

# Spontaneous deracemization of NLC at phase transitions

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The possibility of spontaneous deracemization of nematogenic substances with a low energy barrier between enantiomers is investigated in the Maier–Saupe model. It is shown that the correlation between deracemization and the orientational order parameters results in the appearance of new phase diagrams  $I-1-N-1-C$  and  $I-1-C$  ( $I$  and  $N$  are the racemic isotropic and nematic phases,  $C$  is the deracemic cholesteric phase, and the number 1 indicates the type of transition). In the case when the transition time between enantiomer states is long compared with the time required to establish orientational order, the lifetime of some metastable phases increases, and this could be the reason for the temperature hysteresis of the  $N-1-C$ ,  $I-1-C$ , and  $D-1-C$  phase transitions ( $D$  is the deracemic isotropic phase) and monotropism of the nematic phase.

## INTRODUCTION

A distinguishing feature of mesogenic molecules is their conformational mobility, i.e., the possibility of a change in spatial structure accompanying rotation about the bonds. For this reason, the achiral nematic phase arises not only when the main conformational state is achiral (NLC-1), but also when it is chirally and doubly degenerate under the condition that the energy barrier between the left- and right-hand enantiomers is not very high ( $< 10^5$  J/mole), so that the nematic phase can form due to racemization, i.e., due to equality of the concentrations of the enantiomers (NLC-2).

X-ray structural measurements<sup>1</sup> and quantum-mechanical calculations<sup>2</sup> show that the well-known PAA and MBBA apparently belong to the NLC-2 state. It is obvious that deracemization of NLC-2, being spontaneous and arising due to the intermolecular interaction<sup>3,4</sup> or induced by external action, for example, by circularly polarized light,<sup>5</sup> should result in the formation of a chiral cholesteric phase with a characteristic spiral structure.

The possibility of spontaneous deracemization of NLC-2 owing to intermolecular interaction was first pointed out by Zel'dovich.<sup>3</sup> If the interaction between identical enantiomers is stronger than between opposite enantiomers, then a phase transition (PT) like the transition at the Curie point in ferromagnets is possible in the system. Zel'dovich's calculation<sup>3</sup> was performed in the self-consistent-field model, analogous to Weiss's theory.

Katz took into account in a self-consistent fashion the formation of a helix accompanying spontaneous deracemization of NLC-2.<sup>4</sup> In the case of the helix structure, the induced dipole-quadrupole interaction makes different contributions to the effective interaction energies between the two right-hand and two left-hand enantiomers, giving rise, in this manner, to positive feedback between spontaneous deracemization and the inverse pitch of the helix.

Both models neglect the differences in the orientational order parameters for different enantiomers with spontaneous deracemization and predict a second-order NLC–CLC phase transition.

In the present paper we give a microscopic description of spontaneous deracemization in the Maier–Saupe model. As will be shown below, the correlation between deracemi-

zation and orientational ordering can change the type of NLC–CLC phase transition and the phase diagram as a whole.

## 1. SPONTANEOUS DERACEMIZATION IN THE MAIER–SAUPE MODEL

We shall employ the Maier–Saupe model for a two-component mixture in order to describe the spontaneous deracemization. In this model the self-consistent potentials  $W_\alpha$  for two enantiomers (where  $\alpha$  is a + or – sign) have the form

$$W_\alpha(\theta_\alpha) = - \sum_\beta C_\beta [U_{\alpha\beta}^{(0)} + U_{\alpha\beta}^{(2)} S_\beta P_2(\cos \theta_\alpha)], \quad (1)$$

where  $\theta_\alpha$  is the angle between the long axis of the molecule of the  $\alpha$ th enantiomer and the director,  $S_\beta$  and  $C_\beta$  are, respectively, the orientational order parameter and the concentration of the  $\beta$ th enantiomer ( $\beta$  denotes + or – sign;  $C_+ + C_- = 1$ ), and  $U_{\alpha\beta}^j$  are the coefficients in the expansion of the intermolecular interaction in Legendre polynomials.

