Computer Simulation of a Hard-Rod System: Structural Transitions and Clusters

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Received May 18, 1993*

We have studied by computer simulation a continual 2D hard-rod system with volume topological interaction between the rods. The microstructure of the rods that is obtained can be conveniently analyzed with the help of cluster formation terminology. We have shown that cluster distribution with respect to the numbers of rods can be written as $P(N) = A_0 \exp[(A_1)N]$, where A_0 and A_1 are constants which depend upon the cluster forming criteria and the rod system density, ρ, and N is the number of rods in a cluster. There are two transition regions in the hard-rod system of 2D spherocylinders at the axes ratio $p = 6$. The transition at $\rho = 0.35$–0.40 is the structural transition from the intermediate solution of rods and clusters to the solution of overlapped rods and clusters. The transition at $\rho = 0.50$–0.55 can be associated with the appearance in the system of percolation clustering. The cluster in the 2D rod system can therefore be considered to be a quasi-rod. The implication of this is that thermodynamic calculations for the system should be carried out as they would be for a polydisperse system with a given distribution of quasi-rods.

INTRODUCTION

It is well-known from classical work[1,2] that long-term order in two-dimensional systems is not possible because of unlimited growth in the thermal fluctuations of the orientation director as a consequence of which transition into an oriented state is not a first-order phase transition. The fluctuation growth, which is a logarithmic divergence, is, however, slow, and in a 2D liquid crystal, the ordered regions, or clusters, whose size depends upon the concentration of anisotropic particles, have to appear. Some papers have dealt with numerical simulation[3,4] and analysis[5,6] of 2D systems but were devoted mainly to investigation of the thermodynamic parameters of the system; local structure was not studied sufficiently.

In this connection, it is of interest to study the microstructure of the 2D rod system and to determine the effect upon it of the thermodynamic parameters.

DESCRIPTION OF THE MODEL

The continual 2D hard spherocylinder system has been studied. The only interactions between the spherocylinders are the volume topological interactions characteristic of lyotropic liquid crystals. In addition, the system was perturbed by an external quadrupole field oriented along the x-axis. We used periodic boundary conditions to restrict the boundary effects. Regular initial rod configurations were chosen in order to obtain systems with denser rod packing. To obtain configurations of close-packed rods, two types of initial rod configuration resembling parquet were chosen with order parameters $S = 1$ or $S = 0$ and $S = 2\cos^2\theta - 1$, where θ is the angle between the system orientation director and the rod axis (see Figure 1a). The system density was varied from $\rho = 0.20$ to $\rho = 0.75$ in steps ($\Delta\rho$) of 0.05. All computations were performed on a CDC CYBER 172 computer. The basic cell was chosen as a square containing 40–80 rods. At each time, step, the position and orientation of a randomly chosen rod was changed at random. The movement of the rod center was limited to a rectangle of dimensions $2\Delta X_{max} \times 2\Delta Y_{max}$ and rotation to the angular segment $2\Delta\Phi_{max}$. The values $2\Delta X_{max}$, $2\Delta Y_{max}$, and $2\Delta\Phi_{max}$ were chosen according to the criteria of half-acceptance of new configurations, which ensured the fastest convergence. Starting from two different parquetlike initial configurations, 10^4 one-step configurations were generated. The resulting equilibrium states were then obtained by averaging over the subsequent 10^4N-step configurations. Markov chain equilibrium state was also tested for by system size variation.

To analyze the rod microstructure that results, we propose a cluster formation criterion, as follows. The cluster was determined as the configuration of the rods according to the following equations:

$$d_{ij}, d_{ji} \le \gamma(2D)$$

$$l_{ij}, l_{ji} \le \beta(L/2) \qquad (1)$$

in which d_{ij} is the perpendicular length dropped from the i-rod center on to the axis of the j-rod, l_{ji} is the segment length along the axis from the j-rod center to the intersection point with the perpendicular dropped from the i-rod center. L and D are the rod length and diameter, respectively, and β and γ are the cluster formation parameters. It is clear from Figure 2 that when $\gamma = \beta = 1$, rods A and B belong to the same cluster, while rod C does not belong to this cluster because the perpendicular which is dropped from the C rod center crosses the B rod axis behind the rod. The proposed criteria have some advantages in comparison with cluster definition for spherical particles, and this is thought to be a result of the increased area of contacts on the rod perimeter. The cluster distribution $P(N)$ was determined as the rod portion belonging to N-rod clusters.

