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# Molecular theory for the Leslie viscosities of nematics

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# Molecular theory for the Leslie viscosities of nematics

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Simple analytic expressions for all six Leslie viscosities for nematics are obtained from the molecular theory for rigid prolate molecules. The theory relates the viscosities to the second and fourth moments, $P_2$ and $P_4$, of the molecular distribution function, the aspect ratio $a$ of the molecules, and an isotropic viscosity that accounts for the effects of orientation-independent momentum transport. The theory is obtained by using expressions derived from a molecular theory by Kuzuu and Doi, as well as an approximate formula for the 'tumbling parameter' $\lambda$ in terms of $P_2$ and $P_4$; this approximate formula agrees well with data for many small-molecule nematics. Using the Maier–Saupe potential to compute $P_2$ and $P_4$, we find that the temperature dependencies of all six Leslie viscosities are in surprisingly good agreement with measurements of these viscosities for MBBA.

## 1. Introduction

The phenomenological theory of Leslie and Ericksen [1] shows that there are six viscosities for nematic liquid crystals, five of which are, in principle, independent. The values of these viscosities determine the flow properties of liquid crystals, as well as the transient response of the nematic director to perturbing fields, such as electric fields used in liquid crystal displays. Despite the importance of these viscosities, all six of them are rarely measured as a function of temperature, because it is experimentally difficult and tedious to do so.

Empirical formulas and correlations have been derived for some of these viscosities, especially for $\gamma_1$, the rotational viscosity, as discussed by Kneppe *et al.* [2]. These expressions usually assume that the viscosities are of the form $\gamma_i = f_i(P_2)g(T)$; $i = 1,2$, where $P_2$ is the second moment of the distribution function, also called the order parameter $S \equiv P_2$, and $T$ is temperature. The function $f$ is often taken to be a simple power law. This empirical approach is not very satisfactory, not only because it lacks theoretical justification, but also because it is hard to develop suitable expressions for all the viscosities, which can differ greatly among themselves both in magnitude and in temperature dependence, as well as in sign.

Here we propose a simple molecular theory for prolate molecules from which predictions of these viscosities are obtained analytically in terms of both $P_2$, the second moment of the distribution, as well as $P_4$, the fourth moment, and the molecular aspect ratio $a$. The theory differs from one presented by Marrucci [3] in that both $P_2$ and $P_4$ are involved in the final expressions, and in that a more accurate expression for $\lambda$, the 'tumbling parameter' is derived.

The theory is derived from a Fokker–Planck equation for the orientation distribution function of a nematic liquid composed of prolate objects of aspect ratio $a$. Kuzuu and Doi [4] showed that in the limit of low flow rates, the Leslie viscosities could be derived from this equation in terms of $\lambda$, $P_2$, $P_4$, and $L(a) \equiv (a^2 - 1)/(a^2 + 1)$, as follows:

$$\alpha_1 = -2\bar{\eta}L^2(a)P_4, \tag{1}$$

$$\alpha_2 = -\bar{\eta}L(a)\left(1 + \frac{1}{\lambda}\right)P_2, \tag{2}$$

$$\alpha_3 = -\bar{\eta}L(a)\left(1 - \frac{1}{\lambda}\right)P_2, \tag{3}$$

$$\alpha_4 = \bar{\eta}L^2(a)\tfrac{2}{35}(7 - 5P_2 - 2P_4), \tag{4}$$

$$\alpha_5 = \bar{\eta}L(a)[\tfrac{1}{7}L(a)(3P_2 + 4P_4) + P_2] \tag{5}$$

and

$$\alpha_6 = \bar{\eta}L(a)[\tfrac{1}{7}L(a)(3P_2 + 4P_4) - P_2]. \tag{6}$$

According to the molecular theory, $\bar{\eta}$ is given by $ck_BT/2\bar{D}_r$, where $c$ is the number concentration and $\bar{D}_r$ is the rotary diffusivity of the molecules. The quantity $L(a)$ is near unity, $L(a) \geqslant 0{\cdot}97$, even for modest aspect ratios of $a \geqslant 8$, so we will set $L(a) = 1$ in what follows.

If $\bar{\eta}$ is taken as a fitting parameter, the expressions above give the Leslie viscosities in terms of the measurable quantities $P_2$, $P_4$ and $a$, and one additional quantity $\lambda$. In a simple shearing flow, $\lambda$ is related to the flow alignment, or Leslie, angle $\theta$ by

$$\tan\theta = \left(\frac{\lambda - 1}{\lambda + 1}\right)^{1/2}.$$

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In the event that $\lambda < 1$, there is no flow alignment in shear, but the director tends to undergo 'tumbling' motions. Kuzuu and Doi presented a rather complex numerical procedure to obtain $\lambda$ from the molecular theory.

