

## Temperance in nematic liquid crystals

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*Questa noticina è dedicata alla memoria di Gaetano Fichera, maestro illustre e severo; famoso per fondamentali, corpose memorie di lunga lena, Egli non disprezzava l'occasionale breve "lettera aperta ai colleghi" contenente un esempio critico o probativo.*

RIASSUNTO: *Si dimostra che, accettata una definizione corrente di temperatura assoluta, possono essere raggiunte, in via di principio, entro un elemento di cristallo liquido nematico, temperature negative.*

ABSTRACT: *We show that, in principle, negative absolute temperatures may be achieved in a cell of nematic liquid crystal.*

### 1 – Cues on temperance

As in standard treatises (e.g., [1], sects 14.11 and 14.12) absolute temperature is intended here as a parameter linked to (and in the canonical case fully characterizing) the distribution of energies among particles belonging to a body element. Precisely, if  $\rho$  is the mass density of the element and  $\rho\epsilon$  its energy per unit volume, if  $\gamma(\xi) d\xi$  is the fraction of particles in the element with energy density within the interval  $(\epsilon\xi, \epsilon(\xi + d\xi))$ , so that

$$(1) \quad \int_0^\infty \gamma(\xi) d\xi = 1, \quad \int_0^\infty \xi\gamma(\xi) d\xi = 1,$$

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then, an appropriate factor apart, absolute temperature is given, over the support of  $\gamma$ , by the derivative

$$(2) \quad \theta = -\frac{d\xi}{d(\lg \gamma)} = -\gamma \frac{d\xi}{d\gamma}.$$

Thus only if  $\gamma$  depends on  $\xi$  exponentially does (2) lead to a value for  $\theta$  independent of  $\xi$ . That value need not be positive, however; though, when  $\theta$  is negative, then the normalization conditions (1) alone imply that the support of  $\gamma$  is necessarily compact. Such is the state of affairs in the celebrated experiment of Pound, Purcell and Ramsey. The ensuing realization that infinite absolute temperature is, in principle, achievable and actually offers the gate to negative values, whereas absolute zero cannot ever be reached suggested the acceptance of negatemperature  $-\theta^{-1}$  as the more appropriate parameter. To avoid a compound word, for  $\alpha = \theta^{-1}$ , I adopt, with glee, the name temperance recommended to me by my friend Maurizio Brocato. When the support of  $\gamma$  is the interval  $[0, \hat{\xi}]$  and the dependence of  $\gamma$  on  $\xi$  is exponential

$$(3) \quad \gamma = \frac{\alpha e^{-\alpha\xi}}{1 - e^{-\alpha\hat{\xi}}},$$

then, as a consequence of conditions (1), where now the limits of integration are  $0, \hat{\xi}$ , the temperance  $\alpha$  depends on the choice of  $\hat{\xi}$  through the equation (see, e.g., [2])

$$(4) \quad \alpha - 1 = \frac{\alpha\hat{\xi}}{1 - e^{\alpha\hat{\xi}}}.$$

The most temperant distribution is the asymptotic one, for  $\hat{\xi} \rightarrow 1$  and  $\alpha \rightarrow -\infty$ , when  $\gamma$  tends to a  $\delta$ -function centred at  $\xi = 1$  (when all particles have the same energy). The most intemperant one occurs for  $\hat{\xi} = 2$ ,  $\alpha = 0$  (when all energy levels achievable are uniformly distributed among particles). The canonical distribution ( $\hat{\xi} \rightarrow \infty$ ) has unit temperance  $\alpha = 1$ .

To attach a temperance to non-exponential distributions I recommended in [2] to resort to the opposite of the variation of  $\gamma$  over its support; that choice confirms the value of  $\alpha$  obtained from (2) when the distribution is exponential, but leads to a unique value also when (2)

fails the requirement of constancy. For instance, if  $\gamma$  is monotone and the support is  $[0, \hat{\xi}]$ , then  $\alpha$  is given by

$$(5) \quad \alpha = \gamma(0) - \gamma(\hat{\xi}).$$

Such definition I accept below.

## 2 – Cues on partial order in nematics

When, even locally (i.e., within a material element), the molecules of a nematic liquid crystal are not totally ordered, their locally prevailing direction, if available (the crystal may indeed melt), is insufficient to portray events. A tensor  $M$  of partial order may succour:  $M$  is the average, within the element, of the distribution of tensors  $n \otimes n$  if the direction of  $n$  is that of a molecule. Of course, many different distributions of directions may lead to the same value of  $M$ ; as an archetype, one may quote the simplest one, where the histogram is an ellipsoid. Actually, again for ultimate ease, though with some consequent disappointing forfeiture, I will always take below the disorder in directions to be optically uniaxial, hence in the present instance, the ellipsoid to be axially symmetric and thus  $\gamma$  to be independent of longitude  $\psi$  and varying with colatitude  $\varphi$  (measured from the axis of symmetry) as set by geometry and the normalization condition

$$(6) \quad \gamma = \xi(\delta)(1 - \delta \cos^2 \varphi)^{-1/2} \quad \delta \in [-\infty, 1];$$

negative values of  $\delta$  lead to oblate ellipsoids, positive ones to prolate ellipsoids. In (6)  $\xi(\delta)$  is a positive normalization factor, chosen so that

$$\frac{1}{2\pi} \int_0^{2\pi} d\psi \int_0^{\pi/2} \xi(\delta)(1 - \delta \cos^2 \varphi)^{-1/2} \sin \varphi d\varphi = 1.$$