RESULTS

Figure 1b shows a snapshot of the system configuration at the equilibrium state with $\rho = 0.60$. The forward and rotational diffusion of rods has been investigated in the concentration range $\rho = 0.20$–0.55.

Figure 3 shows the diffusion coefficients of the rods along the field D_x as a function of the concentrations at different values of the oriented field. It has been shown that the asymmetry of forward diffusion can be expressed as

* Abstract published in *Advance ACS Abstracts*, March 15, 1994.

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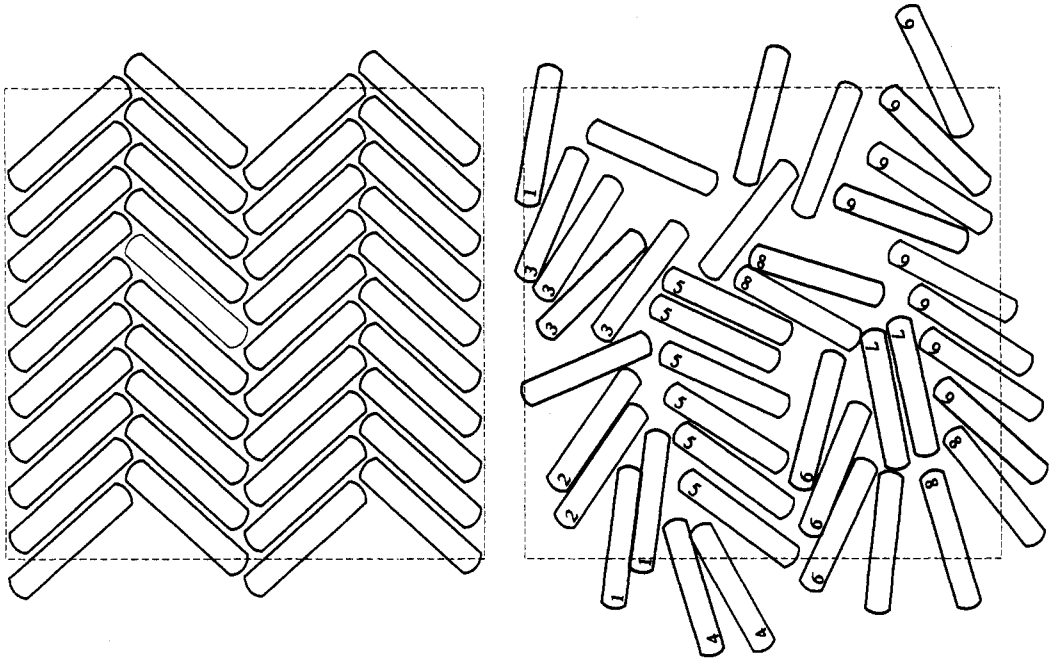

a b

Figure 1. Snapshots of hard-rod Systems: (a) initial (parquet-like) configuration; (b) equilibrium configuration.

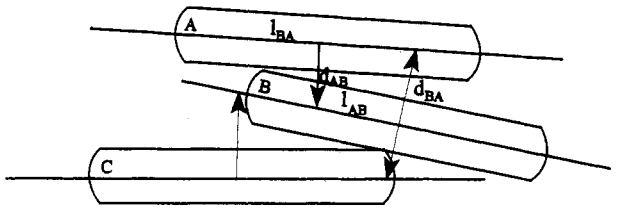

Figure 2. Schematic drawing of a cluster showing local definitions.

