Nematic Potential and Order Parameter Determined from Dielectric Measurements

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The Maier-Saupe theory is employed in order to calculate order parameters S from the nematic potential q. It is found that one of the basic assumptions of the Maier-Saupe theory, $q \sim S$, is approximately fulfilled. The relation between q and S is analysed for various state changes. Previously reported findings for 7 PCH that $q \sim S$, not fulfilled along isochoric changes, can be explained by taking into account the pressure and temperature dependences of q. The procedure described in this paper allows to treat experimental data for the nematic potential in a unique way, without being affected by inadequacies of experimentally determined order parameters.

Key words: Liquid Crystals; High Pressure; Nematic Potential; Dielectric Relaxation.

1. Introduction

We have demonstrated recently that high-pressure dielectric measurements together with the equation of state provide useful information to test molecular statistical theories [1]. In order to analyse the dielectric properties of nematic liquid crystals knowledge of the order parameter S is indispensable. However, high-pressure data for S are very scarce and partially doubtful. Results have been published e.g. for some nCBs [2–4] and 7PCH [5], but the authors point out that many corrections are necessary, partially due to experimental flaws [3, 4]. In spite of these shortcomings we have used the S data for the analysis of the high-pressure behaviour of the nematic potential q (calculated from the retardation factors) under various conditions [1, 6, 7]. In particular, we examined the proportionality between q and S, which is an important assumption in the Maier-Saupe theory [8]. In this analysis both quantities, q and S, were taken from different experiments.

On the other hand, the order parameter can be calculated in the frame of the Maier-Saupe theory from the nematic potential derived from dielectric relaxation measurements. It has been shown that such a theoretical calculation of S agrees fairly well with experimental results obtained by various methods at ambient pressure as well as at higher pressures [9, 10]. In this work we apply

such calculations for the analysis of recently obtained high-pressure dielectric data.

2. Calculation of the Order parameter

In the nematic phase, the order parameter $S = \langle 3 \cos^2\theta - 1 \rangle/2 = 3 \langle \cos^2\theta \rangle/2 - \frac{1}{2}$ can be obtained from the expression

$$\langle \cos^2\theta \rangle = \frac{\int_0^\pi \cos^2\theta \, f(\theta) \sin\theta \, d\theta}{\int_0^\pi f(\theta) \sin\theta \, d\theta} \qquad (1)$$

where θ is the angle between the molecular symmetry axis and the director, and the angular distribution function $f(\theta)$ is taken in the simplest form proposed by Maier and Saupe [8]. It depends on the nematic potential q, or $\sigma = q/kT$:

$$f(\theta) = C \exp[-q/(kT) \sin^2\theta], \qquad (2)$$

Equation (1) was integrated numerically. Some data are gathered in Table 1 in steps of $\sigma = 0.1$. They can be fitted to a polynomial: $S = a_0 + a_1\sigma + a_2\sigma^2 + a_3\sigma^3$ with $a_0 = 0.0375$, $a_1 = 0.1308$, $a_2 = 4.38 \cdot 10^{-3}$, $a_3 = -1.22 \cdot 10^{-3}$. In Fig. 1, $\sigma = q/kT$, and σ/S are plotted as functions of S. Clearly σ is practically proportional to S for $S < 0.6$. Thus, one important assumption of the Maier-Saupe theory ($q \sim S$) seems to be fulfilled, at least partly for isothermal state changes in the lower range of order param-

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Table 1. Order parameter S as a function of the nematic potential in steps of 0.1.

