CRITICAL EXPONENTS OF THE NEMATIC-SMECTIC-A TRANSITION FROM TWIST VISCOSITY (*)

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ABSTRACT — It has been predicted that the twist viscosity γ_1 behaves critically like

$$\gamma_1 = \gamma_1^{\circ} + b \,.\, \left(\frac{T - T_{NA}}{T_{NA}}\right)^{-x}$$

as the temperature approaches the nematic-smectic-A second-order transition point T_{NA}. Experimentally, a wide variety of values for the exponent x have been reported which range from 0.33 to 1.07.

We show that such discrepancy is mainly due to a wrong evaluation of the non-critical part γ_1° of the twist viscosity, for which various «a priori» expressions have been used so far. Using here a new theoretical expression for γ_1° recently deduced by us, which reads

$$\gamma_1^{\circ} = c \,.\, S.^2 \ \exp\left(\frac{\varepsilon S}{kT}\right)$$

and reanalysing the available data, we show that only one critical exponent $x \simeq 0.33$ is compatible with the experimental data. Our analysis also gives the parameters c and ε which have a molecular interpretation and can be independently checked.

1 — INTRODUCTION

Since the prediction that the nematic-smectic-A phase transition (N-A transition) may be continuous [1-3], the interest in evaluating the critical exponents characterizing this transition has been the

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source of a lot of experimental work. The theoretical description of this transition has been based on two main models: a Landau-type one due to McMillan [4], using the mean-field approximation, and, alternatively, De Gennes' model [2, 3] which predicts for this transition the critical exponents of the superfluid transition in Helium-4.

Concerning the twist viscosity, both theories predict a critical divergence of γ_1 like $(T/T_{NA} - 1)^{-x}$ as the temperature T approaches the N-A transition temperature T_{NA}. This enhancement is due to fluctuations of the smectic-A order parameter $\Psi(r) = |\Psi(r)| \, e^{i\phi(r)}$ in the nematic phase. These fluctuations of $\Psi(r)$ (originating cybotactic groups) have a characteristic correlation length ξ, which grows like $(T/T_{NA} - 1)^{-\nu}$ as $T \rightarrow T_{NA}$. Mean field theory predicts $x = \nu = 0.5$ [4] and a calculation of Jähnig and Brochard [5-7] using the model of De Gennes leads to $x = \nu/2 \simeq 0.33$.

The precise determination of the critical exponent x requires an accurate knowledge of the temperature dependence of the regular part, γ_1^0, of the twist viscosity γ_1. Up to now the analysis of experimental data has always been performed by taking for γ_1^0 various «a priori» expressions without theoretical support, and this is one of the reasons for the wide variety of values of x reported in the literature, which range from 0.33 to 1.07.

We have recently derived theoretically an expression describing the temperature dependence of γ_1 in nematics not showing critical behaviour [8], which has the form

$$\gamma_1^0 = c . S^2 \exp\left(\frac{\varepsilon S}{kT}\right) \tag{1}$$

where S is the usual nematic order parameter (as defined in [9]), k is the Boltzmann constant, T is the absolute temperature, ε is a constant related to the Maier-Saupe mean-field potential [10], and c is nearly constant over the temperature range of the nematic phase. Explicit expressions for c and ε are given in ref [8].

In this paper we shall apply expression (1) in order to get the critical exponent x of γ_1 in two nematic materials showing second-order N-A transitions. The total viscosity (experimentally measured) is given by

$$\gamma_1 = \gamma_1^0 + b . \left(\frac{T - T_{NA}}{T_{NA}}\right)^{-x} \tag{2}$$

where γ_1^o is given by (1) and the second term in the right-hand side represents the critical contribution. Expression (2) has been proposed in refs [4] and [6] but without explicitation of the form of γ_1^o (T).

The nematic materials considered here are the following:

1) 40.8: N[4-n-butoxybenzilidene]-4′-octylaniline
2) HAB: 4,4′-di-n-hexylazoxybenzene

These two materials have monomolecular layers in the smectic-A phase.

In the next section we give the results of a least squares fit of expression (2) to the experimental data on γ_1 (T) quoted for 40.8 and HAB from the Bordeaux group [11].

In section 3 we shall discuss our results and compare them with the theoretical predictions [4, 7, 8] and with a similar analysis performed by us [12] for two other materials which have bimolecular layers in the smectic-A phase.

