

Unconventional Mesophases Formed by Condensed Vector Waves in a Medium of Achiral Molecules

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A phenomenological theory that describes the phase transitions from a liquid of achiral molecules to the periodic antiferroelectric mesophases is presented. The transitions are shown to be driven by the vector-wave condensation mechanism. Resulting ordered phases have the structure of a vector wave with linear, circular, or elliptic polarization. The phase diagram, the stability with respect to spatial modulation, and the behavior in an external field are discussed in relation with the recently discovered achiral antiferroelectric liquid crystals. [S0031-9007(98)08201-5]

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Prediction of the ferroelectric phase existence in chiral smectics [1], followed by the discovery of a variety of ferro-, antiferro-, and ferrielectric mesophases [2,3] is a success of the application of symmetry arguments in liquid crystal research. In the media formed by *chiral* molecules the *tilted smectic structure* becomes simultaneously *polar*, which leads to a strong *induced* ferroelectricity (or antiferroelectricity) effect. The more general question of whether the polar ordering could exist in a medium of *achiral* molecules has remained open for a long time, though a considerable effort, both experimental [4] and theoretical [5], has been expended to prove the existence of ferroelectricity in this system. The dipole interaction in conventional liquid crystals was considered to be too weak to produce long-range polar ordering [6], the induced ferroelectric effect is forbidden by the symmetry of achiral medium, and the induced antiferroelectricity was not discussed. However, recent progress in the synthesis of mesogenic molecules with unconventional shape [7,8] resulted in the discovery of new antiferroelectric phases in a media formed by achiral molecules with bent cores (*banana-shaped molecules*) [8–10]. In an external electric field these phases show double hysteresis loops and high saturation polarization. The common striking feature of the new phases is their *chiral symmetry*. In addition, these phases are not miscible with any known mesophase. This fact indicates that their structures should be completely new. The structural models proposed after the first series of experiments use the notions well established for *conventional liquid crystals* to explain the properties of the new mesophases. Sekine *et al.* [11] used the analogy with the helicoidal structure of the smectic-*C** (*Sm-C**) phase in chiral smectics to take into account apparently circular domains revealed by the texture analysis. The type of the thermodynamical instability, which can form that structure has not yet been advanced. Link *et al.* [10] considered the new phase to be also a classical smectic one, in which the chirality is induced by two distinct instabilities of a hypothetical paraelectric structure. Both models

assume implicitly the existence of a *smectic paraelectric phase* which should be stable between the antiferroelectric phase and the isotropic liquid. However, at the same time x-ray diffraction and optical microscopy have shown the absence of the paraelectric *Sm-A* phase in the phase sequence of the compounds under consideration: The antiferroelectric phase condenses directly from the isotropic liquid [8–12]. This essential point clearly distinguishes the new phases from previously studied ferroelectric and antiferroelectric analogs.

The aim of this Letter is to account for these particular features and to propose a phenomenological model of the antiferroelectric phase formation in a system of achiral molecules assuming condensation of a vector wave directly from the isotropic liquid. We show that three distinct phases stabilized by this mechanism have the “*condensed wave*” structure of linear, circular, and elliptic polarization, respectively (Fig. 1). The “waves” polarized circularly or elliptically have chiral symmetry, though in these phases the domains of opposite chirality are energetically equivalent and coexist at the same temperature. The structure of the phase with linear wave polarization is achiral. The unconventional mesophase formation mechanism, which we propose, is fundamentally different with respect to existing mechanisms of liquid crystal formation, namely, those of the liquid to nematic or liquid to smectic phase transitions. The situation is reminiscent of that in the theory of high- T_c superconductors, where the classical *s*-pairing mechanism was replaced by the anisotropic $d_{x^2-y^2}$ -wave pairing [13]. Following the analogy between superconductors and liquid crystals developed by de Gennes [14] *s*-pairing is equivalent to the condensation of a *scalar density wave* $\rho = |\psi|e^{i(\mathbf{k}\cdot\mathbf{r}+\phi)} + \text{c.c.}$, which is responsible for the transition into the *Sm-A* phase. The order parameter (OP) components for this transition are the complex wave amplitudes $\psi = |\psi|e^{i\phi}$ and $\psi^* = |\psi|e^{-i\phi}$. Along the same line, the order parameter of the *vector wave* condensate proposed in this Letter is perfectly isomorphous to the OP of the anisotropic *d*-wave pairing in a

