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Comment on "Direct measurements of the thermomechanical Lehmann coefficient in a compensated cholesteric liquid crystal" by Oswald P. and Dequidt A.

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Abstract. - We resolve the apparent contradiction between experiments and theory regarding the existence of Lehmann effects in compensated cholesterics

Recent direct measurements of the thermomechanical Lehmann effect in a cholesteric liquid crystal [1] showed, in accordance with earlier measurements [2], that it does not vanish at the compensation point, where the helical structure, the twist q_0, vanishes. However, according to a symmetry argument by de Gennes [3], which was also taken over by us [4], the coefficients describing Lehmann effects should be proportional to q_0 and thus vanish at the compensation point. In this Comment we reconcile the discrepancy between experiment and theory by writing the free energy density of cholesteric liquid crystals in a slightly more general form than is usually done.

Concentrating on twist deformations of the nematic director $\hat{\boldsymbol{n}}$, the gradient free energy density in cholesterics is obtained by taking the nematic expression and adding a linear twist term, allowed by the lack of inversion symmetry in chiral systems. This is usually written as [3]

$$f_{twist} = \frac{1}{2} K_2 (\hat{\boldsymbol{n}} \cdot \operatorname{curl} \hat{\boldsymbol{n}} + q_0)^2 \tag{1}$$

Minimizing this expression with respect to twist leads to $\hat{\boldsymbol{n}} \cdot \operatorname{curl} \hat{\boldsymbol{n}} = -q_0$, which is realized by the standard helical structure of the director with a pitch π/q_0. At the compensation point, where the helical pitch tends to infinity, q_0 has to vanish.

However, in eq.(1) the linear twist term is written as $q_0 K_2 \hat{\boldsymbol{n}} \cdot \operatorname{curl} \hat{\boldsymbol{n}}$ with the usual twist elastic coefficient K_2 as prefactor. There is no general law that requires this special choice. In the spirit of Frank [5] the linear twist coefficient k_2 and the quadratic one $k_{22}(= K_2)$ are independent. Of course, the former one must vanish in an achiral system, which is guaranteed by writing $k_2 = q_0 L_2$. With that the (relevant part of the) free energy reads

$$F = \frac{1}{2} K_2 T^2 + \frac{1}{2} \gamma \Delta^2 + q_0 L_2 T + q_0 \tau T \Delta \tag{2}$$

with the twist $T = \hat{\boldsymbol{n}} \cdot \operatorname{curl} \hat{\boldsymbol{n}}$ and with $\Delta = c - c^a_{eq}$ (or $\Delta = \sigma - \sigma^a_{eq}$, or $\Delta = \rho - \rho^a_{eq}$, respectively), the deviations of the scalar variables (concentration c, entropy σ, and density ρ) in the chiral state from their values in the achiral one. There is a bilinear coupling ($\sim \tau$) to twist that is responsible for the static parts of the Lehmann effects [6]. This last term in eq.(2) has also to be proportional to q_0, since it is absent in an achiral system for symmetry reasons.

Minimization leads to the equilibrium values

$$T^{chiral}_{eq} = -q_0 \frac{L_2}{K_2^{eff}} \equiv -q_0^{helix} \tag{3}$$

$$\Delta^{chiral}_{eq} = q_0^2 \frac{\tau}{\gamma} \frac{L_2}{K_2^{eff}} \tag{4}$$

with $K_2^{eff} = K_2 - q_0^2 \tau^2 / \gamma$, giving rise to a reduction of the free energy in the helical state by

$$F^{chiral}_{eq} = -\frac{1}{2} q_0^2 \frac{L_2^2}{K_2^{eff}} \tag{5}$$

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Harmonic deviations from this helical ground state (with pitch π/q_0^{helix}) cost energy

$$F = \frac{1}{2}K_2\left[\hat{\boldsymbol{n}}\cdot\operatorname{curl}\hat{\boldsymbol{n}}+q_0^{helix}\right]^2+\frac{1}{2}\gamma\left(\delta\Delta\right)^2 -q_0\,\tau\left[\hat{\boldsymbol{n}}\cdot\operatorname{curl}\hat{\boldsymbol{n}}+q_0^{helix}\right]\delta\Delta \quad (6)$$

where $\delta\Delta$ stands for $\delta\Delta = c - c_{eq}^a - \Delta_{eq}^{chiral}$ and correspondingly for σ and ρ replacing c.

By eq.(6) the divergence of the pitch of the helix at the helix inversion point (meaning $q_0^{helix}\to 0$), does not necessarily mean $q_0\to 0$, (and thus the vanishing of the Lehmann effects), since $q_0^{helix}\to 0$ can be achieved by $L_2\to 0$ while keeping q_0 finite, according to eq.(3). The conventional description implies $L_2 = K_2$, for which there is no obvious a priori necessity, thereby implying $q_0 = q_0^{helix}$.

