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Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 13 Dec 2006.

To cite this article: T. Carlsson (1982): The Possibility of the Existence of a Positive Leslie Viscosity α_2. Proposed Flow Behavior of Disk Like Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 89:1-4, 57-66

To link to this article: http://dx.doi.org/10.1080/00268948208074469

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Mol. Cryst. Liq. Cryst., 1982, Vol. 89, pp. 57–66
0026-8941/82/8904-0057$06.50/0
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The Possibility of the Existence of a Positive Leslie Viscosity α_2. Proposed Flow Behavior of Disk Like Nematic Liquid Crystals

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(*Received January 25, 1982; in final form April 15, 1982*)

The signs of the Leslie viscosities α_2 and α_3 for nematics consisting of disk like molecules are discussed. It is predicted on theoretical grounds that for disk like molecules α_3 is always positive while α_2 should be able to exhibit both positive and negative values. This is the first time that the possibility of a positive α_2 is discussed in the literature. Provided that the prediction is correct, the nature of the flow behavior of disk like molecules is discussed.

I INTRODUCTION

The flow behavior of nematic liquid crystals is a very complicated matter. For a complete description of the subject one needs to introduce six viscosity coefficients[1] which commonly are called the Leslie viscosities and are denoted by α_i ($i = 1$–6). Of these six coefficients only five are independent due to an Onsager relation which was first noted by Parodi[2] and later discussed by Currie [3,4]

$$\alpha_6 - \alpha_5 = \alpha_2 + \alpha_3 \tag{1}$$

Requiring the entropy production to be positive Leslie derives the following inequalities to be satisfied by the viscosity coefficients

$$\begin{aligned} &\alpha_4 \geqslant 0 && 2\alpha_1 + 3\alpha_4 + 2\alpha_5 + 2\alpha_6 \geqslant 0 \\ &2\alpha_4 + \alpha_5 + \alpha_6 \geqslant 0 && (\alpha_3 - \alpha_2)(2\alpha_4 + \alpha_5 + \alpha_6) \geqslant (\alpha_2 + \alpha_3)^2 \end{aligned} \tag{2}$$

$$\gamma_1 \equiv \alpha_3 - \alpha_2 \geqslant 0 \tag{3}$$

When studying the qualitative flow behavior of a nematic liquid crystal there are however only two of the six viscosity coefficients that are of importance. These are α_2 and α_3. We can see from Eq. (3) that there is one important restriction that these must follow.

In Section II we will give a brief review of the nature of the two types of flow that can occur and how they are related to the two viscosity coefficients just mentioned. In Section III we introduce the reactive parameter λ and discuss how the different types of flow correspond to certain values of λ. We then compare this with a recent calculation by Volovik[5] where λ is calculated as a function of molecular shape. With Voloviks calculations in mind we predict that the newly found disk like molecules[6] might turn up to have a positive value α_2 (and hence α_3 according to the inequality of Eq. (3)). This would be the first time that one discovers a compound with a positive value of α_2. In Section IV we discuss the flow properties of the disk like molecules under the assumption that the predictions of the Leslie viscosities made in Section III are true.

II FLOW ALIGNMENT AND TUMBLING

When shearing a nematic liquid crystal between two parallel glass plates we get two different types of flow behavior[7] depending on the signs of α_2 and α_3. If the product $\alpha_2\alpha_3 > 0$ we have a stable type of flow usually called "flow alignment". When on the other hand $\alpha_2\alpha_3 < 0$ the flow is more complicated and a state denoted "tumbling" will occur. If we examine these conditions together with the restriction of Eq. (3) we can distinguish the following cases.