q/kT	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
2.0	0.297	0.312	0.327	0.342	0.356	0.371	0.385	0.399	0.412	0.426
3.0	0.439	0.452	0.465	0.478	0.490	0.502	0.513	0.525	0.536	0.546
4.0	0.557	0.567	0.577	0.587	0.596	0.605	0.614	0.622	0.631	0.639
5.0	0.646	0.654	0.661	0.668	0.675	0.682	0.688	0.694	0.700	0.706
6.0	0.712	0.717	0.722	0.727	0.732	0.737	0.742	0.746	0.750	0.755
7.0	0.759	0.763	0.766	0.770	0.774	0.777	0.781	0.784	0.787	0.790
8.0	0.793	0.796	0.799	0.802	0.804	0.807	0.809	0.812	0.814	0.817
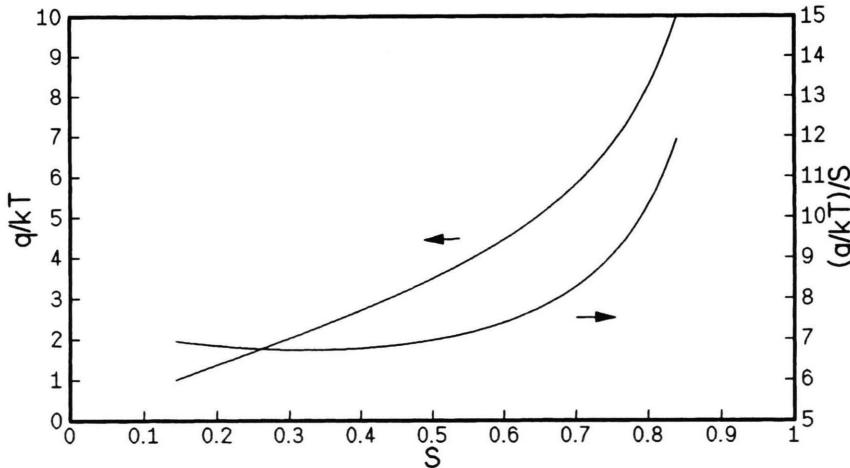
Fig. 1. Nematic potential $\sigma = q/kT$, and σ/S as a function of the order parameter.
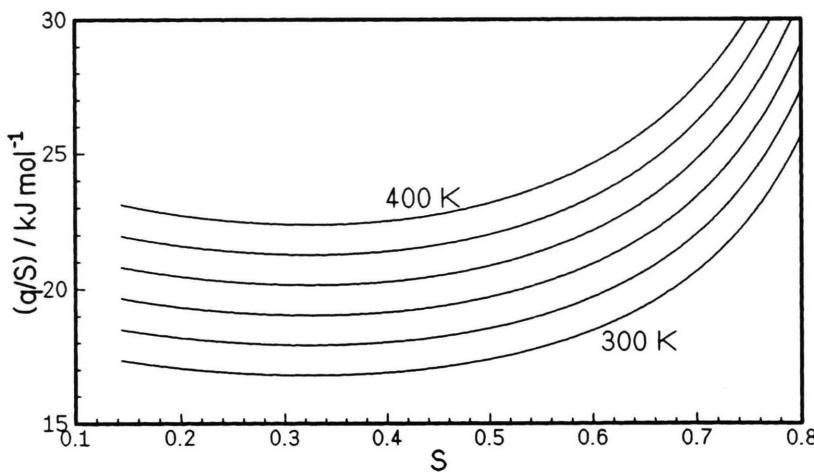
Fig. 2. Nematic potential q/S as a function of the order parameter for various isotherms. The temperatures vary in steps of 20 K from 300 to 400 K.

eters. A comparison with experimental results for other state changes will be given in Chapter 3.

The ratio of $q/S = \upsilon$ is discussed in the literature as an interaction coefficient that has been evaluated in detail for various homologous series of liquid crystals [1, 3, 11,

12]. It is assumed that υ is independent of the temperature, but is a function of the molar volume, usually expressed as a power law: $\upsilon = \upsilon_0 \, V^{-\gamma}$ [1, 13]. In order to discuss the relation between q and S in more detail, we plot q/S as a function of S for temperatures in steps of

20 K between 300 and 400 K, see Figure 2. In this temperature range (that practically covers most of the nematics, which we have been studied in the past) the interaction coefficient increases from ~ 17 to 24 kJ/mol with rising temperature. These values are somewhat higher than experimental findings for υ [1, 3]. Varying values for υ have been related to changes of the intramolecular core or the alkyl chain length [1, 11]. Figure 2 only predicts that higher values are expected, when the nematic range is shifted to higher temperatures. This is roughly the case for the series nCB, nPCH and nCCH in this order.