In section 4 we shall present the main conclusions of this work.

2 — RESULTS

In this section we present the results of a computation of the four parameters c, ε, b, x, needed to characterize the thermal dependence of γ_1, according to Eq. (1) and Eq. (2).

Our method of computation has been discussed elsewhere [12] and consists in an iterative linear regression over expression (2) minimizing the root mean square error (r.m.s. error) taken as a function of the parameters c, ε, b and x. It is also possible to vary slightly T_{NA} within the range of the experimental error in order to obtain a better fit.

For these computations it is necessary to have an analytical expression for the temperature dependence of the nematic order parameter S for each nematic. As we do not know at present the absolute values of S for the materials studied, we have used instead, the values of the anisotropy of the magnetic susceptibility $\Delta\chi$ (T) from ref [13], which are proportional to S.

The two sets of data were fitted with an empirical expression of the form

$$\Delta \chi \times 10^7 \,(\mathrm{c.g.s.}) = [s_1 + s_2 . t^{1/2} + s_3 . \mathrm{t}^{1/4} + s_4 . t^{1/6}]^{1/2} \qquad (3)$$

where $t = \mathrm{T}_{\mathrm{NI}} - \mathrm{T} + \lambda$, T_{NI} is the nematic-isotropic transition temperature of the compound considered, T is the absolute temperature, and all the other symbols represent numerical constants to be computed by the least squares method.

Figure 1 shows the data on $\Delta\chi(\mathrm{T})$ for 40.8, from Ref. [13], fitted with expression (3). A similar fit has been obtained for HAB.

We also tried to fit the same data with a theoretical expression proposed by Hess [14], viz

$$\mathrm{S(T)} = \mathrm{S}(\mathrm{T}_{\mathrm{NI}}) . \left[\frac{3}{4} + \frac{1}{4} \left(1 + \Theta . \frac{\mathrm{T}_{\mathrm{NI}} - \mathrm{T}}{\mathrm{T}} \right)^{1/2} \right] \qquad (4)$$

but with poor results in the temperature range near T_{NI}, as shown in figure 2.

In Table I we present the computed values of c^*, ε^*, b, x, and the r.m.s. error for 40.8, HAB, and, for the sake of completeness,

TABLE I

Material	Origin of data	$\mathrm{T}_{\mathrm{NI}} - \mathrm{T}_{\mathrm{NA}}$ (K)	C^* (Poise)	ε^* (Kcal/mole)	b (Poise)	x	r.m.s. error
CBOOA	[21]	25.02	0.0199 a)c)	2.5230 a)c)	0.0268 c)	0.332 c)	0.0084 c)
CBOOA	[15]	24.75	0.0092 a)	3.1491 a)c)	0.0218 c)	0.330 c)	0.0089 c)
8OCB	[22]	12.347	0.0122 b)	4.0602 b)c)	0.0470 c)	0.352 c)	0.0518 c)
HAB	[11]	38.18	0.0998 a)	1.2273 a)c)	0.1673 c)	0.328 c)	0.0165 c)
40.8	[11]	15.33	0.0642 a)	0.8495 a)	0.0654	0.333	0.0129

a) Computed with $\Delta \chi \times 10^7$ instead of S.

b) Computed with the order parameter S′ of a spin probe dissolved in the nematic phase (see [12]).

c) See ref. [12].

