The influence of lateral substituents on the phase behaviour of nematogenic liquid crystals

M. Ballauff[a]

[a] Max-Planck-Institut für Polymerforschung, Postfach 3148, 65, Mainz, F.R., Germany

PLEASE SCROLL DOWN FOR ARTICLE

The influence of lateral substituents on the phase behaviour of nematogenic liquid crystals

by M. BALLAUFF

Max-Planck-Institut für Polymerforschung, Postfach 3148, 65 Mainz,
F.R. Germany

The influence of lateral substituents or side chains attached to thermotropic nematogens is considered on the basis of the Flory lattice model. The rigid core of the nematogen is characterized by its axial ratio x and the characteristic temperature T^* which measures the strength of the anisotropic dispersion forces operative between the cores. For the side chain an additional parameter zm which is proportional to its hard core volume enters the partition function. Given these quantities and the free volume as obtained from the thermal expansion coefficient, the nematic–isotropic transition temperature T_{NI} and the temperature dependence of the order parameter may be calculated. The results show that the lowering of T_{NI} by lateral substituents is caused by (1) their interference with molecules packing and (2) the dilution of the anisotropic dispersion forces between the central nematogenic cores. As an additional consequence of this the order parameter is lowered considerably. A survey of recent experimental data shows that the decrease of T_{NI} is correlated solely with the hard core volume of the substituent regardless of its chemical structure or polarity, thus corroborating the theoretical predictions.

1. Introduction

It is now well recognized that the stability of a nematic phase is mainly determined by the steric forces resulting from the shape anisometry of mesogenic molecules [1]. At the high density and the close packing occurring in the liquid state, the spatial arrangement of the particles is dominated therefore by the hard core repulsion which would be inferred if one molecule should overlap another. Having characterized the structure of the liquid on these premises the intermolecular attraction may be dealt with in terms of the usual mean field approximation.

A molecular theory of nematic liquids comprising both steric forces as well as intermolecular attraction has been proposed by Flory and Ronca [2, 3]. This mean field approach is an improved version of the lattice treatment of ordered states originated by Flory in 1956 [4]. With the free volume of the nematic liquid being taken into account properly [5, 6], this model may be shown to give an accurate description of neat nematogens and of their mixtures [7, 8]. In addition, the lattice model may be used to describe mixtures of nematogens with flexible polymers [9, 10]. It is interesting to note that the free energy of a system of ordered rods as proposed by Flory and Ronca [2] is very much akin to the result derived by Khokhlov and Semenov [11] on the base of the decoupling approximation introduced by Parsons [12]. This fact adds further credibility to the deductions of the lattice theory.

As in many theories of the nematic state (cf. [1]), the molecules of the nematogenic fluid are viewed by the Flory approach as perfectly rigid rods. This neglects the fact

the real molecules are not shaped like ideal cylinders but may have diameters varying along the long molecular axis. In addition, lateral substituents are sometimes appended to the rigid cores to increase the dielectric constant perpendicular to the long axis. Recently, these laterally substituted thermotropic nematogens have been the subject of a careful study by Osman [13] who showed the decrease of the nematic–isotropic transition temperature to be directly correlated with the hard core volume of the respective lateral substituents. Weissflog and Demus [14, 15] demonstrated that long alkyl chains affixed to aromatic rigid cores do not interfere severely with the ordering process. These laterally substituted nematogens have been studied exhaustively [16–19]. With regard to lyotropic systems, as encountered in solutions of helical polypeptides, it has been pointed out by Flory and Leonard [20] that the side chains in these polymers have a profound influence on their phase behaviour. A lattice treatment of the nematic ordering of rigid rods bearing flexible side chains has been proposed recently [21]. Here these considerations are extended to thermotropic systems along the lines devised previously [5, 6]. Given the structural parameters of the nematogen (axial ratio of the rigid core, hard core volume of the side chain, characteristic temperature of the anisotropic dispersion forces) the nematic–isotropic transition temperature may be calculated by the theory presented here and compared to recent experimental results [13–19].

