Magnetization and polarization of orientationally ordered systems

S. A. Pikin
Institute of Crystallography, Academy of Sciences of the USSR, Moscow

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An exact solution has been obtained for the general Hamiltonian which describes an orientationally ordered system with pre-transition dipole correlations of the ferromagnetic and ferroelectric type. This solution shows that finite magnetization and finite polarization, induced by weak external fields and stabilized by a liquid crystal order, can exist.

There is now no experimental evidence of the existence of intrinsic ferroelectrics and ferromagnets–liquid crystals and polymer ferromagnets. The existence of ferroelectricity in polymer materials is probably attributable to the presence in them of crystal regions (grains) with a ferroelectric order. The reason for the absence of this type of ordering in noncrystalline media is known: The interaction of magnetic and electric dipoles of the neighboring molecules is relatively weak, the dipoles are weakly correlated at relatively large distances, and the fluctuations are strong. Clearly, the indicated ferromagnetic and ferroelectric states are difficult to obtain in a "pure form," but amorphous systems with a strong enough correlation of the dipole moments can exist. Although the magnetization and polarization in such systems, on the average, can be set equal to zero, the susceptibility χ_0 of these systems as a function of the applied magnetic field $\mathscr{E}$ behaves anomalously:

$$\chi_0 \sim \mathscr{E}^{-\alpha}, \tag{1}$$

where α is the critical exponent, usually $\alpha \ll 1$. In the present letter, we postulate that the system has the property described in (1) and a macroscopic orientational (liquid crystal) order and we show that a system with such properties could exhibit magnetization and polarization properties.

Expression (1) corresponds to a plot of the induced moment $\mathcal{M}_0$ versus the applied field, which varies in accordance with $\mathcal{M}_0 \sim \mathcal{E}^{1-\alpha}$, and the singular part of the thermodynamic potential in a certain temperature interval is given by

$$-f(\mathcal{E}) \sim -|\mathcal{E}|^{2-\alpha}. \tag{2}$$

The general Hamiltonian of the system, which gives rise to the thermodynamic function (2), can be written in the form

$$\tilde{\mathcal{H}} = \mathcal{H}_0 - \mathcal{E}\mathcal{M}, \tag{3}$$

where the Hamiltonian $\mathcal{H}_0$ takes into account the interaction energy of the dipoles, which accounts for the above-mentioned strong correlation of the dipoles in the given temperature interval, and $\mathcal{M}$ is the sum of the projections of all the dipoles onto the direction of the external field. Accordingly, $\mathcal{M}_0$ is the expectation value $\langle \mathcal{M} \rangle$ with a Hamiltonian $\tilde{\mathcal{H}}$ in a unit volume of the substance.

If the medium has an orientational order, i.e., if it has a selected direction $\vec{n}$ (the director in a liquid crystal), then the possible interaction of the dipole moments with the orientational degree of freedom must be quadratic in $\vec{n}$. The corresponding contribution to the general Hamiltonian $\mathcal{H}$ can be written as follows:

$$\mathcal{H} - \tilde{\mathcal{H}} = -\frac{\lambda}{2}\mathcal{M}_{\vec{n}}^2 = -\frac{\lambda}{2}(\vec{\mathcal{M}}\vec{n})^2, \tag{4}$$

where the parameter λ characterizes the degree of orientational order and the strength of the indicated interaction. Equation (4) describes the anisotropic nature of the magnetization and polarization of the liquid crystal. In the presence of an external field $\vec{\mathcal{E}}$ the expectation value of the moment $\langle \vec{\mathcal{M}} \rangle$ may stabilize in a certain sense because of the interaction (4) and because of the strong dipole correlations: Upon removal of the field the system may retain a certain expectation value $\langle \vec{\mathcal{M}} \rangle$ because of the presence of the energy barrier, $\sim \lambda \langle \mathcal{M} \rangle^2$ which the system must surmount upon the transition to the paramagnetic state and paraelectric state.

This line of reasoning is consistent with the following analytic description. Assuming that $\mathcal{E}$ and λ in the Hamiltonian $\mathcal{H}$ are independent parameters, we write the thermodynamic potential in the absence of orientational order, i.e., when $\lambda = 0$, in the form

$$\Phi(\lambda = 0) = \Phi_0 - f(\mathcal{E}). \tag{5}$$

We assume for simplicity that the directions of the vectors $\vec{\mathcal{E}}$ and $\vec{n}$ are the same as that of the z axis. In this case, the general Hamiltonian, according to (3) and (4), is

$$\mathcal{H} = \mathcal{H}_0 - \mathcal{E}\mathcal{M}_z - \frac{\lambda}{2}\mathcal{M}_z^2. \tag{6}$$

