Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: J. Y. Denham , R. L. Humphries & G. R. Luckhurst (1977): Computer Simulation Studies of Anisotropic Systems, I. A Linear Lattice, Molecular Crystals and Liquid Crystals, 41:3, 67-74

To link to this article: http://dx.doi.org/10.1080/01406567708071956

Mol. Cryst. Liq. Cryst., Vol. 41 (Letters), pp. 67-74

Printed in the United States of America

COMPUTER SIMULATION STUDIES OF ANISOTROPIC SYSTEMS, I. A LINEAR LATTICE

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Abstract We have studied the static properties of a linear array of rod-like particles using Monte Carlo simulation techniques. The calculated temperature dependence of the energy and specific heat are found to be in very good agreement with the exact thermodynamic properties. The model system is known to be rotationally disordered at all temperatures but this behaviour is only mimicked by the computer simulations when the number of particles exceeds one thousand.

Molecular field theories of nematic,[1] cholesteric[2] and certain smectic[3] liquid crystals have proved to be particularly successful in predicting both the existence of the various phase transitions and the magnitude of the order parameters. However such theories are, by their very nature unable to provide any information concerning the distribution functions involving two or more molecules. As a consequence the predictions, by molecular field theories, of those properties which depend on the short-range order are likely to be in error. Similar, although more severe, problems are encountered in theoretical studies of the molecular organisation in normal liquids. Here considerable progress has been made towards their solution by the use of computer simulation experiments.[4] The same simulation techniques should be equally valuable in theoretical investigations of liquid crystals, where the anisotropic part of the intermolecular potential is of vital importance. Indeed several such studies of the nematic phase in two and three dimensions have already been reported.[5,6,7] However the interpretation of the results of these experiments is not always straight-forward. For example, Monte Carlo calculations on an ensemble of hard spherocylinders failed to discover an orientationally ordered phase.[6] In contrast molecular dynamics experiments on ellipsoids interacting with a continuous short-range potential did demonstrate the existence of a nematic phase.[7] The discrepancy in these two results could be caused by the difference in the anisotropic pair potential or by problems of the simulation techniques when applied to systems capable of forming orientationally ordered phases. It is valuable therefore to apply the technique to models whose properties are known exactly and we present here the results of such an investigation using the Monte Carlo approach.

The model studied is a regular linear array of N rod-like particles constrained to lie in a plane; cylic boundary conditions are imposed in that the first and Nth particles are neighbours. The anisotropic interaction is restricted to nearest neighbours and takes the form

$$U(\theta) = -\varepsilon\, T_2(\cos\theta), \tag{1}$$

where T_2 (cos θ) is the second Chebychev polynomial cos2θ and θ is the angle between the molecular symmetry axes. In the thermodynamic limit, when N tends to infinity, the configurational contributions to the entropy, energy and specific heat are given by [8]

$$S = Nk\ln\{2\pi I_o(\varepsilon/kT)\} - (N\varepsilon/T) I_1(\varepsilon/kT)/I_o(\varepsilon/kT), \tag{2}$$

$$U = -N\varepsilon I_1(\varepsilon/kT)/I_o(\varepsilon/kT) \tag{3}$$

and

$$C_v = \frac{Nk}{2}\left(\frac{\varepsilon}{kT}\right)^2 \left[1+\frac{I_2(\varepsilon/kT)}{I_1(\varepsilon/kT)} - 2\left\{\frac{I_1(\varepsilon/kT)}{I_o(\varepsilon/kT)}\right\}^2\right]; \tag{4}$$

the symbol $I_n(\varepsilon/kT)$ denotes an nth order modified Bessel function. In addition this system does not exhibit a transition to a rotationally ordered phase but remains disordered at all temperatures.[8]

The Monte Carlo calculation was performed following the usual prescription and configurations were generated with a Boltzmann distribution in phase space.[4] The entropy is not readily available from such calculations[4] although both the energy and specific heat were evaluated. We also calculated an order parameter $\overline{T}_2$, defined as the ensemble average of $T_2(\cos\gamma)$, to characterise the long-range orientational order which might be exhibited by the system. Here γ is the angle between the molecular symmetry axis and the preferred molecular orientation which, by analogy with nematics, we call the director. The order parameter is equal to one in a completely ordered system and vanishes for the disordered phase. In the calculations the orientation of each particle is defined by the angle, θ, between its symmetry axis and a laboratory frame parallel to the molecular centres. The order parameter is therefore given by

$$\overline{T}_2 = \overline{\cos 2\theta}\,\cos 2\theta_o + \overline{\sin 2\theta}\,\sin 2\theta_o, \qquad (5)$$

where θ_o is the angle between the laboratory axis and the director. The transformation θ_o is that which maximises $\overline{T}_2$ and is found to be

$$\tan 2\theta_o = \overline{\sin 2\theta} \,/\, \overline{\cos 2\theta}. \qquad (6)$$

During the course of the simulation experiment the orientation of the director may change; consequently we have calculated θ_o for each configuration with the aid of equation (6). This then enables us to determine $\overline{T}_2$ for each configuration and so obtain the final order parameter by averaging over all configurations.

