ON THE VISCOSITY COEFFICIENTS OF NEMATIC MBBA AND
THE VALIDITY OF THE ONSAGER—PARODI RELATION

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From a critical review of the experimental viscosity data for nematic MBBA a complete set of viscosity coefficients is proposed, for which the Onsager—Parodi relation is valid. The temperature dependence of \( \gamma_1 \) can be described by

\[
\gamma_1 \sim S \exp(E/kT).
\]

In this letter viscosity data for N-\((p\text{-methoxybenzylidene})\)\(-p\text{-n-butylaniline}\), MBBA, in the nematic phase are critically reviewed. It is shown that the rotational viscosity \( \gamma_1 \) derived from Gähwiller's complete set of data is in disagreement with results from other measurements. A new complete set of viscosity data is proposed, for which the Onsager—Parodi relation is valid.

The expression for the viscous stress tensor of an incompressible nematic contains six coefficients with the dimension of a viscosity: \( \alpha_1, \ldots, \alpha_6 \) (Leslie coefficients) [1]. Parodi has shown that from Onsager's reciprocal relations, which reflect the time reversal invariance of the microscopic motions, one can derive [2]

\[
\alpha_6 - \alpha_5 = \alpha_2 + \alpha_3. \tag{1}
\]

As the validity of this relation in the case of nematic liquid crystals has been questioned, it would be useful to have experimental tests. This would require many independent measurements, which are usually not available, in which case eq. (1) is simply assumed to be true.

The viscosities that are measured experimentally are usually combinations of the \( \alpha \)'s. In a simple shear experiment for a nematic with a uniform director pattern one can measure the three Miesowicz viscosities (fig. 1a,b,c):

\[
\eta_1 = \alpha_2 - \alpha_3, \quad \eta_2 = \alpha_4, \quad \eta_3 = \alpha_6.
\]

\( \eta_1 \): director parallel to velocity gradient,
\( \eta_2 \): director parallel to flow direction,
\( \eta_3 \): director normal to shear plane.

In Miesowicz' original papers on PAA [3] the definitions of \( \eta_1 \) and \( \eta_2 \) are interchanged; we have retained here the notation of Helfrich [4]. These viscosities are related to the \( \alpha \)'s by

\[
\eta_1 = \frac{1}{2}(-\alpha_2 + \alpha_4 + \alpha_5), \quad \eta_2 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6), \quad \eta_3 = \frac{1}{2} \alpha_4. \tag{2}
\]

If the director is in the shear plane at an arbitrary angle...
with the flow direction a fourth coefficient $\eta_{12} = \alpha_1$ comes into play, that is symmetric in the coordinates (see fig. 1d). If the director is in the shear plane the flow leads to a torque on the director and thus changes the orientation of the director. The corresponding shear-torque coefficients are $-\alpha_2$ and $\alpha_3$ if the director is parallel to the velocity gradient and to the flow, respectively (fig. 1a,b). For an arbitrary angle $\theta$ between the director and the flow direction (fig. 1d), there is a specific angle $\theta_0$ (flow alignment angle) where the shear torque vanishes, given by

$$\tan^2 \theta_0 = \frac{\alpha_3}{\alpha_2} = (\gamma_2 + \gamma_1)/(\gamma_2 - \gamma_1).$$  

(3)

In this expression we have introduced

$$\gamma_1 = \alpha_3 - \alpha_2, \quad \gamma_2 = \alpha_6 - \alpha_5.$$  

(4)

The viscosities $\gamma_1$ and $\gamma_2$ can often be measured directly in experiments where the director is made to rotate. In terms of the experimental viscosities eq. (1) can be written as

$$\eta_2 - \eta_1 = \alpha_3 + \alpha_2.$$  

(5)

Gähwiller has reported on the viscosities of MBBA [5]. From his results a complete set of coefficients can be calculated assuming that eq. (1) is valid. The results are given in table 1. In addition various authors have reported values for $\gamma_1$, which are collected in fig. 2. These results from several different methods indicate at $T_{NI} - T = 18^\circ$ a value $\gamma_1 \approx 95$ cP, which is considerably larger than Gähwiller's result. Considering the Onsager—Parodi relation as stated in eq. (5), we must conclude that either this relation does not hold or that $|\eta_2 - \eta_1|$ as given by Gähwiller is too small. Therefore we shall compare these shear flow results in detail with those of some other methods.