Since even in pure cholesterics the pitch of the helix is much greater than the intermolecular distance, for simplicity we neglect the reciprocal effect of the helix on the intermolecular interaction; then  $U_{++}^{(j)} = U_{--}^{(j)}$ . A qualitative analysis of the effects arising when this approximation is not employed will be presented below. The difference between  $U_{++}^{(j)} = U_{--}^{(j)}$  and  $U_{+-}^{(j)} = U_{-+}^{(j)}$  arises due to the fact that the correlations are taken into account self-consistently.<sup>6</sup>

In this model the free energy per molecule is equal to

$$F = - \frac{1}{2} \sum_{\alpha,\beta} C_\alpha C_\beta (U_{\alpha\beta} + U_{\alpha\beta} S_\alpha S_\beta) + T \sum_\alpha C_\alpha \left[ \ln C_\alpha + \int \rho_\alpha(\theta_\alpha) \ln \rho(\theta_\alpha) d(\cos \theta_\alpha) \right]. \quad (2)$$

Minima of the free energy  $F$  with respect to the orientational distribution functions  $\rho_\alpha(\theta_\alpha)$  and the relative deracemization  $y = C_+ - C_-$  correspond to stable states of the

system. It is obvious that minimizing  $F$  with respect to  $\rho_\alpha(\theta_\alpha)$  gives  $\rho_\alpha(\theta_\alpha) \propto \exp(w_\alpha \cos \theta_\alpha)$  and the consistency equation

$$S_\alpha = Z_\alpha^{-1} \int_0^1 P_2(x) \exp(w_\alpha x^2) Dx, \quad (3)$$

where

$$Z_\alpha = \int_0^1 \exp(w_\alpha x^2) Dx,$$

$$w_\alpha = 3 \sum_\beta S_\beta C_\beta U_{\alpha\beta}^{(2)} / 2T.$$

It is convenient to represent the  $y$ -dependent part of the free energy  $\Delta F(y)$  to use Eq. (3) in the dimensionless form

$$\Delta F/2T = f = f_{is} + f_{an}, \quad (4)$$

where

$$f_{is} = [-y^2 U_0 + (1+y) \ln(1+y) + (1-y) \ln(1-y)],$$

$$f_{an} = -1/6 A [(1+y)^2 S_+ (S_+ + 1) + (1-y)^2 S_- (S_- + 1) + U_2 (1-y^2) \times (2S_+ S_- + S_+ + S_-)] + (1+y) \ln Z_+ + (1-y) \ln Z_-.$$

$$U_0 = (U_{++}^{(0)} - U_{+-}^{(0)}) / 2T, \quad A = 3U_{++}^{(2)} / 2T, \quad U_2 = U_{+-}^{(2)} / U_{++}^{(2)}.$$

## 2. RESULTS AND DISCUSSION

The minimum of  $f$  with respect to  $y$  cannot be found analytically. But, before we present the results of numerical calculations, we analyze the general properties following from the expression (4). It is obvious that  $f_{is}$  and  $f_{an}$  are even functions of  $y$ . For this reason, the points ( $y=0$ ) corresponding to the racemic isotropic ( $I$ ;  $S_+ = S_- = 0$ ) and nematic ( $N$ ;  $S_+ = S_- = S_N$ ) phases are extrema with respect to  $y$ . For racemic phases the expression (4) reduces to the standard expression for a single-component substance and the phase transition  $I-1-N$  (the number 1 indicates the type of transition) should occur at  $T = T_{IN}$ , determined from the condition  $A = A_{IN} = 6.812 \cdot 2 / (1 + U_2)$ . Besides the racemic phases, there can also exist deracemic ( $y \neq 0$ ) isotropic ( $D$ ;  $S_+ = S_- = 0$ ) and cholesteric ( $C$ ;  $S_+ \neq S_-$ ) phases.

