Relations between Nematic Potential and Order Parameters $\langle P_2\rangle$ and $\langle P_4\rangle$

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The Maier-Saupe theory is employed in order to calculate order parameters $\langle P_2\rangle$, $\langle P_4\rangle$ from the nematic potential q. The relation between $\sigma = q/(RT)$ and $S = \langle P_2\rangle$ corresponds well with a recently established formula by Kalmykov. The relation between the order parameters is in accordance with the analytic expression $\langle P_4\rangle = 5/7\ \langle P_2\rangle^2$ proposed by Zanonni, but deviates significantly from the Faber model, according to which $\log \langle P_4\rangle = (10/3) \log \langle P_2\rangle$. Experimental results for 5CB obtained from Raman measurements, however, are in better agreement with the Faber model.

Key words: Liquid Crystals; Nematic Potential; Order Parameters.

1. Introduction

Long range orientational ordering of molecules in the nematic phase can fully be described if the orientational distribution function $f(\theta)$ is known (θ is the angle between the axis of symmetry of the molecule and the director). This allows to calculate a set of order parameters $\langle P_1\rangle$ being expansion coefficients of $f(\theta)$ into Legendre polynomials $P_1(\cos\theta)$ (1 even) [1, 2]. The first two order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ can be obtained experimentally [1]. Thus a knowledge of $f(\theta)$ implies that all the order parameters can be calculated. On the other hand, a knowledge of $\langle P_2\rangle$ and $\langle P_4\rangle$ yields more information about the distribution function [2]. A special form of $f(\theta)$ was postulated by Maier and Saupe (MS) [3] or obtained by solving the Fokker-Planck equation for a given problem [4]. However, in both cases the experimentally determined nematic potential q is needed for the calculation.

In [5], the MS theory [3] was employed in order to calculate the order parameter:

$$S = \langle P_2\rangle = \langle P_2(\cos\theta)\rangle = 3\langle \cos^2\theta\rangle/2 - 1/2, \qquad (1)$$

from the nematic potential q. In this paper we extend the calculation to

$$\langle P_4\rangle = \langle P_4(\cos\theta)\rangle = (35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3)/8, \qquad (2)$$

where the averages of the $\cos\theta$ functions can be obtained from the expressions

$$\left\langle \cos^2\theta \right\rangle = \frac{\int_0^\pi \cos^2\theta\, f(\theta)\sin\theta\, \mathrm{d}\theta}{\int_0^\pi f(\theta)\sin\theta\, \mathrm{d}\theta}, \qquad (3)$$

$$\left\langle \cos^4\theta \right\rangle = \frac{\int_0^\pi \cos^4\theta\, f(\theta)\sin\theta\, \mathrm{d}\theta}{\int_0^\pi f(\theta)\sin\theta\, \mathrm{d}\theta}.$$

The distribution function is taken according to the MS mean field theory [3]:

$$f(\theta) = f(0)\exp(-\sigma \sin^2\theta), \quad \sigma = \frac{q}{RT}. \qquad (4)$$

The nematic potential can be obtained from the retardation factor $g_{||}$, being the measure of the slowing down of the relaxation times at the nematic – isotropic phase transition [6, 7]. The order parameters can be derived from dielectric relaxation measurements that have already been employed by us to 8PCH [8]. The reliability of this procedure will be discussed in a subsequent paper [9] where order parameters derived for several nematics will be compared with those obtained by other experimental methods. In this paper we present some general relations between the order parameters $\langle P_2\rangle$, $\langle P_4\rangle$ and the nematic potential q. Some numerical data for $\langle P_4\rangle$ are gathered in Table 1.

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Table 1. Order parameter $\langle P_4 \rangle$ as a function of the nematic potential q/RT in steps of 0.1.

q/RT	**0.0**	**0.1**	**0.2**	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**	**0.8**	**0.9**
2.0	0.058	0.063	0.070	0.076	0.083	0.089	0.096	0.103	0.111	0.118
3.0	0.126	0.133	0.141	0.149	0.157	0.165	0.173	0.182	0.190	0.198
4.0	0.206	0.214	0.223	0.231	0.239	0.247	0.255	0.263	0.271	0.279
5.0	0.287	0.295	0.303	0.310	0.318	0.325	0.332	0.340	0.347	0.354
6.0	0.361	0.368	0.375	0.381	0.388	0.394	0.401	0.407	0.413	0.419
7.0	0.425	0.431	0.437	0.443	0.448	0.454	0.459	0.465	0.470	0.475
8.0	0.480	0.485	0.490	0.495	0.500	0.504	0.509	0.513	0.518	0.522

