

## Randomness in nanoscopic liquid-crystal droplets —How small is too small?

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(received 7 January 2002; accepted in final form 6 May 2002)

PACS. 61.30.-v – Liquid crystals.

PACS. 71.15.Pd – Molecular dynamics calculations (Car-Parrinello) and other numerical simulations.

PACS. 61.20.Ja – Computer simulation of liquid structure.

**Abstract.** – We have used random matrix theory to obtain an exact result for the probability distribution of the nematic order parameter in a randomly oriented array of rod-shaped molecules. The result for the average order parameter is that  $\langle S(N) \rangle = \sqrt{81/40\pi N} + \mathcal{O}(N^{-1})$ . This disproves a conjecture that  $\langle S(N) \rangle$  should tend to  $\sqrt{2/3N}$ .

In studies of nematic liquid crystals, the order parameter  $S$  describes the tendency to alignment of an assembly of rod-shaped molecules. It takes on its maximum value of 1 when the long axes of the molecules are all perfectly parallel, and vanishes in an infinitely large ensemble in which the molecular orientation is completely random. In a finite ensemble of randomly oriented molecules, however,  $S$  will always be greater than zero, as it is defined as the largest eigenvalue of a traceless matrix. In this letter we present a calculation based on random matrix theory of the probable magnitude of  $S$  in small systems in the absence of any nematic interactions.

It is of considerable interest to be able to predict  $\langle S \rangle$  (the average value of  $S$ ) and its standard deviation in volumes of nematic liquid crystal sufficiently small that the number  $N$  of molecules cannot be considered infinite. For example, a polymer-dispersed liquid crystal [1] consists of a sheet of polymer within which a phase separation process has caused there to be dispersed minute droplets of liquid crystal. When the diameter of these droplets is of the order of the wavelength of visible light the material appears opaque. Application of an electric field, however, may orient the birefringent nematic droplets so that their optical properties match those of the polymer matrix, and the sheet becomes transparent, in effect forming an electrically switchable window blind. If the size of the droplets were reduced below the wavelength of light, a clear, haze-free, switchable birefringent film would result. The optical properties would depend on  $\langle S \rangle$  in the field-on and field-off states.

Another area in which there is a need for information about  $\langle S \rangle$  is in numerical simulations of liquid crystals where limitations on computational resources necessarily force consideration

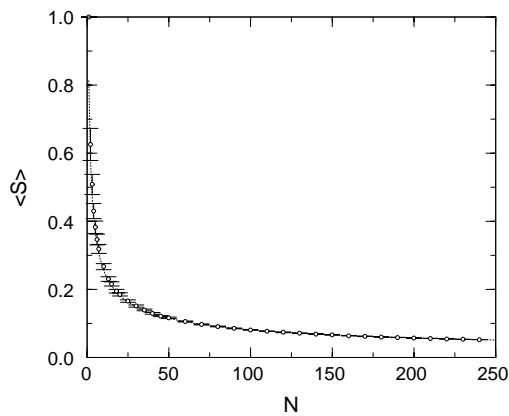


Fig. 1 – The plot shows the results of a numerical experiment to determine the average order parameter and its standard deviation in an ensemble of  $N$  randomly oriented molecules. The dotted line is a plot of  $\sqrt{2/3N}$ .

of small numbers of molecules. Indeed the model we solve below appears to have been first introduced by Eppenga and Frenkel [2] in their seminal Monte Carlo study of an idealized system of rods and plates. The problem of small numbers is particularly acute in the atomistic simulation of liquid crystals by the methods of molecular dynamics. The large number of atoms composing a single molecule (38 even in the simple mesogen 4-n-pentyl-4'-cyanobiphenyl, known as 5CB) makes it difficult to run realistic simulations of large assemblies of molecules. In order to estimate the significance of any apparent nematic order observed in the results of a simulation of a system of modest size it is necessary to know what  $\langle S(N) \rangle$  would be had the orientations of the  $N$  molecules been purely random.

The order parameter  $S$  of an assembly of rod-shaped molecules is defined as the largest eigenvalue of the tensor

$$\mathbf{Q} = \frac{1}{2N} \sum_{i=1}^N (3\hat{u}_i \hat{u}_i - \mathbf{I}), \tag{1}$$

with  $\hat{u}_i$  a unit vector in the direction of the molecular axis and  $\mathbf{I}$  the unit tensor. Eppenga and Frenkel [2] estimated  $\langle S(N) \rangle$  by forming the cubic equation for the eigenvalues and averaging the coefficients before solving it. The result of this procedure was that  $\langle S(N) \rangle$  was predicted to be  $\sqrt{3/4N} + O(N^{-1})$ .

