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Simple experimental assessment of smectic translational order parameters

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A procedure to obtain the smectic translational order parameter Σ from the temperature-dependent intensity I of the fundamental (001) smectic layer peak, observed in small-angle x-ray scattering experiments, is presented. We report results obtained with this procedure on the smectic-A or chiral smectic-A phases of six different liquid crystals, among them a "de Vries"-type 2-{4′-[1″,1″-dihydro-2″-(2″-perfluorobutoxyperfluoroethoxy)- perfluoroethoxy]} phenyl-5′-octylpyrimidine(3M8422) and the antiferroelectric R-4-(1-methylheptyloxycarbonyl)phenyl-4′-octloxybiphenyl-4-carboxylate (MHPOBC) materials. The smectic order parameters obtained are in the range between 0.5 and 0.9. For the "de Vries"-type 3M 8422 we found remarkably high values of Σ in the order of ∼0.9.

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The smectic translational order parameter Σ and the smectic layer spacing d are the most important parameters to characterize the layer structure of any smectic or lamellar liquid-crystalline phase. Experimental measures of d are accurately obtained from the small-angle x-ray scattering (SAXS) of the smectic layers. The translational order parameter for simple molecular crystals was first defined by Kirkwood and Monroe in their theory of fusion [1]. For liquid crystals the smectic translational order parameter Σ was introduced by Kobayashi [2,3] and McMillan [4,5]. McMillan assumed that the formation of a periodic one-dimensional (1D) smectic structure is mainly driven by core-core interactions leading to a layer structure where the highly polarizable aromatic cores of the mesogenic molecules are segregated from the flexible tails. In the resulting density wave $\rho(z)$ the smectic layer spacing d corresponds to its period. The amplitude of this density wave is described by the 1D translational order parameter Σ [4,5],

$$\Sigma = \left\langle \cos\left(\frac{2\pi z_i}{d}\right)\right\rangle, \tag{1}$$

where z_i is the position of the molecule i along the z axes, the origin of which is defined to meet a certain maximum of the density wave.

Even though Σ is the most important parameter to characterize the quality of smectic layering, our empirical knowledge on Σ is limited: To our knowledge experimental values of Σ are reported for less than tens of thousands of smectic materials [6–9]. In these rare cases Σ was always obtained by a method originally proposed by Leadbetter *et al.* [6,10]. This method requires the presence of higher-order x-ray diffraction peaks, which are difficult to observe in the majority of smectic liquid crystals. It further assumes Gaussian positional fluctuations of the smectogenic molecules around their equilibrium z position and, finally, it crucially relies on calculations of molecular structure factors derived from the assumption of a certain dominant molecular conformation. Due to these restrictions of the "Leadbetter method" we started to work on a more general procedure where the smectic translational order parameter is obtained from the temperature-dependent intensity $I(T)$ of the (001) fundamental smectic layer peak, easily observed in SAXS experiments. We now report the results obtained with this procedure which is to some extent analogous to the "Haller method" where the orientational order parameter is determined by an extrapolation of the temperature-dependent optical birefringence to zero absolute temperature [11].

According to Leadbetter [10], Σ is obtained by comparing the (001)-intensity $I(T)$ actually observed at a certain temperature T with the (001)-intensity I_0 which would result from the same smectic structure but with perfect 1D translational order,

$$\frac{I(T)}{I_0} = \Sigma^2. \tag{2}$$

Since I_0 thus refers to a hypothetical state of matter the fundamental problem in any experimental determination of Σ is to find a reasonable estimate of I_0. Whereas the Leadbetter method estimates I_0 by structure-factor calculations we estimated I_0 by a "Haller-like" extrapolation of $I(T)$ to zero absolute temperature where—due to the absence of thermal fluctuations—the smectic structure is assumed to be perfectly ordered. An example of this extrapolation procedure is shown in Fig. 1: The fundamental (001) smectic layer peak in the smectic-A (SmA) phase of octyloxycyanobiphenyl (8OCB) (cf. Fig. 2) is seen in the experimental SAXS profile of the scattered intensity I_s vs the scattering angle θ recorded at 60.8 °C [Fig. 1(a)]. Integration of the peak areas at several temperatures T leads to the temperature-dependent intensity $I(T)$ as shown in Fig. 1(b). The integrated intensity was used instead of the peak maxima since the width of the layer peak is due to quasi-long-range order and instrumental resolution not infinitely small. Following the general theory of phase transitions and critical phenomena we now assume a power-law dependence of the order parameter Σ in terms of the reduced temperature τ,

$$\Sigma = |\tau|^{\beta}, \tag{3}$$

where $\beta > 0$ denotes the order-parameter exponent. In the definition of $\tau \equiv (T/T_c) - 1$ the temperature T_c is the second-

