On the Role of Spherical Symmetry in the Maier-Saupe Theory

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The Maier-Saupe theory of the isotropic-nematic phase transition contains two crucial elements. First the orientational order in the nematic phase is attributed to the anisotropic part of the Van der Waals forces between the anisotropic molecules. In addition, in applying a mean-field approximation spherical symmetry around a central molecule is assumed. In this paper the consequences of this contradiction are investigated within the context of the theory. It is shown that relatively small deviations from spherical symmetry already destroy the orientational order. Hence the success of the Maier-Saupe potential is due to other reasons outside the original theory.

Keywords: Nematic liquid crystals; molecular-statistical theory; phase transitions

At Alfred Saupe's 70th birthday it seems appropriate to describe some aspects of the Maier-Saupe theory of the nematic phase that have probably not been fully appreciated in the literature. This paper relies on notes from my own personal investigations of the Maier-Saupe theory in the early seventies, when I had started research in liquid crystals at the Philips Research Laboratories in Eindhoven. Hence it might provide also some insight in the state of the art at that time. In the history of molecular theories of nematic liquid crystalline behaviour four major steps can be distinguished. The first attempt is from Born [1] who used dipolar interactions to obtain nematic ordering, of course necessarily leading to ferroelectricity, in contrast with experimental observations. Zwetkoff [2] introduced the orientational order parameter which we still use nowadays, thus avoiding Born's problems by taking the second Legendre polynomial. In fact he also constructed an empirical ordering potential using his new order parameter. Onsager [3] used a different approach relying on excluded volume effects to

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obtain orientational order in lyotropic systems. In the Maier-Saupe theory [4, 5] the line from Refs. [1, 2] is taken up again, and the isotropic-nematic phase transition is attributed to the anisotropic part of the van der Waals-forces between anisotropic molecules. The interaction energy is calculated using second-order perturbation theory. Moreover, in applying a mean-field approximation to perform an average over the surroundings of a molecule, spherical symmetry is assumed. In the following the consequences of this inherent contradiction will be investigated within the framework of the theory itself. I will show that relatively small deviations of spherical symmetry already cause the phase transition to disappear. As a consequence the successful applications of the potential are due to other reasons than the physical arguments used in the derivation. This conclusion was later confirmed in a different way by the work on the so-called generalised Van der Waals-theory by Gelbart and coworkers [6].

The order of an ensemble of anisotropic molecules is specified by the distribution function $P(\mathbf{r},\Omega)$, which gives the probability of finding a molecule at a particular position $\mathbf{r}$ and with a particular orientation Ω, where $\Omega = (\phi,\Psi,\theta)$ represents the set of Eulerian angles. For the nematic phase $P(\mathbf{r},\Omega) = \rho f(\Omega)$, where ρ is the uniform mass density and $f(\Omega)$ the normalised orientational distribution function [7]. For the isotropic phase evidently $f(\Omega)$ is a constant. Here I want to restrict the discussion to the uniaxial nematic phase of axially symmetric molecules in which case the orientational distribution function reduces to $f(\theta)$. Now $f(\theta)\,2\pi\sin\theta\,d\theta$ gives the number of molecules with its long axis at an angle between θ and $\theta + d\theta$ with the preferred direction $\mathbf{n}$ (director). The average value of a physical quantity $X(\theta)$ over the orientations of all molecules then is given by

$$\langle X \rangle = 2\pi \int_0^\pi f(\theta)\, X(\theta)\, \sin\theta\, d\theta. \tag{1}$$

In the model used the nematic phase can be characterised by a single order parameter

$$S = \langle P_2(\cos\theta)\rangle = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle = \left\langle 1 - \frac{3}{2}\sin^2\theta\right\rangle. \tag{2}$$

