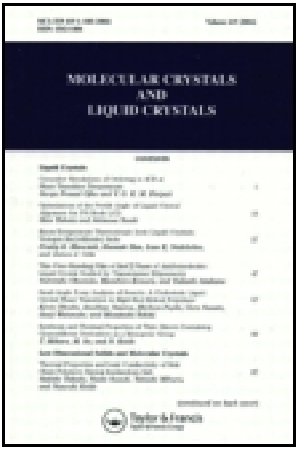

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On the k_{13}-Dependent Energy Term in Nematic Liquid Crystals

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On the k_{13}-Dependent Energy Term in Nematic Liquid Crystals

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The difficulties arising from the inclusion of term k_{13} (div(**n** div **n**) in the expression of the free energy density are discussed. It is shown that they are related to the fact that in this term second order spatial derivatives $n_{i,jk}$ of the nematic director **n** appear. Each term containing a second order derivative would give a distorted configuration of the director field. The global effect is zero in the bulk, owing to the divergence structure of the term, but different from zero near to the boundaries.

Keywords: Nematic, surface energy, elastic energy, variational calculus.

The term

$$k_{13}\, div(\mathbf{n}\ \mathrm{div}\ \mathbf{n}), \tag{1}$$

which appears in the free energy density of nematic liquid crystals, is the most difficult to handle, and its effects on the configuration of the director field are still unknown or, at least, an object of controversy. First introduced by Oseen around 1930,[1] it was generally disregarded for forty years. In 1971 Nehring and Saupe[2,3] found that the induced dipole-induced dipole part of the molecular interactions gives for k_{13} and for the other elastic constants values of comparable magnitude. It seemed obvious to investigate its role in determining the director configuration. Only boundary effects are expected, since the expression (1) may be integrated to give the surface term

$$\iint_{\text{boundary}} \mathrm{k}_{13}\, \mathbf{N}\cdot\mathbf{n}\ \mathrm{div}\ \mathbf{n}\ dS, \tag{2}$$

where **N** is the normal of the surface limiting the nematic sample.

However, this term was omitted in the subsequent papers of Nehring *et al.*[4,5] In 1985 the authors of this paper found out that if the term (2) is incorporated in the

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expression of the free energy density F for nematic liquid crystals, the variational problems of minimizing F become unsolvable.[6] We tried to give an explanation of this surprising result, which is related to the fact that, with this inclusion, F contains volume and surface integrals with spatial derivatives $n_{i,j} = \partial n_i/\partial x_j$ of the same order. In particular we have shown, by considering a well defined case, that no function satisfying the Euler-Lagrange equations in the whole sample, boundary included, may be an extremum of F.

In Reference 6 we noticed that, in the considered case, the boundary conditions given by Hinov[7-9] do not minimize F even in the class of the functions which satisfy the Euler-Lagrange equation. In a very recent paper Hinov[10] considers wrong our analysis, on the basis of rather generic and questionable arguments, and re-proposes the same boundary conditions. Perhaps the fact that his boundary conditions fail in a single case is considered as an inessential accident by him (and by other people too[11]). So we discuss a second even simpler case, in order to confirm the validity of our analysis and to find a way for a correct approach to the physical problem.

We consider a nematic slab between the planes $z = \pm d$, with the director field lying in the (x,z) plane and such that the angle θ between $\mathbf{n}$ and z be an even function of z. This may be obtained by suitable and symmetric boundary conditions. Let the free energy per unit area be

$$F(\theta(z)) = 2\left\{\int_0^d (k/2)\theta'^2\,dz + [(w/2)(\theta - \theta_e)^2 - k_{13}\,\theta\,\theta']_{z=d}\right\}, \quad (3)$$

where k is an average Frank elastic constant, θ_e the angle between the surface easy axis and z, and $\theta' = d\theta/dz$. The last term is the one given by Equation 2 with the approximation $\sin\theta = \theta$.