Recently [5], however, we have shown that by neglecting flow-induced disturbances from a *uniaxial* orientation distribution function, an analytic expression for $\lambda$ could be obtained in terms of $P_2$, $P_4$, and $a$:

$$\lambda = L(a)\frac{15P_2 + 48P_4 + 42}{105P_2}. \qquad (7)$$

This expression is in excellent agreement with experimental measurements of $\lambda$ for most of the nematics for which $\lambda$ has been measured, as long as the temperature is well away from a transition to a smectic phase. For example, figure 1 compares the prediction of equation (7) to an experimentally determined $\lambda$ for MBBA as function of temperature. The values of $P_2$ and $P_4$ as functions of $T/T_{NI}$, where $T_{NI}$ is the clearing temperature, were obtained from the Maier–Saupe [6] potential, as tabulated in the table.

Equations (1)–(7) give the contributions to the viscosities from the rotary diffusive motions of the molecules, in terms of the moments $P_2$ and $P_4$ of the molecular distribution function and the aspect ratio $a$. Since the equations were intended to describe lyotropic nematic polymers, other contributions to momentum transport—which might be important for thermotropic small-molecule nematics—are neglected in these equations. Here, for simplicity, we shall lump all other such contributions into a single, orientation-independent, viscosity $\alpha_0$. This isotropic viscosity is the coefficient of a Newtonian term and therefore affects only one Leslie viscosity, namely $\alpha_4$. Hence equation (4) is modified:

$$\alpha_4 = \bar{\eta}L^2(a)\tfrac{2}{35}(7 - 5P_2 - 2P_4) + \alpha_0. \qquad (4')$$

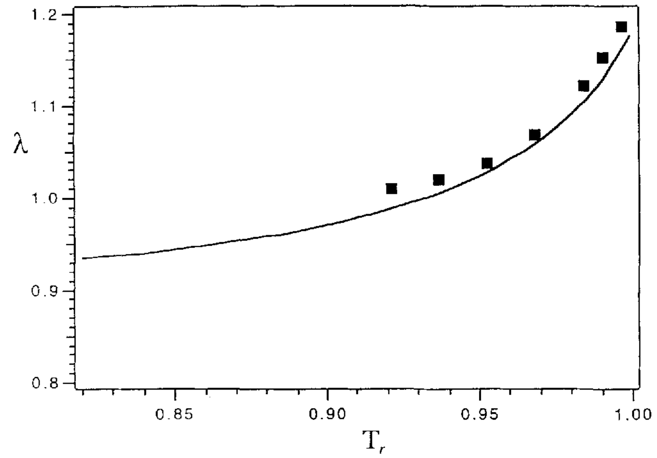

Figure 1. 'Tumbling parameter' $\lambda$ for MBBA (symbols) as a function of reduced temperature $T_r \equiv T/T_{NI}$ compared to the prediction of equation (7), with $P_2$ and $P_4$ taken from the Maier–Saupe theory, and $L(a) = 1$ (lines).

Table. $P_2$ and $P_4$ from the Maier–Saupe theory.

| $T/T_{NI}$ | $P_2$ | $P_4$ | $T/T_{NI}$ | $P_2$ | $P_4$ |
|---|---|---|---|---|---|
| 0·999 | 0·441 | 0·127 | 0·910 | 0·615 | 0·256 |
| 0·990 | 0·471 | 0·145 | 0·900 | 0·627 | 0·268 |
| 0·985 | 0·485 | 0·154 | 0·880 | 0·649 | 0·290 |
| 0·975 | 0·509 | 0·171 | 0·860 | 0·669 | 0·311 |
| 0·965 | 0·530 | 0·186 | 0·840 | 0·687 | 0·331 |
| 0·955 | 0·549 | 0·200 | 0·800 | 0·719 | 0·370 |
| 0·945 | 0·566 | 0·213 | 0·715 | 0·772 | 0·446 |
| 0·930 | 0·588 | 0·232 | 0·505 | 0·864 | 0·619 |
| 0·920 | 0·602 | 0·244 | 0·303 | 0·926 | 0·775 |

From equations (1)–(3), (4′), (5)–(7), we can predict all the Leslie viscosities as functions of temperature, provided that $\lambda$, $P_2$, $P_4$, $a$, $\bar{\eta}$, and $\alpha_0$ are given as functions of temperature. As before, we shall take $P_2$ and $P_4$ from the Maier–Saupe theory, and shall use the approximate equation (7) for $\lambda$. Again, we set $L(a) = 1$. Thus, we need only specify the temperature dependencies of $\bar{\eta}$ and $\alpha_0$. We shall assume that these follow the usual Arrhenius forms, and, noting that in the isotropic state the viscosity $\eta_{iso}$ is given by $\alpha_4/2$ with $P_2 = P_4 = 0$, we obtain from equation (4′):

$$\eta_{iso} = \bar{\eta}/5 + \alpha_0/2 = \exp(B + E_a/RT); \quad r = \frac{\alpha_0}{\alpha_0 + \bar{\eta}} \qquad (8)$$

where the constants $B$, $E_a$, and $r$ must be fitted to data for a given liquid crystal. Two of these three constants, $B$ and $E_a$, can be obtained by the temperature dependence of the viscosity in the isotropic state. Thus, *only one constant, r, needs to be obtained by fits to the Leslie viscosities.*