(a) $\alpha_2\alpha_3 < 0$: Eq. (3) together with this condition gives that $\alpha_2 < 0$ and $\alpha_3 > 0$. This type of nematic liquid crystal is not very common but a few examples are mentioned in the literature.[8-11]

(b) $\alpha_2\alpha_3 > 0$: Eq. (3) now permits two possibilities—

(b1) $\alpha_2 < \alpha_3 < 0$ i.e. both α_2 and α_3 are negative. This is the most common type of nematic liquid crystal and with a few exceptions all compounds that exhibit nematic behavior belong to this group.

(b2) $\alpha_3 > \alpha_2 > 0$ i.e. both α_2 and α_3 are positive. Up to now no one has established such a behavior. The fact is that although there is no thermodynamic restriction against α_2 being positive it is very often

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taken for granted in the literature that it cannot be. The aim of this article is to discuss the flow properties of the disk-like molecules and to point out that these might be candidates for showing up a positive α_2.

III THE REACTIVE PARAMETER

Introducing the reactive parameter λ

$$\lambda = \frac{\alpha_2 + \alpha_3}{\alpha_2 - \alpha_3} \tag{4}$$

we now discuss the different cases mentioned in Section II. Expressing the ratio α_3/α_2 in terms of λ we get

$$\frac{\alpha_3}{\alpha_2} = \frac{\lambda - 1}{\lambda + 1} \tag{5}$$

In the lower part of Figure 1 we have plotted α_3/α_2 as function of λ and we see that we can distinguish the three cases mentioned above.

Case b1: $\lambda > 1$

In this regime $0 < \alpha_3/\alpha_2 < 1$. Together with Eq. (3) this implies that $\alpha_2 < \alpha_3 < 0$. Most known nematic compounds belong to this group having an absolute value of α_2 about 10–100 times larger than that of α_3. This means that $\lambda \gtrsim 1$ in most known cases.

Case a: $-1 < \lambda < 1$

Here α_3/α_2 is negative. The restriction of Eq. (3) thus implies that α_3 is positive and α_2 is negative. As mentioned before we today know a few nematic compounds that belong to this group. A common feature for these compounds is that the nematic phase is preceded by a smectic A phase. Both theoretical considerations[12] and experiment[11] indicate that α_3/α_2 for these compounds diverge when the temperature is lowered and the underlying smectic A phase is approached. Some of these compounds also show negative values of α_3 in the high temperature range. This means that their λ value will be slightly larger than unity near the nematic–isotropic phase transition and then decrease continuously to minus one as the temperature is lowered and the A–N transition is reached.

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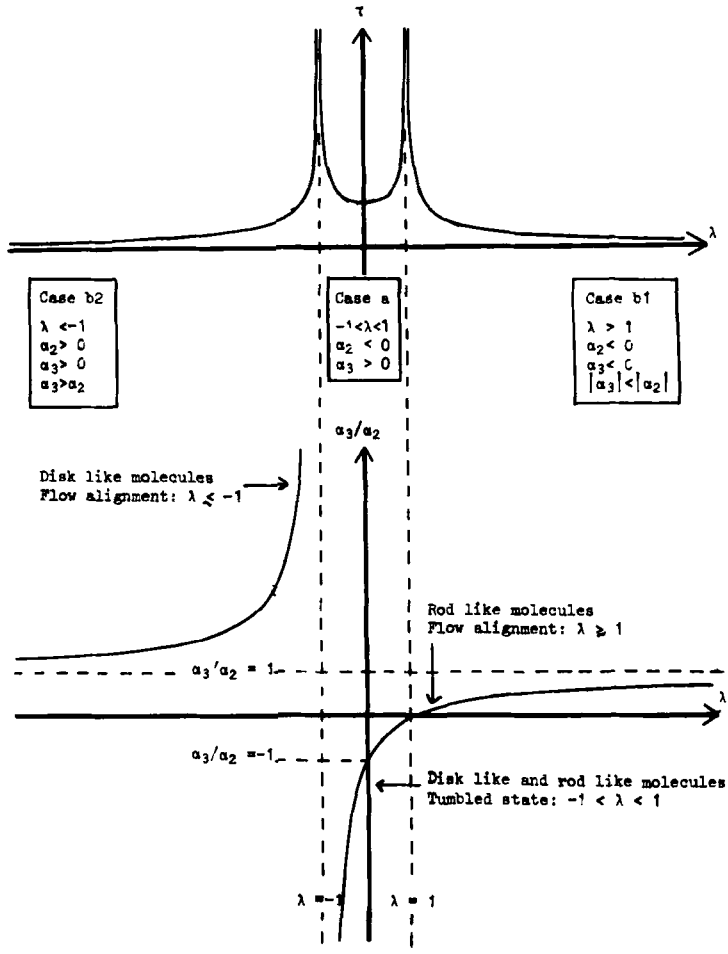

