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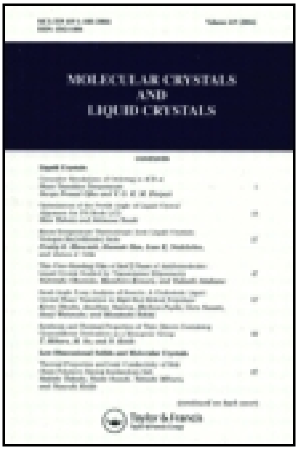

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The Flory Lattice Model of Nematic Fluids

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The Flory Lattice Model of Nematic Fluids

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The Flory lattice theory of neat nematic fluids is reviewed and compared to other current statistical-mechanical treatments of systems of ordered hard rods. It is shown that the model provides a sound description of the nematic state. At intermediate concentrations the free energy derived thereby reduces to the expression given by the decoupling approximation.[1] At low concentrations the result of the Onsager Theory is obtained. The Flory theory is easily extended to include thermotropic systems by introducing the characteristic temperature of anisotropic interaction T*. This parameter is in semi-quantitative agreement with values estimated from optical and thermodynamic data.

INTRODUCTION

The ordering transition from an isotropic to a nematic state in low molecular weight liquid crystals and polymer liquid crystals has found wide-spread attention during the recent years. Although there is now a vast body of experimental data accumulated for these systems, the statistical-mechanical description of ordered states is still a controversial subject. At present, there are two major approaches to a molecular statistical description of nematic phases: 1. the Maier-Saupe theory and its refinements; and 2. the hard-rod theories supplemented by the inclusion of attractive forces introduced in terms of a mean field.[2] Among the theories of the second kind the Flory lattice model has been widely used for the description of polymeric systems and mixtures thereof.[3] However, the treatment of a system of ordered rigid rods by a lattice model requires a number of stringent assumptions which may afflict the final results. Therefore, a comparison of the Flory model with other current hard rod theories of the nematic state will be useful in order to assess its merits and limitations in detail. In the first three sections the treatment of a system of rigid rods by this model will be compared to the theories of References 4 and 1, which provide solutions for the dilute and the semi-dilute case, respectively. Since the Onsager approach has been discussed in great detail recently,[5] a brief summary will suffice here. The fourth section of this review is devoted to the extension of the Flory model to systems of rods with attractive forces. Special attention will be given to the role of fluctuations of the director field when comparing the measured order parameter with its value given by theory.

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1. DILUTE SYSTEMS: ONSAGER THEORY

Consider a gas of N_p long, thin rods of length L and diameter d confined in a volume V. The essential step in the derivation of the partition function Z for the system thus defined is given by the artifice that particles with different orientation may be treated as particles of different kind. In addition, the volume in space available for a rod restricted in its orientation for the solid angle $\Delta\Omega$ surrounding the direction $\underline{a}$ is only $V\Delta\Omega$ rather than $4\pi V$. With the angular distribution function $f(\underline{a})$ being subject to the constraint:

$$\int f(\underline{a})\, d\Omega(\underline{a}) = 1 \tag{1.1}$$

one obtains for the continuous limit[4]

$$\ln Z = N_p\left(\left(1 + \ln\left(\frac{V}{N_p}\right)\right) - \int f(\underline{a}) \ln(4\pi f(\underline{a}))\, d\Omega(\underline{a}) + \frac{N_p}{2V}\iint \beta_1(\underline{a}, \underline{a}')\, f(\underline{a})\, f(\underline{a}')\, d\Omega\, d\Omega' + \ldots\right) \tag{1.2}$$

Equation (1.2) contains all the terms needed in principle for the description of an ordered phase: 1) the ideal gas term; 2) the entropic term describing the loss of entropy due to the orientation of the molecules in the ordered phase; and 3) a term taking into account the excluded volume, here expressed in approximation where only the second virial coefficient is retained.

For the above system of long, thin rods the excluded volume $-\beta_1$ is given[4,6]:

$$-\beta_1 = 2\, L^2 d\, |\sin\gamma| \tag{1.3}$$

where γ is the angle between the two rods. The ordering transition is due to the competition of the second and third term in (1.2): The second term being the entropy of an ideal gas of needles has its maximum in the isotropic phase whereas the third term dealing with the excluded volume of a system of impenetrable rods favors alignment. The evaluation of the distribution function $f(\underline{a})$ can be done by taking the variation of the free energy with regard to the distribution function $f(\underline{a})$ which leads to the non-linear integral equation

$$\ln(4\pi f(\underline{a})) = \lambda - 1 + \frac{N_p}{V}\int f(\underline{a}')\, \beta_1\, d\Omega' \tag{1.4}$$

where λ is the Lagrange multiplier to introduce the constraint (1.1). The solution for the nonlinear integral equation (1.4) has been discussed exhaustively[7] and does not need to be reviewed here. In this context it suffices to note that the Onsager theory predicts a first order transition from an isotropic to a nematic phase. The

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volume fraction of the rods in the ordered phase just at the transition is approximately proportional to the inverse of the axial ratio $x = L/d$. This result can be derived rather easily by the following qualitative argument[8]: Consider an assembly of rods having the length L and a squared base with area $d * d$ (cf. Figure (1)). At dense packing the excluded volume per rod is given by d^2L but in the dilute solution by L^2d if only two rods are assumed to interact. Hence the volume fraction of the rods in solution at which the excluded volume comes into play is given by the ratio of d^2L to L^2d. This suggests that the critical volume fraction of incipient ordering should vary with the inverse axial ratio d/L.

Regarding the value of the critical volume fraction as derived by the Onsager theory it must be kept in mind that its value is the lower bound of this quantity. This may be argued from the fact that the excluded volume is derived solely from binary interaction between two rods. The effect of excluded volume will be diminished when going to higher concentrations (see section 3).