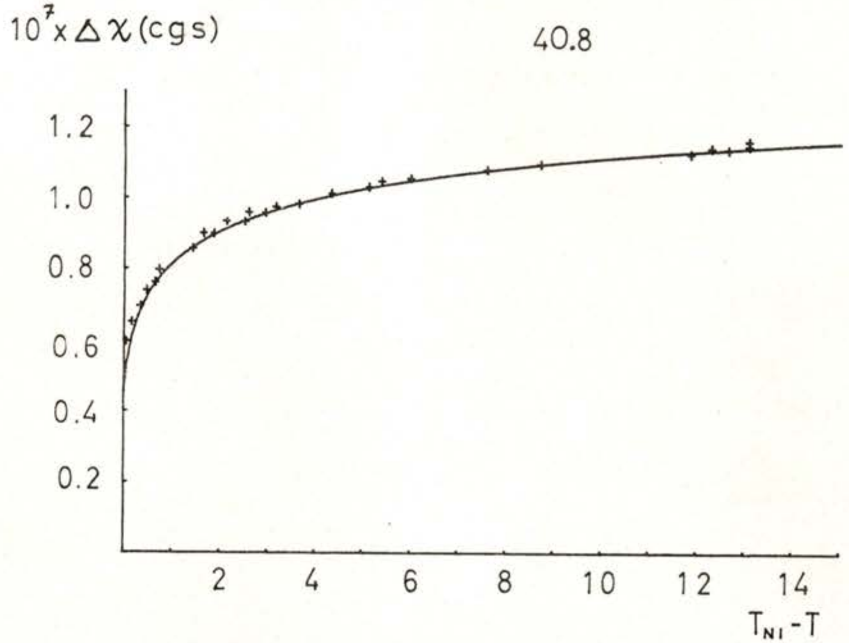

Fig. 1 — Anisotropy of the magnetic susceptibility $\Delta\chi . 10^7$ (C.G.S.) for 40.8. Data points from [13], fitted with expression (3) with $s_1 = -0.45762$, $s_2 = -0.18941$, $s_3 = 1.29634$, $s_4 = 2.7035 \times 10^{-5}$, $\lambda = 0.1$.

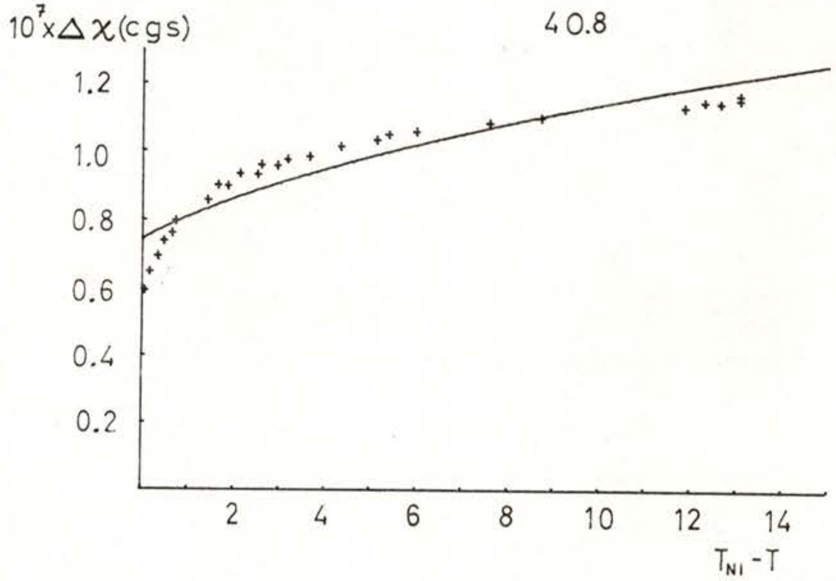

Fig. 2 — The same data of fig. 1, now fitted with expression (4). The best fit (full curve) is for $S(T_{NI}) = 0.75$ and $\Theta = 290$.

also for CBOOA [N-4-cyanobenzilidene-4′-octyloxi-aniline] and 8OCB [4, octyloxy-4′, cyanobiphenyl] [12]. We denote by c^* and ε^* the values of c and ε computed with $\Delta\chi \times 10^7$ instead of S; they are related by:

$$c = c^* \, . \, \frac{\Delta\chi \times 10^7}{\mathrm{S}} \quad \text{and} \quad \varepsilon = \varepsilon^* \, . \, \frac{\Delta\chi \times 10^7}{\mathrm{S}} \tag{5}$$

The plots of $\gamma_1\,(\mathrm{T_{NI}} - \mathrm{T})$ for 40.8 and HAB are presented in figures 3 and 4 respectively, and show good agreement with the experimental data.

We may check our determination of γ_1° by plotting $ln\,(\gamma_1 - \gamma_1^\circ)$ as a function of $ln\,(\mathrm{T} - \mathrm{T_{NA}})$. If γ_1° is correctly evaluated, then the log-log plots must give a straight line *over the whole nematic range.* These plots are presented in figs. 5 and 6, which effectively show straight lines over the whole nematic range. We also note that the r. m. s. errors are nearly the same in each case.