FIGURE 1 The reorientational time, τ, and the ratio, α_3/α_2, as functions of the reactive parameter λ. We can distinguish between three different cases.

Case b1: $\lambda > 1$ For $\lambda > 1$ we have $\alpha_2 < \alpha_3 < 0$. This is the most common behavior for rod like molecules in the nematic state. In general $|\alpha_2|$ is 10–100 times larger than $|\alpha_3|$, so λ is not very much larger than one. In this limit τ diverges as $\sqrt{\alpha_2/\alpha_3}$.

Case a: $-1 < \lambda < 1$ For $-1 < \lambda < 1$ we have $\alpha_2 < 0$ and $\alpha_3 > 0$. This behavior has been observed for a few rod like molecules exhibiting values of λ in the whole range of the interval as the temperature is varied. For low temperatures, near the smectic A–nematic phase transition, there are reasons to believe that $\alpha_3/\alpha_2 \to -\infty$ which means that $\lambda \to -1$. For high temperatures, near the nematic–isotropic phase transition, α_3 may change sign and become negative. When this happens, $\lambda = 1$. There should also be a possibility that some disk like molecules belong to this case.

Case b2: $\lambda < -1$ For $\lambda < -1$ we have $\alpha_3 > \alpha_2 > 0$. This is one of the proposed possible behaviors for disk like molecules. It seems reasonable to expect that $\alpha_3 \gg \alpha_2$ so that λ will not be very much less than -1. In this limit τ diverges as $\sqrt{\alpha_3/\alpha_2}$.

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Case b2: $\lambda < -1$

In this regime $\alpha_3/\alpha_2 > 1$. Together with Eq. (3) this implies $\alpha_3 > \alpha_2 > 0$. Although there is no restriction upon α_2 being positive it is often assumed that it cannot be. We now ask the question: If we are looking for compounds being candidates of having positive α_2, where should one look?

In a recent paper[5] Volovik calculates the value of λ for different shapes of molecules. His results establish that $\lambda = 1$ for ideal rods and $\lambda = -1$ for infinitely thin disks. When nonideality is taken into account, he expects small deviations in his results. We now show that this means that the disk like molecules, when being in the nematic state, are candidates for showing positive values of α_2 (and hence α_3). If the deviation from $\lambda = -1$ is such that $\lambda \lesssim -1$ this implies $\alpha_3/\alpha_2 \to \infty$, both being positive (see Figure 1). This behavior is quite similar to the "ordinary" nematic behavior ("ordinary" nematic is a nematic consisting of rod like molecules), but with the roles of α_2 and α_3 interchanged. What one expects is thus a nematic consisting of disk like molecules where α_3 is always positive and much larger than α_2 ($\alpha_2 > 0$). If on the other hand $\lambda \gtrsim -1$ we will get $\alpha_3/\alpha_2 \to -\infty$, α_3 being positive and α_2 being negative. This change of sign of α_2 would then correspond to the change of sign of α_3 which has been observed for some of the rod like nematics. In the next section we will discuss the nature of the flow behavior for the disk like molecules under these assumptions.