Complete sets of Leslie viscosities are rare; one of the few is for MBBA. For this liquid crystal, Kneppe *et al.* [7], found that the activation energy is $E_a = 25\,000\,\mathrm{J\,mol^{-1}}$. The constant $B$, which can be obtained from the magnitude of isotropic viscosity near $T_{NI}$, is $-13{\cdot}3$ for MBBA. We obtain the constant $r$ by a fit to the Miesowicz viscosities; these are just combinations of the Leslie viscosities, as follows:

$$\eta_1 \equiv (-\alpha_2 + \alpha_4 + \alpha_5)/2; \quad \eta_2 \equiv (\alpha_3 + \alpha_4 + \alpha_6)/2;$$

$$\eta_3 \equiv \alpha_4/2. \qquad (9)$$

Figure 2 ($a$) compares the predicted Miesowicz viscosities with the measured values for MBBA. The measured values are plotted in Kneppe *et al.* [7]; for convenience, we obtained them from the tables of Leslie viscosities given in [2]. The value of $r$ was adjusted to give the best fit to the Miesowicz viscosities; as $r$ increases, the ratios of the predicted Miesowicz viscosities deviate less from unity. A 'best' fit for MBBA yields $r = 3/8$.

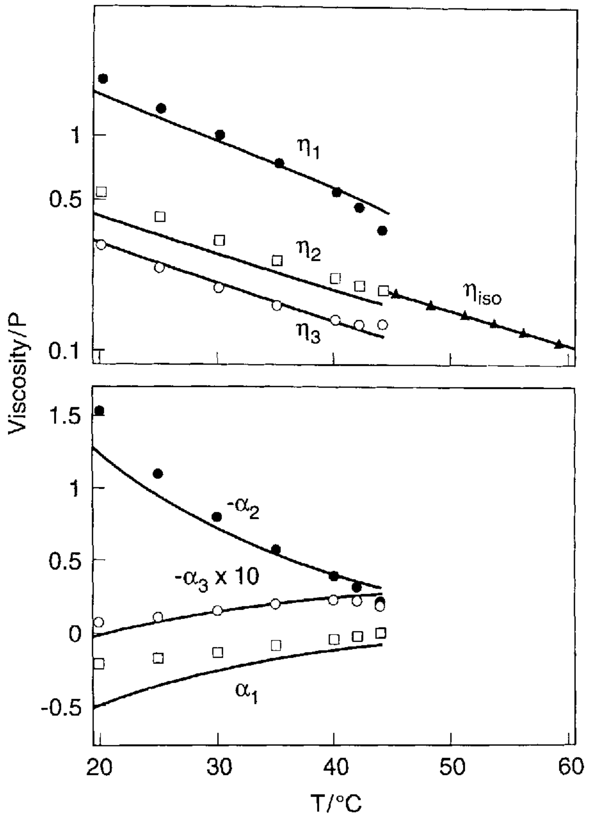

Figure 2. (*a*) The symbols are the Miesowicz viscosities $\eta_1$, $\eta_2$, $\eta_3$ for MBBA as functions of reduced temperature, taken from Kneppe *et al.* [2]; the lines are the predictions of molecular theory, with one adjustable parameter, $r$. Values for the isotropic viscosity $\eta_{\mathrm{iso}}$ were taken from Gähwiller [8]. (*b*) The same as (*a*), except for the viscosities are the Leslie viscosities, $\alpha_1$, $\alpha_2$, and $\alpha_3$.

With all parameters fit, the temperature dependence of the Leslie viscosities $\alpha_1$, $\alpha_2$, $\alpha_3$ are predicted and compared to the experimental measurements of these viscosities in figure 2(*b*). The predicted viscosities agree with the measured values in their sign, magnitude, and the slope of their temperature dependences. Note that the viscosities $\alpha_2$ and $\alpha_3$ depend oppositely on temperature (one is an increasing, and the other a decreasing function of temperature), and the trends in both cases are correctly predicted by the theory. The worst agreement is for $\alpha_1$, where the measured value is a factor of two smaller than that predicted by the theory. Nevertheless, the overall extent of the agreement between theory and experiment is very encouraging, especially considering that there is only one adjustable parameter, if one takes the temperature dependence of the viscosity in the isotropic state to be a measurable input to the theory. Other sets of Miesowicz viscosities reported in the literature show ratios $\eta_1:\eta_2:\eta_3$ similar to that of MBBA [7]; thus, it appears that the value $r \approx 3/8$ might be taken as a rough 'universal' number. If so, then from measured values of the transition temperature $T_{\mathrm{NI}}$ and the constants $B$ and $E_a$ obtained from viscosity in the isotropic state, all Leslie viscosities in the nematic state can be approximated by the simple equations above, for liquid crystals composed of prolate molecules. It would be interesting to see if an analogous theory for oblate ellipsoids is equally successful in describing discotic nematics.

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