SIMPLE MOLECULAR STATISTICAL INTERPRETATION OF THE NEMATIC VISCOSITY γ_1 (*) (**)

A. F. Martins and A. C. Diogo
Centro de Física da Matéria Condensada (INIC)
Av. Gama Pinto-2, Lisboa-4, Portugal

ABSTRACT — We present a theoretical analysis of the rotational viscosity $\gamma_1(T)$ of nematic liquid crystals based on the theory of rate processes and Maier and Saupe's molecular theory. We derive:

$$\gamma_1(T) = c \ S^2 \ \exp(\varepsilon S / kT)$$

where $\varepsilon = 3A/2mV_N^2$ and $c \simeq$ const. (explicitly given). This relation fitts very well the compiled experimental data for p-azoxyanisole (PAA), with $c = 0.177$ poise and $\varepsilon = 0.879$ kcal/mole, and for anisaldazine (AD), with $c = 0.111$ poise and $\varepsilon = 0.890$ kcal/mole. From these values of ε we get the nearest-neighbour coordination numbers $m = 6.3$ for PAA and $m = 6.8$ for AD. The agreement between our theory and experience extends over the entire nematic range including the region close to T_c.

RESUMÉ — Nous présentons une analyse théorique du coefficient de viscosité rotationelle $\gamma_1(T)$ des cristaux liquides nématiques qui nous permet de trouver la relation suivante:

$$\gamma_1(T) = c \ S^2 \ \exp(\varepsilon S / kT)$$

où $\varepsilon = 3A/2mV_N^2$ est défini dans le cadre de la théorie moléculaire de Maier et Saupe et c est une constante dont la forme explicite est donnée. La relation ci-dessus s'accorde très bien avec les résultats expérimentaux relatifs au p-azoxyanisole (PAA), avec $c = 0{,}177$ poise et $\varepsilon = 0{,}879$ kcal/mole, et avec les résultats relatifs à l'anisaldasine (AD), avec $c = 0{,}111$ poise et $\varepsilon = 0{,}890$ kcal/mole. À partir des valeurs du paramètre ε nous obtenons les nombres de coordination $m = 6{,}3$ pour le PAA et $m = 6{,}8$ pour l'AD. L'accord de cette théorie avec l'expérience s'étend sur toute la plage nématique, en particulier il se vérifie tout près de T_c.

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I — INTRODUCTION

The fundamental equations for viscous flow in nematic liquid crystals have first been written down by Leslie [1] and have proved to be consistent with many experimental observations. Essentially, the hydrodynamic equations of Leslie give the motions of two *coupled* fields, the velocity field $\vec{v}(\vec{r}, t)$ and the director field $\vec{n}(\vec{r}, t)$. If the velocity gradients are negligible, the coupling between these fields vanishes and we may separate the equation of motion for the director:

$$\sigma \frac{d\vec{\Omega}}{dt} + \gamma_1 \vec{\Omega} - \vec{N} = 0 . \tag{1}$$

Here $\vec{\Omega} = \vec{n} \times (d\vec{n}/dt)$ is the rotational velocity of the director, $\vec{N} = \vec{n} \times \vec{h}$ is a restoring torque due to the *molecular field* $\vec{h}$ [2], σ is an inertial coefficient associated with director reorientations, and γ_1 is a pure *rotational* viscosity. The effect of an external magnetic field is included in $\vec{N}$.

The viscosity $\gamma_1(T)$ may be measured in a way derived from the application of Leslie equations to the Tsvetkov's experiment [3]. The measurement is performed under stationary conditions such that the director fied $\vec{n} \equiv \vec{n}(t)$ makes a constant angle with an external rotating magnetic fied $\vec{H} \equiv \vec{H}(t)$, and it is assumed that $\vec{n}(t)$ is homogeneous in space, $\vec{v} = 0$, and the temperature is constant.

The inertial term in equation (1) is completely negligible for motions in the frequency range compatible with the continuum theory [2]. To this approximation, equation (1) describes a rotational motion of the director with a definite velocity under given conditions. This is typical of a rate process [4].

In the following part of this paper we will outline a molecular statistical theory of $\gamma_1(T)$ which takes advantage of these facts.

In part III the main results of the theory are contrasted with different interpretations of $\gamma_1(T)$ that have been proposed so far and with experimental data available for *p*-azoxyanisole (PAA) and anisaldazine (AD). These data strongly support our theory.