The Euler-Lagrange equation of the variational problem reads $\theta''(z) = 0$ and its general solution, with the condition $\theta'(0) = 0$ (imposed by the symmetry of the problem), is:

$$\theta(z) = \text{const.} = \theta_1. \quad (4)$$

The boundary condition proposed in Reference 10 (Equation 9) may not be directly applied to this case, since it contains the ratio $\theta''(d)/\theta'(d)$ between two quantities which are both zero (incidentally, in Reference 10 the quantity $2k_{13}$ appears in place of k_{13}, perhaps as a misprint). We therefore consider the term $(k/2)\theta'^2$ as the limiting case for $H \rightarrow O$ of the term $(k/2)\,\theta'^2 + (1/2)\chi_a\,H^2\theta^2$ (whose physical meaning is obvious).

The most general, symmetric, solution of Euler's equation is $\theta(z) = \theta_1 \cos[(\chi_a/k)^{1/2}H\,z]$. By inserting it in Equation 9 of Reference 10, and assuming $\sin 2\theta_1 = 2\theta_1$, one immediately obtains, in the limit $H \rightarrow 0$:

$$\theta_1 = \{1 + (k_{13}/wd)\}^{-1}\,\theta_e. \quad (5)$$

Obviously the integration constant θ_1 may be obtained by directly inserting the function (4) into the Equation (3). This gives $F = w\,(\theta_1 - \theta_e)^2$, which has unique minimum for $\theta_1 = \theta_e$.

Also in this case the boundary equation used by Hinov does not give the correct minimum. But, as already noticed in Reference 12, the most puzzling feature of our variational problem is that no function which satisfies the Euler-Lagrange equation in the closed interval $(0, d)$ may be an extremum of F. In the present case the solutions of the Euler-Lagrange equation are the constant functions. A simple inspection of Equation (3) shows that no constant function gives an extremum for F. In fact the term $k_{13}\,\theta(d)\theta'(d)$ may be arbitrarily decreased by continuously changing the shape of the function $\theta(z) = \theta_1$ in order to make $\theta'(d) \neq 0$, as shown in Figure 1, and for small changes no compensation may arise from the other terms. To be specific let us change the function $\theta(z) = \theta_e$ into the function:

$$\theta(z;\,\theta_0) = \begin{cases} \theta_e + \theta_0 & \text{for } \theta \le z \le d - r)^2 \\ \theta_e + \theta_0 - (\theta_0/r^2)\,(z - d + r)^2 & \text{for } d - r \le z \le d, \end{cases} \qquad (6)$$

which reduces to the original one for $\theta_0 = 0$. The corresponding value of F, which may be easily obtained by inserting $\theta(z;\,\theta_0)$ in Equation 3, is:

$$F = (4\,k/3r)\,\{\theta_0^2 + (3k_{13}/2k)\,\theta_e\theta_0\}. \qquad (7)$$

One may notice that F has a unique minimum for

$$\theta_0 = -(3k_{13}/2k)\,\theta_e, \qquad (8)$$

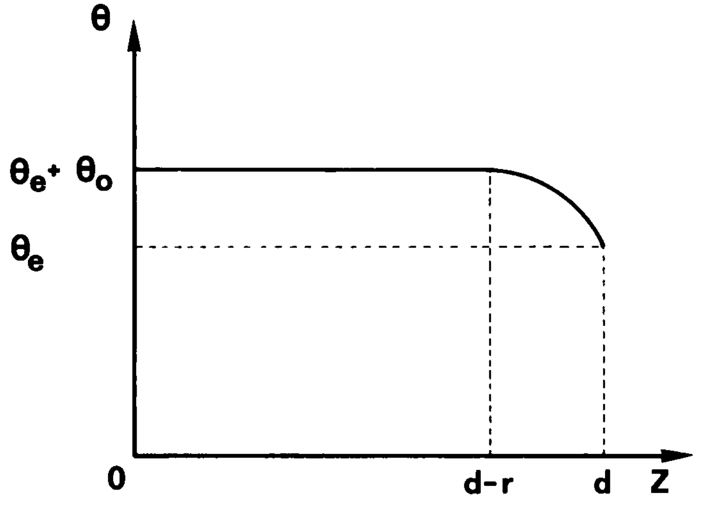

FIGURE 1 Plot of the function $\theta(z) = \theta_e$ (dashed line), and of the variate function $\theta(z;\,\theta_0)$ (continuous line).