2. Theory

We consider a system of rod-like molecules with flexible side chains appended to the rigid core as indicated in figure (1). The lattice is divided into cells of dimensions equal to the diameter of the rod-like part of the particle. The axial ratio x is given therefore by the number of segments constituting the rigid part. To each rod, z side chains are attached each of which comprises m segments. For simplicity, we take the segments of the side chains to be equal to the diameter of the segments of the main chain. The free volume present in the system may be introduced by allowing a corresponding fraction to the lattice sites to remain vacant [5, 6]. It must be noted that the device of assigning the free volume to lattice vacancies is confined to its use in formulating the dependence of the partition function on orientation.

Let the rod-like parts of the molecules be oriented preferentially to the axis of the domain which is taken along one of the axes of the lattice. We shall estimate the number v_{j+1} of positions available to the $(j + 1)$th molecule after having introduced j particles. In doing this we first introduce the rod-like core of the molecules which is subdivided into y submolecules containing x/y segments (see figure 1)). The relation
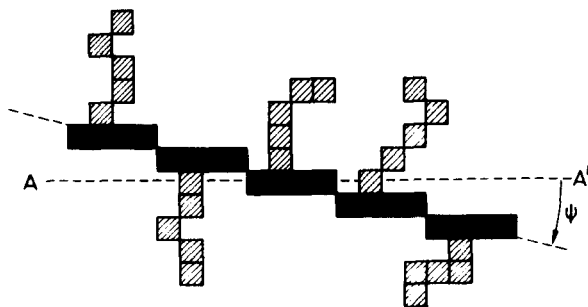

Figure 1.   Representation of a rigid rod with flexible side chains on a cubic lattice.

between the disorder parameter y and the angle ψ of inclination to the preferred axis will be specified later. Let n_0 denote the total number of lattice sites and $f = x + zm$ the overall number of segments per molecule. The number of positions available to the first segment of the first submolecule of particle $j + 1$ is given by the number of vacancies $n_0 - fj$. The expectation of a vacancy required for the $y_{j+1} - 1$ first segments of the remaining submolecules is given by the volume fraction of the vacancies $(n_0 - fj)/n_0$. If a given site is known to be vacant the site following it in the same row can be only occupied by either the initial segment of a submolecule or a segment of a side chain. The conditional probability therefore follows as the ratio of vacancies to the sum of vacancies, submolecules and total number of the segments of the side chains

$$(n_0 - fj) \bigg/ \left(n_0 - fj + \sum_i^j y_i + zmj \right).$$

Since we assume the conformation of the side chains to be independent of the order in the respective phase, the expectancy of a vacancy for the zm segments of the side chain is given by the volume fraction of empty sites $(n_0 - fj)/n_0$. It follows that

$$v_{j+1} = (n_0 - fj) \left(\frac{n_0 - fj}{n_0} \right)^{y_{j+1}-1} \left(\frac{n_0 - fj}{n_0 - fj + \sum_i^j y_i + zmj} \right)^{x - y_{j+1}} \left(\frac{n_0 - fj}{n_0} \right)^{zm}, \quad (1)$$

or, with negligible error,

$$v_{j+1} = \frac{(n_0 - fj)!}{(n_0 - f(j + 1))!} \frac{\left(n_0 - x(j + 1) + \sum_i^{j+1} y_i \right)!}{\left(n_0 - xj + \sum_i y_i \right)!} n^{1 - y_{j+1} - zm}. \quad (2)$$