2. Relations between the Order Parameters and the Nematic Potential

It was already shown in [5] that S is roughly proportional to q (at least for smaller values of S) which is a basic assumption of the Maier-Saupe theory [3]. Numerical data for S versus $\sigma = q/RT$ are given in [5]. Another relation between S and σ has been derived by Kalmykov and Coffey (KC) [10] in solving the Fokker-Planck equation for rotational Brownian motion with the use of the Maier-Saupe mean field potential. The exact solution of the problem can well be approximated by

$$\sigma = \frac{3S(5-\pi S)}{2(1-S^2)} \,. \tag{5}$$

Also this equation was applied to results on 8PCH [8]. In Fig. 1 we present σ as a function of S after MS and KC without referring to a specific substance. The two curves practically coincide, although the relations between q and S have been derived in a completely different manner.

Figure 2 shows the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as functions of σ calculated with (2) and (3). In the whole range $\langle P_4 \rangle$ is significantly smaller than $\langle P_2 \rangle$. This is normally the case when a cylindrical molecule is dissolved in a uniaxial (nematic) phase [2] and is in accord with experimental findings for nematics [1, 11–13]. The majority of the molecules is parallel to the director. Nevertheless, if both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are considered, the mean field theories give better agreement with the experimental data for many characteristic properties of the nematic phase [14, 15]. It should be noted that for special systems $\langle P_4 \rangle$ can even be larger than $\langle P_2 \rangle$ [2].

3. Relations between $\langle P_2 \rangle$ and $\langle P_4 \rangle$

According to theoretical considerations [2, 11, 15, 16] $\langle P_2 \rangle$ and $\langle P_4 \rangle$ should be interrelated. In order to analyse the relation between them in more detail, Fig. 3 shows a plot of $\langle P_2 \rangle$ versus $\langle P_4 \rangle$, where also recent data for 5CB have been included. The latter results have been derived from Raman measurements [13] at various pressures and temperatures. The figure shows that they markedly deviate from the MS theory. Dalmolen *et al.* [17] attributed the deviation from the MS theory (in that $\langle P_4 \rangle$ was too small for the lower members, 5CB, 6CB, of the alkylcyano-biphenyls) to antiparallel molecular associations.

A plot of log $\langle P_4 \rangle$ against log $\langle P_2 \rangle$ yields approximately a straight line, see Fig. 4, where also relations proposed by Zannoni and Faber are shown. The curve calculated in the frame of the MS theory corresponds very well with $\langle P_4 \rangle = 5/7\, \langle P_2 \rangle^2$, reported by Zannoni for $\langle P_2 \rangle$ up to 0.6 [2].

Faber [16] has developed a model, in which the relation $\log \langle P_4 \rangle = 10/3\, \langle P_2 \rangle$ is derived from fluctuations of the nematic director field. The corresponding curve (Fa) deviates significantly from the calculated MS curve. Results (×) from resonance Raman scattering [13], however, seem to be better related to the Faber model. A similar behaviour was previously observed for PCH5 [12]. We shall come back to this discussion in the forthcoming paper [9].

4. Conclusions

The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were calculated on the basis of the Maier and Saupe mean field theory of the nematic state. The dependence of $S = \langle P_2 \rangle$ on the nematic potential $\sigma = q/RT$ agrees well with the formula derived recently by Kalmykov and Coffey [10]. The relationship between $\langle P_4 \rangle$ and $\langle P_2 \rangle$ is quadratic, in agreement with Zannoni's coefficient 5/7. However, recent results derived from Raman measurements indicate that the relationship is better described with the Faber model.

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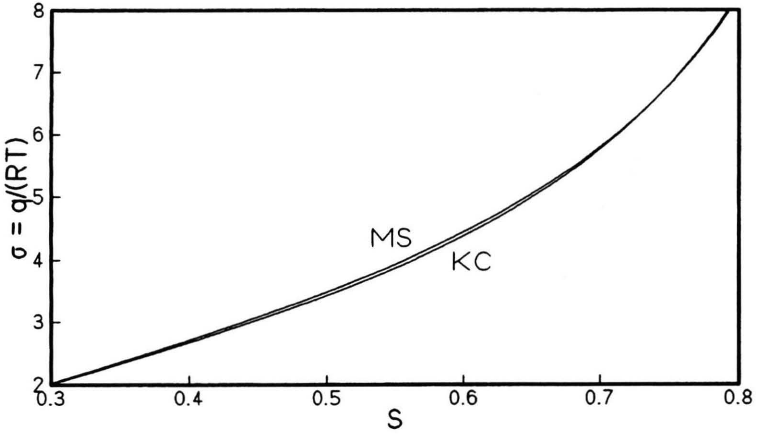

Fig. 1. Nematic potential $\sigma = q/RT$ as a function of the order parameter S. MS: Maier Saupe theory [3], KC: (5).

