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M. Warenghem [a]

[a] Laboratoire de Physique des States Anisotropes, Laboratoire de recherche associe au CNRS no 465, Universite des Sciences et Techniques de Lille, 59655, Villeneuve d'Ascq, Cedex, France

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A Test for Surface Energy Anisotropy Sign Determination

M. WARENGHEM

Laboratoire de Physique des States Anisotropes,† Universite des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France

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Creagh and Kmetz have assumed that the relative values of the nematic to the substrate surface tension permit an estimation of nematic orientation on that substrate. This much discussed assumption is studied in detail in this paper; a new rule will be proposed and a test for the sign of the surface energy anisotropy is applied.

In many display applications using nematic liquid crystals, a regular orientation on plane surfaces is required. There are three different regular orientations recognized for nematic liquid crystals lying on the substrate: planar, homeotropic or tilted. It is useful therefore to know what the characteristics are that give rise to one of these alignments. Creagh and Kmetz,[1] in 1973, proposed a simple rule that allowed the nematic director orientation for different substrates to be estimated. If the surface tension of the substrate, γ_S, is larger than that of the nematic, γ_L, then planar alignment results. If however, $\gamma_S < \gamma_L$, then the nematic forms an homeotropic arrangement. Several later experiments have shown the weakness of this rule[2,3] or have corroborated it.[4,5] In particular Porte[5] gave theoretical support to Creagh and Kmetz's rule. In this paper we propose a development of these results and a new rule for the sign of the surface energy anisotropy. Finally the validity of this rule will be discussed and compared with recent similar work.

† Laboratoire de recherche associe au CNRS no 465.

(A) SOME REMARKS ON THE PORTE CALCULATION

The minimum of the free enthalpy for the nematic substrate system characterizes its equilibrium. Using the surface tension notion, this implies determination of the minimum of γ_{LS}, the surface tension of nematic-substrate interface,[6] as a function of the director orientation.

The first remark concerns the compounds used: Porte has clearly indicated that only dispersion interactions were introduced in previous calculations. In fact many experiments are carried out with compounds having a dipole moment, so they cannot be used to test the validity of the Creagh and Kmetz rule. This is the case, amongst others, with the work of Hiltrop[2] and Haller.[3] The second remark concerns the variation of the surface tension for the nematic with θ, the angle of the director with the normal to the surface. Porte chose a monotonic ascending function for γ_L but did not examine the reverse situation. It is from this viewpoint that we extend the earlier work. As an introduction let us consider again the Porte discussion on the existence of a minimum of $\gamma_{LS}(\theta)$ and carry out a graphical analysis. Using Porte's notation we want to find the minimum of:

$$\gamma_{LS}(\theta) = \gamma_S + \gamma_L(\theta) - W_a(\theta)$$

with the adhesion energy,

$$W_a(\theta) = 2[\gamma_L(\theta)\gamma_S]^{1/2}$$

Thus

$$\gamma_{LS}(\theta) = \{(\gamma_S)^{1/2} - [\gamma_L(\theta)]^{1/2}\}^2 \tag{1}$$

Then choosing[6] a monotonic ascending function for $\gamma_L(\theta)$, we may plot both $(\gamma_S)^{1/2}$ and $[\gamma_L(\theta)]^{1/2}$ *versus* θ (Figure 1). According to the different values of the parameter γ_S, there are three different situations, and minima of $\gamma_{LS}(\theta)$ (formula 1) are obtained for $\theta = 0$ (Figure 1a); $\theta = \theta_0$ (Figure 1b), and $\theta = \pi/2$ (Figure 1c) in agreement with the Porte and Creagh results.

(B) CALCULATION WITH A SIMPLE MODEL IGNORING DISPLACEMENT EFFECTS

In the analytical expression proposed for the nematic surface tension[7]

$$\gamma_L(\theta) = \gamma_\perp + \Delta\gamma \sin^2 \theta, \tag{2}$$

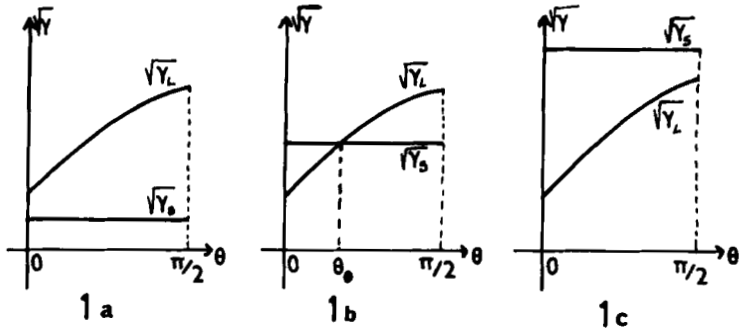

FIGURE 1 Graphical representation of the minimization of $\gamma_{LS} = [(\gamma_S)^{1/2} - (\gamma_L)^{1/2}]^2$.