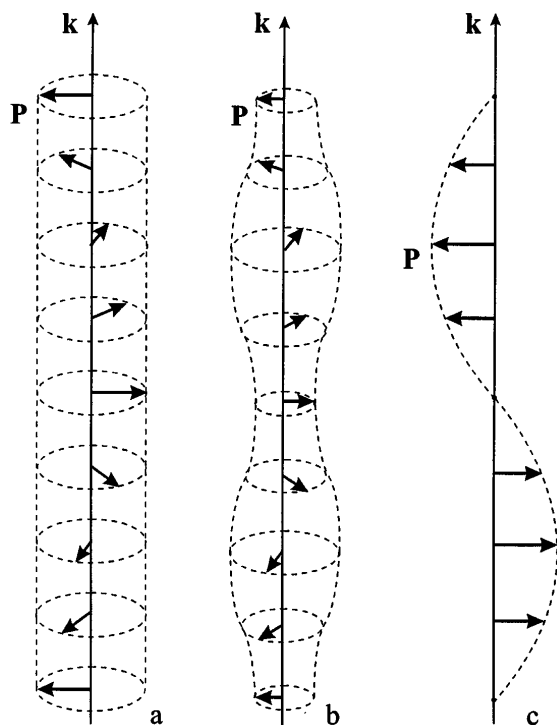


FIG. 1. Condensed wave antiferroelectric structures with (a) circular C , (b) elliptic EL , and (c) linear R polarization.

two-dimensional superconductor which stabilizes three distinct superconducting phases [15]. This analogy opens up the possibility to use numerous results of the d -wave superconductivity theory for the understanding of the proposed unconventional periodic mesophases, namely, the number and the type of phases, phase diagram, critical behavior, vortexlike defects, mixed twist-grain-boundary (TGB)-like states, etc.

The formation of an antiferroelectric phase with local polarization perpendicular to the wave vector of the structure is driven by the condensation of a transverse polar wave $\mathbf{P}(\mathbf{r})$:

$$\mathbf{P}(z) = \mathbf{e}_x[p_x \cos(kz + \varphi_x)] + \mathbf{e}_y[p_y \cos(kz + \varphi_y)], \quad (1)$$

where the z axis is chosen along the wave vector \mathbf{k} , p_x and p_y are the components of the wave amplitude, φ_x and φ_y are the initial phases, and \mathbf{e}_x and \mathbf{e}_y are the unit vectors in the plane perpendicular to the wave vector. The combinations $\eta_1 = p_x e^{i\varphi_x} - ip_y e^{i\varphi_y}$, $\eta_2 = p_x e^{-i\varphi_x} - ip_y e^{-i\varphi_y}$, η_1^* and η_2^* of the complex wave amplitudes span four components of the irreducible representation of the liquid state Euclidean symmetry group $O(3) \times R_3$ and represent the OP components $\eta_1 = |\eta_1| e^{i\varphi_1}$, $\eta_2 = |\eta_2| e^{i\varphi_2}$. The transformation properties of the OP components' permit to calculate the effective free energy associated with the antiferroelectric phase formation depends only on two invariants: $I_1 = \eta_1 \eta_1^* + \eta_2 \eta_2^* \equiv |\eta_1|^2 +$

$$|\eta_2|^2 \text{ and } I_2 = \eta_1 \eta_1^* \eta_2 \eta_2^* \equiv |\eta_1|^2 |\eta_2|^2:$$