The same argument works for the dynamic contributions to the Lehmann coefficients that can be extracted from the dissipation function [6]

$$R = R^a + q_0\left(\boldsymbol{h}\times\hat{\boldsymbol{n}}\right)\cdot\left(\psi_c\boldsymbol{\nabla}\mu_c+\psi_\sigma\boldsymbol{\nabla}T+\psi_e\boldsymbol{E}\right) \quad (7)$$

with μ_c the chemical potential of a mixture, T the temperature, and $\boldsymbol{E}$ the electric field. These additional chiral terms come with a q_0 factor for symmetry reasons again. Partial derivation with respect to the molecular field $\boldsymbol{h}$ leads to torques on the director due to concentration, temperature, pressure gradients or external electric fields that are commonly known as (the dynamic contributions to the) Lehmann effects [6]. They are absent in achiral systems ($q_0 = 0$), but not necessarily at the helix inversion point ($q_0^{helix} = 0$).

In mixtures of chiral molecules of opposite handedness it is also possible to get a helix-free state at a certain concentration. Assuming linear superposition of material properties as the simplest case, the linear and quadratic twist terms in the free energy obtained with the effective prefactors read,

$$q_0^{mix}L_2^{mix} = \Phi\,q_0^{(1)}L_2^{(1)}+(1-\Phi)\,q_0^{(2)}L_2^{(2)} \quad (8)$$

$$K_2^{mix} = \Phi K_2^{(1)}+(1-\Phi)K_2^{(2)} \quad (9)$$

where Φ and $1-\Phi$ are the concentrations of the species with superscripts 1 and 2, respectively. The compensation point, where the helix vanishes, is obtained for $q_0^{mix}L_2^{mix} = 0$. Again, this condition does *not* imply that the Lehmann coefficients, e.g.

$$q_0^{mix}\tau^{mix} = \Phi\,q_0^{(1)}\tau^{(1)}+(1-\Phi)\,q_0^{(2)}\tau^{(2)} \quad (10)$$

also vanish at the compensation point.

On the other hand, for mixture of left- and right-handed molecules of the same type, where the material properties are the same except for the handedness, e.g. $L_2^{(1)} = L_2^{(2)}$, $\tau^{(1)} = \tau^{(2)}$, and $q_0^{(1)} = -q_0^{(2)} = q_0$, the effective

$$q_0^{mix} = \Phi\,q_0^{(1)}+(1-\Phi)\,q_0^{(2)} = q_0(2\Phi-1), \quad (11)$$

is the same for all chiral effects and vanishes for a racemic mixture, $\Phi = 1/2$, and with it the helix and the Lehmann effects.

The question remains as to what q_0 macroscopically means, if it is not directly related to the pitch of the helix. Being a pseudoscalar quantity it characterizes on the macroscopic level all chiral contributions/effects that have to be absent in the achiral case (for symmetry reasons). Since chirality of the phases considered here comes from the chirality of the molecules, the existence of the quantity q_0 is a direct macroscopic consequence of the molecular properties in a cholesteric phase. In a liquid crystalline phase composed of nonchiral molecules q_0 vanishes. The same observation applies to measurable properties such as, for example, optical rotatory power.

What is observable on the macroscopic level are e.g. q_0L_2, $q_0\tau$, $q_0\psi_e$ etc. or, if pitch measurements are compared with Lehmann results, ratios like L_2/ψ_e. Since all phenomenological parameters (susceptibilities, transport coefficients) can still be rather arbitrary (regular) functions of q_0^2, it is not possible to predict within this phenomenological description the q_0 dependence of those ratios. On the other hand, it is conceivable that there are materials with $L_2\approx K_2$ leading to $q_0^{helix}\approx q_0$ and thus to a vanishing of Lehmann effects at the compensation point.

In closing we note that all the arguments presented here apply equally well to chiral smectic phases with a helical superstructure such as smectic C*. Therefore well-controlled experiments near the compensation point in such a system appear to be highly desirable.

* * *

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REFERENCES

[1] Oswald P. and Dequidt A., *Europhys. Lett.*, **83** (2008) 16005; **80** (2007) 26001.
[2] Éber N. and Jánossy I., *Mol. Cryst. Liq. Cryst.*, **72** (1982) 233; **102** (1984) 311; and *Mol. Cryst. Liq. Cryst. Lett.*, **5** (1988) 81.
[3] de Gennes P.G. and Prost J., *The Physics of Liquid Crystals* (Clarendon, Oxford) 1995.
[4] Pleiner H. and Brand H. R., *Mol. Cryst. Liq. Cryst. Lett.*, **5** (1987) 61; **5** (1988) 183.
[5] Frank F. C., *Discuss. Faraday Soc.*, **25** (1958) 19.
[6] Brand H. R. and Pleiner H., *Phys. Rev. A*, **37** (1988) 2736 and in *Encyclopedia of Materials: Science and Technology*, Vol. **5** (Elsevier) (2001) 1214.