COMMENTS

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Comment on ''Phenomenological approach to the problem of the K_{13} surfacelike elastic term in the free energy of a nematic liquid crystal''

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In a recent paper [Phys. Rev. E **48**, 1254 (1993)], an alternative procedure is proposed for obtaining the nematic director field that minimizes the total free energy of a nematic liquid crystal. In this Comment we show that this solution does not correspond to a minimum of the free energy. [S1063-651X(96)01711-4]

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It is known in nematic liquid crystals (NLC's) that the Nehring-Saupe free energy $\mathcal{F}_2$ is not bounded from below due to the presence of the K_{13} surfacelike elastic term. Thus, a minimizing director field cannot be found in the class of continuous functions. This is termed ''the K_{13} problem'' and has been the object of some debate in the literature [1–4]. According to [1], the K_{13}-surface elastic term favors the occurrence of a discontinuity of the director field at the interfaces of the NLC. Obviously, this director discontinuity is an artifact of the elastic theory because $\mathcal{F}_2$ corresponds to a truncated expansion of the total free energy $\mathcal{F}$, which is actually bounded from below. In recent years, different theoretical approaches have been proposed in the literature [2–4] to bypass this problem. In [3] a second order elastic theory has been proposed. In this theory, the elastic contributions up to the fourth order in the director gradients are retained in the expansion of the elastic free energy density. The second order elastic free energy $\mathcal{F}=\mathcal{F}_2+\mathcal{F}_4$ is bounded from below and the minimizing director field is the superposition of a standard slow macroscopic distortion and a sharp interfacial distortion. The characteristic thickness of the interfacial distortion is of the order of a few molecular lengths. From the macroscopic point of view, the interfacial distortion is equivalent to the discontinuity of the director field, which is predicted by the first order elastic theory [1]. In a recent paper [2], a different solution to this problem has been proposed. The author of [2] notes that the higher order elastic terms ($\mathcal{F}_6,\mathcal{F}_8,\ldots$), which are not taken into account by the second order theory, can play an important role and the total free energy $\mathcal{F}$ can appreciably differ from the second order free energy. It is then argued on phenomenological grounds that, if the surface normal derivative ξ exceeds a finite value ξ_m, the total free energy will be very large, whereas for $|\xi|<\xi_m$, $\mathcal{F}=\mathcal{F}_2$. Hence the actual minimum of the total free energy can be found operationally by considering only the first order free energy $\mathcal{F}_2$ restricting the allowed configurations to the class of configurations C_m, where $|\xi|\leq\xi_m$ [Eq. (24) of [2]]. It is further argued in [2] that a minimization over this class of functions can be carried out by considering the Euler-Lagrange equation resulting from $\mathcal{F}_2$ and suitable boundary conditions [Eq. (25) of [2]]. Here we show that minimization over the C_m class of configurations is not equivalent to this Euler-Lagrange equation with these boundary conditions. We do so by solving this Euler-Lagrange equation and boundary conditions for a specific, simple, exactly soluble example. We then show that a small perturbation of this solution, still fulfilling the condition that the configuration normal derivative is smaller than ξ_m, lowers the free energy $\mathcal{F}_2$. Hence this solution does not represent a minimizing solution for $\mathcal{F}_2$ in the class C_m. On the other hand, if there were a minimum for the free energy $\mathcal{F}_2$ within and not at the boundary of C_m, then it should satisfy this Euler-Lagrange equation with these boundary conditions. We conclude that the minimum of $\mathcal{F}_2$ in C_m is (at the least in this example) on the boundary of C_m, that is, that $\xi=\xi_m$. Thus, the minimization of $\mathcal{F}_2$ in the class of configurations C_m is not equivalent to the solution of the Euler-Lagrange equations and boundary conditions suggested in [2].

Let us consider a NLC layer of thickness d sandwiched between two solid parallel plates. The two planar interfaces are at $z=-d/2$ and $z=d/2$, respectively. The director $\mathbf{n}$ makes an angle θ with the z axis in the x-z plane. We restrict our attention here to one-dimensional distortions, where $\mathbf{n}\equiv(\sin\theta(z),0,\cos\theta(z))$; for this case, the free energy per unit surface area of the NLC layer is

$$\mathcal{F}_2=\int_{-d/2}^{d/2}F_b(\theta,\dot{\theta})dz+W_1(\theta_1)+W_2(\theta_2)+f_{13}(\theta_1,\dot{\theta}_1)-f_{13}(\theta_2,\dot{\theta}_2), \tag{1}$$

where $\dot{\theta}=d\theta/dz$, $\theta_1=\theta(-d/2)$, $\theta_2=\theta(d/2)$, and W_1 and W_2 are the anchoring energies at the two planar interfaces, F_b is the bulk free energy density, and f_{13} is the surface elastic free energy density. The explicit form of f_{13} is $f_{13}(\alpha,\dot{\alpha})=(K_{13}/2)\sin(2\alpha)\dot{\alpha}$, where α and $\dot{\alpha}$ are the director angle and its z derivative at the interfaces ($\alpha=\theta_1$ or $\alpha=\theta_2$). The Euler-Lagrange equation for the director angle is

$$\frac{\partial F_b}{\partial \theta}-\frac{d}{dz}\frac{\partial F_b}{\partial \dot{\theta}}=0. \tag{2}$$

According to [2], the equilibrium configuration must be a solution of Eq. (2) everywhere (also at the surfaces). We denote this solution by $\overline{\theta}(z)$ and the corresponding free energy by $\mathcal{F}_2$.