$S = 0$ if the distribution of the long molecular axis is random as in the isotropic phase; $S = 1$ corresponds to a perfectly aligned nematic phase. The variation of S with temperature as obtained from different methods is shown for a particular nematic compund in Figure 1. In the mean-field

approximation as used in the Maier-Saupe theory each molecule is assumed to experience an average potential $U(\theta)$ given by

$$U(\theta) = -A \langle P_2(\cos\theta) \rangle P_2(\cos\theta)$$

$$= -A S \left(1 - \frac{3}{2} \sin^2\theta \right), \tag{3}$$

where A is the strength of the potential. The potential is related to the distribution function by

$$f(\theta) = Z^{-1} \exp[-U(\theta)/k_B T], \tag{4}$$

where Z serves to normalise $f(\theta)$. Under appropriate conditions the attractive anisotropic energy dominates over the counteracting orientational (rotational) entropy. Calculation of both contributions to the free energy leads to a first-order phase transition from the nematic to the isotropic liquid phase where S changes discontinuously from 0.43 to 0. The theoretically predicted behaviour of S versus temperature is shown as the full line in Figure 2.

I will now summarise under what conditions eq. (3) is derived in the original work of Saupe [4,5]. Starting point is the interaction between two neutral molecules 1 and 2, to be described by a system of point charges. Following the original notation, molecule 1 has its centre of mass in the origin of a laboratory-fixed coordinate system; $e_i^{(1)}$ are the charges at $\rho_i^{(1)} = (x_i^{(1)}, y_i^{(1)}, z_i^{(1)})$. $\mathbf{R} = (X, Y, Z)$ is the distance to the centre of mass of molecule 2 with charges $\rho_k^{(2)} = (x_k^{(2)}, y_k^{(2)}, z_k^{(2)})$ with respect to (X, Y, Z). The dipolar part of the electrostatic interaction energy between the two molecules is described by the Hamiltonian

$$\mathbf{H}_{\mathrm{dip}}^{12} = \sum_{i,k} e_i^{(1)} e_k^{(2)} \left\{ \frac{1}{R^3} (\rho_i^{(1)} \cdot \rho_k^{(2)}) - \frac{3}{R^5} (\mathbf{R} \cdot \rho_i^{(1)})(\mathbf{R} \cdot \rho_k^{(2)}) \right\}, \tag{5}$$

which can be substituted in the expression for the second-order perturbation energy to give

$$W_{12} = \sum_{\mu,\nu} \frac{\langle 0^{(1)} 0^{(2)} | \mathbf{H}_{\mathrm{dip}}^{12} | \mu^{(1)} \nu^{(2)} \rangle}{E_{00} - E_{\mu\nu}}. \tag{6}$$
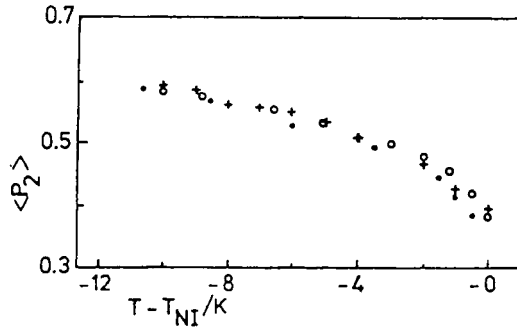
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FIGURE 1   Order parameter $S = \langle P_2(\cos\theta) \rangle$ of 5CB as obtained experimentally with different methods [7].
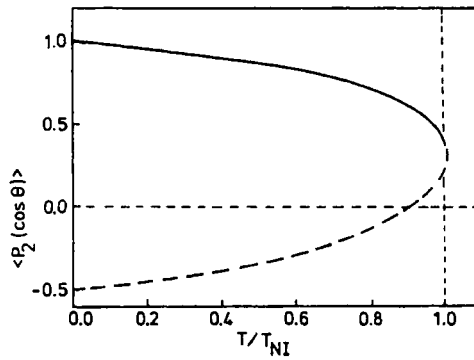

FIGURE 2   Order parameter $\langle P_2(\cos\theta) \rangle$ as obtained from the Maier-Saupe mean-field theory.