The configurational partition function Z_M may be represented by the product of the combinatorial part Z_{comb} and the orientational part Z_{orient} [2]

$$Z_M = Z_{comb} Z_{orient}. \quad (3)$$

The combinatorial part Z_{comb} is related to v_j by

$$Z_{comb} = \left(\frac{1}{n_x!} \right) \prod_1^{n_x} v_j, \quad (4)$$

with n_x being the number of molecules inserted into the lattice. Thus

$$Z_{comb} = \frac{(n_0 - n_x x + \bar{y} n_x)!}{n_x!(n_0 - n_x f)!} n_0^{n_x(1 - \bar{y} - zm)}, \quad (5)$$

where $\bar{y}$ denotes the average of the disorder index y defined by

$$\bar{y} = \sum \frac{n_{xy}}{n_x} y. \quad (6)$$

Here, n_{xy} is the number of molecules whose orientation is specified by y. The orientational partition function Z_{orient} is then given by [2]

$$Z_{orient} = \prod_y \left[\left(\frac{\omega_y n_x}{n_{xy}} \right) \right]^{n_{xy}}, \quad (7)$$

where $\omega_y = \sin \psi$ [2] is the *a priori* probability of disorientation y and ε_y is the

orientation-dependent energy of one segment of the rigid core in the mean field of its neighbours when its disorientation is y; k and T are the Boltzmann constant and the temperature, respectively. The side chains are assumed to be exempt of the ordering process and so their contribution to the orientational partition function can be neglected. This may also be justified from the small anisotropy of alkyl chains which renders their contribution to the anisotropic dispersion forces very small. Hence, the orientation-dependent energy per segment ε_y is given by [2, 22]

$$\varepsilon_y \;=\; -(kT^*/\tilde{V})\,\frac{x}{f}\,S\,(1 - \tfrac{3}{2}\sin^2\psi_y), \tag{8}$$

with the characteristic temperature T^* measuring the strength of the orientation-dependent dispersion forces; $\tilde{V} = V/V^*$ is the reduced volume, i.e. the ratio of the volume of the system to the occupied volume V^*. The factor x/f, i.e. the ratio of the volume occupied by the rod-like part of the particle and its total number of segments, takes into account the dilution of the anisotropic dispersion forces by the side chains. The quantity S is the usual order parameter [3] defined by

$$S \;=\; 1 - \tfrac{3}{2}\langle \sin^2\psi\rangle. \tag{9}$$

The orientation-dependent energy for the whole system obtained by summing equation (8) over all $n_x x/2$ segment pairs is

$$E_{\text{orient}} \;=\; -\frac{n_x x^2 kT}{2\tilde{V}f}\,S^2. \tag{10}$$

Combining these equations and introducing Stirling's approximation for the factorials, we obtain for the reduced free energy (cf. [2])

$$
\begin{aligned}
-\ln Z_u \;=\;& (n_0 - n_x f)\ln\!\left(\frac{n_0 - n_x f}{n_0}\right) + n_x \ln\frac{n_x}{n_0} \\
& - (n_0 - n_x x + n_x \bar{y})\ln\!\left[1 - \frac{n_x x}{n_0}\left(1 - \frac{y}{x}\right)\right] - n_x(1 - \bar{y} - zm) \\
& + n_x \sum_y \frac{n_{xy}}{n_x}\ln\frac{n_{xy}}{n_x \omega_y} - \frac{1}{2}\frac{n_x x^2}{\tilde{V}\theta f}\,S^2,
\end{aligned}
\tag{11}
$$

with the reduced temperature θ being defined by $\theta = T/T^*$. Note that the orientational distribution is still arbitrary at this stage.

