

# MOLECULAR APPROACH TO THE HYDRODYNAMIC VISCOSITIES OF NEMATIC LIQUID CRYSTALS (\*)

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*ABSTRACT* — We discuss the temperature behaviour of the capillary-flow viscosities of nematics and outline a molecular theory of the rotational viscosity  $\gamma_1$ . This theory gives  $\gamma_1(T) = \text{const. } S^2 \exp(\varepsilon S/kT)$ , in good agreement with experimental data. The parameter  $\varepsilon = 3 A/2 m V^2$  comes from the Maier and Saupe's potential and is equal to 0.8795 kcal/mole in the case of *p*-azoxyanisole. From this we get the nearest-neighbor coordination number  $m = 6.3$ .

## 1 — INTRODUCTION

The rheological properties of nematic liquid crystals have received much attention in the past. In particular Miesowicz clearly defined three independent viscosities to characterize the flow of such anisotropic liquids, and latter Porter and Johnson studied experimentally their temperature dependence. More recently Leslie derived a hydrodynamic theory of nematic liquid crystals according to which the rheological properties of incompressible nematics depend on five coefficients. Three of them can be chosen to be the Miesowicz viscosities but this is not always most convenient. For comparison, it is remembered that incompressible isotropic liquids show a single viscosity.

In this paper, the hydrodynamic viscosities of nematic liquid crystals introduced by Leslie are considered from the point of

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view of molecular theories, and we try to explain their temperature behaviour. Particular attention is paid to the rotational viscosity  $\gamma_1(T)$ .

## 2 — TOPICS ON CONTINUUM THEORY

The viscous properties of *incompressible* nematics may be characterized by the following set of five independent coefficients:

$$(1) \quad \left\{ \begin{array}{l} \mu \equiv \mu_1 = A_1 S^2 \\ \lambda \equiv \mu_4 = 2 \nu_{\text{iso}} - a S + A_3 S^2 \\ \frac{1}{2} \gamma_1 \equiv \frac{1}{2} (\mu_3 - \mu_2) = C_1 S + C_2 S^2 \\ \frac{1}{2} \gamma_2 \equiv \frac{1}{2} (\mu_3 + \mu_2) = -B_1 S - B_2 S^2 \\ \frac{1}{2} \gamma_3 \equiv \frac{1}{2} (\mu_6 + \mu_5) = \frac{3}{2} a S + A_2 S^2 \end{array} \right.$$

Here,  $\mu_i$  ( $i=1 \dots 6$ ) are the original viscosities introduced by Leslie in his hydrodynamic theory of nematics [1],  $S$  is the order parameter, and  $\nu_{\text{iso}}$  is the viscosity extrapolated from the isotropic phase ( $S=0$ ). Expansions of the  $\mu$ 's in powers of  $S$  have been considered first by Helfrich and Imura and Okano [2] and used in (1). According to Imura and Okano,  $a$ ,  $A_i$ ,  $B_i$ , and  $C_i$  ( $i=1, 2, \dots$ ) are constants «which are expected to depend on temperature very weakly» [2]. The rotational viscosity  $\gamma_1$  is of fundamental importance in the theory of nuclear spin-lattice relaxation in nematic mesophases [3, 12].

Leslie has shown that  $\gamma_1$  is always positive. The order parameter is usually positive, but it can, in principle, be negative (metastable state). As  $\gamma_1$  must vanish and have a minimum at  $S=0$ , we have  $C_1=0$  and  $C_2 > 0$  in expression (1), so that:

$$(2) \quad \gamma_1 = 2 C_2 S^2$$

This result was first presented by Helfrich [2] who supposed it to be valid only for  $|S| \ll 1$ . The ratio  $\gamma_2/\gamma_1$  is a coupling parameter between molecular orientation and shear flow. There

is evidence [4] that this parameter is continuous across the nematic-isotropic transition, in which case  $B_1 = 0$  and consequently:

$$(3) \quad \gamma_2 = -2 B_2 S^2$$

Using the theory of Leslie [1] and equations (1) we may derive expressions for the temperature dependence of the capillary-flow viscosities  $\eta_{1M}$  and  $\eta_{2M}$  as measured by Miesowicz and others [5, 6]. With  $C_1 = 0$ , but independently of  $B_1$ , we find:

$$(4) \quad \begin{cases} \eta_{1M} = \frac{1}{4} a S + \left[ A_1 \sin^2 \theta_0 \cos^2 \theta_0 + \frac{1}{2} (A_2 + A_3) \right] S^2 + \eta_{iso} - \frac{1}{4} \gamma_1 \\ \eta_{2M} = \frac{1}{4} a S + \frac{1}{2} (A_2 + A_3) S^2 + \eta_{iso} + \gamma_1 \left( \frac{1}{4} + \frac{1/2}{\cos 2 \theta_0} \right) \end{cases}$$