Another argument which casts doubt on the quantitative validity of the Onsager treatment is related to the volume dependence of the cluster integrals.[9] In equations (1.2) and (1.4) the integration over the volume is extended to infinity which implies that the value of the cluster integrals does not depend on the volume. This assumption is justified if the volume per particle $V/N_P = v$ is much greater than the volume v^* per particle in which interaction takes place because outside of v^* the integrand of (1.4) is zero. Thus the cluster treatment requires $v >> v^*$. As an upper bound of v^* one may choose L^3. A smaller perhaps more realistic estimate is given by the covolume per particle L^2d. The particle density at the transition is of the order of $1/L^2d$ (see above) which leads to $v^*/v \simeq L/d$ for $v^* \sim L^3$ which for the long rods under consideration here is much greater than unity. Even if v^* is identified with the covolume per particle the ratio of v^* to v is of the order of unity but not much smaller as required for the validity of the cluster expansion. Since v^* will diminish with increasing order the Onsager approach consequently favors the formation of order states. Accordingly, the density predicted for the onset of phase separation is too low and the order parameter in the nematic phase too high.

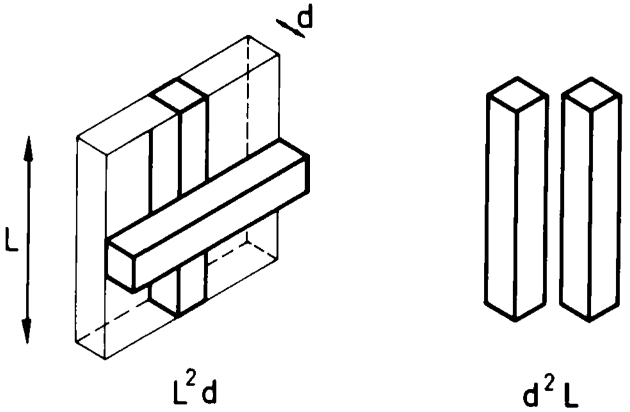

FIGURE 1 Excluded volume for two rods in dilute solution (left) and at dense packing (right).

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Quantitative conclusions drawn from the Onsager theory hence must be regarded cautiously.

A point of great importance which can be addressed qualitatively at the level of approximation of the Onsager theory is the number of mutual orientations the two rods may assume. In the original treatment by Onsager as outlined above the orientation of the rods relative to the preferred direction may vary in a continuous fashion. To facilitate the calculation of the higher virial coefficients it has been suggested[10,11] to restrict the cylinders to three mutually perpendicular orientations. However, Straley[12] was able to show that discrete geometries are not a useful way to study real liquid crystal systems. The argument of Straley rests on an extension of the Zwanzig model from 3 (cubic symmetry) to 6 (dodecahedral symmetry) and to 10 (icosahedral symmetry). The results for the equation of state do not seem to trend towards the Onsager limit (cf. Figure (1) of Reference 12), at least for the rather restricted number of orientations accessible through this argument. The reason for this finding is clearly located in the fact that in the continuous model the angular distribution function is sharply peaked with most rods being oriented within 20° of the preferred direction. The restricted orientations do not sample this distribution well since they differ by at least 45°. Thus the ordered phase in discrete geometries has nearly all the rods pointing into one direction. This implies that all the virial corrections vanish whereas the continuous model leads to a finite value of the second virial coefficient.

It is evident that these shortcomings of the Zwanzig model do not appear only in treatments based on the virial expansion. Any lattice model or computer simulation using a restricted geometries of the rods will come to similar unphysical deductions.[13] The approximations of the Flory lattice theory necessary to introduce a continuous angular distribution function therefore seem to be less stringent than the restriction of the rods to three mutually perpendicular orientations. However, rectangular lattice models may be a very useful device to study the ordering transition of semiflexible polymers.[14,15]

2. TREATMENT OF ORDERED POLYMER SYSTEMS BY LATTICE METHODS

2.1. General considerations

As has been outlined in the first section the Onsager treatment is afflicted by a number of problems which can be traced back to the difficulties of the cluster expansion for a system of long rods. Besides these problems its range of validity is restricted to the range of concentrations where the third virial coefficient may be neglected. Lattice models can circumvent this problem allowing the evaluation of the partition function over the whole range of concentrations. The obvious shortcoming of these theories is clearly given by the necessity of subdividing the molecule into a succession of structural entities, usually called segments each of which is occupying one cell of the lattice. Despite the inherent artificialities of this procedural device the application of lattice methods to polymeric systems has met

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with gratifying success, especially in the deduction of the combinatorial contribution to the partition function of mixtures.[16]

The principal step for the evaluation of the partition function is the estimation of the number ν_{j+1} of sequences of empty lattice sites when j molecules have already been inserted into the lattice containing n_o sites.[16] For the calculation of ν_{j+1} for disordered systems it is sufficient in most of the cases to identify the expectation that a given site is vacant with the *a priori* probability p_{ji}

$$p_{ji} = (n_o - xj - i)/n_o \tag{2.1}$$

of a vacancy in the system (cf. Reference 17 for a further discussion of this point). Here x is the number of segments in the chain and i is the number of segments of particle $j+1$ already assigned to the lattice.[17,18] The combinational part of the partition function for a system consisting of n_2 molecules then follows as

$$Z = (Z_c/n_2!) \prod_1^{n_2} \nu_j \tag{2.2}$$

where Z_c is the intramolecular chain configuration partition function. In the limit of very long chains, *i.e.*, large x we obtain[18]

$$Z = (z_c/e)x^{n_2} \tag{2.3}$$

with z_c being the factor contributed per segment to the intramolecular partition function. From (2.3) it is evident that Z may become much smaller then 1 if the effective number z_c per segment is less than e as it may occur in case of relatively stiff chains. Thus the total number of accessible configurations is less than unity which is physically unacceptable ("entropy castastrophy,"[17]) since there will be at least one totally ordered configuration being available for the system. This argument clearly demonstrates that the treatment of stiff-chain systems has to proceed in a different fashion by directly evaluating the partition function for ordered systems of rigid rods, *i.e.*, the existence of ordered states has to be assumed first.