In the conclusion we briefly refer to expected extensions and improvements of this work.

II — MOLECULAR THEORY OF $\gamma_1(T)$

As it is well known the director $\vec{n}$ is a unit vector used to specify, in equilibrium, the preferred direction of molecular orientation.

When rotational motion is set in a portion of the nematic liquid, as expressed by equation (1), the molecules at each point of the moving liquid will be, on the average, parallel to the director at that point if the condition $\omega\tau << 1$ is fulfilled. Here ω is the frequency characterizing the time variation of $\vec{\Omega}$ and τ is a characteristic molecular decay time. Therefore, under such a condition we may interpret the motion of $\vec{n}$ as a collective motion of the molecules (or, perhaps in some cases, more complex «particles» formed by several molecules).

Besides the collective reorientations represented by the motion of $\vec{n}$, there are single-particle motions in the nematic phase with characteristic times of order τ, most likely to molecular motions in the isotropic liquids.

Single-particle reorientations take place against a potential barrier due to the local field created by all other molecules in the fluid. The instantaneous form of this potential depends on the configuration of the surrounding molecules and its calculation is a formidable task. However, to a good approximation, we may use the smooth form of the potential as given by the Maier and Saupe's mean-field theory [5]:

$$D(\theta) = -\frac{A}{m V_N^2} S P_2(\cos\theta) \tag{2}$$

where S is the degree of order, A is a molecular constant, m is a cluster parameter, V_N is the nematic volume, and θ is the angle made by the long molecular axis with the equilibrium direction. The minima of the potential (2) are separated by π thus reflecting the experimental fact that the directions $\vec{n}$ and $-\vec{n}$ are physically equivalent in all known nematics. The height of the potential barrier is given by

$$E = D(\theta)_{\max} - D(\theta)_{\min} = \frac{3}{2}\,\frac{A}{m V_N^2} S = \varepsilon S \,. \tag{3}$$

The actual packing of the molecules in the nematic state, and their long shape, do not allow for single-particle reorientations over large angles (e. g. rotational jumps of π) unless a previous local «lattice» expansion occurs. The probability of a rotational jump should then be given by the probability of the molecule finding the *necessary free volume* times the probability of attaining *sufficient energy* to cross over the potential barrier, as the two events must happen simultaneously. In equilibrium, the frequencies of molecular jumps clockwise and counter-clockwise are the same, and, within the framework of the rate theory [4], they are given by the following expression:

$$\nu_0 = \frac{k\mathrm{T}}{h} \Pi\,(\mathrm{Z}^e\,,\mathrm{Z}) \exp\left(-\,\varepsilon \mathrm{S}/k\mathrm{T}\right) \tag{4}$$

where $\Pi\,(\mathrm{Z}^e\,,\mathrm{Z})$ is a probability or «steric» factor depending on the partition functions of the molecule in the excited and normal states, k and h are the Boltzmann and Planck constants, and T is the temperature.

In the conditions of the Tsvetkov's experiment, as described above, an external torque due to the magnetic field is constantly applied to the molecules and the frequencies of molecular jumps forward and backward are no more the same. We then have, according to Boltzmann statistics:

$$\nu_{\pm} = \nu_0 \exp\left(\pm\,\mathrm{W}/k\mathrm{T}\right) \tag{5}$$

for the frequencies of molecular jumps in the forward (+) and backward (—) directions. In expression (5), W is the work done by the external torque; it should be computed between normal ($\theta = 0$) and excited ($\theta = \pi/2$) states of the jumping molecule. Note that we are concerned only with molecular rotational jumps of π for these jumps *conserve* the direction of $\vec{n}$ relative to the external field (cf. Tsvetkov's experiment).

