Pseudoscalar liquid crystals

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Liquid crystals that differ from an ordinary liquid by the presence of a pseudoscalar quantity are considered. In this type of liquid-crystalline phase, rotation of the plane of polarization (rotation, for brevity) occurs despite the fact that the substance consists of optically inactive molecules. The rotation can have either sign, and the interface between phases with different signs of the rotation possesses a definite surface tension and energy. A transition from one phase to the other occurs at this interface.

In ordinary molecular crystals, as a rule, both the positions and orientations of the molecules are ordered. However, for many substances there also exist phases with a lower (but nevertheless partially preserved) degree of order. For example, the orientations of the molecules can remain ordered (correlation in the entire volume) in the absence of correlation of their positions. In this case the obstacle to the mutual displacement of the molecules disappears, i.e., the strength and shear modulus vanish, but the anisotropy is preserved. Such phases are called liquid-crystalline phases.

One of the properties of ordinary crystals is the possibility of rotation of the plane of polarization of light by a crystal consisting of an optically inactive substance. A necessary condition for this is the absence of a center of inversion in the lattice. As examples we may cite quartz (SiO_2) or sodium chlorate ($NaClO_3$). The rotation in the case of a cubic crystal is characterized by the magnitude of the pseudoscalar A in the expression for the dielectric constant for a field with wave-vector k_m:

$$\varepsilon_{rn}=\varepsilon_0\delta_{rn}+iA\varepsilon_{rnm}k_m,$$

where δ_{rn} is the Kronecker symbol and ϵ_{rnm} is the completely antisymmetric unit tensor of rank three (cf., e.g., the review[1]).

It is obvious that the same inactive substance gives dextro- and levorotatory crystals with equal probability1). This is the difference between such crystals and the trivial case of crystals which consist of an optically active substance and are therefore rotatory. Dextrorotatory crystals of an inactive substance can be transformed into levorotatory crystals or into a d-l mixture by reaction in the solid phase or after melting and recrystallization. Obviously, this is impossible in the case of an active substance.

In this note we remark that the crystal property that gives rise to rotation by inactive molecules can be conserved after the ordering of the positions and even the ordering of the orientations have vanished. This conclusion follows from the fact that the rotation is determined by a pseudoscalar that does not vanish on averaging over the orientations. It is illuminating to imagine a dextrorotatory monocrystal with cubic symmetry. Its rotation does not depend on the direction of the ray. Such a crystal retains its dextrorotation when crushed and pressed in the form of an isotropic (on average) polycrystal.

For a certain relationship between the forces that maintain the molecules in well-defined positions and the forces that give rise to the rotation (dextro- in the given case) of the crystal, we may imagine that when the temperature is raised the crystal will melt but the rotatory property (a pseudoscalar) will be conserved. A dextrorotatory liquid will be obtained. However, a levorotatory liquid too can consist of the same substance. It may be assumed that there exist substances for which the rotation disappears at a temperature T_c higher than the melting temperature2). The temperature T_c plays a role analogous to that of the Curie point. The liquid is an ordinary, nonrotatory, uniform liquid when $T > T_c$. When the temperature is lowered below T_c the liquid is transformed into a mechanical mixture of dextro- and levorotatory liquids. The dextro- and levorotatory liquids correspond to the minimum free energy, and the nonrotatory liquid is unstable for T below T_c. The phenomenon is similar to a certain extent to the separation of a homogeneous solution into two phases at a critical point, e.g., to the separation of a racemic melt (of dextro- and levorotatory molecules in equal numbers) into two phases with an excess of dextrorotatory molecules in one phase and of levorotatory molecules in the other.

There is, however, an essential difference: in the case under consideration here that of an active liquid of inactive molecules, the amounts of levo- and dextrorotatory liquids obtained from the ordinary liquid on cooling are not specified. One liquid can be transformed into the other. The rotation is determined not by the predetermined conformation of the atoms in the molecule, but by the ordering of the molecules when they interact. It is this ordering which permits us to call such a hypothetical rotatory liquid a "pseudoscalar liquid crystal."

In a certain sense such a body is a limiting case—the least ordered and most liquid of all liquid crystals. It is possible to construct a model of pseudoscalar liquid crystals by considering molecules that can be found in two active, mutually mirror forms d and *l* and, moreover, are easily transformed from one form to the other $d \rightleftarrows l$. It is precisely the rapid transformation that forces us to regard these molecules as inactive, in the time average. In fact, active molecules such as *l*- and d-glucose or *l*- and d-tartaric acid, are distinguished precisely by their stability, i.e., by the fact that the $d \rightleftarrows l$ transition is practically forbidden and does not occur within any foreseeable time. Thus, we shall consider inactive (in this sense) molecules transforming into each other and shall denote their total concentration by $n = d + l$. For small n, in the absence of interaction, obviously $d = l = n/2$ at equilibrium. We shall assume now that the interaction is such that two d-molecules attract each other. Two *l*-molecules attract each other in exactly the same way and with the same potential. However, it does not contradict general principles to assume that unlike molecules d and *l* repel each other, or at least attract each other more weakly. Then it is obvious that when the total concentration is large and the temperature is low a nonsymmetric mixture will be found to be thermodynamically more favorable.