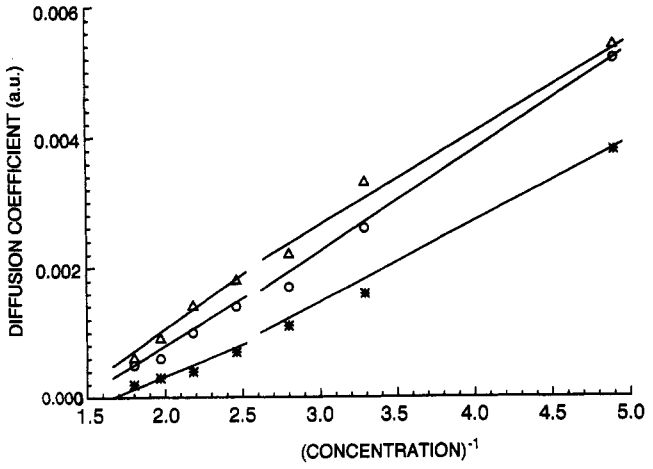

Figure 3. Concentration dependence of forward mobility coefficient for different oriented fields. (*) $H = 0.0$; (○) $H = 0.025$; (△) $H = 0.05$.

$$D_h(H)/D_K(H) = 1 + A(H) \quad (2)$$

where H is the oriented field strength and A is a coefficient which expresses the degree of dependence of diffusion asymmetry on the field. Figure 4 expresses the concentration dependence of the coefficient A. These graphs show that, in the concentration interval $\rho = 0.36$–0.41, there is a transition region which separates two different types of rod mobility. In addition, the time of rod rotational mobilities were found, and their dependence on concentration is shown in Figure 5. In this case, the same transition region was observed between the two different types of relaxation. Figure 6 shows the dependence of rod clustering tendency on concentration at different values of γ and β. It can be seen that there are two special concentration regions: ρ^I (see also Figures 3–5) and $\rho^{II} = 0.51$–0.56 in which changes of the slope of the straight line were observed. Analysis of the cluster distribution showed that the changes can be expressed by the following relation:

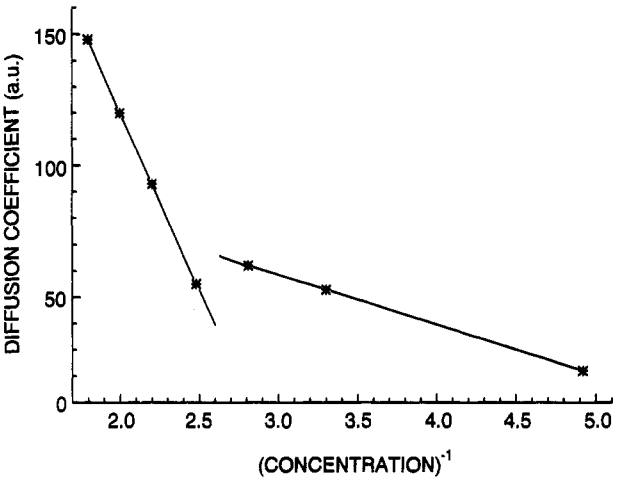

Figure 4. Concentration dependence of asymmetry response on an oriented field.

$$P(N) = A_0 \exp[(A_1)N] \quad (3)$$

where A_0 and A_1 are constants which depend upon the parameters γ and β and the density ρ. Figures 7 and 8 show the concentration dependence of A_0 and A_1.

DISCUSSION

The concentration dependence of the diffusion coefficient shown in Figure 3 indicates a linear relationship between the diffusion coefficient and the concentration. This result is in

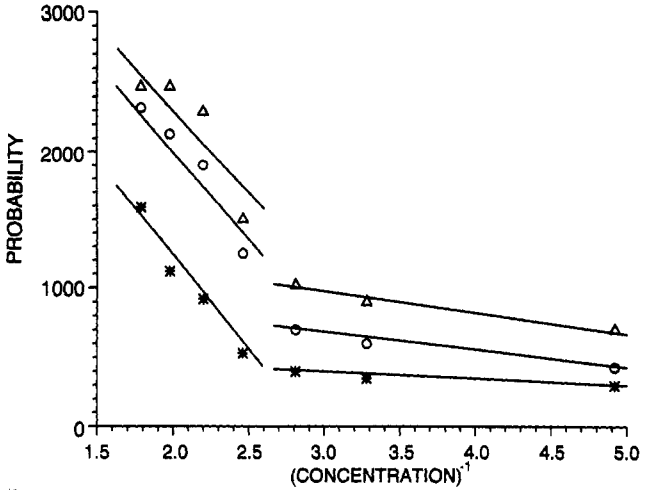

Figure 5. Concentration dependence of rotational mobility time τ^1 for different oriented fields: (*) $H = 0.0$; (○) $H = 0.025$; (△) $H = 0.05$.