Taking into account the distance between minima of the potential barrier, and expression (5), we may introduce a (relative) *mean rotational velocity* of the jumping molecule in the following manner:

$$\Omega^* = \pi\,(\nu_+ - \nu_-) = 2\,\pi\,\nu_0 \sinh\left(\mathrm{W}/k\mathrm{T}\right).$$

In actual experiments we always have $\mathrm{W} << k\mathrm{T}$ so that:

$$\Omega^* = 2\,\pi\,\nu_0\,\frac{W}{k\,T}\,. \tag{6}$$

The work W may be written as:

$$W = N^*\,V_i^*\,\frac{\pi}{2} \tag{7}$$

where N^* is the *mean value* (for $\theta = 0 \rightarrow \pi/2$) of the torque density per molecule, and V_i^* is the volume available for the jumping molecule after the local lattice expansion referred to above. V_i^* is roughly the volume which should dispose each molecule if they were isotropically distributed. If ΔV^* represents the local expansion we may write:

$$V_i^* = V_N^* + \Delta V^* \tag{8}$$

where V_N^* is the volume per molecule in the nematic phase. The change in volume at the nematic-isotropic transition is only a very small fraction of the nematic volume V_N and the temperature variations of V_N and V_I are very similar. V_I is the actual volume in the isotropic phase. As we expect $V_i \simeq V_I^e$ (V_I^e being equal to V_I as extrapolated from the isotropic phase) it is clear that ΔV^* should be nearly temperature independent. On the other hand, the internal pressure variation Δp necessary to produce this volume expansion ΔV^* should be strongly dependent on temperature and increase as the crystalisation point is approached. In fact, the mean field theory of Maier and Saupe [5], predict:

$$\Delta p = \left(\frac{\partial U_{\mathrm{ord}}}{\partial V_N}\right)_S = \frac{N_A}{m}\,\frac{A}{V_N^3}\,S^2 \tag{9}$$

where U_{ord} is the internal energy associated with nematic order and S is the usual order parameter.

From expressions (6) and (7) we have:

$$\gamma_1 = \frac{N^*}{\Omega^*} = \frac{k\,T}{\pi^2\,V_i^*}\,\frac{1}{\nu_0}\,. \tag{10}$$

In order to write this formula in a more convinient way, we now remember the following thermodynamic relation

$$V_i^*\,\chi_i = \Delta V^* / \Delta p$$

where, according to the definition of V_i^* given above, the quantity χ_i denotes the isothermal compressibility of the state with an isotropic distribution of the molecular axes (at the temperature corresponding to V_N). On substituting V_i^* taken from this relation into the expression (10) we get:

$$\gamma_1 = \frac{k T \chi_i}{\pi^2 (\Delta V^*)} (\Delta p) \frac{1}{\nu_0} .$$

If we finally substitute here the value of ν_0 as given by (4) and the value of Δp taken from (9) we find:

$$\gamma_1 = c\, S^2 \exp(\varepsilon S / k T) \tag{11}$$

where c is a roughly temperature independent factor given by:

$$c = \frac{N_A}{m} \frac{h \Lambda \chi_i}{\pi^2 (\Delta V^*) V_N^3 \Pi} . \tag{12}$$

Here N_A is the Avogadro's number, and Π is the probability factor introduced in expression (4); the meaning of the other symbols was given above.

Expression (11) is our central result. It was first published in a previous Note by one of us, Ref. [6], without detailed demonstration (only the principle of our reasoning was given).

The *activation energy* which appears in (11) is proportional to the order parameter S and thus varies strongly with temperature. This behaviour contrasts with what is usual in isotropic liquids, for which E is constant over most practical temperature ranges. Expression (11) also shows that the *rotational* viscosity $\gamma_1(T)$ vanishes in the isotropic phase $(S = 0)$.

To complement the theory we have just outlined, a final remark is in order. In the foregoing discussion we have considered simple nematics where intermolecular position-correlations are not too strong, and the molecules *do not* form well defined clusters or cybotactic groups. If nematic molecules associate to form cybotactic groups or clusters composed of a great number of molecules some deviation from the curve (11) may occur. This point will be discussed elsewhere.

III — EXPERIMENTAL DATA AND DISCUSSION

An expression similar to (11) but with $E = \text{constant}$ was first proposed empirically by Martins [7]. Helfrich proposed $\gamma_1 = b_1 S^2$ with $b_1 = \text{constant}$, for $|S| << 1$, which is not the current case [8].

It may be fruitful to contrast our results with a theory developed by Imura and Okano. From their paper we get:

$$\gamma_1 = 2\, C_1\, S + 2\, C_2\, S^2 \tag{13}$$

where C_1 and C_2 are «constants which are expected to depend on temperature very weakly» [9]. Moreover, the term proportional to S^2 in expression (13) should be negligible as compared to the first.