The majority of calculations were performed with a sample of 256 particles although some larger ensembles were also used. The initial configuration was chosen to be completely random and about 0.2×10^6 configurations were employed to equilibrate the system at a particular value of the reduced temperature, kT/ε. The various averages were then taken over a production run of typically 2×10^6 configurations. An estimate of the error in the averages was obtained by dividing this production run into ten equal blocks, an average was calculated for each block and the standard deviation of these ten averages determined.

The calculated dependence of the reduced energy per particle, $U/N\varepsilon$, on the reduced temperature is shown in Fig.1; the error in $U/N\varepsilon$ is found to be very small and is less than the size of the points on the graph. The true temperature dependence of the energy was calculated from equation (3) and is plotted as the solid line in the figure. The agreement between the Monte Carlo experiments and the exact results is seen to be perfect even at the lowest temperatures.

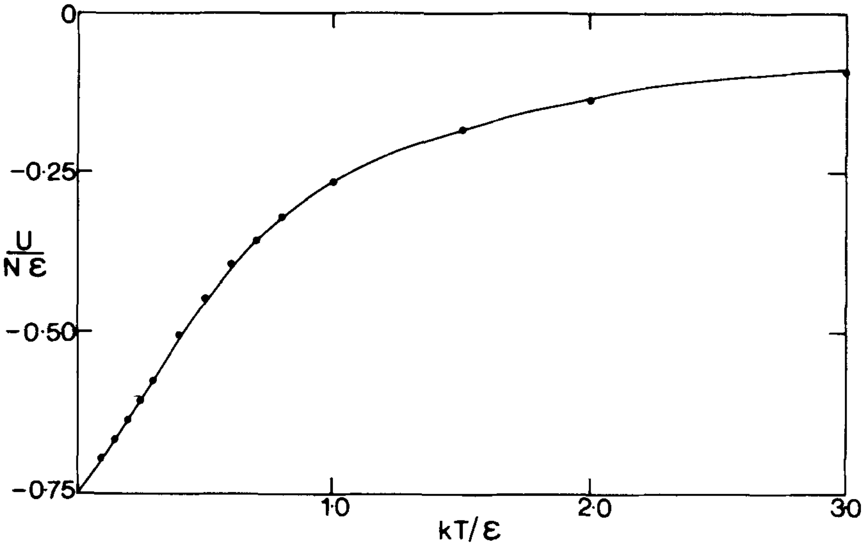

FIGURE 1 The dependence of the reduced energy per particle on the reduced temperature. The points come from the Monte Carlo simulations while the curve gives the exact results.

The specific heat per particle C_v/Nk is plotted as a function of kT/ε in Fig.2. The error in C_v is seen to be large especially at low temperatures; however these large errors are to be expected for a quantity calculated from fluctuations in the energy.[4] None-the-less there is still good agreement with the exact values of the specific heat obtained from equation (4) which are plotted as the solid line in Fig.2.

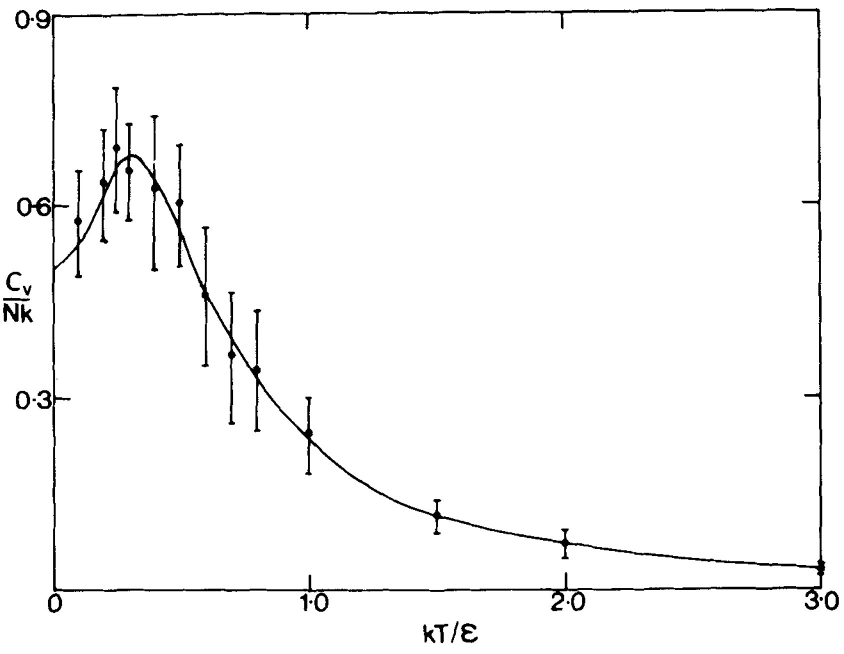

FIGURE 2 The temperature dependence of the specific heat per particle. The curve indicates the true dependence while the points are taken from the simulation experiments.