Since for  $S_+ = S_- = 0$  we have  $f_{an} = 0$ , the isotropic phases  $I$  and  $D$  are described by the term  $f_{is}$ , which is identi-

cal to the expression obtained in Ref. 3. At the temperature  $T = T_{ID}$ , determined from the condition  $U_0 = 1$ , a phase transition  $I-2-D$  should occur between these phases.

In analyzing the numerical calculation it is convenient to represent  $U_0$  in the form  $U_0 = \tilde{U}_0 A / A_{IN}$ . Then the change in the temperature is given by the quantity  $A$ , while  $U_2$  and  $\tilde{U}_0$  are temperature-independent parameters, characterizing the intermolecular interaction. The normalization of  $\tilde{U}_0$  and  $U_2$  is chosen so that the values  $\tilde{U}_0 = 1$  and  $U_2 = 1$  are special values. The inequality  $\tilde{U}_0 > 1$  is the condition for the appearance of the  $D$ -phase prior to the transition into the nematic phase. For  $U_2 = 1$  the anisotropic part of the free energy  $f_{an}$  does not depend on  $y$  and the order parameters  $S_+ = S_-$  are independent of  $y$ . Then spontaneous deracemization is described by the expression for  $f_{is}$  obtained in Ref. 3. It should occur at  $T = T_{ID}$  irrespective of whether or not this temperature corresponds to the isotropic or liquid-crystalline phases (in the latter case, naturally, an  $N-2-C$  transition should occur).

Figure 1a shows the curves  $f(y)$ , calculated  $\tilde{U}_0 = 0.32$  and  $U_2 = 0.45$  and under the condition that the consistency equation (3) holds. Since for  $\tilde{U}_0 < 1$  the qualitative form of the dependence  $f_{is}(y)$  does not change in the temperature interval of interest to us near  $T_{IN}$ , Fig. 1a shows only one dashed curve, corresponding to  $T = T_{IN}$ . The curve has a single temperature-independent minimum  $f_{is}(0) = 0$ , corresponding to a racemic isotropic liquid. At high temperatures (curve 1) there are no minima corresponding to orientationally ordered phases, since nonzero solutions of Eq. (3) do not exist for all values of  $y$ . At  $T = T_N^* = 1.01199 T_{IN}$  a metastable minimum appears (curve 2), which corresponds to the nematic phase and which at  $T = T_{IN}$  becomes equal to the isotropic minimum, and an  $I-1-N$  phase transition occurs (curve 3). At  $T = T_C^*$  an additional cholesteric minimum with  $y \neq 0$  (curve 4) arises on the liquid-crystal branch. This minimum rapidly becomes deeper, and at  $T = T_{NC}$  becomes equal to the nematic minimum (curve 5) and gives rise to a first-order  $N-1-C$  phase transition with jumps in the deracemization parameter ( $0 \rightarrow y_C$ ) and the order parameter ( $S_N \rightarrow S_+, S_-$ ). As the temperature decreases further the barrier between the cholesteric and nematic phases decreases and vanishes completely at  $T = T_N^{**}$  (curve 6), determining the lower limit of metastability of the nematic phase. Thus for the chosen parameters  $U_2$  and  $\tilde{U}_0$  the phase transition temperatures and limits of metastability form the following sequence:

