) at \( \mu \neq 0 \) indicate that isostructural N-paranematic (pN) transitions take place at \( 0 < \mu < \mu_A \approx 0.012 \) in systems of conformationally rigid particles and at \( 0 < \mu < \mu_B \approx 3 \) in systems of flexible ones. Differences between low and high temperature phases disappear while reaching magnetic fields \( \mu = \mu_A \) and \( \mu = \mu_B \), respectively, just as it happens in “pressure-temperature” variables in the classical critical liquid-gas point. By order of magnitude a value of the sizeless critical field \( \mu_A \) at the fixed molecular parameters \( \epsilon = 6, \gamma = 0.9 \) coincides with the one calculated in [17]. This indicates that in absolute units the magnetic field \( H_A \approx 0.8 \times 10^5 \) kOe corresponds, according to [32], to the value \( \mu_A \) and the value \( H_A \) exceeding it approximately by two orders corresponds to the value \( \mu_B \). We note that to date the critical “A” point is revealed within the limit of experimental opportunities for creation of orienting fields [19,32] and, hence, the critical “B” point is most likely unachievable in the experiment. A conclusion of practical importance follows from here: investigation of properties of mesophases in magnetic fields in the critical point vicinity is connected with lowest efforts in the class of systems of rigid molecules.

Figure 3a,b shows the dependences of the orientational order \( \langle P_2 \rangle_N, \langle P_2 \rangle_pN \) and conformational disorder \( \varphi_N, \varphi_pN \) parameters in points of N-pN phase transitions on the value \( \mu \) in systems of conformationally rigid molecules. It is seen that the curves \( \mu_A - \mu = \varphi_1(\langle P_2 \rangle_N) \) and \( \mu_A - \mu = \varphi_2(\langle P_2 \rangle_pN) \) form together a parabola symmetrical with respect to the axis \( (\mu_A - \mu) \) which coincides precisely with the corresponding result of the papers [2,20,32]. However, a similar curve in coordinates \( \varphi_N - (\mu_A - \mu) \) and \( \varphi_pN - (\mu_A - \mu) \) is essentially asymmetrical (“skewed parabola” in Fig. 3b). A situation contrary to the described one is observed in systems of conformationally flexible molecules: the combined curve in coordinates \( \varphi_N - (\mu_B - \mu) \) and \( \varphi_pN - (\mu_B - \mu) \) is parabolic (Fig. 3d) and the one in coordinates \( \langle P_2 \rangle_N - (\mu_B - \mu) \) and \( \langle P_2 \rangle_pN - (\mu_B - \mu) \) is an “asymmetrical parabola” (Fig. 3c). This conclusion can be considered as a characteristic one for distinguishing experimentally mesomorphic systems described adequately by approximations of rigid and flexible molecules.

Figure 4 shows phase diagrams of the model in the “field-temperature” coordinates calculated by means of formulae (2, 3) at \( \epsilon = 6 \) and different values of the molecular rigidity parameter \( \gamma \). It is seen from figure 4a, b that a standard situation described in theoretical papers [2,16,17] and supported experimentally [20] takes place in the approximation of rigid particles \( (\gamma \to 1) \). And besides, the results of the paper [17] are quantitatively reproducible. It follows from figure 4c,d that in the approximation of flexible particles the curve dividing N and pN phases corresponds to a square dependence \( T(H) \) in relatively weak magnetic fields only and passes into a dependence close to the linear one in strong fields. These results are characteristic for the class of systems
Fig. 3. — (a,b) Functional relationship between magnitudes of the magnetic field and values of orientational order parameters in the nematic \((P_2)_N\) and paranematic \((P_2)_pN\) phases (a) and, respectively, of conformational disorder parameters \(x_N\) and \(x_{pN}\) in these phases (b) in points of orientational transitions in the system of conformationally rigid particles \((\gamma = 0.8)\).

(c,d) Functional relationship between magnitudes of the magnetic field and values of orientational order parameters in the nematic \((P_2)_N\) and paranematic \((P_2)_pN\) phases (c) and, respectively, of conformational disorder parameters \(x_N\) and \(x_{pN}\) in these phases (d) in points of orientational transitions in the system of conformationally flexible particles \((\gamma = 0.3)\). \(\mu_A, \mu_B\) are critical magnetic field values at which the first order nematic-paranematic phase transition changes for the second order one in systems of conformationally rigid and flexible molecules, respectively.

Fig. 4. — "magnetic field \((\mu) - temperature \((\tau)\)" phase diagrams of mesomorphic systems of conformationally rigid (a,b) and flexible (c,d) molecules with different values of the rigidity parameter \(\gamma = 0.9\) (a), 0.8 (b), 0.3 (c), 0.2 (d).
of flexible molecules and can be, as a matter of principle, verified experimentally, in spite of the fact that critical points, as has been shown above, cannot be achievable in such systems in the experiment. Figure 4 shows tendencies of alteration of the critical fields $\mu_A$ and $\mu_B$ values decreasing with the molecular rigidity parameter increase both in systems of conformationally rigid molecules (Fig. 4a,b) and in those of flexible particles (Fig. 4c,d).

In conclusion we note that, since the diamagnetic susceptibility of dielectrics has small values, then for verification of the conclusions obtained investigations of mesophases in electric fields can prove to be more preferential than in magnetic ones.

**Designations.**

N - nematic, pN - paranematic; A,B - end critical points in lines of isostructural transformations N-pN in systems of conformationally rigid (Fig. 4a,b) and flexible (Fig. 4c,d) molecules, respectively.

**References**


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