Here $|\mu^{(1)}\rangle$ and $|v^{(2)}\rangle$ are the orthonormal eigenfunctions of molecule 1 and 2, respectively, with associated energies E_μ and E_v. The ground state is given by $\mu = v = 0$, and is excluded from the summation. If we now introduce

$$x_\mu^{(1)} = \sum_i \langle 0^{(1)} | \rho_i^{(1)} x_i^{(1)} | \mu^{(1)} \rangle, \tag{7}$$

and similarly for $x_v^{(2)}$, and moreover corresponding expressions in y and z, we can write the result as (suppressing the superscripts 1 and 2)

$$W_{12} = \frac{1}{R^6} \sum_{\mu,v} (E_{00} - E_{\mu v})^{-1} \left[\left(3\frac{X^2}{R^2} - 1 \right) x_\mu x_v + \left(3\frac{Y^2}{R^2} - 1 \right) y_\mu y_v \right.$$

$$+\left(3\frac{Z^2}{R^2}-1\right)z_\mu z_v + \frac{3XY}{R^2}(y_\mu x_v + x_\mu y_v) + \frac{3YZ}{R^2}(z_\mu y_v + y_\mu z_v)$$

$$+\frac{3XZ}{R^2}(z_\mu x_v + x_\mu z_v)\Bigg]^2. \tag{8}$$

This equation is the basis for further manipulations. In order to make the appropriate averages over the orientations and positions of the molecules (which are assumed to be independent), eq. (8) must be transformed to a molecule-fixed coordinate system (ξ, η, ζ) related to (x, y, z) via the Euler angles (ϕ, Ψ, θ). Assuming a uniaxial nematic phase consisting of uniaxially symmetric molecules, the angles ϕ and Ψ are randomly distributed. In addition all expressions should be invariant under the transformation $\theta \to \pi - \theta$. Defining the integrals ξ_μ, η_μ, and ζ_μ similarly to those in the laboratory system (see eq. 7), Maier and Saupe find that the interaction energy depends on the isotropic and anisotropic part of the molecular transition moments defined as

$$f_\mu = \frac{1}{3}(\xi_\mu^2 + \eta_\mu^2 - \zeta_\mu^2),$$

$$\delta_\mu = \zeta_\mu^2 - \frac{1}{2}(\xi_\mu^2 + \eta_\mu^2). \tag{9}$$

The final result for the interaction energy then can be written as

$$W = R^{-6} \sum_{\mu,v}(E_{00} - E_{\mu v})^{-1}\Bigg\{f_\mu f_v A(R)$$

$$+\left[f_\mu \delta_v\left(1 - \frac{3}{2}\sin^2\theta_1\right) + f_v\delta_\mu\left(1 - \frac{3}{2}\sin^2\theta_2\right)\right]B(R)$$

$$+\delta_\mu \delta_v\left(1 - \frac{3}{2}\sin^2\theta_1\right)\left(1 - \frac{3}{2}\sin^2\theta_2\right)C(R)\Bigg\}. \tag{10}$$

This is essentially eq. (8) of Ref. [5] where, however, the coefficients $A(R)$, $B(R)$ and $C(R)$ were not made explicit. They can be written as

$$A(R) = 6,$$

$$B(R) = 3Z^2/R^2 - 1, \tag{11}$$

$$C(R) = 1 - 8Z^2/R^2 + 9Z^4/R^4.$$

Note that in eq. (10) three terms may contribute to the interaction energy. The first one is proportional to the product of the isotropic parts of the molecular transitions moments, the last one to the anisotropic parts, while in between a cross-term arises. In the subsequent mean-field approximation molecule 1 is singled out, and a summation is made over all other molecules. The average over the angles θ_2 can be expressed using the order parameter S given by eq. (2). This leads to

$$U(\theta, S) = \sum_{\mu, v} (E_{00} - E_{\mu v})^{-1} \left\{ f_\mu f_v \sum_k 6/R^6 \right.$$

$$+ \left[f_\mu f_v \left(1 - \frac{3}{2} \sin^2\theta \right) + f_v \delta_\mu S \right] \sum_k B(R)/R^6$$

$$\left. + \delta_\mu \delta_v \left(1 - \frac{3}{2} \sin^2\theta \right) S \sum_k C(R)/R^6 \right\}. \tag{12}$$

