LIQUID CRYSTAL-LIKE PHASE SEPARATION IN SYSTEMS OF MACROSCOPIC RODS

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ABSTRACT

Experiments with monolayers of macroscopic rods indicate separation into isotropic and aligned phases at greater-than-critical concentrations. This behavior is qualitatively similar to that of rodlike liquid crystalline polymers, which in turn has been modelled successfully in three dimensions by Flory and Ronca. We have adapted their approach to predict the ordering of rods in two dimensions. A preliminary phase diagram is presented. The critical rod concentration at which an aligned phase can appear first is a decreasing function of rod axial ratio. Rods of a given axial ratio will phase separate at lower overall concentrations in two dimensions than in three.

INTRODUCTION

Macroscopic rods, in the form of fibers or whiskers, are used as reinforcing agents in a wide variety of composite materials. Strength, stiffness and toughness all are increasing functions of the attainable volume fraction of rods [1-3]. There are several available and potential processing methods for inducing global rod alignment, thus allowing them to pack more densely. However, the properties of the finished artefact are then necessarily anisotropic. For situations where isotropic properties are desirable, it is of fundamental interest to determine whether clusters of aligned rods can develop spontaneously. While such alignment would allow accommodation of a greater rod volume fraction than is possible if the rods are independently and randomly oriented, it is not clear whether the presence of the clusters would improve the mechanical properties. If the matrix material is brittle, the clusters may act as crack-initiating defects. In either case, it is of value to understand and predict the formation of such clusters.

Evans and Gibson [4] suggest that the maximum packing density for randomly oriented macroscopic rods is comparable to the phase boundary marking the appearance of the nematic phase in a system of rod-like liquid crystalline polymer molecules. They contend that macroscopic rods have no analog to diffusion as a means of effecting their rearrangement into an aligned state. Chick and Aksay [5] suggest that the vibrations and turbulence that prevail during the processing of many composites may facilitate such rearrangement. If phase separation does occur, we should expect an athermal model to apply, since the interactions between rods will be dominated by steric repulsion. A notably successful model for phase separation in athermal systems of rodlike particles has been derived by Flory and Ronca [6]. It is found to be qualitatively applicable to a number of polymer - solvent systems [7]. We have set out to investigate the applicability of this model to the systems of macroscopic and truly athermal rods that pertain to composite materials in the absence of forced alignment. Our analysis is confined to two dimensions (a monolayer of rods), for the following reasons: Firstly, it is simpler to observe clustering in two dimensions than in three, both for models that are generated statistically in a computer and also for real systems. (In real three-dimensional systems, the container walls constrain those configurations that are readily visible; it is difficult to characterize the bulk configurations.) Secondly, practical composites frequently are built up from laminated sheets that individually contain a two-dimensional distribution of fibers or whiskers.

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THE MODEL IN TWO DIMENSIONS

Our approach is directed by the model of Flory and Ronca [6], which is derived for three dimensions. We shall use the notation (FRxx) to refer to equation (xx) in their work. If the Flory-Ronca model were exact, adapting it to two dimensions would only require modification to parameters that characterize rod orientations. The model contains three such parameters. One is a disorientation index y, defined for each molecule in terms of the lattice model that constitutes the basis of the Flory-Ronca approach. y is the number of adjacent lattice rows occupied by a molecule, where rows are defined as lying parallel to the direction of preferred molecular orientation X. Other parameters that describe molecular orientation are ψ, the angle between a rod and X, and ω_y, the fractional range of *solid* angle associated with molecules having a given value of y. In the two-dimensional case of present interest, we have to redefine ω_y as a fractional range of *planar* angle. Thus

$$y = (4/\pi)x \sin\psi \tag{FR27}$$

and

$$\omega_y = \sin\psi\,(d\psi/dy) \tag{FR28}$$

are replaced in two dimensions by

$$y = 1 + (x - 1)\sin\psi \tag{1}$$

and

$$\omega_y = d\psi/dy = (\sec\psi)/(x - 1) \tag{2}$$

Here x is the axial ratio of the rods, which are assumed to be monodisperse. However, if we effect these simple substitutions only, we find that the model does not predict any phase separation, and so does not agree with experiment (Fig. 1). Some further refinements are therefore necessary.

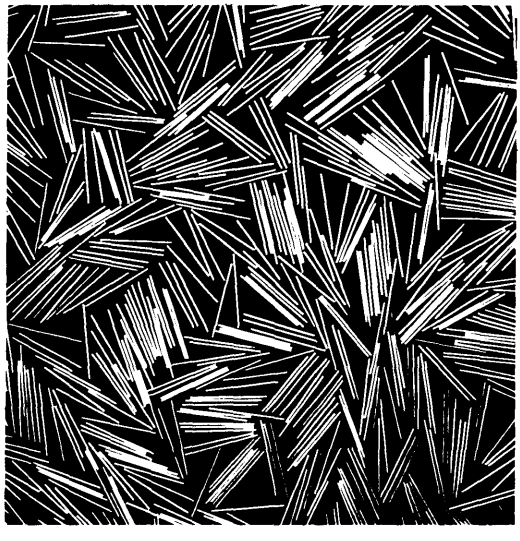

Figure 1

Wooden rods (2mm diameter) with an axial ratio of 25. Rods were scattered onto a horizontal substrate, forming a random pile several rods deep. The substrate was then vibrated until the rods formed a monolayer. Since all the rods can be accommodated in two dimensions, their distribution after prolonged vibration should be independent of the density and surface finish of individual rods.