3 — DISCUSSION

We have already remarked that the choice of different expressions for γ_1° leads to different values for x. It can be shown that even within a narrow region near $\mathrm{T_{NA}}$, where the regular part γ_1° of the twist viscosity is nearly constant, the slope y found by plotting $\log \gamma_1$ vs. $\log(\mathrm{T} - \mathrm{T_{NA}})$ is a function of the ratio $\zeta = \gamma_1^\circ / \tilde{\gamma}_1$. This explains why the plots of $ln\,\gamma_1$ vs. $ln\,(\mathrm{T} - \mathrm{T_{NA}})$ give a curve that tends only asymptotically (as $ln\,(\mathrm{T} - \mathrm{T_{NA}}) \rightarrow \infty$) to a straight line with a slope equal to the critical exponent x. The result given by this type of fit depends on the temperature range $\mathrm{T} - \mathrm{T_{NA}}$ over which data are retained for the definition of the «straight line». The value of x found in this way is controled by the last points retained and not by the points close to $\mathrm{T_{NA}}$ as it should be. This explains the large dispersion of values for the critical exponent x reported so far.

Fundamental in our method of analysis is the original way of accounting for the regular part of the viscosity. In the analyses reported so far, the thermal dependence of the regular part of the viscosity had been assumed in all cases, and in various forms. By

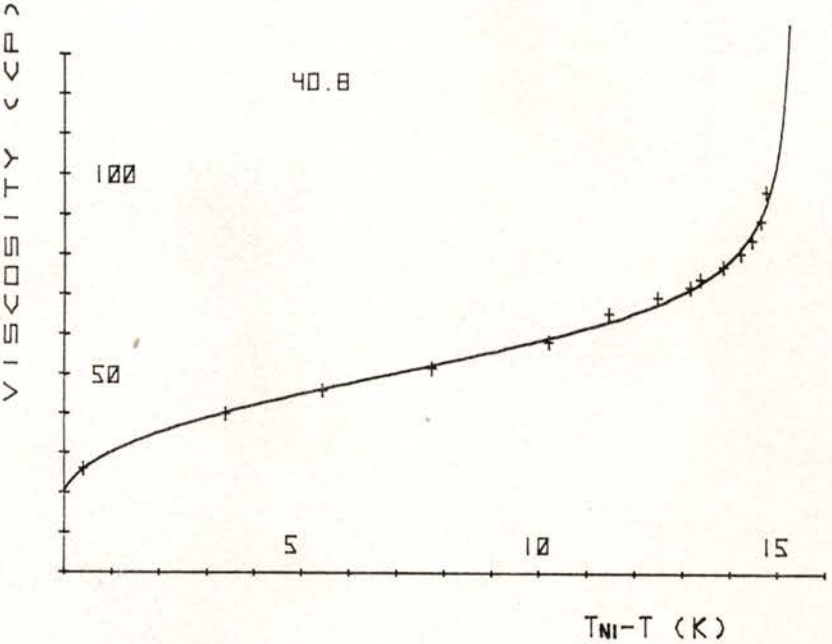

Fig. 3 — Twist viscosity γ_1 (T_{NI} -T) for 40.8. Data from [11] fitted with expression (2) (see Table I).

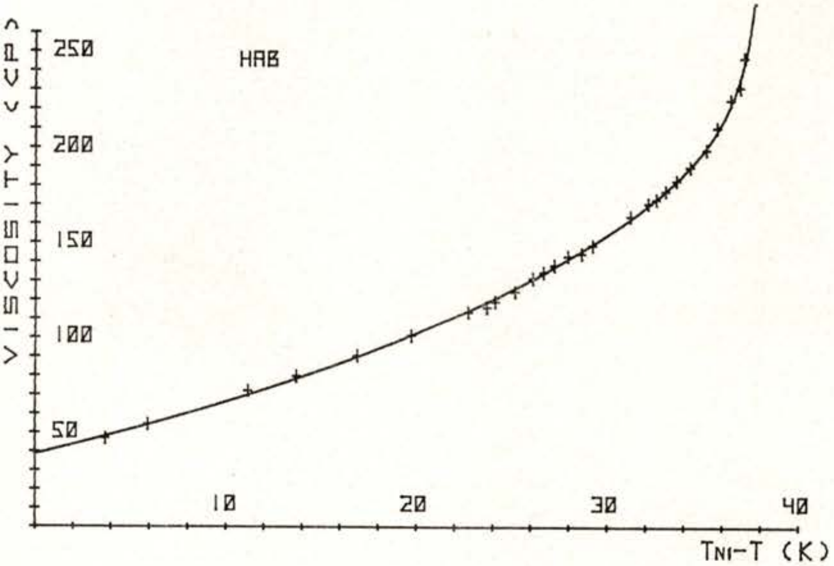

Fig. 4 — Twist viscosity for HAB. Data points from [11] fitted with expression (2) (see Table I).