The crucial next step is to evaluate the average values of the quantities Z^2/R^2 and Z^4/R^4. Maier and Saupe assume spherical symmetry, in which case these reduce to 1/3 and 1/5, respectively, leading to $B(R) = 0$ and $C(R) = 2/15$. As a consequence the cross-term in eq. (12) disappears. Moreover, the term proportional to $f_\mu f_v$ (which depends on the excluded volume) is for spherical symmetry independent of orientation. Hence only the last term forms the nematic potential, which can be written in the well-known form of eq. (3). The fundamental point is not only the form of the potential (which was already given by Zwetkoff, as correctly noted by Maier and Saupe), but also the origin of the orientational order in the nematic phase being attributed to the anisotropic part of the dispersion interactions between the molecules. This point was strongly emphasised in an earlier note by Maier and Saupe [8] preceding their main paper. In Ref. [5], but especially in Saupe's thesis [4], the assumption of spherical symmetry in combination with anisotropic molecules has been extensively discussed. It will be clear from eq. (12) as given above, that if we do not make this assumption of spherical symmetry two differences come in.

(i) The coefficient $B(R)$ in the second term does not average out to zero anymore, and the physical effect of this term has to be investigated.

(ii) The term proportional to $f_\mu f_v$ now depends on the shape and the orientation of the central molecule, and thus may also contribute to the orientational energy.

We shall first investigate the first point. The general problem of calculating $\Sigma B(R)/R^6$ and $\Sigma C(R)/R^6$ is rather complicated. In Figure 3 results are given for the special case of a uniaxial excluded volume, for which both a spheroid and a spherocylinder are taken. Details of the calculation are given in the appendix. Such an axially symmetric excluded volume can only be expected for $S = 1$. Nevertheless the results probably also give a qualitatively correct idea of the relative variations of $\Sigma B(R)/R^6$ and $\Sigma C(R)/R^6$ with length/width ratio L/D for arbitrary S. From Figure 3 we note that $\Sigma B(R)/R^6$ has the opposite sign of $\Sigma C(R)/R^6$, while its absolute magnitude increases relatively fast with L/D. Already for $L/D > 1.35$ we find that $|\Sigma B(R)/R^6| > |\Sigma C(R)/R^6|$. For typical nematogenic mole- cules we can estimate that $f_\mu \cong \delta_\mu$ [9]. Hence incorporation of the cross-term in $f_\mu \delta_v$ of eq. (12) leads for any sizeable value of L/D to destruction of the nematic phase because its destabilising effect is larger then the stabilising effect of the term proportional to $\delta_\mu \delta_v$. Evidently the success of the Maier-Saupe theory depends critically on the assumption of spherical symmetry.

The contradiction described above can be understood from the later work of Gelbart and coworkers [6]. They considered essentially the coupling between the isotropic part of the dispersion forces proportional to $f_\mu f_v$ and the anisotropic orientation dependent excluded volume (point ii
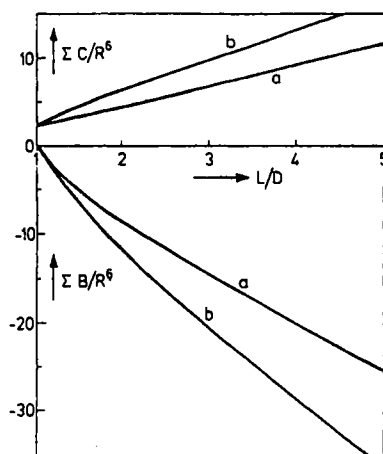

FIGURE 3   Variation of $\Sigma B(R)/R^6$ and $\Sigma C(R)/R^6$ with length/width ratio for a spheroidal (a) and a spherocylindrical (b) excluded volume.