2.2. Flory-Ronca theory: athermal systems

Consider a system of rods having an orientation with regard to a preferred axis measured by an angle of inclination Ψ (see Figure (2)). The essential step in the Flory model[19] consists in breaking up the rods into a sequence of y consecutive submolecules. In this two-dimensional rendition the relation of the "disorder index" y to the number of segments x and the angle Ψ may be written as[19]

$$y = x \sin \Psi \tag{2.4}$$

The exact relationship between y and Ψ will be discussed in more detail below. The calculation of ν_{i+1} of situations accessible to the i + 1th rod after i particles have been assigned to the lattice now proceeds as follows[19]: For the first segment of the first submolecule there are n_o − ix empty cells. In a mean-field treatment

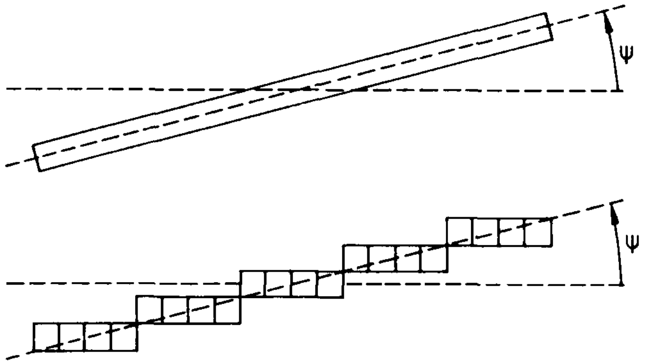

FIGURE 2 Representation of a rod in a cubic lattice. (see Reference 19).

of a nematic phase it may be assumed that the sequences of segments occuring in a given row of cells parallel to the preferred axis are uncorrelated with those in adjacent rows. Hence, the expectation of vacancy at the site required for an initial segment of the remaining $y_{i+1} - 1$ submolecules is the volume fraction of vacancies $(n_o - ix)/n_o$. Having established that one of these sites is vacant one requires the conditional probability that the next site in this row is vacant to be occupied by the remaining segments of the submolecule. This conditional probability is given by the number fraction of vacancies in the rows parallel to the preferred axis given by the ratio of the number of vacancies to the sum of vacancies and submolecules. Thus the required expectation that all the cells for the x segments of rod $i + 1$ being arranged in y_{i+1} submolecules is[19]

$$\nu_{i+1} = (n_o - ix)\left(\frac{n_o - ix}{n_o}\right)^{y_{i+1}-1}\left(\frac{n_o - ix}{n_o - ix + \Sigma\, y_j}\right)^{x - y_{i+1}} \tag{2.5}$$

It is important to note that *a priori* probabilities are employed for propagation along direction perpendicular to the preferred axis, *i.e.*, for placement of the first segments of the submolecules whereas inserting the remainder $x/y - 1$ segments requires the probability of finding a vacant pair of lattice cells.[20] Applying *a priori* probabilities for the latter process would lead to the Flory-Huggins result for isotropic systems, of course.

As in the Onsager theory the partition function Z is split into a combinatorial part Z_{comb} depending on the excluded volume and an orientational part Z_{orient} referring to an ideal gas of cylinders with restricted orientation.

$$Z = Z_{comb}\, Z_{orient} \tag{2.6}$$

Insertion of (2.5) into (2.2) and subsequent consolidation leads to the first factor[21]

$$Z_{comb} = \frac{(n_1 + n_x\bar{y})!}{n_1!\, n_x!}\, n_o^{\,n_x(1-\bar{y})} \tag{2.7}$$

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Here n_1 and n_x are the number of solvent molecules and rodlike particles, respectively; $\bar{y}$ is the mean value of the disorder index y defined by

$$\bar{y} = \sum n_{xy}\, y/n_x \tag{2.8}$$

where n_{xy}/n_x the orientational distribution specifying the fraction of the molecules with disorientation y. As in the Onsager approach the orientational part Z_{orient} follows as[21]

$$Z_{\text{orient}} = \prod_y (\sigma\, \omega_y\, n_x/n_{xy})^{n_{xy}} \tag{2.9}$$

with σ being constant to be specified later. Because of the cylindrical symmetry of the problem the statistical weight ω_y results to[21]

$$\omega_y = \mathit{sin}\ \Psi_y \tag{2.10}$$

Substitution of (2.7) and (2.9) into (2.6) followed by introduction of Stirling's approximation for the factorials gives

$$-\ln Z = n_1 \ln v_1 + n_x \ln(v_x/x) - (n_1 + n_x y)\ln\left(1 - v_x\left(1 - \frac{\bar{y}}{x}\right)\right)$$
$$+ n_x(\bar{y} - 1) + n_x \sum_y \frac{n_{xy}}{n_x} \ln\left(\frac{n_{xy}}{n_x\, \omega_y}\right) - n_x \ln \sigma \tag{2.11}$$

where $v_1 = n_1/(n_1 + n_x x)$ and $v_x = n_x x/(n_1 + n_x x)$ are the volume fractions of the respective components. Note that at this stage the orientational distribution function is not yet specified.

There are two limiting cases of Equation (2.11) to be considered: 1) For perfect alignment each rod only consists of one submolecule, thus $\bar{y} = y = 1$. In this case (2.11) must be reduced to the ideal mixing law a requirement being fulfilled if

$$\sigma = 1/\omega_1 \tag{2.12}$$

Random disorder requires $n_{xy}/n_x = \omega_y$. Then (2.11) reduces to the well-known Flory-Huggins expression for the free energy of mixing of a polymer with a solvent.[16]

The distribution function n_{xy}/n_x at equilibrium disorder may be derived as follows: The last molecule inserted into the lattice may be taken as a probe for the expected number of situations available to a particle the disorder of which is specified by y. Since

$$v_y \sim (1 - v_x(1 - \bar{y}/x)) \tag{2.13}$$

We have[21]

$$n_{xy}/n_x = f_1^{-1}\, \omega_y \exp(-ay) \tag{2.14}$$

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where

$$a = -\ln(1 - v_x(1 - \bar{y}/x)) \tag{2.15}$$

and

$$f_1 = \int_0^{y_{\max}} \omega_y \exp(-ay)\, dy \tag{2.16}$$

The orientational part then follows as

$$\ln Z_{\text{orient}} = n_x[\ln(f_1\sigma) + a\bar{y}] \tag{2.17}$$

and, after insertion into (2.9)

$$\begin{aligned} -\ln Z = {} & n_1 \ln v_1 + n_x \ln(v_x/x) - n_1 \ln(1 - v_x(1 - \bar{y}/x)) \\ & + n_x(\bar{y} - 1) - n_x \ln(f_1\sigma) \end{aligned} \tag{2.18}$$

The equation is only valid, of course, if $\bar{y}$ assumes its equilibrium value.[21] Alternatively, the orientational distribution function at equilibrium may be derived by taking the variation of (2.11) with regard to n_{xy}/n_x.

