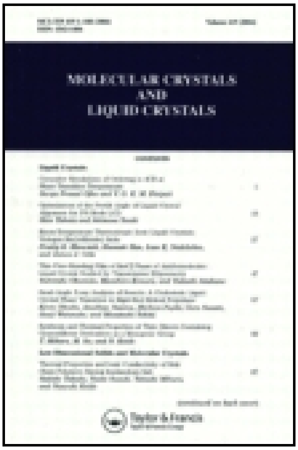

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Negative Order Parameters For Nematic Liquid Crystals?

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NEGATIVE ORDER PARAMETERS FOR NEMATIC LIQUID CRYSTALS?

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Abstract A model for a mesophase composed of rod-like molecules between which repulsive forces are dominant is discussed and shown to lead to values of $\bar{P}_2$ which are always positive. Under certain conditions however, the model leads to negative values of the order parameter $\bar{P}_4$. One negative experimental value for $\bar{P}_4$ has already been reported from Raman light scattering studies.

The orientational order of a single rod-like molecule in a uniaxial liquid crystal mesophase is only completely defined by the ensemble averages of all the even Legendre functions, $P_L(\cos\beta)$. Here β is the angle between the molecular symmetry axis and the director. The first of these averages, $\bar{P}_2$, is available from a variety of experimental techniques; its magnitude and temperature dependence then provide valuable tests of statistical mechanical theories of liquid crystals. One of the more successful theories of nematics was proposed by Maier and Saupe who employed a molecular field approximation.[1] Their expression for the single particle orientational pseudo-potential has since been generalised to

$$U(\beta) = \sum_{L(\text{even})} \bar{u}_L \bar{P}_L P_L(\cos\beta), \tag{1}$$

where $\bar{u}_L$ is determined by the average of the distance dependent expansion coefficients in the intermolecular potential.[2] Comparison of the observed and theoretical values of $\bar{P}_2$ reveals that the orientational pseudo-potential is apparently dominated by the first term, with L equal to two.[1,2] A further test of the theory would be provided if the higher order parameters were known, but, at present, only $\bar{P}_4$ is claimed to be available. The intensities of the vibrational lines in Raman light scattering experiments are related to $\bar{P}_4$[3] and this fact has been employed to measure $\bar{P}_4$.[4,5] The values of the higher order parameter are found to be considerably lower than those predicted by the Maier-Saupe theory and, in one instance, $\bar{P}_4$ is observed to be negative.[4] The discrepancy between theory and experiment may stem from the uncertainties of the light scattering technique[6] and this view is supported by electron resonance determinations of $\bar{P}_4$ for a spin probe, which are in good accord with theory.[7] Despite the uncertainty surrounding the values of $\bar{P}_4$ obtained from light-scattering experiments it is of interest to see if any model of a mesophase composed of rod-like molecules can lead to such negative values.

Within the context of the molecular field approximation the angular dependence of the pseudo-potential given in Eq. (1) is quite general although the form of the expansion coefficients, $u_L\bar{P}_L$, does depend on further approximations. Knowledge of the order parameters, $\bar{P}_2$ and $\bar{P}_4$, allows us to assess the reliability of the first term in the expansion without making any assumptions concerning the dependence of the expansion coefficients on the order parameters. The dependence of $\bar{P}_4$ on $\bar{P}_2$ predicted by the pseudo-potential, restricted to the first term, is shown, as the dashed line, in Fig. 1 and clearly provides a poor representation of the results obtained for 4'-n-heptyl-4-cyanobiphenyl[5] and for 4'-n-butylbenzylidene-4-cyanoaniline dissolved in 4-methyloxybenzylidene-4'-n-butylaniline.[4] The potential employed in the calculation is relatively weak as we can see from the slow variation of the singlet orientational distribution function shown in Fig. 2. The curve was

$$p(\beta) = \exp\{c_2P_2(\cos\beta)\}/\int\exp\{c_2P_2(\cos\beta)\}\sin\beta\, d\beta \quad (2)$$

calculated with c_2 equal to 2.3 which corresponds to an order parameter $\bar{P}_2$ of 0.5, typical of a real nematic. It is reasonable to assume that harsher repulsive forces are important in a liquid crystal mesophase and these could be incorporated into the theory by the retention of more terms in the expansion of the pseudo-potential. However this addition would introduce adjustable parameters into the theory and would also necessitate some assumption concerning the form of the expansion coefficients. We shall therefore adopt the other extreme and assume that the repulsive forces are dominant; under such conditions the singlet distribution function might be expected to adopt the rectangular form illustrated in Fig. 2. This