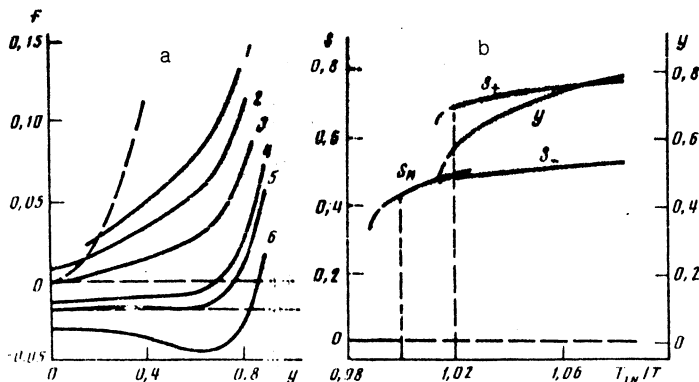


FIG. 1. a— $f(y)$  for  $\tilde{U}_0 = 0.32$  and  $U_2 = 0.45$  for different temperatures  $T$ : 1— $1.02300 T_{IN}$ , 2— $T_N^* = 1.01199 T_{IN}$ , 3— $T_{IN}$ , 4— $T_C^* = 0.98699 T_{IN}$ , 5— $T_{NC} = 0.98230 T_{IN}$ , and 6— $T_N^{**} = 0.97172 T_{IN}$ . The dashed line depicts the curve  $f_{is}(y)$  at  $T = T_{IN}$ . b—Temperature dependence of the orientational order parameters  $S_N$ ,  $S_+$ , and  $S_-$  and of the relative deracemization  $y$ . The dashed line designates the regions of metastability.  $\tilde{U}_0 = 0.32$  and  $U_2 = 0.45$ .

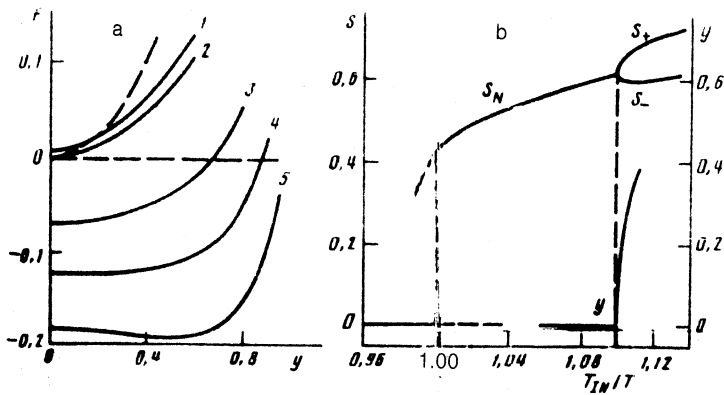


FIG. 2. a— $f(y)$  for  $\tilde{U}_0 = 0.4$  and  $U_2 = 0.6$  for different temperatures  $T$ : 1— $T_N^* = 1.01199 T_{IN}$ , 2— $T_{IN}$ , 3— $0.91256 T_{IN}$ , 4— $T_N^{**} = T_{NC} = 0.90963 T_{IN}$ , 5— $0.88562 T_{IN}$ . b—same as Fig. 1b, for  $\tilde{U}_0 = 0.4$  and  $U_2 = 0.6$ .

$$T_N^* > T_{IN} > T_C^* > T_{NC} > T_N^{**}$$

The temperature dependences of the orientational order and deracemization parameters are presented in Fig. 1b.

An increase in  $U_2$ , corresponding to a decrease in the difference in the anisotropic interaction between the identical and different enantiomers, results in a gradual decrease to zero in the jumps in  $y$  and  $S$  at  $T = T_{NC}$ . Figure 2a shows a sequence of dependences  $f(y)$  for  $U_2 = 0.6$  and  $\tilde{U}_0 = 0.4$ . This series shows that in this case the NLC-CLC phase transition is of second order (curve 4). The order parameters  $S_+$ ,  $S_-$ , and  $y$ , presented in Fig. 2b, have square-root temperature dependence for  $T < T_{NC}$ . This is apparently a general property of second-order phase transitions in self-consistent field models with a linear relation between the order parameters ( $S_+ - S_- \propto y \propto (T_{NC} - T)^{1/2}$ ).