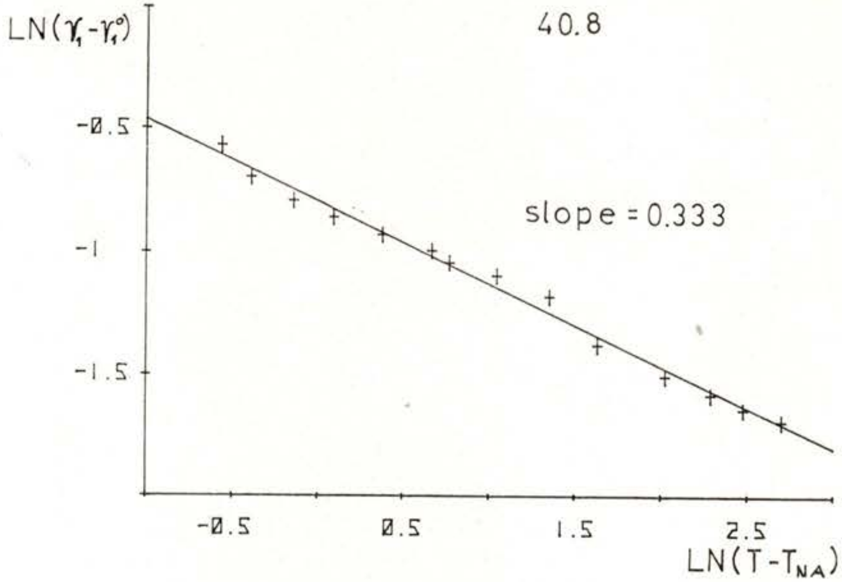

Fig. 5 — Plot of $ln(\gamma_1 - \gamma_1^o)$ vs $ln(T - T_{NA})$ for 40.8; γ_1^o is given by (1) and the straight line is determined by a least squares fit.

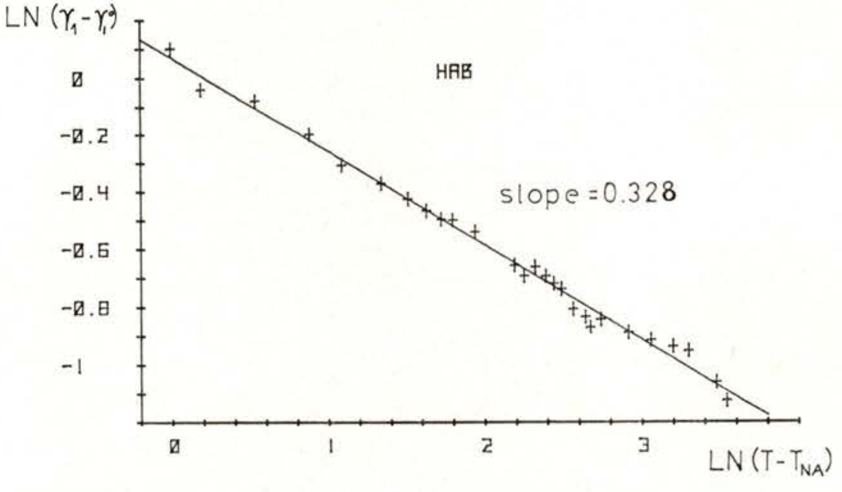

Fig. 6 — Plot of $ln(\gamma_1 - \gamma_1^o)$ vs $ln(T - T_{NA})$ for HAB; γ_1^o is given by (1) and the straight line is determined by a least squares fit.

contrast, our analysis is based upon expression (1), which has been theoretically derived and experimentally tested in appropriate conditions [8]. The plots of $\log(\gamma_1 - \gamma_1^\circ)$ vs. $\log(T - T_{NA})$ shown in this paper give straight lines over the full nematic range and so give a meaningful result for the critical exponent.