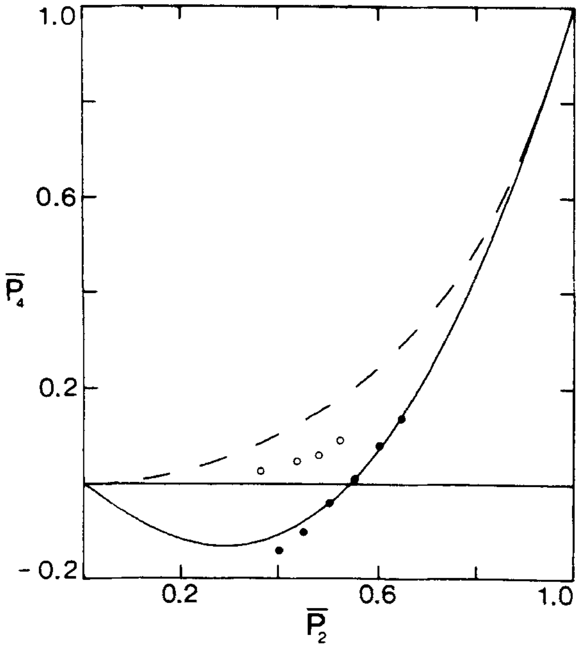

FIGURE 1 The dependence of the order parameter $\bar{P}_4$ on $\bar{P}_2$; the dashed line was calculated from Eq. (2) and the solid line from Eq. (3). The points correspond to 4'-n-butylbenzylidene-4-cyanoaniline in 4-methoxybenzylidene-4'-n-butylaniline (●) and 4'-n-heptyl-4-cyanobiphenyl (○).

would correspond to the purely repulsive pseudo-potential

$$\left.\begin{aligned} &U(\beta) = 0, \ \beta < \beta_0, \\ \text{and}\quad &U(\beta) = \infty, \ \beta > \beta_0; \end{aligned}\right\} \qquad (3)$$

the rectangular distribution function in Fig. 2 was calculated with β_0 equal to 52°, which also corresponds to $\bar{P}_2$ of 0.5. Such a potential would be experienced by a rod constrained to reside with its centre on the axis of a cylinder and executing maximum fluctuations of ± β_0. The orientational order parameters are readily calculated from this potential and are found, for example, to be

$$\bar{P}_2 = \cos\beta_0 (\cos\beta_0 + 1)/2 \qquad (4)$$

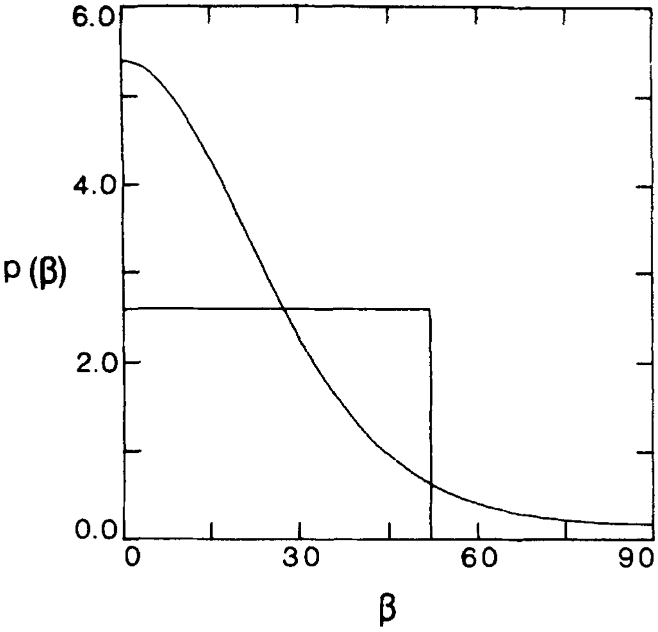

FIGURE 2 The two extreme orientational singlet distribution functions.

$$\bar{P}_4 = \cos\beta_0 (\cos\beta_0 + 1)(7\cos^2\beta_0 - 3)/8 \qquad (5)$$

These and the higher order parameters are readily obtained from the following general result

$$\bar{P}_L = \{P_{L+1}(\cos\beta_0) - P_{L-1}(\cos\beta_0)\}/(2L+1)(\cos\beta_0 - 1). \quad (6)$$

We can now see, from Eq. (4), that with this simple potential the order parameter $\bar{P}_2$ is always positive but that according to Eq. (5) $\bar{P}_4$ will be negative provided β_0 is greater than $\cos^{-1}(\sqrt{3/7})$, which is about 50°. The dependence of $\bar{P}_4$ on $\bar{P}_2$ calculated for this model is also given in Fig. 1, as the solid line, and this clearly shows the predicted negative regime which is in remarkably good agreement with one set of experimental results. The other set of results could be accounted for by taking some combination of the pseudo-potentials for the two extremes which we have considered but we prefer not to enter into such curve fitting exercises. The apparent success of this extreme form of the orientational pseudo-potential should not be taken to imply the dominance of repulsive forces in liquid crystals, until the values of the higher order parameter $\bar{P}_4$ have been confirmed.

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