Equation (2.18) gives the free energy of a system of n_x rigid rods immersed in a solvent containing n_1 at orientational equilibrium with the order being present in the anisotropic phase being measured by the disorder index y. For calculating the concentrations in the coexisting isotropic and anisotropic phases the chemical potential has to be determined by partial differentiation of (2.18). At orientational equilibrium, we have[21]

$$\left(\partial \ln Z / \partial \left(\frac{n_{xy}}{n_x}\right)\right) = 0 \tag{2.19}$$

The resulting equilibrium condition leads to

$$\ln\left(\frac{v_x'}{v_x}\right) = (x - 1)v_x - (\bar{y} - 1)v_x' + \ln(f_1) \tag{2.20}$$

It remains to evaluate the relation of the disorder index y and the corresponding angle Ψ. Adopting the result given by Equation (2.4) would lead to erroneous results because of the two-dimensional rendition of the problem which requires

$$\omega_y = 1/x \tan \Psi \tag{2.21}$$

instead of the correct relation (2.10). This difficulty of the model[22] can be remedied by considering the projection of one rod on a cross section of the cubic lattice perpendicular to the preferred direction[21]: The transverse axes are labelled Y_1 and

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Y_2; Ψ denotes the azimuthal angle between the axis of the rod (heavy line in (Figure 2)) and φ is the angle of rotation about the domain axis. It is apparent that the number of lattice cells required for the representation of the projection of the into the Y_1-Y_2 plane is approximated by the sum of the magnitudes of the components y_1 and y_2 of the length of the rod on the axes Y_1 and Y_2. Hence,

$$y = |y_1| + |y_2| = x \sin \Psi \, (|\cos \varphi| + |\sin \varphi|) \tag{2.22}$$

Averaging over φ one obtains[21]

$$y = \frac{4}{\pi} x \sin \Psi \tag{2.23}$$

It must be noted[21] that (2.23) is consistent with expression (2.10) for the statistical weight ω_y. Then

$$n_{xy}/n_x = f_1^{-1} \sin \Psi \exp(-\alpha \sin \Psi) \tag{2.24}$$

with

$$\alpha = (4/\pi)\, a\, x \tag{2.25}$$

where the quantity a is defined by Equation (2.15). The integral f_1 now may be evaluated according to

$$f_p = \int_0^{\pi/2} \sin^p \Psi \exp(-\alpha \sin \Psi)\, d\Psi \tag{2.26}$$

with $p = 1$. The average values of sin Ψ and y are consequently given by

$$\langle \sin \Psi \rangle = f_3/f_1 = \frac{2}{3}(1 - S) \tag{2.27}$$

and

$$\bar{y} = (4/\pi) \times f_2/f_1 \tag{2.28}$$

with S being the common order parameter. The self-consistency relations (2.27) and (2.28) together with the equilibrium condition (2.20) now furnish a complete set of equations which upon numerical solution lead to the concentrations in the respective phases as well as to the disorder index $\bar{y}$ at equilibrium.

2.3. The "1956" approximation

Significant simplification of the above treatment of the angular distribution function can be achieved by assuming n_{xy}/n_x to be uniform out to a certain angle Ψ' and

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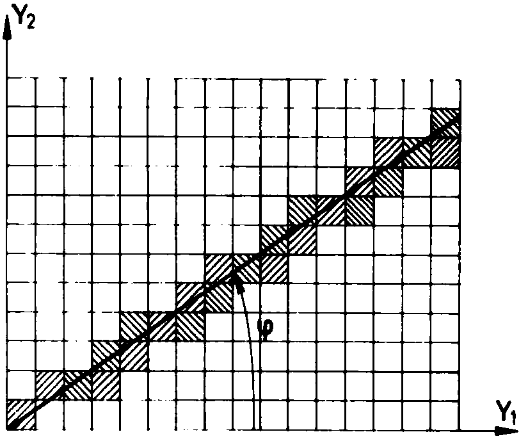

FIGURE 3 Projection of a rod onto the plane perpendicular to the preferred axis.

zero beyond that value. Then the orientational part Z_{orient} will be proportional to $(\omega)^{n}x$ with Ψ being the solid angle within $\Psi \leq \Psi'$. In good approximation, ω is proportional to $\bar{y}^2$ leading to the expression[19]:

$$Z_{\text{orient}} = (\bar{y})^{2n_x} \tag{2.29}$$

The "1956" approximation can be derived from the above treatment by developing the integrals f_p into powers of α which facilitates the numerical solution of the self-consistency relations (2.27) and (2.28) by avoiding the cumbersome numerical evaluation of the integrals (2.26). Furthermore, it can be shown that this approximation leads to rather accurate results in the limit of high axial ratios.[21]

Straley[22] has concluded that the Flory model in this "1956" approximation gives unphysical results because of the problems originating from Equation (2.4). However, in its original derivation[19] the formulation of Z_{orient} by Equation (2.29) circumvents these difficulties by using (2.29).[21] Direct application of (2.4) for the calculation of the orientational part of the partition function would be indeed followed by a finite degree of ordering at all concentrations.

2.4. Problems

The above derivation shows that the parameter $\bar{y}$ gives the average value of the projection of the rods onto the plane defined by the preferred axis. This parameter thus is a direct measure for the steric hindrance exerted by the assembly of densely packed rods on a probe rod to be introduced into the lattice. A number of problems, however, become apparent when specifying the relation of y to the angle of inclination Ψ which may be traced back to the inherently discontinuous character of the lattice rendition. From $y = 4/\pi\, x \sin\Psi$ it is obvious that in fully aligned systems y should vanish whereas the lattice meaning of this parameter requires $y = 1$ in that case. Thus a small fraction of angles refering to values of y smaller than 1 is excluded.[23] However, this problem only comes into play for very small axial ratios hardly exceeding unity as is evident from the above relation (2.23). Since real liquid crystal systems to be treated by the model consist of molecules with x greater than 3 or 4, this inconsistency is of minor importance at the present level of approximation.

Another problem arises when taking the average of y over Ψ in the isotropic phase leading to $\bar{y}_{\text{iso}} = x$. This requires values of y exceeding x a condition which is difficult to be reconciled with the lattice model. However, the free energy of the isotropic phase given by the model is identical to the expression derived from the Flory-Huggins theory thus obviating the need for a description of a disordered system in terms of the parameter y. The order in the nematic phase, on the other hand, is quite high and $\bar{y}$ is much smaller than x and the lattice calculation is expected to come to valid conclusions.