Since the disorder index y is given by [2]

$$y \;=\; (4/\pi)\,x\sin\psi \tag{12}$$

we obtain for n_{xy}/n_x (cf. [2] and [22])

$$n_{xy}/n_x \;=\; \omega_y/f_1 \exp\!\left[-\frac{4}{\pi}\,ax\sin\psi - \frac{3x^2 S}{2\tilde{V}\theta f}\sin^2\psi\right], \tag{13}$$

where the normalization factor f_p is given by

$$f_p \;=\; \int_0^{\pi/2} \sin^p\psi \exp\!\left[-\frac{4}{\pi}\,ax\sin\psi - \frac{3x^2 S}{2\tilde{V}\theta f}\sin^2\psi\right]d\psi \tag{14}$$

with $m = 1$, and the quantity a is

$$a \;=\; -\ln\!\left[1 - \frac{x}{\tilde{V}f}\left(1 - \frac{\bar{y}}{x}\right)\right]. \tag{15}$$

Thus, $\bar{y}$ and S follow as

$$\bar{y} = \frac{4}{\pi} x f_2/f_1, \tag{16}$$

$$S = 1 - \tfrac{3}{2} f_3/f_1. \tag{17}$$

The total number of lattice sites may be expressed by

$$n_0 = n_x f \tilde{V}, \tag{18}$$

and so the free energy at orientational equilibrium is

$$-\ln Z_M = n_x f(\tilde{V} - 1)\ln(1 - \tilde{V}'^{-1}) - n_x \ln(\tilde{V}'f)$$

$$+ n_x f\left(\tilde{V}' - \frac{x}{f}\right) a - n_x(1 - \bar{y} - zm) - n_x \ln f_1 - \frac{n_x x^2}{\tilde{V}'\theta f} S\left(1 - \tfrac{1}{2} S\right). \tag{19}$$

Here, primes are associated with quantities which may differ from those in the isotropic phase. It has to be noted that only the product of z and m matters [21], i.e. the free energy depends solely on the volume fraction of the side chains as compared to the volume fraction of the main chain. The corresponding expression for the isotropic phase may be obtained by equating $\bar{y}$ to x and S to 0; hence,

$$-\ln Z_M = n_x f(\tilde{V}' - 1)\ln(1 - \tilde{V}^{-1}) + n_x \ln(\tilde{V}f) - n_x(1 - f). \tag{20}$$

To a good approximation the difference in density of the coexisting nematic and isotropic phases may be ignored [5, 6]. Therefore, the condition for equilibrium is given by

$$f\left(\tilde{V} - \frac{x}{f}\right) a + \bar{y} - x - \ln f_1 - \frac{x^2 S}{\tilde{V}\theta f}\left(1 - \tfrac{1}{2} S\right) = 0. \tag{21}$$

Since x, zm and the reduced volume $\tilde{V}$ are known, equation (21) together with the relations (16) and (17) lead, upon numerical solution, to the equilibrium values of the order parameter S, the disorder index $\bar{y}$ and the reduced temperature at the transition. Simultaneous numerical solution of the self-consistency relation in equations (16) and (17) then gives the values of $\bar{y}$ and S in the nematic phase as a function of temperature.

3. Results and discussion

As we have seen in the previous section, the nematic–isotropic transition is determined by the following molecular parameters: the axial ratio x of the rod-like core of the mesogen, and zm, the product of the number z of side chains per rigid core and the number of segments per side chain m; the characteristic temperature T^* measuring the strength of the anisotropic dispersion forces, and the reduced volume $\tilde{V}$, calculated from the thermal expansion coefficient in the usual way [23]. The axial ratio x of the central core is determined from structural data of the molecule under consideration and the diameter of the rigid core defines the size of the lattice sites (see [5], [6]). The parameter zm counting the number of segments of the side chains then follows as the hard core volume of the side chains as expressed in units of the lattice cells. Note that the final equation (21) does not contain any direct reference to the artificial lattice parameters but only the ratio of x to $x + zm$. Given the free volume $\tilde{V}$ as function of temperature, T^* may be treated as the only adjustable parameter.
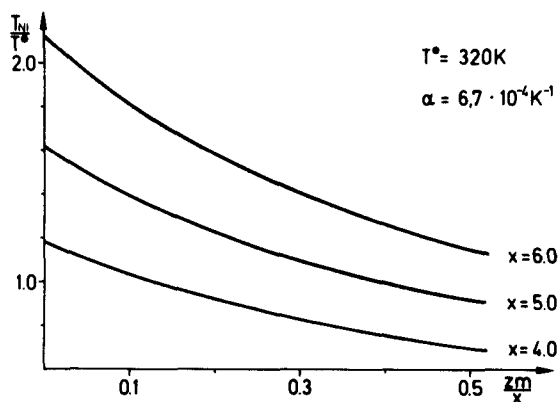
Figure 2.   Reduced temperature of the nematic–isotropic transition versus the ratio of zm, the total number of side chain segments attached to one rod and the axial ratio x of the rigid core. The quantity T^* denotes the characteristic temperature of the anisotropic dispersion forces; α is the thermal expansion coefficient.