As a first approximation, we may take  $\eta_{1M} \sim \eta_{iso} - (1/4) \gamma_1$  and  $\eta_{2M} \sim \eta_{iso} + (3/4) \gamma_1$ . These functions reproduce qualitatively the data compiled by Porter and Johnson [6], including the rapid increase of  $\eta_{1M}$  and decrease of  $\eta_{2M}$  just below the transition point to the isotropic state. Near  $T_c$  the agreement is quantitative. In the opposite side, near  $T - T_c = -15^\circ \text{C}$  the difference between this approximation and experimental data is only about 11% for  $\eta_{1M}$  and 8% for  $\eta_{2M}$ . We have taken  $\eta_{iso} = 2.871 \times 10^{-5} \exp(2867/T)$  poise, as calculated from data in ref. [6], extrapolating the experimental curve relative to the isotropic phase.

### 3 — A MOLECULAR THEORY OF $\gamma_1(T)$

Let us now discuss the viscosity  $\gamma_1$  from a molecular-statistical point of view. This viscosity concerns only the molecular reorientational motions, which take place against a potential barrier whose height is given by:

$$(5) \quad E = D(\theta)_{\max} - D(\theta)_{\min} = \frac{3}{2} \frac{A}{mV^2} S = \epsilon S$$

where  $D(\theta)$  is the mean field potential given by the Maier and Saupe's theory of nematics [7]. Expression (5) shows that the



activation energy  $E$  is nearly proportional to the order parameter  $S$  and so varies strongly with temperature. This behaviour contrasts with what is usual in isotropic liquids, for which  $E$  is constant over most practical temperature ranges.

The molecular motion which we have in mind (reorientation) is a rate process and may be treated in a manner similar to the one introduced by Eyring [8] in his study of the shear viscosity  $\eta$  of isotropic liquids. In the case of the *rotational* viscosity  $\gamma_1$  we must, of course, consider an applied couple-density  $B$  and the proportional angular velocity  $N$  (flux proportional to force) instead of the velocity difference  $v$  and the force-density  $f$ . We must further remark that for the reorientation to be possible a local lattice expansion around the reorienting particle must take place. The microscopic volume  $V_N^*$  generated in this way can be related to the corresponding volume  $V_I^*$  of the isotropic phase by a spherical harmonic expansion. To lowest order, in the mean field approximation, we find:

$$(6) \quad V_N^* \propto V_I^* S^2.$$

With these results in mind, we may apply the general theory of rate processes to calculate the (statistical) rotational velocity  $N$  of the molecules submitted to the applied couple-density  $B$  and finally obtain:

$$(7) \quad \gamma_1 = c S^2 \exp(\epsilon S/kT)$$

where  $c = \text{constant}$ . Expressions (6) and (7) will be derived in more detail in a forthcoming paper.

By comparing expressions (2) and (7) we see that  $C_2$  varies exponentially with temperature in contrast with the above mentioned expectation of Imura and Okano. Our result is significant because, in expression (2),  $S^2$  is a statistical measure of the order and  $C_2$  must contain the physical nature and have the physical dimensions of a viscosity.

Fig. 1 gives a compilation of the so far reported experimental data on  $\gamma_1$ , for *p*-azoxyanisole (PAA), as a function of temperature. The data have been fitted to equation (7) by the least squares method, giving  $c = 0.1767 \text{ g cm}^{-1} \text{ s}^{-1}$  ( $\equiv$  poise) and  $\epsilon = 0.8795 \text{ kcal/mole}$ . We have used the  $S$  values calculated by Chandrasekhar, which have been successfully contrasted with

experience [9]. The agreement between our result and experimental data is very good. The broken line in the figure shows that  $\gamma_1$  cannot be simply proportional to  $S^2$ . An Arrhenius-type law with constant activation energy [10] is contradictory with accepted theories, e. g. ref. [7], and gives a not so good fit. Substituting in expression (5) the foregoing value of  $\epsilon$  and the value of  $A/V^2$  given by Maier and Saupe [7] we find  $m = 6.3$