where $\Delta\gamma = \gamma_{\parallel} - \gamma_{\perp}$ and the subscripts refer to parallel or perpendicular to the surface. The surface tension anisotropy $\Delta\gamma$ can be positive or negative, so besides the case $\Delta\gamma > 0$ studied by Porte, there is the opposite case, for $\Delta\gamma < 0$. A similar graphical analysis then gives readily the minimum of γ_{LS}, i.e.

if

$$\gamma_S < \gamma_L\left(\frac{\pi}{2}\right) \rightarrow \theta_{\min} = \frac{\pi}{2}$$

$$\gamma_S > \gamma_L(0) \rightarrow \theta_{\min} = 0$$

$$\gamma_L\left(\frac{\pi}{2}\right) < \gamma_S < \gamma_L(0) \rightarrow \theta_{\min} = \theta_0$$

We have summarized the two results in Table I.

TABLE I

An extended Creagh and Kmetz rule; notations: see text.

	Possible values for γ	Orientations
a	$\Delta\gamma > 0$; $\gamma_S < \gamma_{\perp}$	Homeotropic
	$\Delta\gamma < 0$; $\gamma_S > \gamma_{\perp}$	
b	$\Delta\gamma > 0$; $\gamma_S > \gamma_{\parallel}$	Planar
	$\Delta\gamma < 0$; $\gamma_S < \gamma_{\parallel}$	
c	$\gamma_S \in [\Delta\gamma]$	Tilted

Using formulae 1 and 2 we have plotted γ_{LS} *versus* θ and obtained three trends, (Figure 2) for each of the cases a, b, c of Table I.

The values of θ_0 can be calculated with the expression 2

$$\frac{\partial}{\partial\theta}\gamma_{LS}(\theta) = \Delta\gamma\{1 - [\gamma_S/\gamma_L(\theta)]^{1/2}\} \sin 2\theta$$

This derivative vanishes for $\Delta\gamma = 0$, $\theta = 0$, $\theta = \pi/2$ and $\theta = \theta_0$ where

$$\sin^2\theta_0 = [\gamma_S - \gamma_\perp]/[\gamma_\parallel - \gamma_\perp] \tag{3}$$

We have tested this formula with values for γ_S, $\gamma_\perp$, $\Delta\gamma$ and θ_0 given in the literature, and particularly with the Porte results[5] which concerned MBBA ordered on glass surfaces covered with monomolecular films of aliphatic monodomains. This author gives θ_0 for different γ_S, and to test formula 3 we need values for $\gamma_\perp$ and $\Delta\gamma$ for MBBA. Many authors have calculated these quantities and Parsons,[8] for instance, expresses γ and $\Delta\gamma$ in term of S the order parameters. It is noteworthy that $\Delta\gamma$ was always negative, but this has raised little discussion. Bernasconi *et al.*[9] found theoretically the value of $\Delta\gamma/\gamma$ to be 0.2 for PAA and Okano *et al.*[10] confirmed this result. Otherwise the MBBA dispersion contribution to the surface tension is evaluated[11] as 29 dyn/cm. Then we have used for MBBA the following values: $\gamma_\perp = 29$ dyn/cm, $|\Delta\gamma| = 6$ dyn/cm.

The values for the tilt angle θ_0 found from formula 3 using the γ_S values given by Porte are reported in Table II. The first three columns are the experimental results taken from Ref. (5) and the last two give the values of θ_0 calculated using formula 3 for $\Delta\gamma > 0$, and $\Delta\gamma < 0$. The first result concerns the sign of $\Delta\gamma$. Contrary to the Parsons results, for MBBA, experimental observation and theoretical calculation only agree if $\Delta\gamma > 0$.

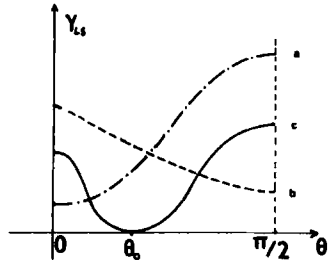

FIGURE 2 Different trends of curves for $\gamma_{LS}(\theta)$.

TABLE II

Comparison between Porte experimental results and theory; n refers to the aliphatic chain length of the substrate, γ_S is the related surface tension, θ_0 the tilt angle of MBBA.

n	γ_S (dyne/cm)	θ_0(deg)	$\theta_0^{th}(\Delta\gamma>0)$	$\theta_0^{th}(\Delta\gamma<0)$
16	23.0±0.3	0	0	90
14	24.0±0.3	0	0	66
12	26.0±0.3	0	0	0
10	29.7±0.3	12	20± 5	0
9	30.8±0.3	22	33± 3	0
8	32.1±0.3	30±8	46± 3	0
7	33.2±0.6	55± 8	57± 6	0
6	34.0±0.8	70±4	70±12	0

In this work we have not tried to improve the values of parameters $\gamma_\perp$ and $\Delta\gamma$, but only to examine experimental results using an expression obtained with an over simple expression for $\gamma_L(\theta)$.