For the proof we shall minimize the free energy per unit volume

$$F={}^1/_2 a(d^2+l^2)+bld+kT(d\ln d+l\ln l)$$

with the additional condition $d + l = n$. Introducing $(d-l)/2n \equiv \alpha$, we rewrite:

$$F=\frac{b+a}{4}n^2+\frac{(a-b)n^2}{4}\alpha^2+nkT\ln\frac{n}{2}+\frac{n}{2}kT\Big[\ln(1-\alpha^2)$$
$$+\alpha\ln\frac{1+\alpha}{1-\alpha}\Big]\longrightarrow\text{const}+\alpha^2\Big[\frac{n}{2}kT+\frac{(a-b)n^2}{4}\Big],\quad \alpha\ll1,$$

whence it can be seen that the critical condition has the form $kT_c = n(b-a)/2$. For $T < T_c$ the symmetric state is unstable and we find

$$\alpha_{eq}=\pm[\text{const}\cdot(T_c-T)]^{1/2}.$$

Because of the symmetry of the problem, a second-order transition occurs at T_c. On cooling of the ordinary liquid at a finite rate, supercooling and delay in the formation of the rotatory phases will not arise. It is not easy to determine the initial dispersity of the phases (we shall return to this somewhat later). For $T < T_c$ the transformation of one phase into the other is a first-order transition, since the difference between the phases is finite. However, this transition is degenerate: scalar bulk quantities (such as the energy) are strictly the same in the two phases, and only the pseudoscalars differ by a finite amount. The boundary between the phases has a definite surface energy (surface tension). It can be calculated by adding a term proportional to the square of the gradient of the pseudoscalar to the total energy density. In the first place, hydrodynamic motion occurs under the influence of the surface tension, transforming closed volumes of a given phase (e.g., volumes of the d-phase, surrounded by l-phase) into spheres with volume equal to the original volume, but with a minimum surface area for the given volume. In the next stage (and evidently more slowly) the inner phase (d in the example above) is transformed into the outer l-phase surrounding it, i.e., the surface is displaced relative to the liquid in a direction determined by the curvature of the surface. It is obvious that the kinetics of the process as a whole will be dependent on the initial distribution of the interfaces with respect to sizes and topological types (simply-connected closed surfaces; multiply-connected closed surfaces; surfaces going away to infinity ?).

It is apparent that the initial state of the process of enlargement of the regions can be obtained by considering the state above the critical temperature. In this state there is at each moment of time a certain random field of the quantity $A(x, y, z)$, or of the quantity $\alpha(x, y, z)$ (proportional to A) in the model of d- and l-molecules. This field is characterized by a definite Fourier-expansion spectrum. We may consider that, for small amplitude α, the individual Fourier components are statistically independent. It is likely that the high-frequency edge of the spectrum is cut off by the surface tension. If this is not the case, we cut it off artificially, havingthe subsequent processes in mind.

The elimination of the high-frequency harmonics ensures that the function $A(x, y, z)$ is smooth. This function is alternating in sign, since above T_c the average $\bar{A}$ equals zero. We shall consider the surface $A = 0$ separating the dextrorotatory $(A >)$ from the levorotatory $(A < 0)$ regions. It is this surface which will be transformed into the interface after cooling.

Thus, there arises the difficult but extremely interesting problem of the statistics of the sizes and properties of zero surfaces and functions specified by a random field with a given spectrum. I hope that this note will attract the attention of mathematicians to this problem.

This note (similar ideas have been expressed by I. F. Gol'dman of Erevan), which pertains to macroscopic physics, was prompted by recent ideas in the theory of elementary particles, namely, by the idea of a degenerate, nonunique state of the vacuum. In this connection one considers the transition of the vacuum from a symmetric to a nonsymmetric state, the appearance of domains, and the explanation of the violation of the symmetry of right and left and of particles and antiparticles (Weinberg et al., Kirzhnits, Linde, and Lee). Meanwhile, recourse to particle theory is not required for a reading of the above material, and therefore references to the literature are omitted.

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[1] In the case of quartz, twins consisting of grown dextro- and levorotatory crystals are called "Brazilian."

[2] Only experiment can answer the question of whether such substances exist in reality. It is appropriate to begin the search with the molten phases of substances that are rotatory in the monocrystalline state.

[1] V. A. Kizel', Yu. I. Krasilov and V. I. Burkov, Usp. Fiz. Nauk 114, 295 (1974) [Sov. Phys.-Uspekhi 17, 745 (1975)].

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