After this methodological remark we shall discuss the values of the parameters b and x found from this analysis. The critical part of γ_1 is [4, 6] given by:

$$\tilde{\gamma}_1 = b\left(\frac{T - T_{NA}}{T_{NA}}\right)^{-x} = \frac{\pi}{4}\frac{kT}{d^2}\frac{\tau}{\xi_{11}} = \frac{3}{2}B_N^\circ\,\tau^\circ\left(\frac{T - T_{NA}}{T_{NA}}\right)^{-x} \qquad (6)$$

where d is the interlayer spacing of the smectic phase, ξ_{11} is the correlation length in a direction parallel to the nematic director and τ is a characteristic time of the cybotactic groups (mean lifetime). B_N may be considered as the rigidity modulus of the smectic layers of the cybotactic groups. Using de Gennes, model, Jähnig and Brochard [6, 7] found $\tau = \tau_o\,(T/T_{NA} - 1)^{-3\nu/2}$ and $\xi_{11} = \xi_{11}^\circ\,(T/T_{NA} - 1)^{-\nu}$, where $\nu \simeq 0.66$.

Taking $d \simeq 25$ Å for 40.8 [16] we find, using (6), $B_N^\circ \cdot \xi_{11}^\circ = 0.388$ erg. cm^{-2}, and $\tau_o / \xi_{11}^\circ = 0.124$ s cm^{-1}. From data [17] on the critical part of the bend elastic constant $\tilde{K}_3 = B_N^\circ\,(\xi_{11}^\circ)^2 \times (T/T_{NA} - 1)^{-0.66}$ we get $B_N^\circ\,(\xi_{11}^\circ)^2 \sim 1.6 \times 10^{-8}$ erg. cm^{-1}, so that we can find $\xi_{11}^\circ \sim 4$ Å and $\tau_o \sim 5 \times 10^{-9}$ s, in accordance with an order of magnitude evaluation by Brochard [5]. For HAB we take d 23 Å (~ molecular length) and find $B_N^\circ \cdot \xi_{11}^\circ = 0.396$ erg. cm^2 and $\tau_o / \xi_{11}^\circ = 0.282$ s cm^{-1}. Unfortunately we have not enough data to calculate ξ_{11}° but assuming $\xi_{11}^\circ \sim 10$ Å we find $\tau_o \sim 3 \times 10^{-8}$ s which compares well with the value obtained from acoustic attenuation measurements on a similar compound [18].

For the regular part of γ_1 we expect [8] that

$$\frac{\pi^2 V^*}{N_A kT} \cdot \gamma_1^\circ = \frac{1}{\nu_o} \qquad (7)$$

be comparable with τ_d^1 the dielectric relaxation time for the rotation of the nematic molecules around their short molecular axis. V^* is roughly the molar volume at the temperature T as extrapolated fom the isotropic phase, and N_A is Avogadro's number. For HAB, and with $T_{NI} - T \sim 13°$, we find $\gamma_1^\circ \sim 0.393$ P . In the lack of data for V^* in HAB we take $V^* \sim 322$ cm^3 mole^{-1} from data in ref. [19] about 4-4′ dipentyloxiazoxybenzene, a molecule of similar dimensions. We then find, from expression (7), $1/\nu_o \sim 4.8 \times 10^{-8}$ s, which is near the experimental value [20] $\tau_d^{(1)} \sim 10.8 \times 10^{-8}$ s.

From Maier-Saupe theory [9–10] we know that

$$\varepsilon = 1/m \times 1.355 \times 10^{-2} \times T_{NI} \text{ (Kcal mole}^{-1}\text{)} \tag{8}$$

where m is a cluster parameter which accounts for steric short range order. Assuming $\Delta\chi \times 10^7/S \sim 1.5$ for 40.8 and $\Delta\chi \times 10^7/S \sim 1.4$ for HAB, using eq. (8) and Table I, we find $m = 3.7$ for the former, and $m = 2.6$ for the latter of these compounds. These values are rather satisfactory.

4 — CONCLUSION

The main conclusion of this work is that the use of expression (1) for the regular part of the twist viscosity γ_1 provides:

a) an unique value for the critical exponent of the twist viscosity divergence near a nematic-smectic-A phase transition ($x \simeq 0.33$) which agrees with De Gennes theory [2, 3] and the subsequent calculation of Jähnig and Brochard [6, 7], based on dynamical scaling;

b) the values of the parameters c and ε which are related to the intermolecular potential of Maier-Saupe [9, 10] and are characteristic of the nematic material;

c) a similar critical behaviour in nematic materials which give monomolecular smectic-A layers and in those which give bimolecular smectic-A layers [12];

d) a complete description of the temperature dependence of the twist viscosity over the whole nematic range.

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