IV DISCUSSION

The main aim of this article is to discuss the values of the viscosity coefficients α_2 and α_3 for disk like molecules in the nematic phase, pointing out the possibility of finding nematics with positive values of α_2 and to discuss the nature of the flow behavior that this would give rise to. To do so, we now give the expression for the viscous torque, Γ_y^h, in the stationary state (i.e. $\partial/\partial t \equiv 0$) exerted on the director in shear flow with the shear rate u'.

$$\Gamma_y^h = (\alpha_3 \sin^2 \theta - \alpha_2 \cos^2 \theta)u' \tag{6}$$

The coordinates are defined in Figure 2. The y-axis is pointing inwards which means that a positive torque Γ_y^h will give rise to a clockwise rotation of the director. If we assume that the distance between the glass plates is large enough, we can neglect the influence of elasticity induced by the walls and give a qualitative description of the flow. Looking for

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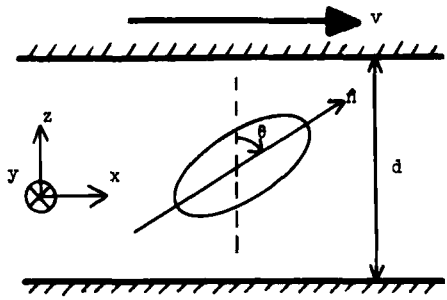

FIGURE 2 Definition of coordinates in the present work. The lower plate is at rest, while the upper one is moved in the x-direction with the velocity v. The z-direction is normal to the plates and the y-axis is pointing inwards. The angle which the director makes with the z-axis is denoted θ counting θ positive for a clockwise rotation.

a stable flow we demand Γ_y^h to be zero giving

$$\alpha_3 \sin^2 \theta - \alpha_2 \cos^2 \theta = 0 \tag{7}$$

This can only be satisfied if α_2 and α_3 are of the same sign. A disk like molecule where α_3 is positive and α_2 is negative would therefore give rise to some kind of tumbled state under shear, which would correspond to the not very well understood tumbled state for rod like nematics. If on the other hand α_2 and α_3 are of the same sign, we get a solution to Eq. (7). This equilibrium angle is commonly called the flow alignment angle and is here denoted by θ_n.

$$\tan \theta_n = \pm \sqrt{\alpha_2/\alpha_3} \tag{8}$$

To chose the right sign in Eq. (8) we proceed as follows. In Figure 3 we have plotted Γ_y^h as a function of θ. Both α_2 and α_3 are assumed to be positive. We now have the two possible equilibrium angles denoted θ_{n_1} and θ_{n_2} as the intersections of the graph of Γ_y^h and the θ-axis. To state which is the stable equilibrium, we have to see what happens with the torque if we permit the director to make a small fluctuation from it's equilibrium value. Beginning with θ_{n_1} (corresponding to the minus sign in Eq. (8)) we see that if we decrease θ with a small amount from θ_{n_1}, the torque exerted on the director is positive, thus working against the fluctuation. A small increase of θ will on the other hand give rise to a negative torque also this tending to bring θ back to its original value of θ_{n_1}. Thus θ_{n_1} is a stable solution of Eq. (7). By similar arguments we can see that θ_{n_2} will correspond to an unstable equilibrium. Consequently we have to choose the minus sign in Eq. (8) when both α_2 and α_3 are positive. If instead both α_2 and α_3 are negative, the graph of Γ_y^h will be