A point of criticism raised by Warner[13] is concerned with the free energy of the isotropic phase. As pointed out in the previous section the free energy (2.18) reduces to the Flory-Huggins result for flexible polymers in this case. In absence of a solvent we obtain

$$-\ln Z = -\ln x + (x-1) \tag{2.30}$$

In the theory of Warner[13] the steric hindrance in the system is calculated by using the projection of the rods into the plane of the probe rod to be introduced into the system. In the limit of high ordering both treatments come to similar conclusions. However, the corresponding free energy of the isotropic phase results to

$$-\ln Z = -\ln x - \left(\frac{(x-1)4/\pi + 1}{1 - \pi/4}\right)\ln\left(\frac{x-1}{x}\frac{\pi}{4} + 1/x\right) \tag{2.31}$$

Considering systems of rather short rods both Equations (2.30) and (2.31) come to comparable entropies in the isotropic state. Going to high axial ratios the difference in ΔF for the isotropic state differ markedly but these systems only exhibit a transition into the disordered state upon dilution where entropy is dominated by the solvent contribution. However, the proper evaluation of the free energy of a system of disordered rods is certainly a problem in need of further elucidation.

3. COMPARISON WITH OTHER APPROACHES

3.1. The "decoupling approximation"[1]

Having introduced the essential steps of the lattice theory, its further implications may be discussed best in a comparison with other models currently being applied to nematic phases. One of the most general and significant contributions to this field has been made by Parsons[1] by introducing the "decoupling approximation." A similar approach[24] has been given recently. Here we outline briefly Parson's theory in the following section.

Consider a system of N long rods in equilibrium at a number density n. As in the Onsager theory $f(\Omega)d\Omega$ is the probability of finding a rod at the solid angle Ω.

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The interactions between the rods are assumed to be of the pair type. Let $\phi(\underline{r},\Omega_{12})$ be the pair interaction. The energy contribution to the free energy may be written in terms of the pair correlation function $g(\underline{r},\Omega_{12})^{25}$:

$$pV/NkT = 1 - \frac{N}{6VkT}\int d^3\underline{r}d\Omega_1 d\Omega_2\, f(\Omega_1)f(\Omega_2)\,(r\frac{\partial}{\partial \underline{r}}\phi\,(\underline{r},\,\Omega_{12})g(\underline{r},\,\Omega_{12}) \quad (3.1)$$

The entropic part of $-\ln Z$ referring to an ideal gas of needles may be expressed by the second term of (1.2) derived by Onsager (cf. Section 1)

$$-\ln Z = NkT\int f(\Omega)\ln f(\Omega)d\,\Omega + F' \quad (3.2)$$

where F' is the additive free energy due to interaction. Applying the relation $p' = (n^2/N)\,(\partial F'/\partial n)_f$ at constant angular distribution and subsequent combination of (3.1) and (3.2) we have[1]

$$-\ln Z = \int d\,\Omega\, f(\Omega)\ln f(\Omega)$$

$$- \frac{1}{6kT}\int d^3\underline{r}d\Omega_1 d\Omega_2 f(\Omega_1)\, f(\Omega_2) * \int_0^n dn'\, r\,\frac{\partial\phi}{\partial r}\, g(\underline{r},\Omega_{12},n) \quad (3.3)$$

which is case of dilute systems ($g \approx \exp(-\phi/kT)$) reduces to the Onsager result (1.2).[2]

To evaluate (3.3) at higher concentrations a pair potential of the form $\phi(r/\sigma,n)$ is introduced where $\sigma = \sigma(\Omega_{12})$ is an angle-dependent parameter. In this "decoupling approximation" ϕ is the same analytical function for all mutual orientations of the two molecules.

With regard to the pair correlation function the decoupling approximation amounts to equating $g(\underline{r},\Omega_{12})$ to $g(r/\sigma)$. Both the pair potential as well as the pair correlation function are exact at low concentrations but certainly only an approximation at higher densities. With these premises of the model it can be shown that (3.3) may be evaluated to give[1]

$$-\ln Z = \int d\Omega\, f(\Omega)\ln f(\Omega) + \frac{J(n)}{2}\int d\Omega_1\, d\Omega_2 f(\Omega_1)\, f(\Omega_2)\, V_{excl}(\Omega_{12}) \quad (3.4)$$

with

$$J(n) = \int_0^n \alpha\,(n')\,dn' \quad (3.5)$$

and

$$V_{excl} = \frac{1}{3}\int d\hat{r}\,\sigma\,(\hat{r},\Omega_{12}) \quad (3.6)$$

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where $\alpha(n)$ is

$$\alpha(n) = -\int_0^\infty dy\, y^3 \frac{\partial\phi}{\partial y} g(y,n) \tag{3.7}$$

To perform the integration in (3.7) we may replace $g(y,n)$ by $g(y,n)\exp(+\phi(y))$. Then:

$$\alpha(n) = -\int dy\, y^3 g(y,n) \exp(+\phi) \frac{\partial}{\partial y} \exp(-\phi(y)) = g(1,n) \tag{3.8}$$

since $\exp(-\phi(y))$ is the Heaviside step function the derivative of which is the Dirac δ-function. Hence[26]

$$J(n) = \int_0^n dn'\, g(1,n') \tag{3.9}$$

The determination of the steric contribution to the free energy (3.4) is thus reduced to the calculation of the excluded volume of a pair of cylinders and the pair correlation function of a system of hard spheres at contact. At the present level of approximation the latter function may be approximated by[26]

$$g(1,n) = 1/(1 - \frac{c}{c_{\max}}) \tag{3.10}$$

where $c_{\max}$ is the maximum concentration of spheres in the system. Combining (1.3) with (3.4) and (3.10) we obtain for the complete free energy

$$-\ln Z = \ln n + \int d\Omega\, f(\Omega) \ln f(\Omega)$$
$$+ c_{\max} L^2 d \ln\left(\frac{1}{1 - c/c_{\max}}\right) * \int |\sin\gamma|\, f(\Omega_1) f(\Omega_2)\, d\Omega \tag{3.11}$$

As first recognized by Khokhlov and Semenov[26] this expression is equivalent to the free energy derived from the lattice model at a highly ordered dense state. Then $\langle\sin\Psi\rangle = \pi/4\, \bar{y}/x$ is much smaller than 1 and Equation (2.11) reduces to

$$-\ln Z = \ln n + \pi/4\, x \langle\sin\Psi\rangle \ln(1/(1 - v_x)) + \int d\Omega\, f(\Omega) \ln f(\Omega) \tag{3.12}$$

Since $x = L/d$ and $v_x = c/c_{\max}$ where

$$c_{\max} = \frac{4}{\pi} d^{-2} L^{-1} \tag{3.13}$$

we arrive at Equation (3.11) again.