Using the standard relation for the potential $\Phi(\lambda, \mathscr{E})$

$$-2\frac{\partial\Phi}{\partial\lambda} = \left(\frac{\partial\Phi}{\partial\mathscr{E}}\right)^2 \tag{7}$$

which is valid within statistical accuracy when the average is taken with the Hamiltonian (6), we can find a general solution of the nonlinear differential equation (7) with the initial condition (5).[1] This solution is the set of algebraic equations

$$\Phi = \Phi_0 + \frac{1}{2\lambda}(\mathscr{E} - x)^2 - f(x), \quad \frac{\partial\Phi}{\partial x} = 0$$

or

$$\Phi = \Phi_0 - f(x) + \frac{\lambda}{2}(f'(x))^2, \quad x = \mathscr{E} + \lambda f'(x). \tag{8}$$

Solution (8) is described in detail in Ref. (1). In our case it describes a usual phase transition upon the reversal of sign of the field, $\mathscr{E}_z$. Since x and Φ, according to (8) where $f'(x) \sim \chi^{1-\alpha}$ are multi-valued functions of $\mathscr{E}$, the point $x = 0$ on the phase diagram $(\Phi, \mathscr{E})$ is situated in the region of absolute instability for positive values of the parameter λ (Fig. 1). The value $\mathscr{E} = 0$ corresponds to the crossing of two branches of the potential Φ and two different points x^+ and x^- on these branches. In this case we have $\Phi(x^+) = \Phi(x^-)$, $x^+ = -x^- = [(2-\alpha)\lambda]^{1/\alpha}$, where it is assumed that $x^+ \ll 1$; i.e., the condition $\lambda^{1/\alpha} \ll 1$ is satisfied. Accordingly, at $\lambda > 0$ a first-order phase transition occurs at the point $\mathscr{E}_z = 0$. The metastable region in this case corresponds to the following interval of values of $\mathscr{E}_z$:

$$\mathscr{E}(\tilde{x}^-) < \mathscr{E}_z < \mathscr{E}(\tilde{x}^+), \quad \tilde{x}^+ = -\tilde{x}^- = [(2-\alpha)(1-\alpha)\lambda]^{1/\alpha}. \tag{9}$$

At $\mathscr{E}_z = 0$ the abrupt change in the dipole moment $\Delta\langle\mathscr{M}_z\rangle$ is given by $\langle\mathscr{M}_z(x^+)\rangle = -\langle\mathscr{M}_z(x^-)\rangle = -\partial\Phi/\partial\mathscr{E}_z|_{x=x^+}$,

$$< M_z(x^+) >= (2-\alpha)^{1/\alpha}\lambda^{(1-\alpha)/\alpha}, \quad \Delta < M_z >= 2 < M_z(x^+) > . \tag{10}$$

Consequently, the susceptibility has a finite value near the transition point:

$$\chi(x^\pm) = \frac{1-\alpha}{\alpha\lambda}. \tag{11}$$

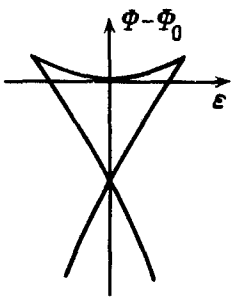

FIG. 1. Thermodynamic potential versus the applied field.

Results (9)–(11) show that in the absence of a critical dipole–dipole correlation (the exponent $\alpha = 0$), the weak interaction with the orientational degree of freedom ($\lambda \ll 1$) does not lead to a stabilization of the induced moment: $\mathscr{E}(\tilde{x}^{\pm}) = \langle \mathscr{M}_z(x^{\pm}) \rangle = 0$, $\chi(\dot{x}^{\pm}) \to \infty$. Any finite value of the exponent α for small values of λ should lead to the given effect. We note that in the absence of a field ($\mathscr{E} = 0$) the system cannot have a uniformly distributed moment, $\langle \vec{\mathscr{M}} \rangle \neq 0$: it is unstable with respect to the formation of regions with an arbitrary orientation of the local moments. A small but finite value of the field of particular orientation induces in an orientationally ordered system a finite average moment $\langle \vec{\mathscr{M}} \rangle$ which depends only slightly on the applied field. This effect may play a noticeable role if the system with the described properties has some dispersed sources of the field such as grains, whose field falls off rapidly upon moving away from the surface of the grain into its interior. In the case under consideration, the average moment remains constant far from such a surface and is determined largely by the distribution parameter and orientational-order parameter λ. Such effects, in principle, can occur in systems predisposed to the existence of ferromagnetic, ferroelectric, and other states such as the superconducting state.

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[1] I. I. Larkin and S. A. Pikin, Zh. Eksp. Teor. Fiz. **56**, 1664 (1969) [Sov. Phys. JETP **29**, 638 (1969)].

Translated by S. J. Amoretty