An increase in  $\tilde{U}_0$  gives rise to deracemization of the system. Thus for  $\tilde{U}_0 = 0.65$  and  $U_2 = 0.5$  (Fig. 3a) as the temperature decreases the cholesteric phase arises before the nematic phase (curves 1 and 2). The metastable nematic phase appears in a narrow temperature interval between  $T_N^*$  (curve 3) and  $T_N^{**}$  (curve 4) below  $T_{IC}$ . In this case we have  $f_N > f_I > f_C$ , and in addition the nematic minimum is very shallow ( $\sim 10^{-3}$ ), since the barrier between the  $N$  and  $C$  phases in Fig. 3a is hardly discernible. As one can see from Fig. 3b,  $S_N < S_+$ ,  $S_-$ , i.e., deracemization increases the orientational ordering of both enantiomers.

For  $\tilde{U}_0 > 1$  in the temperature range of interest to us the dependence  $f_{is}(y)$  describing isotropic phases changes qualitatively (dashed curves in Fig. 4a). At  $T = T_{ID}$  (curve 1)

the spontaneous deracemization  $I-2-D$  predicted by Zel'dovich in Ref. 3 occurs in the isotropic phase. The solid lines represent the  $f(y)$  curves for orientationally ordered phases. The nematic phase does not arise in this case, the cholesteric phase forms at  $T = T_C^*$  as a metastable state (curve 2), and at  $T = T_{DC}$  the cholesteric minimum becomes equal to the isotropic minimum (curve 3) and the  $D-1-C$  phase transition occurs. As one can see from Fig. 4a,  $f_{is}(y)$  has a much smoother minimum than  $f(y)$ , and it changes significantly more slowly as a function of the temperature. For this reason, in the  $D$  phase strong fluctuations of the concentration of the enantiomers should be superposed on the square-root dependence  $y \propto (T_{ID} - T)^{1/2}$  (Fig. 4b). The  $D-1-C$  phase transitions are accompanied by a significant jump in the relative deracemization parameter  $y$  and a sharp decrease of the concentration fluctuations.

The dependence of the phase diagrams on the parameters  $U_2$  and  $\tilde{U}_0$  is shown in Fig. 5.

On the basis of the model under consideration, for  $U_2 < 1$  the cholesteric phase should always be realized at low temperatures. If, however,  $T_{NC}$  lies significantly below  $T_{IN}$ , then there is not enough time for the cholesteric phase to form, since crystallization occurs before deracemization. Curve 1, delimiting the region  $I$  where the cholesteric phase is absent, was obtained under the assumption that crystallization starts at  $S_N = 0.7$ .

In order to analyze the type of  $N-C$  phase transition it is convenient to represent  $f(y)$  in the form of a power series:

$$f(y) = f_N + ay^2 + by^4 + cy^6 + \dots$$

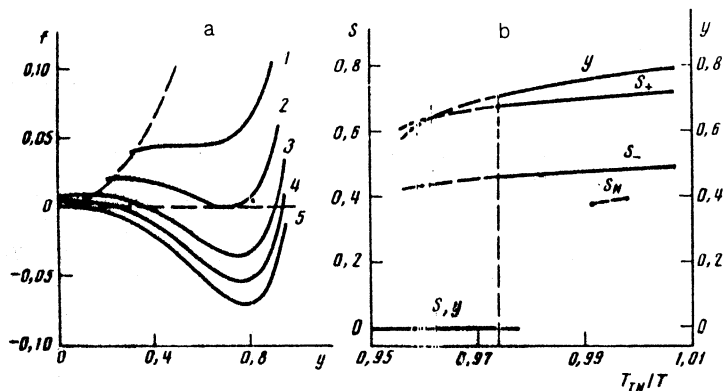


FIG. 3. a— $f(y)$  for  $\tilde{U}_0 = 0.65$  and  $U_2 = 0.5$  at different temperatures  $T$ : 1— $T_C^* = 1.04698 T_{IN}$ , 2— $T_{IC}^* = 1.02634 T_{IN}$ , 3— $T_N^* = 1.01199 T_{IN}$ , 4— $T_N^{**} = 1.00616 T_{IN}$ , 5— $T_{IN}$ . b—same as Fig. 1b, for  $\tilde{U}_0 = 0.65$  and  $U_2 = 0.5$ .

