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Banani Adhikari[ab]; Gurupada Chaudhuri[ab]; Ranjit Paul[ab]
[a] Physics Department, North Bengal University, Siliguri, India [b] Physics Department, Raiganj University College, Raiganj, W. Bengal, India

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Comparison of experimental order parameters of nematogens with Faber's theory

by BANANI ADHIKARI, GURUPADA CHAUDHURI and RANJIT PAUL*
Physics Department, North Bengal University, Siliguri-734430, India
† Physics Department, Raiganj University College, Raiganj, W. Bengal, India

Orientational order parameters $\langle P_4\rangle$, $\langle P_6\rangle$ and $\langle P_8\rangle$, as calculated from our X-ray diffraction studies with aligned nematic samples, have been compared with the predictions of Faber's continuum and Maier–Saupe mean-field theories. In contradiction to our previous finding regarding $\langle P_2\rangle$ and $\langle P_4\rangle$, the agreement with Faber's theory is not good. However, experimental inaccuracies and truncation errors during calculations preclude any definite conclusion on this matter.

In continuation of our previous study [1] comparing the experimental orientational order parameter (OOP) values $\langle P_2\rangle$ and $\langle P_4\rangle$, obtained in our laboratory from X-ray diffraction studies on aligned nematic samples, with those calculated from the continuum theory of Faber [2], we here compare the higher OOPs with theory. We have calculated the orientational distribution function $f(\beta)$ from the X-ray diffraction intensity distribution $I(\psi)$, using the expression derived by Leadbetter and Norris [3]

$$I(\psi)=C\int_{\beta=\psi}^{\pi/2} f(\beta)\sec^2\psi\,[\tan^2\beta-\tan^2\psi]^{-1/2}\sin\beta\,d\beta.$$

For the meaning of the symbols and the derivation of this equation, the reader is referred to the original paper [3]. A method of calculating $f(\beta)$ as a polynomial of $\cos^2\beta$ is given by Bhattacharjee *et al.* [4]. We reanalysed all our previous measurements of $I(\psi)$ to calculate normalized $f(\beta)$ up to the $\cos^{14}\beta$ term. Since the coefficients of $\cos^n\beta$ in the expression for $f(\beta)$ at first increase, but later decrease with increasing n, not much error is incurred by truncating the series after the term containing $\cos^{14}\beta$. Then, integrating $P_{2n}f(\beta)$ over all possible orientations, $\langle P_{2n}\rangle$ ($n=1$ to 5) can be obtained easily.

We also tried an alternative method of calculating $\langle P_n\rangle$. Using the relation,

$$f(\beta)=\sum_{n=1}^{5}\frac{4n+1}{2}\langle P_{2n}\rangle P_{2n}(\cos\beta), \tag{1}$$

one can write the P_{2n}s as polynomials in $\cos^2\beta$ and hence equate the coefficients of $\cos^2\beta$, $\cos^4\beta,\dots,\cos^{10}\beta$ on either side of equation (1). The coefficients on the right hand side of the equation contain $\langle P_2\rangle$, $\langle P_4\rangle,\dots,\langle P_{10}\rangle$. By solving the five simultaneous equations, the values of $\langle P_2\rangle$ etc. were determined. However, these values are quite different from those obtained from the previous method. Sometimes the calculated value of $\langle P_2\rangle$ was even greater than 1. The reason for this is not difficult to understand. The coefficient of $\cos^{10}\beta$ contains only $\langle P_{10}\rangle$ and its value is determined by the coefficient of $\cos^{10}\beta$ in the $f(\beta)$ expansion. However, the higher coefficients are more likely to have larger relative errors; hence not only is the $\langle P_{10}\rangle$

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* Author for correspondence.

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calculated in this manner subject to large error, but also this error is added to the value of $\langle P_8 \rangle$ when it is calculated from the coefficient of $\cos^8 \beta$, and so on. Hence, all errors accumulate in the value of $\langle P_2 \rangle$, which often becomes unrealistic. Hence this method is not used here to calculate order parameters.

In our last publication [1], we analysed data for 20 nematogens. Since then we have obtained X-ray diffraction data for two more compounds, *viz*, ethyl and heptyl members of the 5-(4-alkylcyclohexyl)-2-(4-cyanophenyl)-pyrimidine series [5]. We have obtained X-ray data at three and six different temperatures for the heptyl and ethyl compounds respectively.

Faber's continuum theory [2] predicts that $\ln\langle P_n \rangle/\ln\langle P_m \rangle = n(n+1)/m(m+1)$, independent of both the nature of the compound and the experimental temperature. We have already shown that this relation holds surprisingly well for the ratio of the logarithms of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ [1]. In the table, we have compared the ratios containing higher order parameters, as obtained from our experimental data, with those predicted from Faber's theory. We find from the table that the ratios with higher OOPs deviate progressively more from Faber's theory. There is also more scatter in the experimental data, which is reflected in the rather large values for the standard deviation of these ratios in the table.

In figure 1, we have plotted experimental $\ln\langle P_6 \rangle$ values against $\ln\langle P_4 \rangle$, together with the best fitted straight line through the experimental points and the curves according to the theories of Faber and of Maier and Saupe. The best fitted straight line has the following form:

$$\ln\langle P_6 \rangle = 0{\cdot}4721 + 1{\cdot}5203 \ln\langle P_4 \rangle. \qquad (2)$$

We had to exclude one experimental point from our calculations, since the $\langle P_6 \rangle$ value for this point was negative.