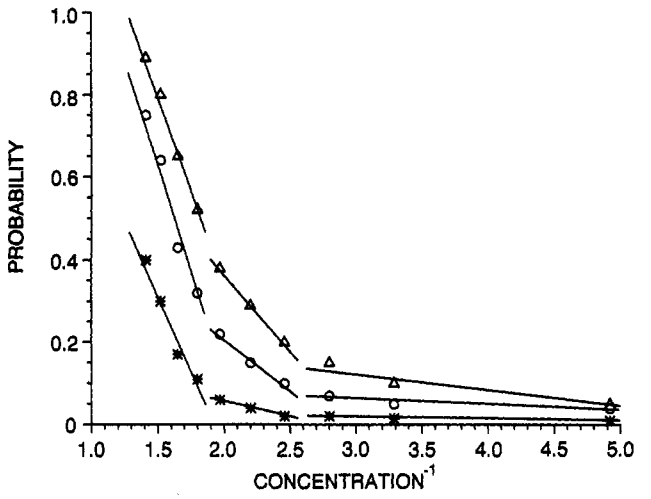

Figure 6. Probability of a rod belonging to a cluster (see text): (*) $\beta = 0.4$, $\gamma = 0.6$; (○) $\beta = 0.6$, $\gamma = 0.7$; (△) $\beta = 0.8$, $\gamma = 0.8$.

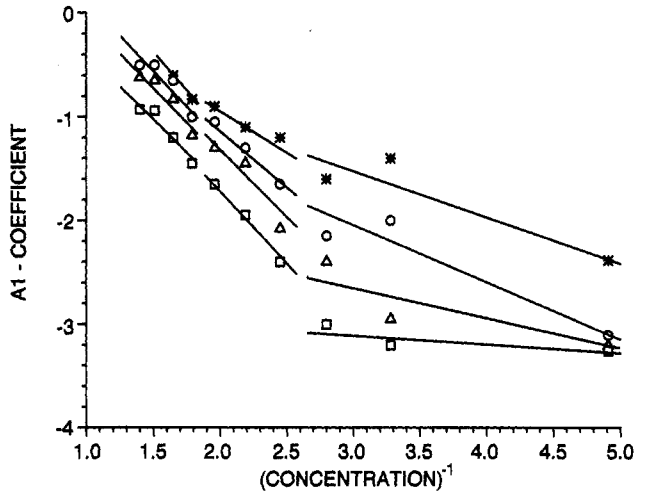

Figure 7. Concentration dependence of the coefficient A_1 in $P(N) = A_0 \exp(A_1 N)$: (*) $\beta = 1.0$, $\gamma = 1.0$; (○) $\beta = 1.0$, $\gamma = 0.8$; (△) $\beta = 1.0$, $\gamma = 0.7$; (□) $\beta = 1.0$, $\gamma = 0.6$.

good agreement with the calculations of Binder et al.[7] It should be noted, however, that comparison with real experimental systems is difficult due to the "vacuum" character of the calculations performed. This is also discussed by Binder.[7]

Analysis of the results of computer simulation shows that cluster formation at low concentrations and the tendency of rods to join clusters both increase with increasing concentration. Clusters which are formed at high values of the parameters γ and β are more sensitive to system size. They are more porous and have more large linear sizes at a constant number of rods in the cluster. It can be assumed that, in the concentration range $\rho^I = 0.36$–0.41, there is a structural transition from intermediate to concentrated rods and clusters solution. It should be noted that, in the concentration region ρ^I, the total amount of large clusters and the probability that a rod will belong to a cluster are both increased. This result is in agreement with analytical predictions concerning transitions from isotropic to anisotropic phases in the same concentration region.