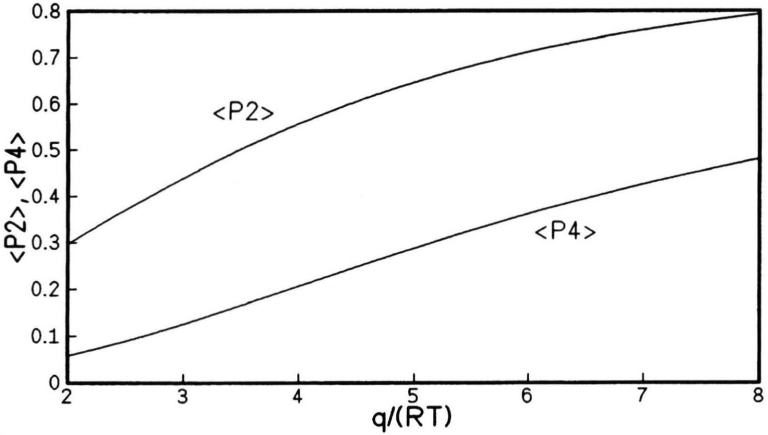

Fig. 2. $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as a function of the nematic potential q/RT.

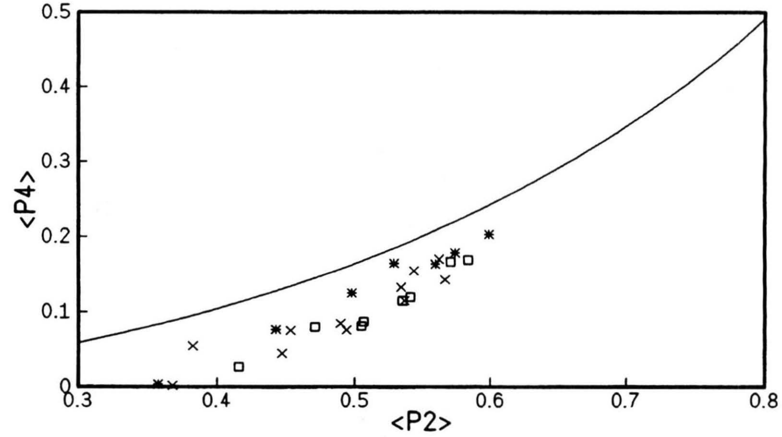

Fig. 3. $\langle P_4 \rangle$ as function of $\langle P_2 \rangle$, calculated in the frame of the MS theory (solid line) in comparison with experimental results for 5CB [13]: × 35 °C, ✱ 60 °C, □ 49 °C.

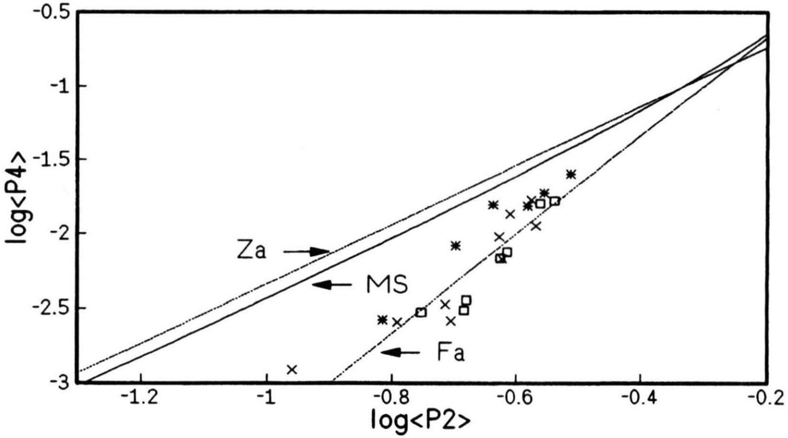

Fig. 4. log $\langle P_4 \rangle$ against log $\langle P_2 \rangle$, MS: calculation after Maier-Saupe, Za: Zannoni [2], Fa: Faber model [16], × 35 °C, ✱ 60 °C, □ 49 °C: experimental results for 5CB after Raman measurements [13].

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