We show here that $\overline{\theta}(z)$ does not minimize $\mathcal{F}_2$, even in the restricted class C_m. Consider, for instance, the function $\theta(z)=\overline{\theta}(z)+\Delta\theta(z)$, where $\Delta\theta=\varepsilon f(z)$. ε is a small perturbative coefficient and $f(z)$ is a function that vanishes at both the interfaces $[f(-d/2)=f(d/2)=0]$ and satisfies the condition

$$\Delta g=\sin(2\overline{\theta_1})\dot{f}(-d/2)-\sin(2\overline{\theta_2})\dot{f}(d/2)\neq 0. \tag{3}$$

We substitute $\theta(z)=\overline{\theta(z)}+\Delta\theta(z)$ in Eq. (2) and make a power expansion at the first order in the small perturbation $\Delta\theta(z)$. Simple calculations give

$$\begin{aligned}\mathcal{F}_2=\overline{\mathcal{F}_2}&+\int_{-d/2}^{d/2}\left(\frac{\partial F_b}{\partial \theta}-\frac{d}{dz}\frac{\partial F_b}{\partial \dot{\theta}}\right)\Delta\theta dz\\&+\left(\frac{\partial F_b}{\partial \dot{\theta}_2}+\frac{\partial W_2}{\partial \theta_2}-\frac{\partial f_{13}}{\partial \theta_2}\right)\Delta\theta_2\\&+\left(-\frac{\partial F_b}{\partial \dot{\theta}_1}+\frac{\partial W_1}{\partial \theta_1}+\frac{\partial f_{13}}{\partial \theta_1}\right)\Delta\theta_1\\&+\frac{\partial f_{13}}{\partial \dot{\theta}_1}(\Delta\dot{\theta})_1-\frac{\partial f_{13}}{\partial \dot{\theta}_2}(\Delta\dot{\theta})_2+O(\Delta\theta^2),\end{aligned} \tag{4}$$

where $\overline{\mathcal{F}_2}$ is the free energy per unit area of solution $\overline{\theta}(z)$; $(\Delta\dot{\theta})_1$ and $(\Delta\dot{\theta})_2$ are the z derivatives of function $\Delta\theta(z)$ at $z=-d/2$ and $z=d/2$, respectively, and $O(\Delta\theta^2)$ represents contributions of second order in $\Delta\theta$. The integrand in Eq. (4) vanishes because $\theta(z)$ is a solution of Eq. (2), while the contributions proportional to $\Delta\theta_1$ and $\Delta\theta_2$ are zero because the function $\Delta\theta(z)$ vanishes at the interfaces. Therefore the free energy for the perturbed function reduces to

$$\mathcal{F}_2=\overline{\mathcal{F}_2}+\frac{K_{13}\Delta g}{2}\varepsilon+O(\varepsilon^2), \tag{5}$$

where $\Delta g\neq 0$ is defined in Eq. (3). Hence $\overline{\theta}(z)$ is not a minimizing function even in the class C_m ($\varepsilon\ll 1$). This is the main reason why the function $\theta(z)$ does not satisfy the test of the elastic torque [4].

To make our theoretical result clearer, let us consider the simpler example in which the two solid plates strongly anchor the director at the tilted angle $\theta=\theta_s$ with respect to the z axis in the x-z plane. We assume isotropic elastic constants ($K_{11}=K_{33}=K$). The $\theta(z)$ solution for the present problem is the uniform alignment $\theta=\theta_s$ everywhere. The free energy of the uniform solution $\theta=\theta_s$ is $\mathcal{F}_2=0$. Now consider the function $\theta(z)=\theta_s+a\cos[\pi z/d]$, where a is an arbitrary constant. This function still satisfies the boundary conditions $\theta_1=\theta_2=\theta_s$. Its free energy per unit surface area is

$$\mathcal{F}_2=\left\{\frac{K\pi^2}{4d}\right\}a^2+\left\{\frac{K_{13}\sin(2\theta_s)\pi}{d}\right\}a. \tag{6}$$

The minimum value of the free energy per unit area is attained for $a=-2R\sin(2\theta_s)/\pi$, where $R=K_{13}/K$. Hence, the uniform solution $\theta=\theta_s$ ($a=0$) does not minimize the free energy if $K_{13}\neq 0$. Furthermore, $\theta=\theta_s$ is also not a minimizing solution in the restricted class C_m of functions $\theta(z)$ having $|\dot{\theta}(z)|<\xi_m$, i.e., the functions $\theta(z)=\theta_s+a\cos[\pi z/d]$ with $|\pi a/d|<\xi_m$. Indeed, whatever is the value of ξ_m, any function with $K_{13}a\leq 0$ and $|a|<|2R\sin(2\theta_s)/\pi|$ has a free energy lower than $\mathcal{F}_2=0$. We infer that the minimum of $\mathcal{F}_2$ in the class C_m cannot be obtained by solving the Euler-Lagrange equation and the boundary conditions proposed in [2].

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