The Flory-Ronca implementation of the lattice model starts out by contemplating the number of situations v_j available to the j^{th} rod, if it is to be incorporated into an existing configuration of $(j-1)$ rods. An explicit formula for v_j is given as Eq.(FR1). The derivation is equally applicable to either two or three dimensions. However, Flory and Ronca express clear reservations about the validity of the equation at large disorientations of the rods. Also [8], the equation permits the model to contain intersecting rods as shown in Fig.2.

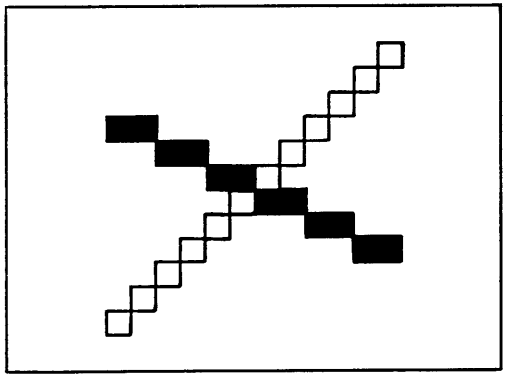

Figure 2

Flory and Ronca's lattice model allows the situation shown alongside, where rods can intersect provided that their segments do not overlap.

While the approximations inherent to Eq.(FR1) do not seem to present a problem in three dimensions, they apparently become significant when the overall number of rod configurations is limited by working in two dimensions. We therefore choose to rely on Monte Carlo techniques to obtain values of v_j. We postulate that v_j is given consistently by:

$$\frac{v_j}{n_o} \propto \frac{1}{< T_j >} \tag{3}$$

where n_o is the total number of lattice cells in the two-dimensional model. The quantity $< T_j >$ is the average number of tries required for the Monte Carlo algorithm to place the j^{th} rod in an existing configuration of $(j-1)$ rods. The algorithm first chooses an angle for the j^{th} rod, and then tries combinations of positional coordinates until the rod is placed successfully. $< T_j >$ necessarily increases with increasing rod concentration, since, at each concentration, it is inversely proportional to the fraction of situations available in the existing configuration as stated in Eq.(3). For the isotropic phase, the program calls upon a random number generator to choose the orientation of each rod. For the aligned phase, the program uses two random numbers to generate orientations that follow a normal distribution with a user-defined standard deviation [9]. An appropriate initial standard deviation of 10° was estimated by using the Flory-Ronca model to calculate the average $<\psi>$ from Eq.(FR27). Flory and Ronca claim that $<\psi>$ is insensitive to x; using their model, we found that $<\psi>$ changes by less than 20% as x varies between 10 and 100. Although the values of $<\psi>$ thus calculated are pertinent to three dimensions, we feel that they represent a useful initial estimate for the value in two dimensions.

Three separate Monte Carlo runs were averaged to estimate $< T_j >$ at each value of j. For both the isotropic and anisotropic phases, we found that the empirical relationship between $\ln < T_j >$ and j can be fitted closely by a quadratic equation:

$$\ln < T_j > = Aj^2 + Bj + C \qquad (4)$$

The constant C is necessarily equal to zero. We substitute Eq.(4) into Eq.(3) to obtain values of v_j.

Our approach then parallels that of Flory and Ronca in calculating total configurational entropy Z_M as the product of combinatory (steric) and orientational factors. Since we are dealing with an athermal system, there is no enthalpic contribution to the free energy. We can therefore determine phase separation at a given value of x by plotting $-\ln Z_M$ as a function of the area fraction of rods (xj / n_o) for both the isotropic and the anisotropic phase, and then searching for a common tangent to both curves. Our expressions for Z_M in both phases are derived analogously to Eq.(FR7).

RESULTS AND DISCUSSION

Our preliminary predictions for phase separation in two dimensions are shown in Fig.3. For the purposes of comparison, the results for phase separation in three dimensions as predicted by Flory and Ronca are also given. It is evident that separation occurs at lower rod packing fractions in two dimensions. Qualitatively, this would be predictable on the basis of the restricted number of orientations available in two dimensions. We are at present investigating the extent to which our diagram for two dimensions is sensitive to the assigned standard deviation of orientations in the anisotropic phase.