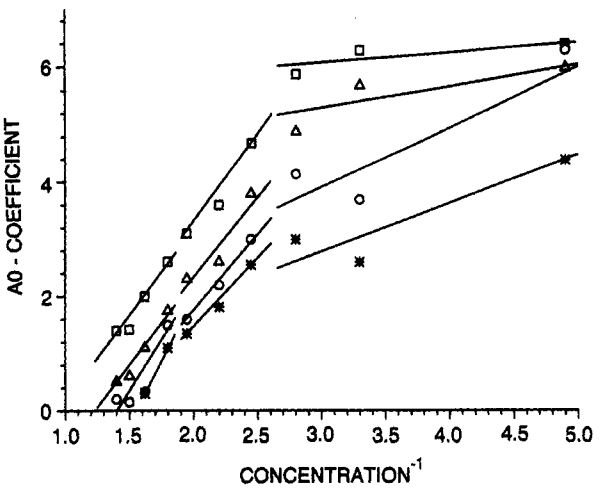

Figure 8. Concentration dependence of the coefficient A_0 in $P(N) = A_0 \exp(A_1 N)$: (*) $\beta = 1.0$, $\gamma = 1.0$; (○) $\beta = 1.0$, $\gamma = 0.8$; (△) $\beta = 1.0$, $\gamma = 0.7$; (□) $\beta = 1.0$, $\gamma = 0.6$.

In the concentration region $\rho = 0.55$, rods are less mobile and only the cluster statistics were investigated. It can be seen from Figures 6–8 that the transition region at ρ^{II} is smoother than that at ρ^I. We assume that the second transition, at ρ^{II}, results from the formation of percolation clusters in the system (see, for example, cluster 9 in Figure 1b). Support for this assumption is found in the observation[8] that the percolation threshold for 3D systems of elongated ellipsoids at $\rho \approx 0.16$ does not depend upon the ratio of the axes of the rods and is in good agreement with experimental data for lyotropic liquid crystal polymers.[9] It should be noted that the concentration ρ^{II} is in quantitative agreement with the value of the percolation threshold for the 2D rod system.[8] The transition at $\rho \approx 0.56$ has been described[3] as a first-order phase transition from the isotropic to the anisotropic state, but a similar transition was not found[4] in the 2D ellipsoid system. The nature of the transition in the concentration region $\rho \approx 0.56$ is still therefore an open question.

In conclusion, it should be noted that clustering terminology can be very useful in the theoretical analysis of 2D rod lyotropic systems. Computer simulation results have shown that clusters in 2D rod systems are best described as "quasi-rod" and have their own properties. Consequently, thermodynamic calculations for such systems should be done as for polydispersed systems with a quasi-rod distribution, as described in eq 3.

ACKNOWLEDGMENT

The authors are grateful to Professors T. M. Birnshtein and Y. Y. Gotlib for continual support and helpful discussions. Support from the International Science Foundation is kindly acknowledged.

REFERENCES AND NOTES

(1) Landau, L. D. About Phase Transition Theory. II. (Russian). *JETP* **1937**, *7*, 627–632.
(2) Stanley, H. E. *Phase Transitions and Critical Phenomena*; Oxford University Press: New York, 1971.
(3) Viellard-Baron, J. Phase Transitions of the Classical Hard-Ellipse System. *J. Chem. Phys.* **1972**, *56*, 4729–4744.
(4) Ward, D. A.; Lado, F. Structure, Thermodynamics and Orientational Correlations of the Nematic Hard Ellipse Fluid from the Percus-Yevick Equation. *Mol. Phys.* **1988**, *63*, 623–638.
(5) Cotter, M. A. Molecular Theories of Nematic Liquid Crystals. *Mol. Cryst. Liq. Cryst.* **1983**, *97*, 29–47.
(6) Merkyrieva, A. A.; Birnshtein, T. M. Oriental Ordering in Two-Dimensional Non-Thermal Systems. (Russian). *Vysokomol. Soed.* **1991**, *33*, 141–147.
(7) Binder, K.; Kaloos, M. H. In *Monte Carlo Methods in Statistical Physics*; Binder, K., Ed.; Springer-Verlag: Berlin, 1979; Vol. 6, Chapter 6.2, p 262.
(8) Stauffer, D. Scaling Theory of Percolation Clusters. *Phys. Rep.* **1979**, *54*, 1–74.
(9) Straley, J. P. The Gas of Long Rods as a Model for Lyotropic Liquid Crystals. *Mol. Cryst. Liq. Cryst.* **1973**, *22*, 333–357.