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In this context it is important to note that the scaled particle theory (SPT) of a system of hard spherocylinders leads to the same form of the free energy of ordered states, namely, $-\ln Z$ is the sum of the entropy term already being present in the Onsager treatment and the product of $\langle \sin\Psi \rangle$ and a function λ^* which only depends on the density and the dimensions of the cylinders.[27,28] One might suspect therefore that the SPT is in essence a decoupling approximation but this point is in need of further elucidation.

From the above comparison of the approaches of Onsager, Parsons and Flory it has become evident that these theories only differ with regard to the steric part of the partition function. In the limit of high order, *i.e.*, intermediate concentrations the Flory result reduces to that given by Parsons, for very long rods both theories coincide with the Onsager free energy (1.2) in the limit of dilute systems as will become evident by expansion of the logarithmic term in front of $\langle \sin \Psi \rangle$.

4. THERMOTROPIC SYSTEMS

Thermotropic nematic liquid crystals and semiflexible polymers transform into the isotropic state at a well-defined transition temperature T_{ni}. This experimental fact implies that the transition in these systems is followed by a change of energy. The concomitant latent volume change is too small to account for the latent heat of transition which in consequence must be traced back to an increase of the intermolecular cohesion energy when going from the isotropic state to the ordered phase. At constant volume, this change of the interaction energy cannot be caused by isotropic dispersion forces since in a dense liquid system the overall number of mutual contacts between the rods in the system will not change upon ordering.

Therefore the dependence of the intermolecular energy on the degree of order must be attributed to the anisotropic dispersion forces.[29] Isotropic dispersion forces promote the ordering transition only in an indirect manner by adjusting the density, *i.e.*, the void volume present in the system. This difference between the molar hard core volume V^* of the molecules and the observed volume V may be treated in terms of the lattice representation as unoccupied sites. In this approach akin to the mean-field lattice gas model[30] and the empty sites replace the solvent molecules present in lyotropic systems (cf. Equation (2.11)). In both cases a decrease of the volume fraction of the rods will be followed by a lowering of the transition temperature.[31]

Accordingly, the extension of the lattice calculation for lyotropic systems as outlined in Section 3 to thermotropic liquid crystals may be done in two steps.[3]

The free volume present in the system[32] is introduced in terms of the reduced volume $\tilde{V} = V/V^*$, *i.e.*, the total number of lattice sites is $n_o = \tilde{V}\, x n_x$ and the volume fraction of voids follows as $1 - 1/\tilde{V}$. Secondly, we require the anisotropic dispersion interaction energy of a rod with inclination Ψ towards the domain axis in the mean-field of all other rods. Following Warner and others,[33-35] the interaction energy of two ellipsoidal particles results to

$$\epsilon = -\frac{C}{r^6} \sum_{i,j} \alpha_i \alpha_j \left[(\underline{u}_i\, \underline{u}'_j)^2 - 6(\underline{u}_i\, \underline{u}'_j)(\underline{\hat{r}}\, \underline{u}_i)(\underline{\hat{r}}\, \underline{u}'_j) + 9(\underline{\hat{r}}\, \underline{u}_i)^2 (\underline{\hat{r}}\, \underline{u}'_j)^2 \right] \quad (4.1)$$

where the prime marks the second molecule. The α_i are the i-th component of the polarizability tensor α of the molecules, the $\underline{u}_i$ are unit vectors in the principal directions of the molecule and $\hat{r} = \underline{r}/r$ is the unit vector joining the centers of the two molecules. Application of Equation (4.1) requires that 1) the temperatures are low enough that the thermal frequencies lie well below the transition frequencies for the molecule; 2) the retardation effect is negligible; and 3) replacement of all transitions by a single frequency in terms of a Drude model.[33] Condition 3 particularly applies best to aromatic cores where the single step represents the π to π^* transitions. Accordingly, special caution must be exerted when using the above scheme for nematogens consisting of hydrocarbon moieties.

More elegantly, Equation (4.1) may be written as[34,36]

$$\epsilon = -\frac{C}{r^6}\left[\operatorname{tr}(\alpha\,\alpha') - 6\,(\underline{\hat{r}}^{T}\,\alpha\,\alpha'\,\underline{\hat{r}}) + 9\,(\underline{\hat{r}}^{T}\,\alpha\,\underline{\hat{r}})\,(\underline{\hat{r}}^{T}\,\alpha'\,\underline{\hat{r}})\right] \tag{4.2}$$

The polarizability tensor α can be represented by its symmetric, cylindric and acylindric part:

$$\alpha = \bar{\alpha}\,\underline{E} + \Delta\alpha\ \mathrm{diag}\left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}\right) + \Delta\alpha^{+}\ \mathrm{diag}\left(0, \frac{1}{2}, -\frac{1}{2}\right) \tag{4.3}$$

with

$$\bar{\alpha} = \frac{1}{3}\operatorname{tr}(\underline{a}) \tag{4.4}$$

To derive a mean field potential that a given molecule is subject to, Equation (4.2) must be averaged over configurations of the other molecule. For this purpose we first assume that the molecules can rotate freely about their long axes so that all contributions from the third term in (4.3) vanish. Averaging over the orientations of the cylindrical axis of molecule 2 as well as over the vector $\underline{\hat{r}}$ yields an energy $\epsilon(\Psi)$ where Ψ is the angle that the cylindrical axis of molecule 1 forms with the domain axis. If $\underline{\hat{r}}$ is assumed to be distributed isotropically in space one obtains[36]

$$\epsilon = \epsilon_{\mathrm{iso}} + \epsilon_{\mathrm{an}}\,(\Psi) \tag{4.5}$$

with

$$\epsilon_{\mathrm{iso}} = -\frac{6\alpha^{-2}C}{\tilde{V}\,r^{*6}} \tag{4.6}$$

where r^* is the intermolecular distance at dense packing ($\tilde{V} = 1$); and

$$\epsilon_{\mathrm{an}}(\psi) = -\frac{2}{15}\,\frac{C}{r^{*6}\tilde{V}}\,(\Delta\alpha)^2\ S\ P_2\,(\cos\Psi) \tag{4.7}$$

or

$$\epsilon_{\mathrm{an}}(\psi) = -\frac{kT^*}{\tilde{V}}\ S\ P_2\,(\cos\Psi) \tag{4.8}$$