The order parameter, T_2, calculated for various reduced temperatures, is listed in the Table together with the number of particles, N, and the length of the production run. For an ensemble of 256 particles the order parameter is found to be about 0.07 at high temperatures; this is close to the value of $N^{-1/2}$ expected for a disordered system of finite size. As the temperature is lowered T_2 increases until at kT/ε of 0.1 it is as large as 0.26 which indicates an orientationally ordered phase. The real system is known to remain disordered at all temperatures and we attribute this discrepancy to the small number of particles employed in the simulation. Several of the calculations were therefore repeated with larger ensembles and as the Table shows the order parameter was found to decrease.

TABLE The dependence of the orientational order parameter on the reduced temperature and the size of the ensemble; the last column gives the length of the production run.

kT/ε	$\overline{T}_2$	N	$L/10^6$
3.0	0.062	256	2.0
2.0	0.071	256	2.0
1.5	0.074	256	2.0
1.0	0.077	256	2.0
0.7	0.093	256	2.0
0.6	0.096	256	2.0
	0.063	576	4.5
0.3	0.158	256	1.0
	0.117	256	2.0
0.25	0.217	256	1.0
	0.129	576	4.5
0.2	0.180±0.07	256	3.0
	0.116±0.05	576	3.0
	0.078±0.02	1156	5.0
	0.048±0.02	2500	7.0
0.1	0.260	256	2.0
	0.127	576	4.5
0.05	0.290	576	4.5

The most complete set of results was obtained at a reduced temperature of 0.2 and here $\overline{T}_2$ decreased from an unrealistic value of 0.180 for 256 particles to a value of 0.048 for 2500 particles, which is essentially zero for an ensemble of this size. In contrast the values of the energy and specific heat were observed to be independent of the sample size.

In conclusion we note that the Monte Carlo technique gives both the energy and specific heat of a linear array of anisotropic particles in almost perfect agreement with their true values for ensembles of only 256 particles. In contrast the order parameter is very sensitive to the number of particles especially at low temperatures and here large ensembles must be employed to reproduce the disordered state exhibited by the model. However, this investigation provides us with some confidence in the use of computer simulation techniques to study real liquid crystals, although of course each system may well present its own problems.

Acknowledgement We are grateful to the Science Research Council for the award of a Research Fellowship to Dr. R.L. Humphries and a Studentship to Mr. J.Y. Denham.

REFERENCES

1. W. Maier and A. Saupe, Z. Naturforsch., 14a, 882 (1959); 15a, 287 (1960); R.L. Humphries, P.G. James and G.R. Luckhurst, J.C.S. Faraday Trans.II, 68, 1031 (1972); G.R. Luckhurst, C. Zannoni, P.L. Nordio and U. Segre, Mol. Phys., 30, 1345 (1975).

2. W.J.A. Goosens, Phys. Lett., 31A, 413 (1970); Mol. Cryst. Liquid Cryst., 12, 237 (1970); B.W. van der Meer and G. Vertogen, Phys. Lett., 59A, 279 (1976).

3. W.L. McMillan, Phys.Rev., 4A, 1238 (1971); 6A, 936 (1972); F.T. Lee, H.T. Tan, Y.M. Shih and C. Woo, Phys. Rev. Lett., 31, 1117 (1973).

4. See, for example, J.P. Hansen and I.R. McDonald, The Theory of Simple Liquids (Academic Press, London, 1976).

5. J. Vieillard-Baron, J. Chem. Phys., 56, 4729 (1972); G. Lasher, Phys. Rev., 5A, 4350 (1972); P.A. Lebwohl and G. Lasher, Phys. Rev., 6A, 429 (1972); H.J.F. Jansen, G. Vertogen and J.G.J. Ypma, Mol. Cryst. Liquid Cryst., 38, 87 (1977).

6. J. Vieillard-Baron, Mol. Phys., 28, 809 (1974).

7. J. Kushich and B.J. Berne, J. Chem. Phys., 64, 1362 (1976); A.L. Tsykalo and A.D. Bagmet, Russ. J. Phys. Chem., 50, 439 (1976).

8. B.C. Freasier and L.K. Runnels, J. Chem. Phys., 58, 2963 (1973).