mentioned above). The principle is illustrated in Figure 4, where for the sake of the argument the full isotropic polarisability is concentrated in the centre of mass of the molecule. It will immediately be clear that for parallel molecules not only the entropy associated with the excluded volume favours alignment, but that also the attractive forces contribute to the orientational order because of the shorter distance between the attractive centres. In order to appreciate the possible importance of this effect it should be realised that $|\Sigma 6/R^6|$ is at least an order of magnitude larger than either $|\Sigma B(R)/R^6|$ or $|\Sigma C(R)/R^6|$. For a spheroid $|\Sigma 6/R^6|$ varies from 105 for $L/D = 1$ to 316 for $L/D = 5$, which can be compared with the numbers from Figure 3. As a consequence the relative sign and magnitude of $\Sigma B(R)/R^6$ and $\Sigma C(R)/R^6$ – and thus the possible destabilising effect mentioned above – become irrelevant. To become more precise, Gelbart et $al.$ [6] consider an attractive pair potential between two molecules 1 and 2 of the form

$$U_{12} = -C_{\text{is}}/R_{12}^6 - (C_{\text{an}}/R_{12}^6)\cos^2\theta_{12}, \tag{13}$$

where C_{is} and C_{an} are assumed to be independent of R. The Maier-Saupe form of the potential can be obtained again if the spherocylinder for which eq. (13) is derived is reduced to a sphere of diameter d. In that case eq. (13) leads to a mean-field potential

$$U(\theta) \approx A_0 + A_2 S\left(1 - \frac{3}{2}\sin^2\theta\right), \tag{14}$$
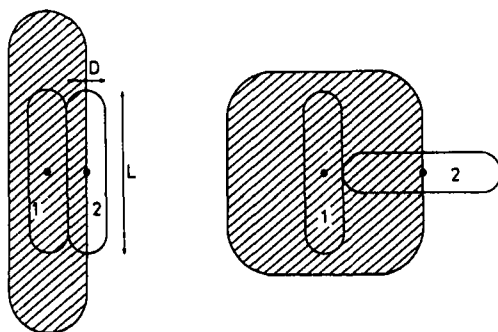

FIGURE 4   Illustration of the effect of the relative orientation of two spherocylinders on their excluded volume.

which is equivalent to eq. (3) with

$$A_0 = -4\pi (C_{an} + 3C_{is})/(9d^3),$$

$$A_2 = -8\pi C_{an}/(9d^3). \tag{15}$$

As in Maier and Saupe's theory, A_2 depends in the limit of spherical symmetry only on the anisotropic part of the dispersion forces. For a spherocylinder the resulting potential can still to a good approximation be written in the form of eq. (14). However, now the coefficient A_2 of the angle-dependent term depends on both C_{is} and C_{an}, with $C_{is} > 8C_{an}$ dominating the contribution to the attractive potential [6].

In conclusion I would like to recall a statement made by P. G. de Gennes during a talk in The Hague shortly after he received his Nobel prize. He mentioned that a certain approximation could only be very bad, and added 'hence let us make another one and hope that their effects compensate somehow'. This is exactly what happens in the Maier-Saupe theory of the nematic phase, where the assumption that the anisotropic part of the dispersion forces if responsible for the orientational order combines with the subsequent use of a spherical average to give a correct and useful nematic potential. Already in the seventies it had been noted by several authors [10] that the original interpretation of the strength of the potential is quantitatively not correct. In perspective the Maier-Saupe potential (with a different strength than originally proposed) can be motivated from the physics of a coupling of the isotropic part of the dispersion forces with an anisotropic orientation dependent excluded volume. This new interpretation certainly serves to provide the Maier-Saupe potential with a prolonged life, which seems an appropriate statement to finish a paper dedicated to Alfred Saupe's 70th birthday.

APPENDIX

In this appendix we shall calculate $\Sigma B(R)/R^6$ or $\Sigma C(R)/R^6$ as to be used in eq. (12), for the special case of a spheroid with its long axis parallel to the director. From eq. (11) we see that in order to do so we have to integrate

three functionals, $1/R^6$, Z^2/R^8 and Z^4/R^{10}, over the volume outside the spheroid. We shall use cylindrical coordinates with $R^2 = x^2 + y^2 + z^2 = r^2 + z^2$. The spheroid has short and long semi-axes b and a, respectively. Then the excentricity is defined as: $e^2 = 1 - b^2/a^2$. On the surface of the spheroid

$$R^2 = R_0^2 = b^2 + e^2 z^2;$$

$$r^2 = r_0^2 = b^2 + e^2 z^2 - z^2.$$

The particle density is given by:

$$N = \frac{1}{V} = \frac{3}{4\pi ab^2}. \tag{A1}$$

Now we can proceed to the actual integration, where the volume outside the ellipsoid will be denoted by τ. This first integration is

$$\sum_k R^{-6} \approx N \iiint R^{-6} d\tau$$

$$= 4\pi N \left[\int_0^a dz \int_{r_o}^\infty \frac{rdr}{(r^2 + z^2)^3} + \int_a^\infty dz \int_0^\infty \frac{rdr}{(r^2 + z^2)^3} \right]$$