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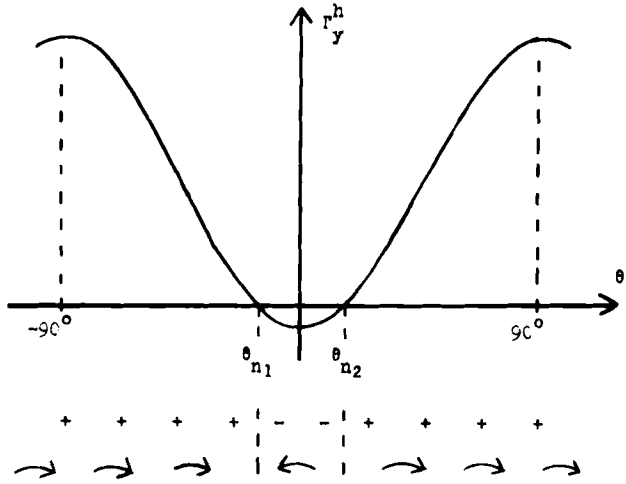

FIGURE 3 The hydrodynamic torque, $\Gamma_y^h = (\alpha_3 \sin^2 \theta - \alpha_2 \cos^2 \theta)u'$, plotted as a function of θ. Both α_2 and α_3 are assumed to be positive and $\alpha_3 = 10\alpha_2$. Flow alignment can occur when $\Gamma_y^h = 0$, and is possible when θ equals θ_{n_1} or θ_{n_2}. In the lower part of the figure the sign of Γ_y^h for the different values of θ is marked out. The arrows indicate the direction of the rotation of the molecules in a nonequilibrium situation. In this case we see that θ_{n_1} is the one of the two possible equilibrium angles which is stable against fluctuations.

mirrored in the θ-axis. Similar arguing now gives θ_{n_2} to be the stable equilibrium as is well known.

When concerning the reorientational times for the director, it is easy to calculate[7] that a typical relaxation time τ is given by

$$\tau = \frac{\alpha_3 - \alpha_2}{2u'\sqrt{|\alpha_2\alpha_3|}} \tag{9}$$

where u' is the shear rate. Rewriting τ as a function of α_3/α_2 and further on (using Eq. (5)) as a function of λ we get

$$\tau = \frac{1}{2u'} \frac{|1 - \alpha_3/\alpha_2|}{\sqrt{|\alpha_3/\alpha_2|}} = \frac{1}{u'\sqrt{|(\lambda - 1)(\lambda + 1)|}} \tag{10}$$

This function is plotted in the upper part of Figure 1.

We now summarize the consequences of Voloviks calculations.

$\lambda \simeq 1$: Rod like molecules

Volovik calculates $\lambda = 1$ for ideal infinite thin rods. When he takes into account the finite thickness of the molecules he expects λ to be

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close to +1. As is mentioned earlier most nematics exhibit values of λ which are slightly greater than one, $\lambda \gtrsim 1 (\alpha_3/\alpha_2 \gtrsim 0)$. This is in agreement with calculations by Helfrich,[13,14] where Helfrich assumes the molecules to be rigid prolate ellipsoids of revolution with the long axis $2a$ and the short axis $2b$. He then gets the result $\alpha_3/\alpha_2 = (b/a)^2$. This means that $\alpha_3/\alpha_2 \to 0$ in the limit of ideal rods and $\tan \theta_n \to \infty$ (Both α_2 and α_3 are negative so the + sign in Eq. (8) is valid). θ_n then lies close to 90° and we will have the well known situation as in Figure 4a. The relaxation time according to Eq. (10) in this limit will be approximated as

$$\tau \simeq \frac{1}{2u'} \sqrt{\alpha_2/\alpha_3} \tag{11}$$

$\lambda \simeq -1$: Disk like molecules

For infinite thin disks Volovic gets $\lambda = -1$. Taking into account the finite thickness of the molecules he expects small deviations from this result. Assuming $\lambda \lesssim -1$ one gets by inspecting Figure 1 that $\alpha_3/\alpha_2 \to \infty$. With Eq. (3) in mind it is clear that in this case both α_2 and α_3 must be positive. If it in Helfrich's calculations is permitted to interchange the roles of the long and the short axis of the ellipsoids without changing anything else, thus making the ellipsoids oblate, we see that Helfrich's results are consistent with the assumption $\lambda \lesssim -1$. When α_3/α_2 is large (both being positive and thus choosing the minus sign in Eq. (8)) we get $\tan \theta_n \to 0^-$, i.e. θ_n is small and negative. In Figure 4b we have pictured the molecules in this type of flow. In the limit of large α_3/α_2, the relaxation time τ can be approximated by (compare with Eq. (11) which is valid for rod like molecules)