The lowering of the nematic–isotropic transition temperature T_{NI} with increasing volume fraction of the lateral substituent is shown in figure 2 where the ratio of T_{NI} and the characteristic temperature T^* is plotted versus the ratio of zm and x, i.e. the ratio of the hard core volumes of the lateral substituents and the central core of the particle. The characteristic temperature chosen in these examples is typical for aromatic cores connected by ester groups [6]; the thermal expansion coefficient corresponds directly to the value measured for the oxybenzoate series [8]. The decrease of T_{NI} as shown in figure 2 with increase of zm is appreciable; nevertheless the present result demonstrates the nematic phase to be stable even for a high volume fraction of the side chains. This unexpected stability of the ordered state is partially due to the fact that the lowering of T_{NI} by the lateral substituent is followed by a decrease of the reduced volume $\tilde{V}$. Hence, the disturbance of the packing of the particles in the nematic fluid as well as the dilution of the anisotropic dispersion forces are partially reduced by the decrease of the free volume in the system since both are affected by the lateral substituent.

For a comparison of these predictions with experimental data a system of nematogens composed of a central rigid core with a lateral substituent varying in size is needed. Thus the main rigid part of the mesogen should not contain any flexible moieties like n-alkyl groups. Only a few systems described in literature meet these conditions. The laterally substituted 1,4-bis-(-4-trans-pentylcyclohexyl)-benzenes studied in detail by Osman [13] are only partially suitable for this purpose because of the flexible pentyl tails. However, figure 1 of Osman's work [13] clearly reveals a monotonic decrease of T_{NI} with increasing hard core volume of the lateral substituents regardless of its chemical nature and polarity. This experimental result is in accord with the theoretical deduction of T_{NI} being reduced with the raising of zm, i.e. with a higher hard core volume of the side group (cf. figure 2).

Another example of laterally substituted nematogens is given by the 1,4-bis-(-4-methoxybenzoyl)-2-n-alkylbenzenes studied in great detail by Weissflog and Demus [14]. Here, the central core does not contain any flexible group which makes this system more suitable for comparison with the predictions given here. The principal result obtained by Demus and co-workers [14–20] in their studies of this system and