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with S being the common order parameter; P_2 (cos Ψ) the second Legendre polynomial and T* the characteristic temperature of anisotropic interaction. With $\epsilon_{\mathrm{iso}} = p^* V_s^*/\tilde{V}$ where p^* denotes the characteristic pressure of the fluid[32] and V_s^* the hard core volume of one segment of the molecule we have[36]

$$kT^* = 2\,\sigma\,p^*\,V_s^*\left(\frac{\Delta\alpha}{\bar{\alpha}}\right)^2 \tag{4.9}$$

The constant σ is located between 1/45 calculated for a spherical distribution of segments (see above) and 1/6 by fixing the neighboring molecule at a location r in a direction perpendicular to the long axis.[36]

Equation (4.9) demonstrates that the characteristic temperature T* measuring the strength of anisotropic interaction may be correlated to thermodynamic and optical data through a purely geometric constant σ. Thus the comparison between T* and the cylindrical part $\Delta\alpha$ of the polarizability tensor furnishes a comprehensive test of the Flory model of thermotropic nematic fluids. Table I summarizes the respective data for two homologous series of rod-like nematogens.[36-39] Despite the uncertainties with regard to the values of p^* and $\Delta\alpha$ this comparison shows the value of constant σ to be located indeed in the range predicted by theory.

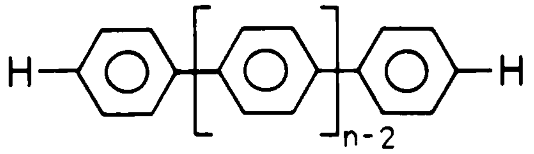
The experimental data displayed in Table I furthermore demonstrate directly the need for the description of the nematic–isotropic transition in terms of the steric forces. The anisotropic dispersion forces per segment as expressed by the quantity T* remains virtually constant throughout the oligomers of a given series. The strong rise of T_{ni} with ascending axial ratio then can be traced back to the increase of the steric thus affected.

To elucidate the influence of attractive forces in more detail, let us consider the nematic–isotropic transition temperature as function of $\tilde{V}$ and axial ratio x. Figure 4 displays the theoretical transition temperatures calculated for a given axial ratio x as function of $\tilde{V}$ for a reasonably chosen characteristic temperature (cf. Table I). There is a strong upturn in T_{ni} when approaching a densely packed system at $\tilde{V} = 1$. It is thus evident that isotropic attraction which adjusts the density of the system has a profound but indirect influence on T_{ni} through an increase of the steric forces when diminishing the free volume. Only anisotropic attraction as given by Equation (4.8) will directly promote ordering.

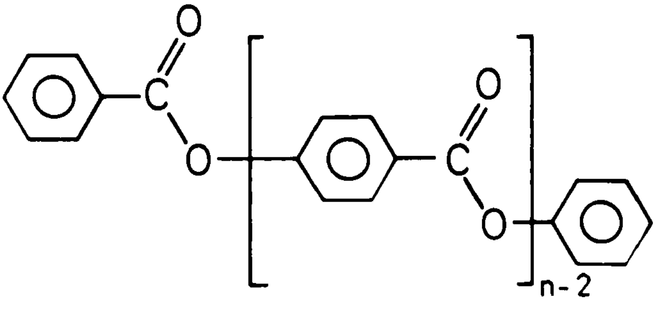
5. ORDER PARAMETER AND FLUCTUATIONS

As has been outlined in the previous section the Flory model seems to describe the nematic to isotropic transition in neat, thermotropic nematogens rather well. The theory has met with similar success when applied to mixtures of nematic liquid crystals.[31,39] However, the order parameter S predicted by this approach is located between 0.6 and 0.7 which is significantly higher than typical values of low molecular liquid crystals (~0.3–0.4) at the transition. This problem is not restricted to the Flory theory but seems to be common to all approaches starting from a system of rigid rods.[2] It has been pointed out by a number of authors[40-42] that this dis-

TABLE I



n	T_{ni}/K	x	$\tilde{V}(T_{ni})$	$\frac{\Delta\alpha}{\alpha}$	σ	T^*/K
4	523	3.9	1.38	0.96	0.07	573
5	691	4.8	1.50	1.02	0.066	630
6	838	5.5	1.56	1.13	0.054	650



n	T_{ni}/K	x	$\tilde{V}/(T_{ni})$	$\frac{\Delta\alpha}{\alpha}$	σ	T^*/K
3	373	3.8	1.216	0.54	0.13	343
4	527	5.1	1.284	0.58	0.10	316
5	737	6.4	1.364	0.60	0.092	306

agreement is due to the neglect of fluctuations in a mean-field approach rather than to insufficiencies in the physical description of the nematic phase. As indicated by Ian and Stephen[43,44] fluctuations may be neglected if