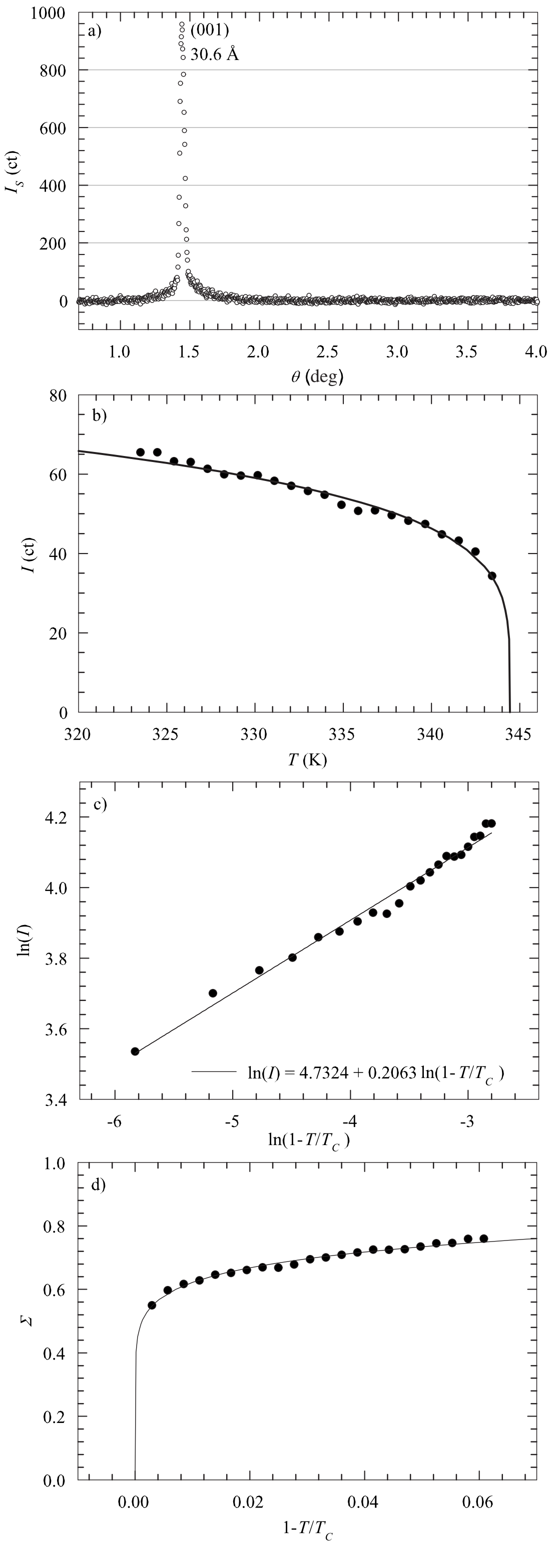

FIG. 1. Determination of the smectic order parameter Σ for the smectic A phase of 8OCB. For explanations see the text.

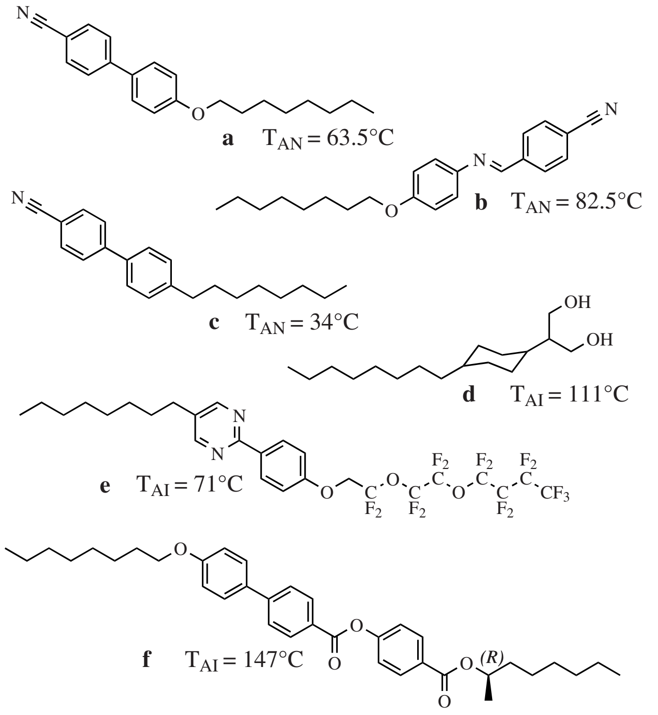

FIG. 2. The six different liquid crystals investigated: 8OCB (a), 4-cyanobenzylidene-4′octyloxyaniline (CBOOA) (b), and octylcyanobiphenyl (8CB) (c) show the simple phase sequence of crystalline–smectic-A–nematic–isotropic and are well-known standard liquid crystal materials. Furthermore, the amphotropic 2-(trans-4-octylcylcyclohexyl)-propane-1,3-diol (DIOL) (d), the "de Vries"-type substance 3M 8422 (e), and the antiferroelectric MHPOBC (f) were studied. T_{AI} and T_{AN} denote the smectic-A–to–isotropic and smectic-A–to–nematic transition temperatures, respectively.