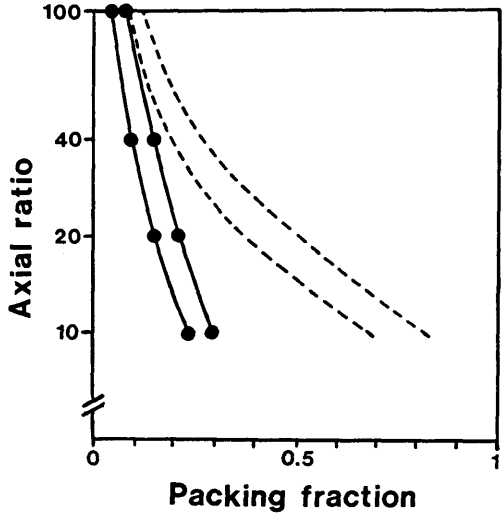

Figure 3

Preliminary (partial) phase diagram for rods in two dimensions (solid lines). Phase boundaries have been calculated for aligned rods that follow a normal distribution having a standard deviation of 10°. Flory and Ronca's phase diagram for three-dimensional systems is also shown (broken lines).

While neither the Flory-Ronca model nor our own provides an exact formula for v_j, it is interesting to note that both approaches lead to surprisingly similar results (Fig.4). Since our

approximation leads to a prediction that agrees at least qualitatively with experiment, we can deduce that the Flory-Ronca approximation tends to underestimate v_j at high axial ratios, and that it overestimates v_j at low axial ratios.

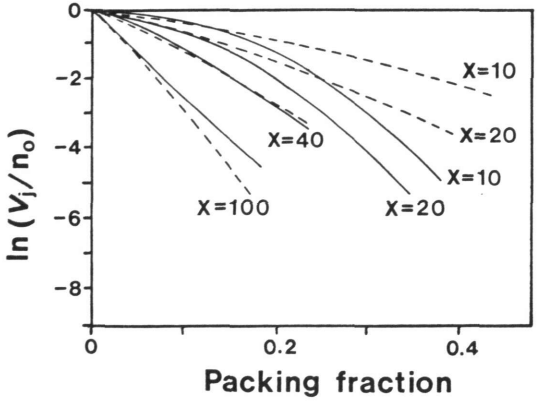

Figure 4

Comparison of $\ln(v_j / n_o)$ *versus* rod concentration for our model and the Flory-Ronca model.
Solid lines were calculated from Eq.(3) and Monte Carlo data. Broken lines were calculated from Eqs.(FR1) and (1), with $\bar{y} = 1 + (x - 1)\sin < \psi >$. Here $< \psi >$ is set equal to 8°, consistent with the standard deviation of 10° chosen for our normally distributed rod orientations.

The athermal separation of rods into isotropic and anisotropic phases can also be demonstrated by our Monte Carlo program for randomly oriented rods, with the area fraction of rods increased beyond the critical value defined by the common tangent construction. Fig.5 shows clusters of aligned rods, with random alignment persisting in the intervening spaces. However, once a rod is placed successfully by the Monte Carlo program, subsequent motion is disallowed. For this reason, the configuration in Fig.5 cannot be associated with the minimum free energy for the given rod aspect ratio and packing fraction.

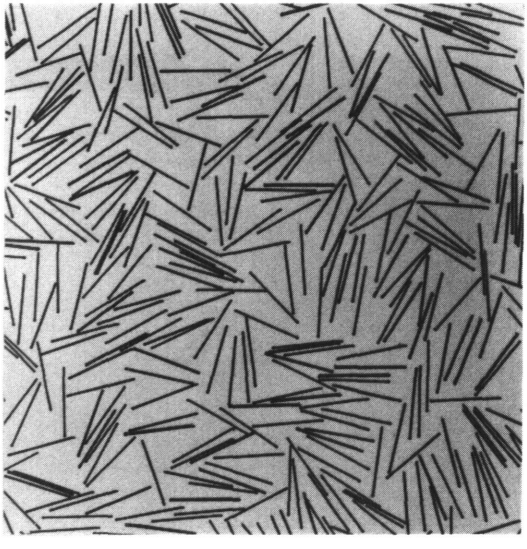

Figure 5

Configuration produced by Monte Carlo program for rods with an aspect ratio of 40. The area fraction shown, 0.12, is in the middle of the two-phase region on the proposed phase diagram (Fig.3).

Simulated annealing should lead to growth and coalescence of ordered clusters. By developing selection rules to identify whether any one rod belongs to a particular cluster or not, we anticipate being able to predict the *scale of the microstructure, i.e.* the average ordered domain size, as a function of the length of anneal. This will add to our ability to predict and therefore control the properties of fiber- or whisker-reinforced composite materials.

CONCLUSIONS

1. With some modifications, Flory and Ronca's model for the athermal phase separation of rodlike particles in three dimensions can be adapted for two-dimensional systems.
2. In two dimensions, as in three, the critical rod concentration at which an aligned phase can appear first is a decreasing function of rod axial ratio.
3. Rods of a given aspect ratio will phase separate at lower overall concentrations in two dimensions than in three.
4. Microstructures of the phase-separated and single phase anisotropic systems can be calculated by Monte Carlo techniques. This offers the possibility of predicting microstructural scale in such systems.

ACKNOWLEDGEMENTS

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