Hence

$$\begin{aligned} \xi(\delta) &= \frac{\delta^{1/2}}{\arcsin \delta^{1/2}} \quad \text{when } \delta \in (0, 1]; \\ \xi(\delta) &= \frac{|\delta|^{1/2}}{\text{Arsh } |\delta|^{1/2}} \quad \text{when } \delta < 0; \quad \xi(0) = 1. \end{aligned}$$

The semiaxes of the ellipse, section of the ellipsoid, are equal to  $(1 - \delta)^{-1/2}\xi(\delta)$  along the line of symmetry and  $\xi(\delta)$  in the orthogonal direction. The measure of triaxiality vanishes and that of prolation  $s$  is a function of  $\delta$  alone (see, e.g., (2.3) of [3]).

In another (actually degenerate) distribution, relevant for our later developments, all molecules are uniformly distributed over a cone with aperture  $2\hat{\varphi}$  ( $\hat{\varphi} \in [0, \frac{\pi}{2}]$ ); an easy calculation shows that, for such distribution, the measure of prolation  $\hat{\rho}$  is given by

$$\hat{\rho} = 1 - \frac{3}{2} \sin^2 \hat{\varphi}.$$

In a cell where the value of  $M$  is everywhere the same, the energy density of an element is deemed to be a function of the second and third invariants of  $M$ ; when triaxiality vanishes, those invariants can be expressed in terms of  $s$  only (see, e.g., (3.2) of [3])

$$\text{II} = \frac{1}{3}(1 - s^2) \quad ; \quad \text{III} = \frac{1}{27}(1 + 2s^3 - 3s^2).$$

Then  $\epsilon$  itself becomes a function of  $s$ ; here the interest centres on circumstances when the minimum of energy density occurs at  $s = 1$  (perfect order) and the maximum at  $s = -\frac{1}{2}$  (distribution in a plane) with a steady increase through the uniform distribution at  $s = 0$ . Thus, under the circumstances the condition  $\frac{\partial \epsilon}{\partial s} < 0$  is of the essence, and, vying for extreme simplicity and striving for the barest example, I quote below explicit calculations for the case  $\epsilon = -\bar{\epsilon}s$ , ( $\bar{\epsilon}$ , a constant) so that, for the conical distributions,  $\epsilon = \bar{\epsilon}(\frac{3}{2} \sin^2 \hat{\varphi} - 1)$ .

### 3 – Temperance in partially ordered nematics

Each axially symmetric distribution may be imagined as a blend of conical distributions, such that  $2\pi\gamma(\varphi)\sin\varphi d\varphi$  counts the fraction of molecules with direction within the sliver delimited by cones of aperture  $2\varphi$  and  $2(\varphi + d\varphi)$ . Thus  $\hat{\gamma}(\varphi)$  determines both the tensor  $M$  and, as we shall see, also the associated temperance.

Using for Cartesian reference the principal axes of  $M$  (and the symmetry line as the third axis) we have

$$\begin{aligned} M &= \frac{1}{2\pi} \int_0^{2\pi} s\psi \int_0^{\pi/2} n \otimes n \hat{\gamma}(\varphi) \sin \varphi d\varphi = \\ &= \frac{1}{2} \int_0^{\pi/2} \hat{\gamma}(\varphi) \begin{pmatrix} \sin^2 \varphi & 0 & 0 \\ 0 & \sin^2 \varphi & 0 \\ 0 & 0 & 2 \cos^2 \varphi \end{pmatrix} d\varphi. \end{aligned}$$

When  $\bar{\gamma}$  is constant, the normalization condition

$$\int_0^{\pi/2} \bar{\gamma} \sin \varphi d\varphi = 1$$

requires  $\bar{\gamma}$  to be equal to 1; hence all three eigenvalues of  $M$  have the same value  $1/3$ . If  $\bar{\gamma}$  is monotone and decreasing with  $\varphi$  the two equal eigenvalues are less than  $1/3$ , whereas the third eigenvalue is larger than  $1/3$ ; thus the ellipsoid representing the distribution is prolate; vice versa, if  $\bar{\gamma}$  is monotone increasing the two equal eigenvalues exceed the third one and the ellipsoid is oblate. On the other hand the sign of the temperance is bound by (5) to the slant of the distribution.

Thus we have reached the main goal of this note, which was to show that positive temperance goes with prolate distributions, null temperance with the uniform one and negative temperance with oblate distributions. Perhaps the latter distributions are much more difficult to achieve in an experiment, except fleetingly, because of their presumable instability.

## REFERENCES

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