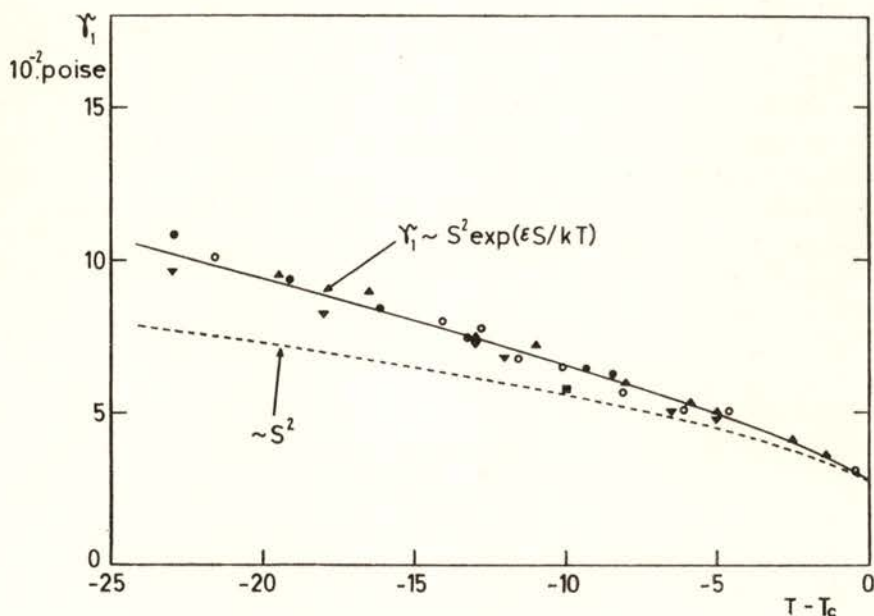


Fig. 1 — Rotational viscosity  $\gamma_1(T)$  of PAA. Experimental points: full circles, from ref. [10]; square, from ref. [14]; open circles, from ref. [15]; triangles, from ref. [16].

for the nearest-neighbor coordination number. This is a meaningful result since  $m$  is equal to 6 in the Monte Carlo calculation of Lebwohl and Lasher [11] and we expect the real value to be larger, due to incoherent diffusion, but only slightly larger because in PAA the diffusion correlation time is about one order of magnitude greater than the correlation time for reorientation [12]. Note that the  $\epsilon$ 's definition of Lebwohl and Lasher ( $\epsilon_{LL}$ ) is not the same as that given by expressions (5) and (7): within the mean field approximation we have  $\epsilon_{LL} =$

$= -\frac{2}{3}\epsilon$ . They give  $-\beta\epsilon_{LL} = 0.77$  (mean field) and we have

found from data on  $\gamma_1$  that  $\frac{2}{3}\beta\epsilon = 0.73$ , in good agreement.

Another grateful result of the present theory is the value of  $\epsilon S_c = 0.293$  kcal/mole. This is about twice the heat of transition  $\Delta Q_c = 0.137$  kcal/mole reported in ref. [13], as expected.

Expression (7) with the above values of  $c$  and  $\epsilon$  gives  $\gamma_1 = 0.0742$  poise at  $122^\circ\text{C}$  ( $T - T_c = -13^\circ\text{C}$ ). This, together with the values of the viscosities measured by Miesowicz [5] allows us to compute all the six coefficients introduced by Leslie. Results are displayed in Table 1 for three values of the flow-orientation angle  $\theta_0$  (at  $122^\circ\text{C}$ ) frequently found in the literature. Which of them is the relevant one, if any, remains an unsolved problem. For comparison, the values found by the Orsay Group from light scattering experiments [14] are also displayed in the table.

Results for some other liquid crystals are being prepared and a comparative study should be published soon.

TABLE 1

Leslie's viscosity coefficients for PAA, at  $122^\circ\text{C}$ , expressed in poise for three values of the flow-orientation angle

	$\theta_0 = 0^\circ$	$\theta_0 = 9.1^\circ$	$\theta_0 = 19.7^\circ$	Ref. [14]
$\mu_1$	—	0.35	0.17	
$\mu_2$	-0.074	-0.076	-0.085	-0.064
$\mu_3$	-0.000	-0.002	-0.011	-0.006
$\mu_4$	0.068	0.068	0.068	0.083
$\mu_5$	0.042	0.040	0.031	0.025
$\mu_6$	-0.032	-0.038	-0.065	-0.045



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