and that the derivative of $dF/d\theta_0$ does exist and is different from zero for any other value of θ_0. In particular it is different from zero for $\theta_0 = 0$, *i.e.* for the unique value of θ_0 which reduces $\theta(z; \theta_0)$ to a solution of the Euler-Lagrange equation. Since the same argument is valid for any other solution, we are definitively convinced that no solution of the Euler-Lagrange equation is an extremum of F. We have deliberately approached the problem in the most elementary and direct form, without using any theorem of the variational calculus, in order to avoid any discussions about its limits of validity. This may obscure the essence of the problem, which is indeed very simple.

The physical interpretation of this unexpected result is given in References 12 and 13. We only add the following considerations.

From the mathematical point of view, we remember that a standard problem of the calculus of variations is the one where the function G under the integral depends linearly on θ'. In this case the variational problem does not, as a rule, have any solutions in the class of continuous functions (see f.i. Reference 14, page 313). Furthermore, if G may be exactly integrated the variational problem may become meaningless. In a sense, this paper and the previous ones[6,12,13] can be considered as an extension of this well known results to the case where G contains a term which depends linearly on θ'' and is integrable. Of course, we are convinced that the underlying physical problem does have a meaning, and that the mathematical difficulties come from some unsuitable analytical formulation, due to an oversimplification.

To this purpose, we notice that the energy term (1) has been introduced as a bulk energy density, and integrated in order to obtain the "surface" term (2). But the concept of boundary "surface" is a geometrical abstraction. In nature we have atoms and molecules. In the molecular approach of Reference 2, the expression (1) is obtained by making use of the concept of "volume elements," whose dimensions must be large enough to contain many molecules, but small with respect to the range r of the molecular interactions. In order to correctly apply the results of Reference 2 to the present case we must use a similar procedure.

To be specific, let us consider the induced dipole-induced dipole interactions (see f.i. Reference 3). It is easily found that even for an undistorted director configuration, a torque arises between two volume elements whose distance is smaller than r. In the bulk the total torque acting on a volume element is zero, for symmetry reasons. For oblique anchoring the torques may not exactly compensate if the volume element is near to a boundary. A boundary distortion, similar to the one represented in Figure 1, is therefore to be expected, even in the case of strong anchoring. To this purpose we recall that the considered interaction gives a negative value for the ratio k_{13}/k which appears in Equation 8.

More generally, a simple term linear in the second order derivative of any director components seems incompatible with the experimental fact that the minimum free energy of nematic liquid crystals is given by the uniform configuration. Actually some terms of this type are present, and are so related to give a divergence structure to the resulting expression: this means that the distorting effects of the various terms cancel each other in the bulk, but not in a boundary layer of thickness r, as evident. It is also evident that the divergence term given by Equation (1), which was obtained by an integration over a sphere of radius r, is not correct near to a boundary. The impossibility of solving the variational problem is simply due to the fact that it has not been correctly formulated. A more correct approach requires an extension of the molecular approach to the boundary region. This problem is under study. It is not an easy task. However we are able to anticipate some preliminary, well established, results:

1) a description of the free energy in term of Frank's elastic constants is no longer possible; more precisely twist, splay and bend energy terms explicitly depend on the angle θ between the director **n** and the surface normal **N**, and on the distance z from the surface, even in the case where the order parameter is constant.

2) New terms appear, which in the bulk, by symmetry considerations are shown to be identically zero, or simple additional constants. In particular the free energy density associated to a uniform director field depends on θ, and z, and in the limit where the boundary layer thickness is negligible, plays the role of the well known Rapini-Papoular surface energy terms.

3) If the molecular interaction is such as to give a contribution to the k_{13}-dependent term, necessarily a new term appears, giving rise to a splay distortion in the boundary layer. With the addition of this new term some difficulties related to the k_{13}-dependent energy term are solved, as already pointed out by qualitative considerations.[6,12,13]

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