3. Presentation of Experimental Data for the Nematic Potential

In Fig. 3 we present q as a function of S for the same isotherms as in Figure 2. The figure shows as an example previously reported q-data for 7 PCH [7] under isobaric and isochoric conditions. Apparently, the relation $q \sim S$ is not fulfilled along the isochoric line as was reported in [7]. The absolute S-values for 7 PCH, however, are smaller than derived from Emsley et al. [5, 7]. On the other hand, for the points belonging to the isobaric lines, $q \sim S$ is roughly valid. This can be understood, when we take into account the following experimental findings. For all nematics so far studied we observe that q increases with pressure but decreases with temperature:

$$\left(\frac{\partial q}{\partial p} \right)_T > 0, \quad \left(\frac{\partial q}{\partial T} \right)_p < 0, \qquad (3)$$

According to well-known thermodynamic relations we can write

$$\left(\frac{\partial q}{\partial T} \right)_V = \left(\frac{\partial q}{\partial T} \right)_p + \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial q}{\partial p} \right)_T . \qquad (4)$$

Since $(\partial p/\partial T)_V > 0$, we find from (3) and (4) that $(\partial q/\partial T)_V$ is less negative than $(\partial q/\partial T)_p$. This means that "jumping" from one isotherm to another in Fig. 3 causes a smaller decrease in q along an isochore than along an isobar; thus the isochore deviates more strongly from $q \sim S$ than the isobar. Strictly speaking, also for an isobaric line $q \sim S$ is not exactly fulfilled. The ratio q/S becomes smaller than the slope along an isotherm, but this may be concealed by experimental scatter. Moreover, with increasing S the ratio q/S increases along an isotherm (see Fig. 2), and this fact compensates the "decrease" along the isobar. Thus we find that for isothermal changes (in particular at lower S values) and for isobaric changes (in particular at higher S values) the proportionality between q and S is roughly fulfilled, whereas for isochoric changes a stronger deviation is expected. This result is just opposite to what one would expect from the volume dependence of υ, according to which $\upsilon = q/S$ should be constant along an isochore. It should be noted that the phenomenological consideration above does not explain the failure of the MS-theory. In a forthcoming paper [14] other recently obtained experimental results will be analysed in a similar way. Possible corrections of (2) due to a fourth-rank order parameter $P_4 (\cos \theta)$ [3, 15] will also be considered.
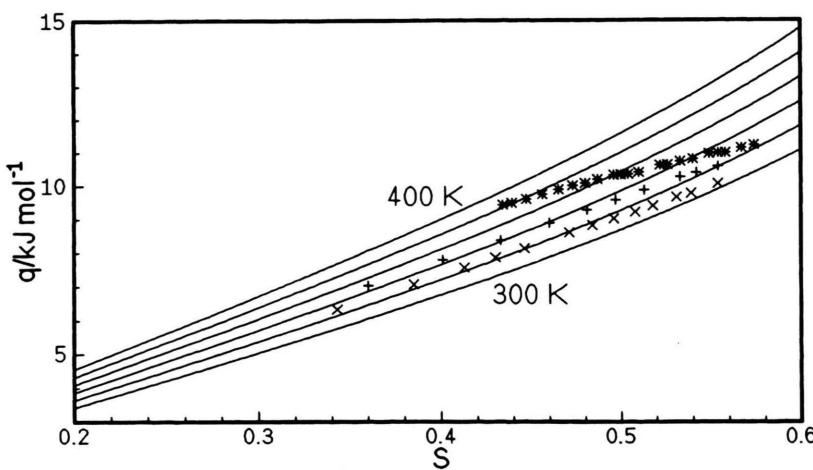

Fig. 3. Nematic potential q for 7 PCH as a function of the order parameter for various isotherms. The temperatures are the same as in Figure 2. * isochore at VM = 292 cm^3 mol^{-1}, + isobar at 43 MPa, × isobar at 1 atm.

Anyway, within the limitations of the MS-theory the procedure described in this paper is independent of the experimental data for the order parameter. This allows one to treat experimental findings for the nematic potential in a unique way, without being affected by experimental inadequacies of order parameter.

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