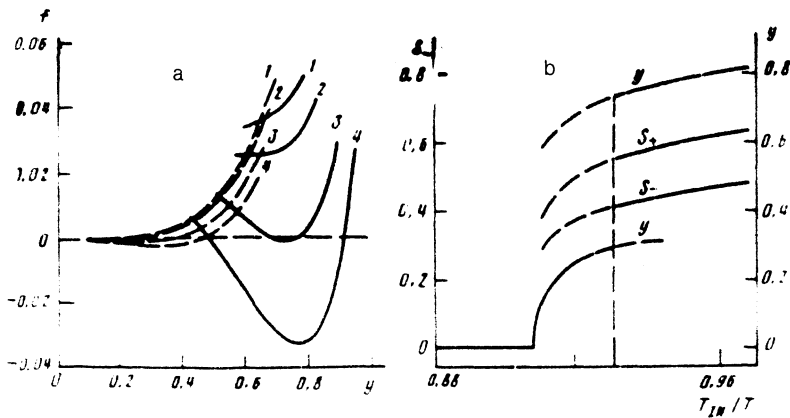


FIG. 4. a— $f_N^-(y)$  (dashed lines) and  $f(y)$  (solid lines) for  $\bar{U}_0 = 1.1$  and  $U_2 = 0.65$  at different temperatures  $T$ : 1— $T_{ID} = 1.10001T_{IN}$ , 2— $T_C^* = 1.09390T_{IN}$ , 3— $T_{DC} = 1.07390T_{IN}$ , 4— $1.05764T_{IN}$ . b—same as Fig. 1b, for  $\bar{U}_0 = 1.1$  and  $U_2 = 0.65$ .

where the coefficients  $a$ ,  $b$ , and  $c$  take into account the  $y$ -dependence of  $S_+$  and  $S_-$ . The temperature  $T_N^{**}$  is the limit of stability of the nematic phase with respect to deracemization, so that  $a(T_N^{**}) = 0$ . It is obvious that the type of phase transition is determined by the sign of the coefficient  $b$  at  $T = T_N^{**}$ . For this reason, the curve found from the condition  $b(T_N^{**}) = 0$  is the line of tricritical points with characteristic temperature dependence  $y \propto (T_N - T)^{1/4}$  (Ref. 7). The curve 3 delimits the regions II and III, for which a stable nematic phase exists, and it is the line of triple points ( $f_I(T_{IN}) = f_N(T_{IN}) = f_C(T_{IN})$ ). The curve 4 delimits the part of the region IV where the nematic can exist in a metastable state. The curve 5 is the limit of the appearance of deracemized isotropic phase and is simultaneously the triple line ( $f_{is}^I(T_{ID}) = f_{is}^D(T_{ID}) = f_C(T_{ID})$ ). It intersects the straight line  $\bar{U}_0 = 1$  only with  $U_2 = 1$ , since for  $U_2 < 1$  and  $\bar{U}_0 = 1$ ,  $T_{IN} < T_{IC}$ .

The rates at which equilibrium values of the orientational order and deracemization parameters are established can differ significantly, since they are determined by different processes at the molecular level: change in the orientation of the long axis of a molecule and conformational transitions between enantiomers. The rate of the first process is virtually independent of the individual features of the substance and lies in the range  $10^6$ – $10^7$  sec $^{-1}$ . For this reason,

the transition from the metastable state into a stable state as a result of orientational ordering should occur quite rapidly, even in the presence of a barrier in the free energy between them. At the same time, the rate  $\omega_{conf}$  of the transition between enantiomer states is determined by the structure of the molecule and can be quite low. In the latter case the lifetimes of the metastable states, transitions from which are related with the change in the concentration of enantiomers, increase significantly. As a result, the  $N$ – $1$ – $C$  phase transition will actually occur not at  $T = T_{NC}$ , but rather at  $T = T_N^{**}$  as the temperature decreases and at  $T = T_C^*$  as the temperature increases. The temperature hysteresis which arises could be responsible for the monotropism of the nematic phase, when this phase arises only on cooling. The range of values of the parameters  $\bar{U}_0$  and  $U_2$ , which corresponds to a monotropic  $N$  phase, is bounded by curves found from the conditions  $T_{IN} = T_N^{**}$  (curve 3') and  $T_{IN} = T_C^*$  (this curve is practically identical to the curve 3 and is not presented in Fig. 5).