$$F = a_0(T - T_c)I_1 + a_2 I_1^2 + b_1 I_2 + b_2 I_2^2 + \dots \quad (2)$$

Minimization of the free energy with respect to the OP components provides four stable states: (I) the high symmetry liquid phase denoted L when $|\eta_1| = |\eta_2| = 0$. (II) For $|\eta_1| \neq 0$, $|\eta_2| = 0$ (or equivalently $|\eta_1| = 0$, $|\eta_2| \neq 0$) an antiferroelectric phase denoted C and represented by a *circularly polarized wave* with the period $2\pi/k$ is stabilized. In the uniaxial chiral symmetry group $G_C = \infty_1 22 (D_\infty)$ of this structure, the continuous translations t_z are broken as well as the continuous rotations R_θ . By contrast, all the helical combinations $t_{\theta/k} R_\theta$ remain symmetry elements of the state. (III) For $|\eta_1|^2 = |\eta_2|^2$, one obtains the phase R with a biaxial achiral symmetry group $G_R = mma (D_{2h})$ and a *linearly polarized wave* structure. (IV) The intermediate phase EL , characterized by $|\eta_1| \neq |\eta_2|$, corresponds to the *general transverse wave with elliptic polarization* and biaxial chiral symmetry group $G_{EL} = 2_1 22 (D_2)$ (see Fig. 1).

Let us note that the vector wave condensation induces as a secondary OP the condensation of the scalar density wave $\rho = |\Psi| e^{i(2kz + \alpha)} + \text{c.c.}$ with the wavelength equal to the half-period of the vector wave. The corresponding coupling free energy has the form $F_{\text{coupl}} = \gamma[|\eta_1| \times |\eta_2| |\Psi| \cos(\varphi_1 - \varphi_2 - \alpha)]$ and induces smectic order in the phases with linear (R) and elliptic (EL) vector wave polarization. However, in the phase C with circular polarization the coupling energy vanishes and the structure does not become smectic. This fact shows that these new mesophases can be *periodic* but, however, *not smectic* and illustrates the difference with conventional liquid crystals. A typical phase diagram presenting stability regions for all the phases is shown in Fig. 2. In this simplest diagram the isotropic liquid is separated from the C phase by a line of second-order phase transformation. The transition between L and R phases changes its order from second to

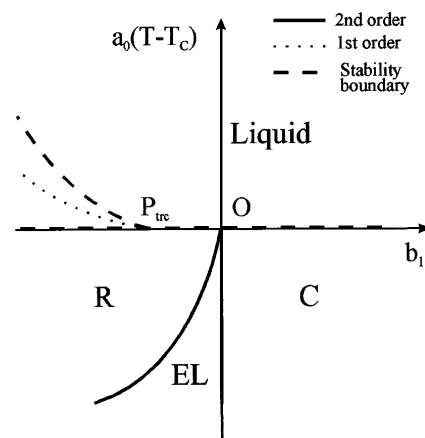


FIG. 2. Phase diagram associated with the free energy Eq. (2).

first at a tricritical point P_{trc} . The stability region of the elliptic phase EL is limited by lines of second-order phase transitions into the phases C and R . All three phases merge at a so-called Landau point O [16].

Before we present a detailed description of the structures involved in the phase diagram we first point out that for an isotropic liquid formed by achiral molecules the axial vector wave (e.g., a wave of molecular tilt with respect to the wave vector direction) and the polar vector wave span the same representation of the symmetry group. This fundamental property has several important physical consequences: (i) The free energy of the system, the type, and the symmetry of the phases remain exactly the same if we replace the polar vector wave $\mathbf{P}(z)$ defined in (1) by the axial vector wave $\mathbf{A}(z) = \tilde{\mathbf{e}}_x[a_x \cos(kz + \tilde{\varphi}_x)] + \tilde{\mathbf{e}}_y[a_y \cos(kz + \tilde{\varphi}_y)]$, where $\tilde{\mathbf{e}}_x$ and $\tilde{\mathbf{e}}_y$ are the unit axial vectors. The OP of this wave is defined by $\xi_1 = a_x e^{i\tilde{\varphi}_x} - ia_y e^{i\tilde{\varphi}_y}$ and $\xi_2 = -a_x e^{-i\tilde{\varphi}_x} + ia_y e^{-i\tilde{\varphi}_y}$. (ii) From the thermodynamical point of view the strong coupling between two waves is expressed by the bilinear term in the free energy $F_{\text{PA}} = \delta(\eta_1 \xi_1^* - \eta_2 \xi_2^* + \eta_1^* \xi_1 - \eta_2^* \xi_2)$, where δ is a phenomenological coupling constant. Consequently, the condensation of the tilt wave necessarily induces the polarization wave, and vice versa.