$$b\,\xi^3 >> kT \tag{4.10}$$

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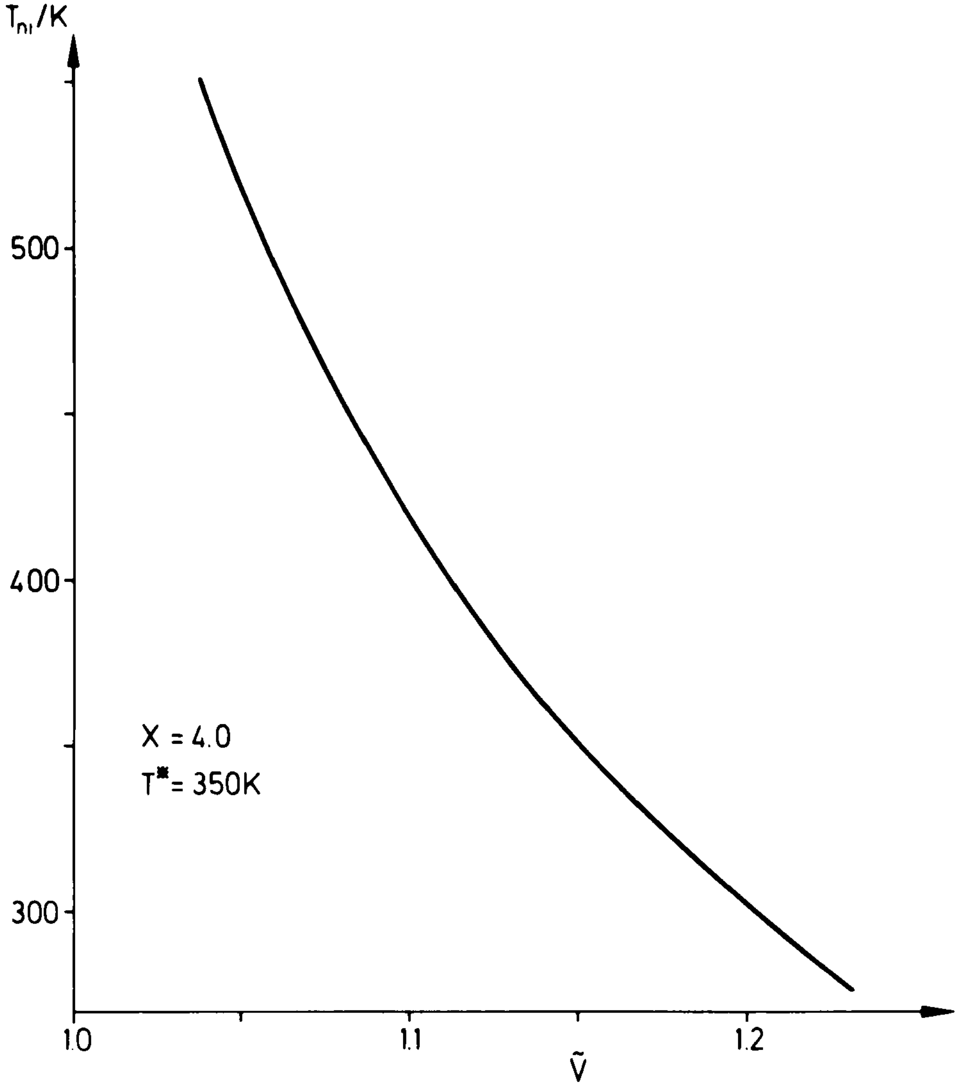

FIGURE 4 Nematic–isotropic transition temperatures calculated with the Flory lattice theory[31] as function of the reduced volume. The characteristic temperature is fixed to 350°K, the axial ratio of the rods is 4.0.

where *b* is the height of the barrier separating the ordered and the disordered state. The quantity ξ denotes the correlation length accessible through light scattering.[6] Calculations for well-investigated liquid crystals like MBBA or PAA,[43,44] confirm that in all but a small range of temperature the left-hand side of (4.10) is greater, *i.e.*, the thermal energy does not suffice to induce a transition into the disordered state in a volume of linear dimensions ξ.

Although fluctuations have a weak effect on thermodynamics they are easy to create and will affect profoundly an observable as the order parameter $\langle P_2 \rangle$. This problem has been analyzed in detail[45] by decomposing the observed order parameter Δ into a degree of order S_0 with respect to the preferred direction within a domain and an average of the fluctuations of the director $\langle P_2(\cos(\lambda(\underline{r}))\rangle$:

$$\Delta = \langle P_2 (\cos(\lambda(\underline{r}))\rangle \cdot S_0 \tag{4.11}$$

where $\lambda(\bar{r})$ denotes the angle of the director at $\bar{r}$ with respect to the observation axis. If the decoupling expressed in (4.11) is assumed to be valid, one may show that in absence of magnetic fields[45]

$$\langle P_2 (\cos(\lambda(\underline{r}))\rangle = 1 - \frac{3kT}{\pi\aleph}\frac{1}{\mathrm{L}} \tag{4.12}$$

where $\aleph$ is the elastic constant in the one-constant approximation[6] and the length L is the minimum wavelength of director distortions. Assuming a macroscopic value to L directly leads to $\Delta = S_0$. In this case the observed order parameter can be identified with the result of the mean-field calculation. To get an estimate of L, Warner[45] argues that this length may be taken as the limit of applicability of continuum theory. Below this length scale the order in the system has to be described in terms of S_0. The ordering of rigid rods on a local scale is clearly governed by steric constraints forbidding overlap of the molecules. Here the continuum theory treating order fluctuations in terms of a macroscopic modulus $\aleph$ certainly will not be applicable anymore. Thus L may be identified with the length scale where the steric constraints begin to be felt in the elastic distortions.[45] Accordingly, insertion of a microscopic value into (4.11) (L ~ twice the molecule length[45]) leads to an appreciable difference of Δ and S_0 ($\Delta/S_0 \sim 0.65$ for PAA).[45] Independent estimates of L from depolarized light scattering and NMR measurements will help to test this prediction experimentally.

From the above considerations it is evident that the fluctuations of the nematic director will cause an appreciable difference of the observed and the calculated order parameter. The magnitude of this distortion is determined by the cut-off length L and the modulus $\aleph$ [cf. Equation (4.12)]. Therefore the discrepancy between Δ and S_0 should be greatly diminished when increasing the length of the rods. There is indeed evidence for a better agreement of the measured order parameter with the Flory prediction in solutions of stiff-chain polymers.[46] According to (4.10) fluctuations of the director should be less important in thermotropic phases of polymers since b as well as the correlation length ξ are higher than in the low-molecular-weight systems.

A final point to be discussed in this context is the influence of the imperfect shape of real nematogens on the order parameter. Again this problem may be treated in terms of the lattice theory[47] leading to the conclusion that deviations from the ideal cylindrical shape caused by, *e.g.*, lateral substituents will greatly reduce the magnitude of S_0. In addition, this distortion is followed by a much stronger dependence of S_0 on temperature. Hence, apart from the discrepancy between the measured order parameter and the value, S_0 deduced from theory certainly must be traced back to idealization of nematogens as ideal rods or spherocylinders.

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