In figure 2, the same procedure is followed for $\langle P_6 \rangle$ and $\langle P_8 \rangle$. Here we had to discard 18 experimental points because of negative $\langle P_8 \rangle$ values. It may not be out of place to mention that in no case did we obtain negative $\langle P_2 \rangle$ or $\langle P_4 \rangle$ values from our experimental data. The best fitted straight line for this case is:

$$\ln\langle P_8 \rangle = 0{\cdot}5937 + 1{\cdot}2151 \ln\langle P_6 \rangle. \qquad (3)$$

Both these figures show that the experimental lines are closer to the Maier–Saupe curve than to the Faber curve. However, no great significance should be attached to this, since experimental uncertainties and truncation errors due to series termination certainly make the experimental values of $\langle P_6 \rangle$ and $\langle P_8 \rangle$ more unreliable than those for $\langle P_2 \rangle$ or $\langle P_4 \rangle$. Estimated errors in the calculated $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values are ±0·02. We are unable to estimate the errors in our calculated $\langle P_6 \rangle$ and $\langle P_8 \rangle$ values. However, these may be somewhat larger than 0·02.

We have found before [1] that the ratio R1 ($=\ln\langle P_2 \rangle/\ln\langle P_4 \rangle$) is significantly larger for compounds having long rigid cores. However, in the present work, we do not

Comparison of theoretical with experimental values of ratios of orientational order parameters.

Ratio	Continuum theory	Mean expt. values (±s.d.)
$R1 = \ln\langle P_2 \rangle/\ln\langle P_4 \rangle$	0·300	0·308±0·018
$R2 = \ln\langle P_4 \rangle/\ln\langle P_6 \rangle$	0·476	0·530±0·053
$R3 = \ln\langle P_6 \rangle/\ln\langle P_8 \rangle$	0·583	0·739±0·075

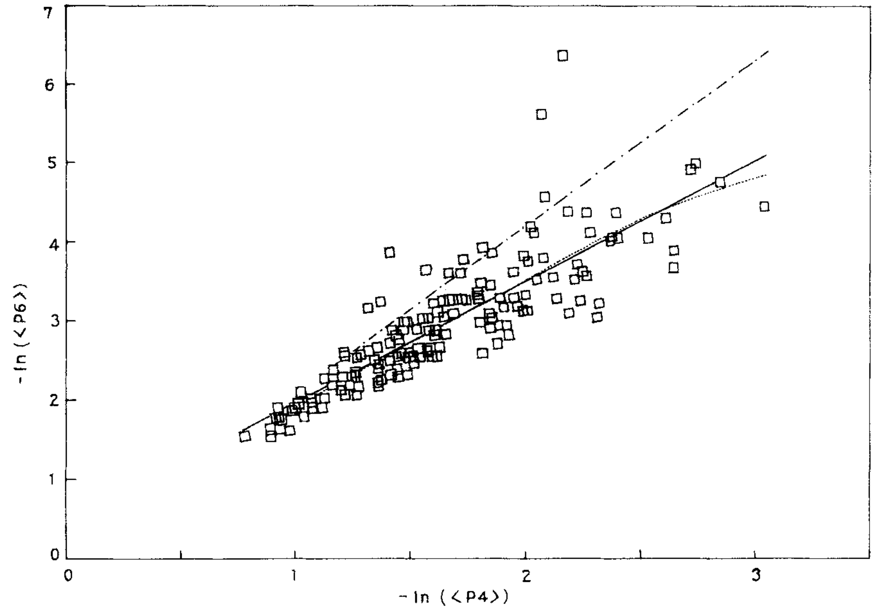

Figure 1. Comparison of trends in experimental $\langle P_4 \rangle$ versus $\langle P_6 \rangle$ values with those from different theories: □, experimental values; (·····), Maier–Saupe mean field theory; (—·—), Faber's theory; (——), linear least square fit (equation (2)).

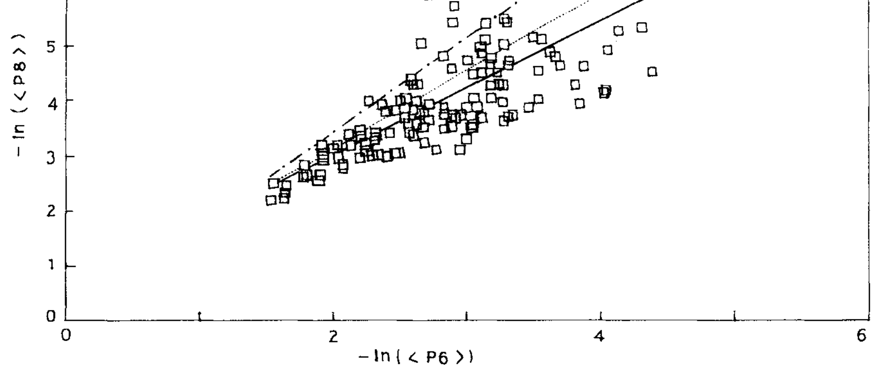

Figure 2. Comparison of trends in experimental $\langle P_6 \rangle$ versus $\langle P_8 \rangle$ values with those from different theories: □, experimental values; (·····), Maier–Saupe mean field theory; (—·—), Faber's theory; (——), linear least square fit (equation (3)).

find such a variation in the ratios R2 and R3 for these molecules. We think that more accurate experimental data are needed before any definite conclusion may be reached in this respect.

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