The part of the region IV between the curves 3' and 4 (the latter curve was found from the condition  $T_N^* = T_N^{**}$ ) corresponds to the values of the parameters  $\bar{U}_0$  and  $U_2$  for which a temperature interval of the metastable nematic phase with  $f_N > f_I$  exists.

### 3. CONCLUSIONS

This paper is an elaboration of the investigation of the possibilities of spontaneous deracemization in nematics, begun in Refs. 3 and 4, where the possibility of second-order  $I$ – $2$ – $D$  and  $N$ – $2$ – $C$  phase transitions was predicted.

The effects considered above arise when the orientational ordering and relative deracemization are taken into account in a self-consistent manner. The correlation between them results in interaction of the order parameters  $S_+$ ,  $S_-$ , and  $y$ , and can significantly expand the possible types of phase diagrams:

a) the  $N$ – $C$  phase transition can become a first-order phase transition (Fig. 1);

b) deracemization can occur simultaneously with orientational ordering (the  $I$ – $1$ – $C$  phase transition) (Fig. 3); and,

c) the  $D$ – $1$ – $C$  phase transition is accompanied by a jump in the deracemization parameter  $y$  (Fig. 4).

The calculations were performed in the Maier–Saupe model, but the observed effects are characteristic for systems with interacting order parameters<sup>7</sup> and they can probably

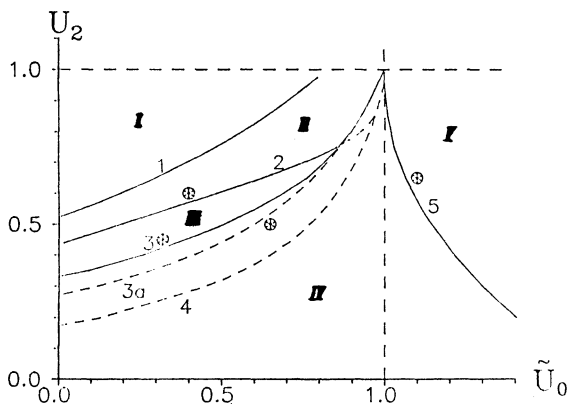


FIG. 5. Phase diagrams as a function of the parameters  $\bar{U}_0$  and  $U_2$ : I— isotropic liquid (IL)–NLC–crystal; II— IL–NLC–2–CLC; III— IL–NLC–1–CLC; IV— IL–1–CLC; V— IL–2–deracemized IL–1–CLC. The dots indicate the values of the parameters  $\bar{U}_0$  and  $U_2$ , corresponding to Figs. 1–4.

also be obtained by alternative methods (on the basis of the Landau-de Gennes theory, taking into account correlations, etc.). We note that the quantitative relations between the temperatures  $T_{IN}$ ,  $T_C$ , and  $T_C^*$  are approximate, especially since, strictly speaking, the parameters  $\tilde{U}_0$  and  $U_2$  also are slightly temperature dependent.

In contrast to the orientational ordering, the change in the relative deracemization depends significantly on the structure of the molecules and can be quite slow. In the latter case, temperature hysteresis of the  $N-1-C$  phase transition should be observed right up to complete vanishing of the nematic phase on heating.

The results presented above were obtained neglecting the feedback between the molecular interaction and the formation of a cholesteric helix, which could itself be the reason for spontaneous deracemization of the nematic phase.<sup>4</sup> This effect will not give phase diagrams of a new type, but sponta-

neous deracemization will occur at higher temperatures, which will shift all curves in Fig. 5 upwards.

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