related compounds is the observation that even long n-alkyl side chains do not destroy the nematic ordering of the central cores. To compare the experimental transition temperatures given in [14] with calculated data, the quantity zm has to be evaluated for different side groups. The mean diameter of the central aromatic core may be approximated by $4 \cdot 7 \text{Å}$ [8] corresponding to a hard core volume of 104Å^3 per segment. From the data of Flory *et al.* [23] the respective quantity for a CH_2 group follows as about $14 \text{cm}^3/\text{mole}$ or 23Å^3 per CH_2. Therefore zm per CH_2 unit may be calculated as the ratio $23/104 \sim 0 \cdot 22$. Since the thermal expansion coefficient of the series under consideration is not given in [14], only a model calculation using reasonable estimates for the respective parameters may be performed here. Figure 3 shows the results of a calculation (solid line) assuming the central core to be characterized by an axial ratio of 5, a characteristic temperature T^* of 320 K and a thermal expansion coefficient of $6 \cdot 7 \times 10^{-4} \text{K}^{-1}$. The number of carbon atoms in the side chain has been converted to zm using the factor of $0 \cdot 22$. The experimental transition temperatures [14] are denoted by crosses and connected by a dashed line. It should be noted that in the course of the calculation the thermal expansion coefficient as well as the value for T^* was kept constant for all members of the series. Hence, the result of the theory displayed by the solid line in figure 3 can be compared with the experimental data only in a qualitative manner. A quantitative comparison would require accurate values of the expansion coefficients and T^* throughout the whole series. Unfortunately, density data are only available for similar series bearing hexoxy end groups [16]. Because of these flexible tails the axial ratio of the members of the respective series cannot be calculated unambiguously. Since this quantity is of utmost importance, these data cannot give a quantitative comparison with theory. However, the expansion coefficient measured for the series having the hexoxy end groups goes through a maximum as a function of the side chain length. The difference of α at the transition, especially
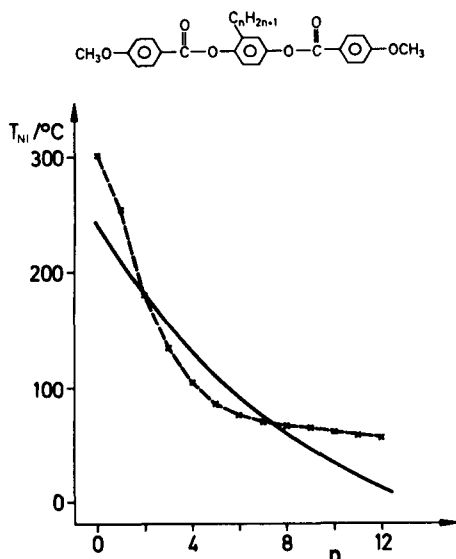

Figure 3. The nematic–isotropic transition temperature versus n, the number of carbon atoms in the alkyl side chains. The experimental data (crosses) are taken from the work of Weissflog and Demus [14]; the solid line shows the prediction of the model calculation (see text for explanation).

when comparing the unsubstituted nematogen with the compound bearing a methyl substituent, is appreciable ($7 \cdot 94 \times 10^{-4} \, \mathrm{K}^{-1}$ and $9 \cdot 47 \times 10^{-4} \, \mathrm{K}^{-1}$, respectively). A similar effect, i.e. the decrease of molecular packing, is expected to occur for the series under consideration here (cf. figure 3) as well. Thus the decrease of T_{NI} when going from $n = 0$ (unsubstituted nematogen) to $n = 1$ will be much steeper if the increase of the free volume is taken into account in the calculation. This certainly will improve the agreement between theory and experiment. Also, the value of T^* might change upon attaching an alkyl substituent. Nevertheless figure (3) demonstrates that the present calculation, disregarding the change of α, already leads to a good qualitative agreement of theory with experiment. The theory derived here can explain easily the unexpected stability of the nematic phase even in the presence of long side chains. An alternative explanation may be sought [19] in the assumption of a special conformation of the n-alkyl chains. A quantitative comparison of theory and experiment using the equation of state data of these compounds certainly would give a definitive answer to this question.

In addition to these experimental results, Weissflog and Demus [14] showed that the nematic–isotropic transition temperatures, measured for members of the series with hexoxy end groups, decreases smoothly with the hard core volume for a great variety of lateral substituents (cf. figure 2 of [17]) in agreement with the findings of Osman [13] and the theory presented here. The transition temperature only deviates from the common curve if two of the three phenyl groups are hydrogenated (series II of [17]) which can be ascribed to the drastic change in T^* caused by this.