We have used the least squares method to fit the experimental data on PAA and AD to equation (13) and have found that the contribution of the term in S^2 is dominant. We may conclude that $\gamma_1(T)$ as given by expression (13) cannot be approximated to first order in S. A similar situation is expected for some other viscosities of nematic liquid crystals [6].

On the other hand, the equations proposed by Imura and Okano contain only one activation energy which is defined in the isotropic phase by the usual Arrhenius' law. The theory outlined here predicts one more activation energy which is characteristic of rotational motions. The activation energy measured in the isotropic phase is characteristic of translational motions (as is the usual shear viscosity).

Let us now compare the predictions of our theory with experimental data. We start with the case of PAA and consider first expression (10) which is equivalent but simpler than expression (11). As $V_i \approx V_I^c$, and the volume change at the nematic-isotropic transition is $\Delta V_c = 0.0035\, V_{N,c}$ [5], we may write $V_i^* \simeq 1.0035\, V_N^* = 3.712 \times \times 10^{-22}\, \text{cm}^3/\text{molec}$. On the other hand we expect, to a good approximation that $1/\nu_o \simeq \tau_d^{(1)}$, where $\tau_d^{(1)}$ is a dielectric relaxation time relative to the orientational motion of the component of the permanent electric dipole parallel to the long molecular axis. With $\tau_d^{(1)} = 4.3 \times 10^{-9}\, \text{s}$ at 125° C [10] expression (10) gives $\gamma_1 = 0.064$ poise which is in excelent agreement with experience (see Fig. 1).

The experimental data on $\gamma_1(T)$ so far reported for PAA have yet been analysed in Ref. [6] in terms of expression (11). These data are again displayed in Fig. 1 and their analysis repeated here for a matter of completeness. The data have been fitted to equation (11) by the least squares method, giving $c = 0.177$ poise and $\varepsilon = 0.879$ kcal/mole. In this calculation we have used the values of S as given by Chandrasekhar, which have been successfully contrasted with experience [11]. The data agree very well with our theoretical

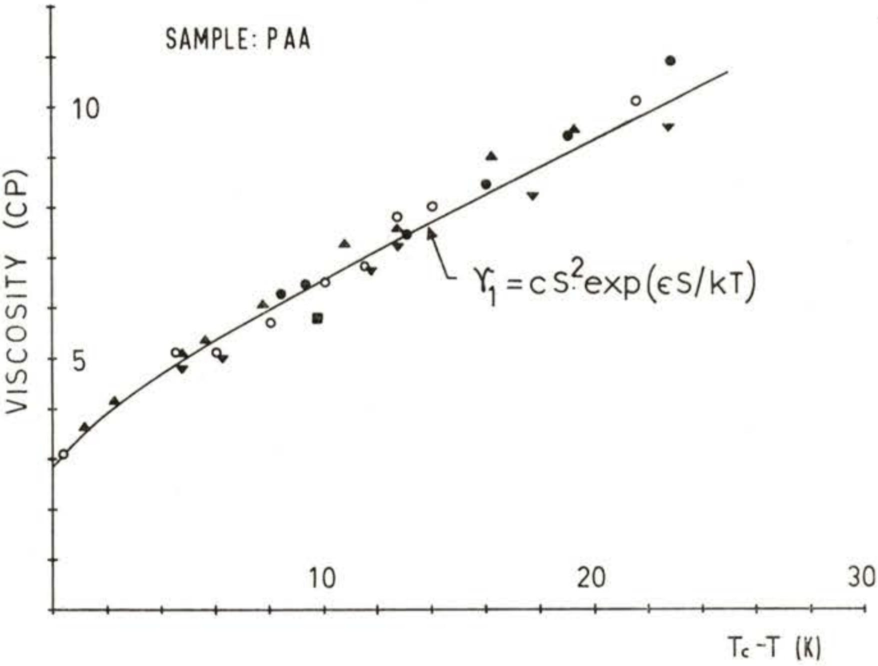

Fig. 1 — Rotational viscosity γ_1 (T) of PAA. Experimental points: open circles from ref. [3]; triangles from ref. [14]; full circles from ref. [16]; square from ref. [17].