The integrals can be evaluated using

$$\int \frac{rdr}{(r^2 + z^2)^{n+1}} = \frac{-1}{2n(r^2 + z^2)^n}, \tag{A2}$$

leading to

$$\sum_k R^{-6} \approx \frac{1}{9}\pi^2 N^2 \left[4\left(\frac{b}{a}\right)^2 + 6 + \frac{6a}{eb}\text{arctg}\left(\frac{ea}{b}\right) \right]. \tag{A3}$$

The second integration is

$$\sum_k Z^2/R^8 \approx N \iiint Z^2 R^{-8} d\tau$$

$$= 4\pi N \left[\int_0^a z^2 dz \int_{r_o}^\infty \frac{rdr}{(r^2 + z^2)^4} + \int_a^\infty z^2 dz \int_0^\infty \frac{rdr}{(r^2 + z^2)^4} \right].$$

Using eq. (A2) this can be evaluated similarly as above, leading to

$$\sum_k Z^2/R^8 \approx \frac{1}{9}\pi^2 N^2 \left[\left(\frac{8}{3} - \frac{2}{e^2}\right)\left(\frac{b}{a}\right)^2 + \frac{1}{e^2} + \frac{1}{e^3}\frac{a}{b}\,\text{arctg}\left(\frac{ea}{b}\right) \right].$$ (A4)

Finally we obtain for the third integration

$$\sum_k Z^4/R^{10} \approx N \iiint Z^4 R^{-10} d\tau$$

$$= 4\pi N \left[\int_0^a z^4 dz \int_{r_0}^\infty \frac{r\,dr}{(r^2 + z^2)^5} + \int_a^\infty z^4 dz \int_0^\infty \frac{r\,dr}{(r^2 + z^2)^5} \right].$$

Again using eq. (A2) this leads to

$$\sum_k Z^4/R^{10} \approx \frac{1}{9}\pi^2 N^2 \left[\left(2 - \frac{1}{e^2} - \frac{3}{4e^4}\right)\left(\frac{b}{a}\right)^2 \right.$$

$$\left. + \frac{3}{8e^4} + \frac{3}{8e^5}\frac{a}{b}\,\text{arctg}\left(\frac{ea}{b}\right) \right].$$ (A5)

Using eqs. (A3–A5) we calculate

$$\sum_k B(R)/R^6 = \frac{1}{9}\pi^2 N^2 \left[\left(4 - \frac{6}{e^2}\right)\left(\frac{b}{a}\right)^2 \right.$$

$$\left. + \left(\frac{3}{e^2} - 6\right)\left\{1 + \frac{1}{e}\frac{a}{b}\,\text{arctg}\left(\frac{ea}{b}\right)\right\} \right],$$ (A6)

$$\sum_k C(R)/R^6 = \frac{1}{9}\pi^2 N^2 \left[\left(\frac{2}{3} + \frac{7}{e^2} - \frac{27}{4e^4}\right)\left(\frac{b}{a}\right)^2 \right.$$

$$\left. + \left(6 - \frac{8}{e^2} + \frac{27}{8e^4}\right)\left\{1 + \frac{1}{e}\frac{a}{b}\,\text{arctg}\left(\frac{ea}{b}\right)\right\} \right].$$ (A7)

In the limit $a \to b$ eqs. (A6) and (A7) give 0 and $(32/135)\pi^2 N^2$, respectively; the values expected for a sphere. From, these equations the curves labelled a in Figure 3 were calculated numerically (in units of N^2).

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