It has to be kept in mind that in the systems introduced by Osman [13] and by Demus et al. [14] the lateral substituent is not expected to disturb strongly the conformation of the mesogenic core. Hence, in these examples the axial ratio as well as T^* will be nearly independent of the size of the substituent. As shown by Gray [24], lateral substituents causing a further twisting in the mesogenic biphenyl moiety diminish T_{NI}. Since in this case the axial ratio of the mesogen is independent of the twisting angle, the decrease of T_{NI} is clearly related to a decrease of T^*. Also, lateral substituents attached to the nematogenic core in a protected position as may be realized for the naphthalene system [24] may increase the transition temperature because this substitution does not broaden the molecule but improves the rod-like shape of the particle. This effect, of course, is beyond the scope of the present treatment which assumes the central core to assume a perfect cylindrical shape.

Having shown that the transition temperatures for mesogens with lateral substituents can be predicted by the present model at least in a semiquantitative way, a further point of interest to be addressed by theory is the order of the nematic phase. Figure 4 shows the order parameter S as a function of the reduced temperature difference $(T_{NI} - T)/T^*$ calculated. For a perfect rod ($zm = 0$) and for a rod with a lateral substituent ($zm = 2.2$) corresponding to a decyl side chain in the above series of Weissflog and Demus [14] (cf. figure 3). First of all, the order parameter at the transition is smaller in the presence of a side chain, a finding again being in qualitative agreement with experimental data (cf. figure 7(b) of [17]). A second point of importance is the different dependence of S on temperature; the slope of the $S(T)$ curve is much steeper in the presence of a lateral group than for a perfect rod. Due to the disturbance of the molecular packing and the dilution of the anisotropic dispersion forces, the degree of ordering in the nematic phase is considerably lower if a side chain is attached to the central core. Despite the fact that theory seems to be correct in a qualitative manner (cf. [17], figure 7(a)), the absolute values of the order parameter at the
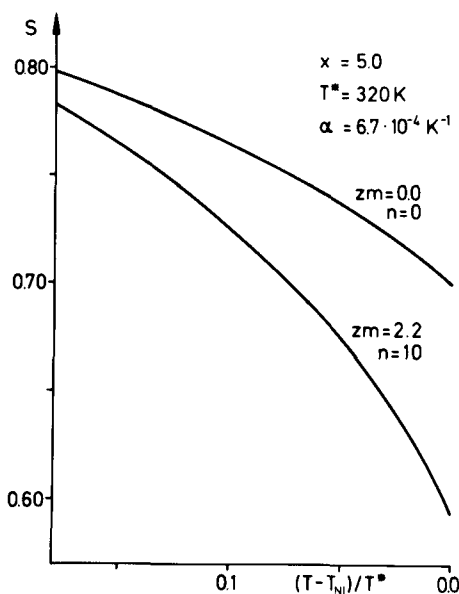
Figure 4. Order parameter S of the nematic phase as a function of the reduced temperature difference $(T - T_{NI})/T^*$, where T^* denotes the characteristic temperature, x is the axial ratio of the central rigid core and α the thermal expansion coefficient. The quantity zm is the total number of side chain segments attached to one rod and n is the number of alkyl carbon atoms (cf. figure 3) corresponding to the respective value of zm (see text for details of the model calculation).

transition is still too high. This deficiency, i.e. the overestimation of molecular order in a nematic phase, appears to be a feature common to most theories of the nematic state (cf. [1] for a detailed discussion of this point, also cf. figures 7 (*a*) and (*b*) of [17]). One of the reasons for this discrepancy might be sought in the neglect of higher terms from the expansion of equation (8). Another problem not addressed by the present mean field treatment is the influence of fluctuations effects on the actually measured order parameter. A detailed discussion of this point has been given by Warner [25].

A final point of importance in the present discussion is the influence of lateral substituents on the formation of layered structures, i.e. smectic phases. In most of the cases studied so far [13, 14, 24] lateral groups will suppress the layering, thus favouring the less ordered nematic phase. However, if the central backbone becomes very long as is the case in stiff chain liquid-crystalline polymers, the strong demixing tendencies of rods and coils [9, 26], together with requirements of molecular packing, may lead to the formation of layered structures [27].