$$\tau \simeq \frac{1}{2u'} \sqrt{\alpha_3/\alpha_2} \tag{12}$$

By comparing Figures 4a and 4b we can see that although the values of θ_n are quite different in the two cases, the physical situations are not. In Figure 4a we have rods lying almost parallel to the glass plates, while in Figure 4b we have disks which are oriented with the disk planes almost parallel to the glass plates. This should not be surprising if one imagines some kind of steric forces to be responsible for the flow alignment.

A reactive parameter $\lambda \simeq -1$ as expected for the disk like molecules could of course also give rise to a state where no flow alignment occur ($\lambda \gtrsim -1$; $\alpha_3 > 0$ and $\alpha_2 < 0$). This would again give some kind of tumbled state resembling the situation described by Refs. 8–11. Thus

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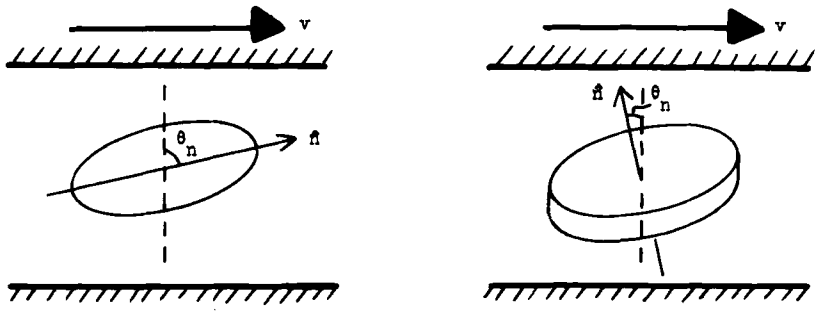

FIGURE 4 (a) Flow alignment angle, $\tan\theta_n = \sqrt{\alpha_2/\alpha_3}$, for rod like molecules. Both α_2 and α_3 are negative and $|\alpha_2| \gg |\alpha_3|$. (b) Proposed flow alignment angle, $\tan\theta_n = -\sqrt{\alpha_2/\alpha_3}$, for disk like molecules. Both α_2 and α_3 are positive and $\alpha_3 \gg \alpha_2$.

we see that the disk like molecules are very likely to be similar to the "ordinary" rod like nematics in their flow behavior, showing flow alignment or tumbling, and with reorientational times for the director which are corresponding. We also see that the roles of the viscosity parameters α_2 and α_3 are interchanged between the two different types of molecules. For rod like molecules α_2 is always negative while α_3 can be negative (flow alignment) or positive (tumbling). For disk like molecules α_3 is always positive while α_2 can be positive (flow alignment) or negative (tumbling).

Note on the relaxation time

Finally it might be interesting to compare the relaxation time for the reorientation of the director with the amount of "nonideality" of the molecules. The ideal rods and disks have values of λ which are $+1$ and -1 respectively. In this limit τ goes to infinity. In order to decrease τ we have to change λ. If $|\lambda|$ is permitted to go to infinity, we see that τ goes to zero. Of course the liquid crystalline behavior demands that the molecules at least resembles rods or disks, so $|\lambda|$ is probably not allowed to be too large if we want to keep the liquid crystal properties of the molecules. However it might be worth noting when designing molecules for technical applications that to decrease τ the molecules should be "as nonideal as possible", i.e. $|\lambda|$ should be as large as possible.

Acknowledgment

The author wishes to express his thanks to Dr. K. Skarp for many stimulating discussions of the hydrodynamics of nematic liquid crystals.

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