Taking into account the experimental precision we note reasonable agreement between the Porte experimental results and our theoretical calculations. Note this also gives agreement with the Bernasconi *et al.* evaluation of $\Delta\gamma/\gamma$ for PAA, contrarily to Naemura[12] who found $\Delta\gamma/\gamma \simeq 10^{-3}$.

It appears therefore that the results presented in Table I constitute a broadening of the Creagh and Kmetz rule, and may also be used to determine the sign of $\Delta\gamma$ for a compound without dipole moment. Effectively if the substrate is chosen with $\gamma_S \ll \gamma_L$ (then both conditions $\gamma_S < \gamma_\perp$, $\gamma_S < \gamma_\parallel$ are fulfilled) and following Table I, the mesogen will align homeotropically if $\Delta\gamma > 0$ or homogeneously if $\Delta\gamma < 0$. Opposite results occur for $\gamma_S \gg \gamma_L$. This experiment can be readily carried out using a polarizing microscope and there is no need for precise calculation.

When dipole moments exist, γ_{LS} can be written as follows[13]

$$\gamma_{LS} = \gamma_{LS}^d + \gamma_{LS}^p = \gamma_L^p + \gamma_S^p - W_a^p + \gamma_L^d + \gamma_S^d - W_a^d$$

Where superscripts P and d refer respectively to polar and dispersion contributions to the surface tension. The adhesion energy W_a is:[13]

$$W_a^d = 2(\gamma_S^d \gamma_L^d)^{1/2}; \quad W_a^p = 2(\gamma_L^p \gamma_S^p)^{1/2}$$

and therefore

$$\gamma_{LS}(\theta) = \{[\gamma_S^d]^{1/2} - [\gamma_L^d(\theta)]^{1/2}\}^2 + \{[\gamma_S^p]^{1/2} - [\gamma_L^p(\theta)]^{1/2}\}^2 \quad (4)$$

The analytical expression 3 is always valid for γ_L^d and a similar one has been proposed[12] for γ_L^p:

$$\gamma_L^p(\theta) = \gamma_1^p + \Delta\gamma^p \sin^2(\theta - \theta_p) \tag{5}$$

where θ_p is introduced because of the non-parallelism of dipole moment and director. Thus γ_{LS}^p has the same three trends as those shown in Figure 2, but translated by θ_p and with different amplitudes. Then γ_{LS} which is the sum of γ_{LS}^p and γ_{LS}^d may have somewhat complicated trends so we cannot generalize for the minimum of γ_{LS} and the results of Table I cannot be extended simply for dipole interactions. Before concluding, let us clearly state the limits of this proposed rule and compare it with other recent work.

(C) LIMITS AND COMPARISONS

To use these results correctly we must know exactly their limitations. These calculations are based on the Perez *et al.*[6] assumption that the system equilibrium is fulfilled if γ_{LS} is a minimum which requires an interface area constant.

The liquid crystal surface tension depends little on temperature;[14] however near the clearing point we may expect variations of orientation with temperature.

The different surface tensions depend markedly on impurities.[15] Experimentally it is necessary to measure the surface tension of the compound used or to verify its purity grade.

The γ_S introduced in this work takes the possible substrate treatment into account, and this is compatible with the results for different orientations obtained with different densities of surfactant.[12,16,17]

The surface tension is a macroscopic notion and this work is compatible with the molecular interpretations of liquid crystal alignment of surfactants.[6,11,18]

Let us now compare our results with other recent research. First Naemura[12] did almost analogous work but his discussion and conclusions differ because he found values of $\Delta\gamma/\gamma$ of about 10^{-3}. Therefore he did not consider tilted orientation. He then adjusts the numerous parameter $\gamma_S^{p,d}$, $\gamma_L^{p,d}$, θ_p to obtain either homogeneous or homeotropic orientation. (The electrostatic screen effect of the same substrate is well established.)

Uchida *et al.*[17] noted, after experimental study of nematic alignment

on different substrates, that the Creagh and Kmetz rule is not verified because of the neglected dipolar interaction.

(D) CONCLUSION

In conclusion we can confirm that the Creagh, Kmetz and Porte assumption is correct for compounds and substrates without dipolar interactions. We have proposed a new rule in Table I. These results can be summarized as follows:

$$\gamma_S \ll \gamma_L \text{ if homeotropic} \rightarrow \Delta\gamma > 0$$
$$\text{homogeneous} \rightarrow \Delta\gamma < 0$$
$$\gamma_S \gg \gamma_L \text{ if homeotropic} \rightarrow \Delta\gamma < 0$$
$$\text{homogeneous} \rightarrow \Delta\gamma > 0$$

which suggests that very straightforward experiments would allow the sign of $\Delta\gamma$, the surface tension anisotropy, to be determined. When the different parameters $\Delta\gamma^{P,d}$, $\gamma^{P,d}$, θ_p and their relationships are better known, the results will be improved.

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