The phenomenological description and molecular symmetry permit us to model the distribution of molecules in each phase. Banana-shaped molecules of C_{2v} symmetry possess a permanent dipolar moment \mathbf{p}_0 . Its local average value has the meaning of the polar vector \mathbf{P} . By contrast, the axial vector \mathbf{A} cannot be attributed to a single molecule and characterizes a property of the molecular orientation distribution function. In the C phase the vector \mathbf{A} has a simple geometrical meaning. It can be presented as a tilt of molecules with respect to the local plane formed by the polarization vector \mathbf{P} and the wave vector (Fig. 3). The molecular distribution in the C phase can be understood then as a spiral formed by the banana-shaped molecules tilted to the constant angle β out of the local (\mathbf{P}, \mathbf{k}) plane

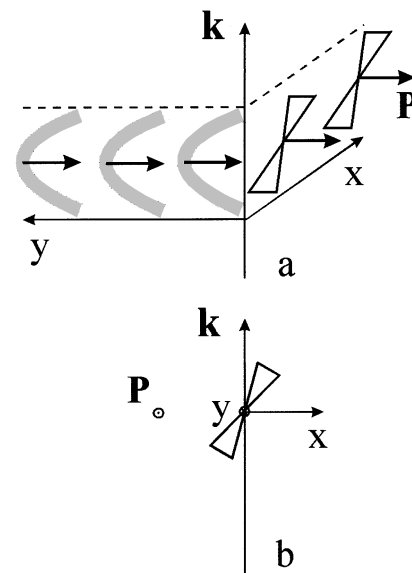


FIG. 3. Local structure of the antiferroelectric phase C with circular wave polarization (a) in a plane perpendicular to the wave vector; (b) relation between the molecular plane tilt, the polarization \mathbf{P} , and the wave vector \mathbf{k} .

(Fig. 3). In the R phase the axial vector \mathbf{A} has no so simple image as it is the case in the C phase. Nevertheless, the smectic character of the linear phase R permits its presentation in a simplified way in the region far from the transition from the liquid state. When the smectic layers are well pronounced the structure can be represented as a simple bilayer antiferroelectric phase. A similar structure was proposed by Takezoe and Watanabe [17] to interpret the dielectric and optical properties of the bent achiral twin dimers. In the elliptic phase EL the structure combines the features of the C and R phases.

In order to study the spatial variation of the order parameter along the wave vector direction we have to consider in addition to (2) the inhomogeneous part of the free energy which contains in the simplest case three terms:

$$F_{\text{inh}} = \lambda[\eta_1(\partial\eta_1^*/\partial z) - \eta_1^*(\partial\eta_1/\partial z) - \eta_2(\partial\eta_2^*/\partial z) + \eta_2^*(\partial\eta_2/\partial z)] \\ + g[(\partial\eta_1/\partial z)(\partial\eta_1^*/\partial z) + (\partial\eta_2/\partial z)(\partial\eta_2^*/\partial z)] + \kappa[\eta_1\eta_2^*(\partial\eta_1^*/\partial z)(\partial\eta_2/\partial z) + \eta_2\eta_1^*(\partial\eta_2^*/\partial z)(\partial\eta_1/\partial z)].$$