References

[1] COTTER, M. A., 1983, *Molec. Crystals liq. Crystals*, **97**, 29.
[2] FLORY, P. J., and RONCA, G., 1979, *Molec. Crystals liq. Crystals*, **54**, 289.
[3] FLORY, P. J., and RONCA, G., 1979, *Molec. Crystals liq. Crystals*, **54**, 311.
[4] FLORY, P. J., 1956, *Proc. R. Soc.* A, **234**, 73.
[5] FLORY, P. J., and IRVINE, P. A., 1984, *J. chem. Soc. Faraday Trans, I*, **80**, 1807.

[6] BALLAUFF, M., and FLORY, P. J., 1984, *Ber. Bunsenges. phys. Chem.*, **88**, 530.

[7] IRVINE, P. A., FLORY, P. J., and DACHENG WU, 1984, *J. chem. Soc. Faraday Trans. I*, **80**, 1795.

[8] BALLAUFF, M., DACHENG WU, FLORY, P. J., and BARRALL II, E. M., 1984, *Ber. Bunsenges. phys. Chem.*, **88**, 524.

[9] BALLAUFF, M., 1986, *Ber. Bunsenges. phys. Chem.*, **90**, 1053.

[10] BALLAUFF, M., 1986, *Molec. Crystals liq. Crystals Lett.*, **4**, 15.

[11] KHOKLOV, A. R., and SEMENOV, A. N., 1985, *J. statist. Phys.*, **38**, 161.

[12] PARSONS, J. D., 1979, *Phys. Rev. A*, **19**, 1225.

[13] OSMAN, M. A., 1985, *Molec. Crystals liq. Crystals*, **128**, 45.

[14] WEISSFLOG, W., and DEMUS, D., 1984, *Crystal Res. Technol.*, **19**, 55.

[15] WEISSFLOG, W., and DEMUS, D., 1985, *Molec. Crystals liq. Crystals*, **129**, 235.

[16] HAUSER, A., RETTIG, R., SELBMANN, CH., WEISSFLOG, W., WULF, J., and DEMUS, D., 1984, *Crystal Res. Technol.*, **19**, 261.

[17] DEMUS, D., HAUSER, A., SELBMANN, CH., and WEISSFLOG, W., 1984, *Crystal Res. Technol.*, **19**, 271.

[18] DEMUS, D., HAUSER, A., ISENBERG, A., POHL, M., SELBMANN, CH., WEISSFLOG, W., and WIECZOREK, S., 1984, *Crystal Res. Technol.*, **20**, 1413.

[19] DEMUS, D., DIELE S., HAUSER, A., LATIF, I., SELBMANN, CH., and WEISSFLOG, W., 1985, *Crystal Res. Technol.*, **20**, 1547.

[20] FLORY, P. J., and LEONARD, W. J., JR., 1965, *J. Am. chem. Soc.*, **87**, 2102.

[21] BALLAUFF, M., 1986, *Macromolecules*, **19**, 1366.

[22] FLORY, P. J., 1984, *Adv. Polym. Sci.*, **59**, 1.

[23] FLORY, P. J., ORWOLL, R. A., and VRIJ, A., 1964, *J. Am. chem. Soc.*, **86**, 3507.

[24] GRAY, G. W., 1982, *Polymer Liquid Crystals*, edited by A. Cifferi, W. R. Krigbaum and R. B. Meyer (Academic Press).

[25] WARNER, M., 1984, *Molec. Phys.*, **52**, 677. See also FABER, T. E., 1983, *Phil. Trans. R. Soc. A*, **309**, 115.

[26] FLORY, P. J., 1978, *Macromolecules*, **11**, 1138.

[27] BALLAUFF, M., 1986, *Makromol. Chem. rap. Commun.*, **7**, 407.