prediction over the entire nematic range. Substituting in expression (10) the foregoing value of ε and the value of A/V_N^2 as given by Maier and Saupe [5] we find $m = 6.3$ for the nearest-neighbour coordination number. This seems to be a meaningful result. It is to be compared with the value $m = 6$ characteristic of a simple-cubic lattice considered by Lebwohl and Lasher in their Monte Carlo calculation [12]. Although this calculation gives very good results, we expect the actual value of m to be slightly larger than 6 because of the contribution of incoherent diffusion not considered in the lattice model. This contribution should have a rather little effect in this case because the diffusion correlation time of PAA is about one order of magnitude greater than the correlation time characteristic of molecular reorientations [7]. Translational diffusion should be completely negligible if the time required for a molecule to diffuse through a distance comparable with the inter-molecular separation were much longer than the characteristic time of reorientation. In such a situation the molecules could be treated as fixed at the lattice points.

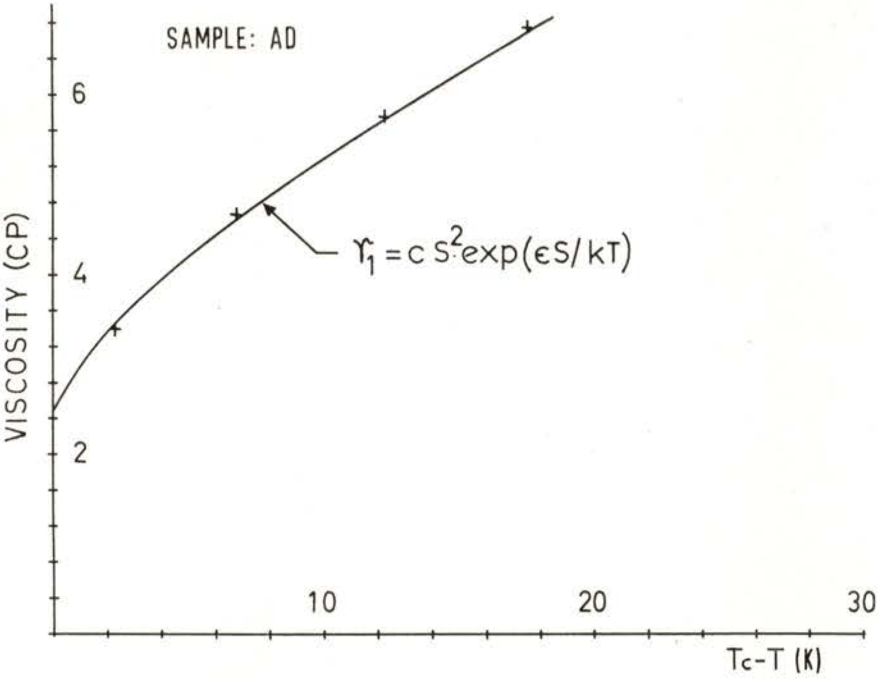

Fig. 2 — Rotational viscosity $\gamma_1(T)$ of AD. Experimental points from ref. [14].

In Fig. 2 are displayed the results we have obtained for anisaldazine (AD). This material clears at 454 K and its order parameter is known from the work of Madhusudana et al. [13]. The data on $\gamma_1(T)$ were reported by Yun [14]. Again, the agreement between expression (11) and experimental data is very good. We find now $c = 0.111$ poise and $\varepsilon = 0.890$ kcal/mole. From the equation $A = 4.55\, k\, T_c\, V^2_{N,c}$ established by Maier and Saupe [5] the value

$T_c = 454\,K$, and the value $V_{N,c} = 257.775\ cm^3/mole$ computed from the density data of Porter and Johnson [15], we find $m = 6.8$. This result compares well with that found for PAA. It may be less accurate as it has been computed from much less experimental data.

IV — CONCLUSION

We have outlined a molecular theory of the nematic rotational viscosity $\gamma_1(T)$ in the spirit of the theory of rate processes. Although established along very simple lines, our theory furnishes a new expression for $\gamma_1(T)$ which is strongly supported by the experimental data available for *p*-azoxyanisole and anisaldazine. Of particular importance is the agreement obtained near T_c.

It is our hope that this theory should be reformulated more rigorously and applied to other cases. Materials with a smectic A-nematic transition should be studied with particular interest near this transition. In any case, precise measurements of the degree of order are required, together with the measurements of $\gamma_1(T)$. We should also try a molecular interpretation of the other viscosities characterizing nematics. Preliminary arguments on this problem have been already presented elsewhere [6, 9].

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