The addition of the gradient terms leads to the trivial consequences in the phases C and R . Their structures remain homogeneous but their actual wave vectors become temperature dependent: $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{q}(T)$. By contrast, the homogeneous EL phase is unstable with respect to the spatial modulation. Its structure becomes incommensurate and can be presented by the following wave:

$$\mathbf{P}(z) = \mathbf{e}_x\{p_x \cos[(k + q_1)z] + p_y \cos[(k - q_2)z]\} + \mathbf{e}_y\{-p_x \sin[(k + q_1)z] + p_y \sin[(k - q_2)z]\}.$$

The corresponding point symmetry decreases from D_2 to C_2 and allows *a priori* nonzero polarization and axial vector. However, due to the chiral symmetry of this phase it should be helically wound in the direction perpendicular to the twofold axis and to the wave vector and

cancel the resulting polarization. This can lead to a TGB-like state formation mentioned as a possible candidate for the low-temperature phase in 1,3-phenylenebis[4-(4-*n*-alkyloxyphenyl-iminomethyl)benzoates] (P-*n*-O-PIMB) [11] on the basis of the x-ray diffraction data.

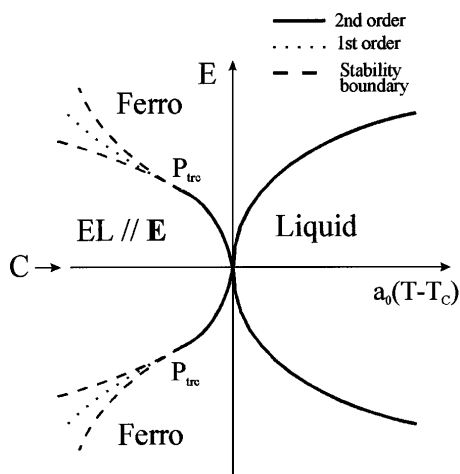


FIG. 4. The calculated electric field–temperature phase diagram. The case of $b_1 > 0$ (C -phase stable in zero field) is considered.

We studied the behavior of the antiferroelectric mesophases under an external electric field perpendicular to the wave vector of the structure. For this purpose we added to the free energy (2) the term $F_{EP} = E^2|\eta_1||\eta_2| \times \cos(\varphi_1 + \varphi_2)$ which is responsible on the coupling of the antiferroelectric OP with the field. The calculated temperature–field diagram is conditioned by the value of the b_1 constant in the free energy expansion (2). For positive b_1 the state C is stabilized for $T < T_c$ in zero field. Small field application induces elliptic distortion of the circular wave C structure, the long elliptic axis being oriented along the applied field. The point symmetry of the state changes from D_∞ to the C_2 group of the incommensurate elliptic phase EL. Such symmetry breaking can be checked experimentally using the second harmonic generation (SHG) technique. In zero field the D_∞ symmetry class gives a zero SHG tensor $\hat{d}_{ijk} = 0$; after field application the components d_{zxx} , d_{zyy} , d_{zzz} , and d_{xyz} become nonzero according to C_2 symmetry [18]. Similar behavior has been observed in the high-temperature antiferroelectric phase of achiral P-*n*-O-PIMB [19]. In the strong field the system can respond in two different ways. The elliptically distorted C phase undergoes for the finite field value a transition to the ferroelectric state and this transition can be either second order in the very vicinity of T_c , or first-order transformation with a typical double-loop hysteresis curve. The corresponding calculated T - E phase diagram is presented in Fig. 4. The final ferroelectric state stable in the region of high fields has a linearly polarized wave structure (similar to that of the R phase) but with nonzero macroscopic polarization averaged over the

period of the phase. The plane of the wave polarization of the structure is parallel to the applied field and the symmetry of the state becomes C_{2v} .

In summary, we have developed a phenomenological theory of the direct phase transition from the isotropic liquid of achiral molecules to the periodic antiferroelectric mesophase. The proposed mechanism involves a *single* instability associated with a four-dimensional order parameter and leads to three ordered states with the structures of the condensed vector wave being polarized linearly, circularly, or elliptically. These phases have no analog among the known mesophases. Their structures and their response to an external electric field make of them likely candidates for the antiferroelectric phases in liquid crystals of banana-shaped molecules.

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