More recently, Doerr and Taylor [3] performed a numerical experiment in which they repeatedly constructed arrays of  $N$  randomly oriented rods and tabulated the observed values of  $\langle S(N) \rangle$ . Their numerical results are shown in fig. 1. They found that the dotted line, which represents  $\sqrt{2/3N}$ , gave a good approximation to the observed values, and conjectured that  $\langle S(N) \rangle = \sqrt{2/3N}$  might be an exact result for the asymptotic form at large  $N$ . Here we shall analyze the full probability distribution of  $S(N)$  and find in particular that  $\langle S(N) \rangle = \sqrt{81/40\pi N}$ , very close to the form inferred by Doerr and Taylor.

The first step in the analysis is to determine the distribution of the quadrupole moment matrix. By making the assumption that the molecules are independent and randomly oriented, it is easy to show that the quadrupole moment vanishes on average and to determine the

covariance of the matrix elements. We find

$$\begin{aligned}\langle Q_{xx}^2 \rangle &= \langle Q_{yy}^2 \rangle = \langle Q_{zz}^2 \rangle = \frac{1}{5N}, \\ \langle Q_{xy}^2 \rangle &= \langle Q_{xz}^2 \rangle = \langle Q_{yz}^2 \rangle = \frac{3}{20N}, \\ \langle Q_{xx}Q_{yy} \rangle &= \langle Q_{xx}Q_{zz} \rangle = \langle Q_{yy}Q_{zz} \rangle = -\frac{1}{10N}.\end{aligned}\quad (2)$$

Since  $Q$  is traceless, we expect  $\langle (Q_{xx} + Q_{yy} + Q_{zz})^2 \rangle = 0$  and indeed eqs. (2) are consistent with this expectation.

To analyze the eigenvalue distribution, however, we need the full joint probability distribution of the six independent quadrupole matrix elements ( $Q_{xx}$ ,  $Q_{yy}$ ,  $Q_{zz}$ ,  $Q_{xy}$ ,  $Q_{xz}$  and  $Q_{yz}$ , the other off-diagonal elements being determined by the requirement that  $Q$  be symmetric). For large  $N$  this is given by

$$P(Q) = C \delta(\text{Tr } Q) e^{-b \text{Tr } Q^2}. \quad (3)$$

Here  $C$  is a normalization constant and  $b = 5/3N$ . Note that this distribution is rotationally invariant. The delta-function ensures that the quadrupole matrix be traceless. It is easy to verify that the distribution above leads to the correct covariance of the matrix elements. That it is the exact asymptotic distribution for large  $N$  follows from the central-limit theorem, since, according to eq. (1),  $Q$  is a sum of  $N$  independent, identically distributed random quantities.

Translating the distribution for the quadrupole matrix into the distribution for its eigenvalues is a formidable problem. Fortunately random matrix theory supplies the solution [4]. Random matrix theory was originally developed as a statistical theory of slow neutron resonances in nuclear physics. Its methods have since found many applications ranging from acoustics to zeta-function number theory. Applying a basic theorem of random matrix theory to our problem [5], we conclude that the eigenvalues of the quadrupole matrix should have the distribution

$$P(\omega_1, \omega_2, \omega_3) = A(\omega_1 - \omega_2)(\omega_1 - \omega_3)(\omega_2 - \omega_3) \delta(\omega_1 + \omega_2 + \omega_3) e^{-b(\omega_1^2 + \omega_2^2 + \omega_3^2)}. \quad (4)$$

It is assumed that the eigenvalues are in the order  $\omega_1 > \omega_2 > \omega_3$  and  $A$  is a normalization constant. Note that the distribution is highly correlated and the probability of degeneracy vanishes linearly with the separation of eigenvalues, an effect dubbed level repulsion in the random matrix literature.

Our main results follow from eq. (4). The average order parameter is

$$\begin{aligned}\langle S \rangle &= \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\omega_1} d\omega_2 \int_{-\infty}^{\omega_2} d\omega_3 \omega_1 P(\omega_1, \omega_2, \omega_3) \\ &= \sqrt{\frac{81}{40\pi N}}.\end{aligned}\quad (5)$$

In order to verify this result an extensive set of simulations were performed. The values of  $\langle S \rangle$  were determined for ensembles of  $N$  rods generated with random orientations. Because eq. (5) is an asymptotic value, it was necessary to extrapolate the results of the simulation to infinite  $N$ . This was achieved by plotting  $S\sqrt{N}$  as a function of  $1/\sqrt{N}$ , as shown in fig. 2. From this plot we see that the asymptotic value of  $\langle S \rangle$  at large  $N$  is clearly very close to the prediction of eq. (5), and definitely lies below the Doerr-Taylor conjecture of  $\sqrt{2/3N}$ . In addition, we see that the next term in the series expansion is given by the slope of the plot, giving

$$\langle S \rangle = \sqrt{\frac{81}{40\pi N}} + (0.115 \pm 0.002)N^{-1} + \mathcal{O}(N^{-3/2}). \quad (6)$$