Using the attenuation of ultrasound Martinoty and Candau [13] have measured the quantities

$$\eta_2 = \eta_2 - \frac{1}{3} \alpha_3(1 + \gamma_2/\gamma_1), \quad \eta_3 = \eta_3.$$  

(6)

Because of the small value of $\theta_0$ one has $|\alpha_3| \ll |\alpha_2|$, and consequently $\eta_2 \approx \eta_2$. The experimental results are $\eta_2 = 27$ cP and $\eta_3 = 42$ cP, in good agreement with the results of table 1. Summerford et al. [14] have argued that Gähwiller's result for $\eta_1$ is too small. To maintain a uniform director pattern the torque due to the applied magnetic field must be much larger than the shear torque. In this particular configuration (director parallel to velocity gradient) this means

$$\Delta \chi H^2 \approx -\alpha_2 \delta,$$  

(7)

where $\delta$ is the shear rate. With the fields and shear rates used by Gähwiller this condition is only approximately fulfilled. However, the results of Summerford et al. are probably not trustworthy, because they also report rather high values for $\eta_3$ and for the viscosity in the isotropic phase, for which quantities this argument

Fig. 2. The rotational viscosity $\gamma_1$ versus reduced temperature for MBBA; ●: rotating magnetic field [6,7]; ○: motion of walls [8]; ◆: light scattering [10]. (This method gives $K_{22}/\gamma_1$, from which $\gamma_1$ is calculated with $K_{22}/\Delta \chi$ from ref. [11], and $\Delta \chi$ from ref. [12]).

Table 1

| Viscosity coefficients for MBBA at 25°C ($T_{NI} - T = 18^\circ$ C) in cP. |
|-----------------|-----------------|
| Experimental a) | Calculated       |
| $\eta_1$ = 103.5 ± 1.5 | $\alpha_1 = 6.5 ± 4$ |
| $\eta_2$ = 23.8 ± 0.3  | $\alpha_2 = -79 ± 2$ |
| $\eta_3$ = 41.6 ± 0.7  | $\alpha_3 = -0.9 ± 0.3$ |
| $\eta_{12}$ = 6.5 ± 4 | $\alpha_4 = 83.2 ± 1.5$ |
| $\theta_0 = 6^\circ ± 1^\circ$ | $\alpha_5 = 45 ± 5$ |
|                     | $\alpha_6 = -34 ± 2$ |
| $\gamma_1 = 78 ± 2$ | $\gamma_2 = -80 ± 2$ |

a) Ref. [5].
Table 2
Revised viscosity coefficients for MBBA at $T_{NI} - T = 18^\circ\text{C}$ (cP).

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Calculated</th>
</tr>
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<tbody>
<tr>
<td>$\eta_2 = 23.8 \pm 0.3$ a)</td>
<td>$\alpha_1 = 6.5 \pm 4$</td>
</tr>
<tr>
<td>$\eta_3 = 41.6 \pm 0.7$ a)</td>
<td>$\alpha_2 = -96 \pm 3$</td>
</tr>
<tr>
<td>$\eta_{12} = 6.5 \pm 4$ a)</td>
<td>$\alpha_3 = -1.1 \pm 0.2$</td>
</tr>
<tr>
<td>$\theta_0 = 6^\circ \pm 1^\circ$ a)</td>
<td>$\alpha_4 = 83.2 \pm 1.5$</td>
</tr>
<tr>
<td>$\gamma_1 = 95 \pm 3$ b)</td>
<td>$\alpha_5 = 63 \pm 12$</td>
</tr>
<tr>
<td>$\gamma_2 = -97 \pm 3$</td>
<td>$\alpha_6 = -34 \pm 2$</td>
</tr>
<tr>
<td>$\eta_1 = 121 \pm 4$</td>
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a) Ref. [5]. b) From fig. 2.

...does not hold. Nevertheless, their objection to the value of $\eta_1$ seems to be correct. Not including $\eta_1$ in experimental results, but still assuming that the Onsager—Parodi relation is valid, we have therefore recalculated the viscosity coefficients of MBBA (see table 2). The new higher value of $\eta_1$ would influence the much wider nematic range.

Now a further check on the results of table 2 is possible using viscosity data from light scattering experiments. From table 2 we calculate

$$\eta_{\text{bend}} = \gamma_1 - \alpha_2^2/\eta_1 = 19 \text{ cP.}$$

Experimental results for this quantity range from 19 to 21 cP [15,16]. Although these results are not very accurate, because they depend on the value chosen for $K_{33}$, which is somewhat uncertain, we see that the agreement is excellent. Hence we can conclude that within the experimental accuracy the Onsager—Parodi relation has been verified for MBBA.

There has been some controversy regarding the temperature dependence of $\gamma_1$ [17,18]. From the present results we can calculate $\gamma_1/\Delta\chi^m$, where $\Delta\chi^m = \Delta\chi/\rho$ is the anisotropy of the mass susceptibility. Assuming that the molecules are effectively axially symmetric around their long axis, one has $\Delta\chi^m \sim S$, where $S$ is the nematic order parameter. From the plot in fig. 3 we see that the temperature dependence of $\gamma_1$ can be described by

$$\gamma_1 \sim S \exp(E/kT).$$

Because the nematic temperature range of MBBA is rather limited, other pre-exponential factors like 1 or $S^2$, although less probable, cannot be completely ruled out. Eq. (9) is in agreement with results of Prost et al. [18] for a different nematic compound with a much wider nematic range.

[1] See, e.g., P.G. de Gennes, The physics of liquid crystals (Clarendon, Oxford, 1974) Ch. 5, where references can also be found to the original literature.