order phase transition temperature from the SmA phase into either the nematic or the isotropic phase. In the more common case of a first-order (isotropic-to-SmA or nematic-to-SmA) transition T_c is the upper stability limit (superheating limit) of the SmA phase which appears slightly above the first-order transition temperature T_0. For the SmA phase at temperatures $T < T_0 < T_c$ we thus obtain

$$\Sigma = [1 - (T/T_c)]^{\beta} \tag{4}$$

and with Eq. (2) the temperature-dependent intensity $I(T)$ is given by

$$I(T) = I_0[1 - (T/T_c)]^{2\beta}. \tag{5}$$

Equation (5) is fitted to the experimental data in a double-logarithmic plot,

$$\ln I = \ln I_0 + 2\beta \ln[1 - (T/T_c)], \tag{6}$$

with T_c, β, and (the desired) I_0 being the parameters to fit. As seen in Figs. 1(b) and 1(c), the experimental $I(T)$ data are well described by Eqs. (5) and (6), respectively. Finally, with the I_0 known from the experimental data fit the order parameters $\Sigma(T)$ are calculated according to Eq. (1). The results for the SmA phase of 8OCB are shown in Fig. 1(d).

This procedure relies on less assumptions and simplifications than the Leadbetter method and can be applied to all smectic liquid crystals, provided the smectic-A temperature range is sufficiently wide to allow for a reliable extrapolation.

We thus applied the extrapolation procedure to SAXS re-

TABLE I. Values of the fit parameters β and T_c in Eq. (3) obtained for the liquid crystal materials under investigation (cf. Fig. 2).

Substance	8OCB	CBOOA	8CB	DIOL	3M 8422	MHPOBC
T_c [°C]	71.3	88.0	36.5	113.0	72.7	149.1
β	0.103	0.037	0.083	0.041	0.054	0.081
Phase above SmA	N	N	N	Iso	Iso	Iso

sults on the SmA or SmA* phases of the six different smectic liquid crystals shown in Fig. 2, among them a “de Vries”–type (3M 8422 [12,13]) and an antiferroelectric (MHPOBC [7,14]) material. Values of β and T_c obtained from the fit procedure for each of these materials are listed in Table I. As seen in Fig. 3 the smectic order parameters obtained for the three mesogens 8CB, 8OCB, and MHPOBC are in the typical range between 0.5 and 0.7 which is consistent with theoretical predictions and earlier experimental results from the Leadbetter procedure. In the case of the antiferroelectric MHPOBC, high values of the smectic order parameter of about 0.8 were reported for its smectic-C^*_{anti} phase in accordance to the anticlinic structure of this phase, which is expected to suppress out-of-layer fluctuations [7]. The high degree of smectic order seems not to be conserved in the SmA* phase of MHPOBC.

According to the present understanding of “deVries” materials the appearance of “de Vries” behavior is promoted by the (rather rare) combination of low orientational order (S) and high smectic translational order (Σ) [12]. A first example which clearly supports this view is the “de Vries”–type material 3M 8422, which combines a low orientational order parameter of ~0.5 [13] with a remarkably high smectic order parameter in the order of ~0.9. Among the other two mesogens (CBOOA, DIOL) with exceptionally high smectic order parameters of more than 0.8 is the amphiphilic DIOL, the smectic layer structure of which is known to be enhanced by intermolecular hydrogen bonds between the terminal hydroxy groups [15].

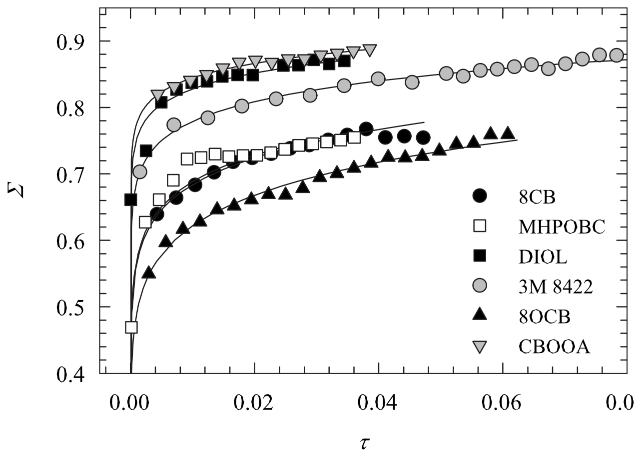

FIG. 3. Smectic order parameters Σ vs reduced temperatures t for the smectic-A phases of all six substances under investigation (cf. Fig. 2).

In conclusion, the extrapolation procedure seems to allow for a simple experimental assessment of smectic translational order even though it is based on fewer assumptions and simplifications than the classic “Leadbetter procedure.” Provided the smectic-A temperature range is sufficiently wide to allow for a reliable extrapolation this method opens a promising way to systematic studies of smectic translational order in homogeneous bulk phases as well as in complex, surface controlled geometries [16–19].

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