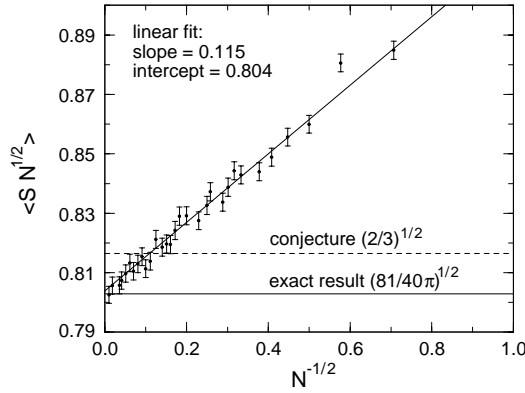


Fig. 2 – This plot shows that  $S\sqrt{N}$  as a function of  $1/\sqrt{N}$  approaches the exact asymptotic value of  $\sqrt{81/40\pi}$  (solid line) rather than the conjectured value of  $\sqrt{2/3}$  (dashed line) as  $N \rightarrow \infty$ . A straight-line fit to the data gives the leading correction term.

From the distribution (4) we can also determine that the standard deviation is  $\langle \delta S^2 \rangle^{1/2} = \sqrt{(0.0804\dots)/N}$ . Integrating over  $\omega_2$  and  $\omega_3$  yields the entire distribution for the order parameter:

$$\begin{aligned}
 P_N(S) &= \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\omega_1} d\omega_2 \int_{-\infty}^{\omega_2} d\omega_3 \delta(\omega_1 - S) P(\omega_1, \omega_2, \omega_3) \\
 &= \sqrt{\frac{6b}{\pi}} e^{-6bS^2} - \sqrt{\frac{3b}{2\pi}} (2 - 9bS^2) e^{-\frac{3}{2}bS^2}
 \end{aligned}
 \tag{7}$$

(see fig. 3). Note that for small  $S$ ,  $P(S) \rightarrow S^4$ . Thus, for any finite  $N$  it is very improbable that  $S$  will be substantially smaller than the average value.

The integrals over the eigenvalues evade the usual methods of random matrix theory due to the delta-function in eq. (4). They are most simply evaluated by making a change of variables

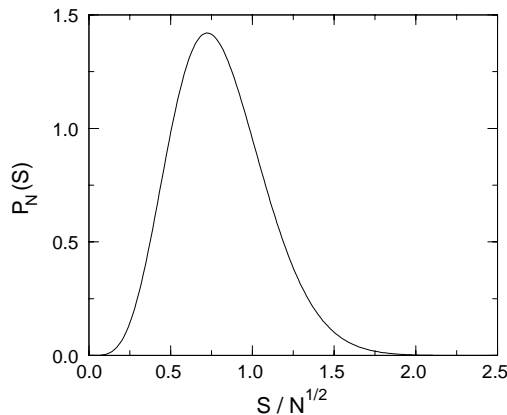


Fig. 3 – Exact distribution of the order parameter for large  $N$ .

via the orthogonal transformation

$$\begin{aligned}\omega_1 &= \frac{1}{\sqrt{3}} y_1 + \frac{1}{\sqrt{2}} y_2 + \frac{1}{\sqrt{6}} y_3, \\ \omega_2 &= \frac{1}{\sqrt{3}} y_1 - \frac{1}{\sqrt{2}} y_2 + \frac{1}{\sqrt{6}} y_3, \\ \omega_3 &= \frac{1}{\sqrt{3}} y_1 - \frac{2}{\sqrt{6}} y_2.\end{aligned}$$

The condition that  $\omega_1 > \omega_2 > \omega_3$  is enforced by restricting the integral in the  $y_2$ - $y_3$  plane to the  $60^\circ$  wedge defined by  $0 < y_2 < \sqrt{3}y_3$ .

The small- $S$  behavior of  $P(S)$  is due to level repulsion. For the order parameter to vanish the eigenvalues of  $Q$  must be threefold degenerate. That  $P(S)$  vanishes as the fourth power of  $S$  may be understood by noting that the threefold degenerate  $Q$  matrix is an isolated point in the five-dimensional space of traceless symmetric  $Q$  matrices.

The significance of this result is seen in the case of a nanoscopic droplet of 5CB of diameter 7 nm, and thus containing about 300 molecules [6]. The average order parameter would be about 0.05 even in a completely randomly oriented system, and so a value of  $S$  of at least 0.10 would be required to demonstrate the presence of any true nematic ordering in such a small system.

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This work was supported by the National Science Foundation under grants DMR98-04983 and DMR00-72935 and by the Donors of the Petroleum Research Fund. The authors acknowledge helpful conversations with P. PASINI and M. TSIGE.

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