PHYSICAL REVIEW A VOLUME 21, NUMBER 6 JUNE 1980

Scaled particle theory of hard rods in two dimensions: Effect of variable rod size and attractive interactions

H. L. Scott, Jr.
Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078

(Received 3 December 1979)

The thermodynamic properties of hard-rod fluids confined to a plane are derived using scaled particle theory, and restricting the number of possible orientations to six. Results for simple systems are compared with earlier results for three-dimensional spherocylindrical systems. Mixtures of rods of different lengths are also studied as possible models for systems in which the constituent molecules may change conformation. Upon inclusion of a van der Waals attractive potential energy, interesting and unusual phase changes can occur.

The method of scaled particle theory (SPT), introduced several years ago in studies of hard spheres and disks,[1] has proved useful in the study of hydrocarbon chain packing in lipid bilayers and biological membranes[2,3] as well as liquid crystals.[4,5] In many such systems molecules are large and may exhibit many conformational states. Changes in molecular size disrupt molecular packing so that in closely packed systems these conformational changes may be related to changes in the long-range order of the system. In recent papers Cotter and Wacker[4,5] have presented an elegant extension of the SPT to mixed anisotropic systems containing molecules with different shapes, and this theory forms a natural basis for the study of the effects of conformational changes at the molecular level. As a first effort in this direction, I have considered several types of two-dimensional hard-rod fluids. The purpose of this paper is to present the properties of these models. In the next section I describe the computational technique and the models studied. The final section contains the results.

MODELS STUDIED

Consider a system of hard rectangular rods confined to a plane. Let the rods have length a and width b. For simplicity in the numerical computations, each rod is allowed to be in one of M orientations, and α_k ($k=1\cdots M$) is the fraction of molecules having orientation k. For a given set $\{\alpha_n\}$ the Gibbs free energy of the system can be written as

$$\frac{G}{Nk_BT}=\ln\rho+\sum_k \alpha_k\left(\ln\alpha_k+\frac{1}{k_BT}\,\omega_k(\rho,a,b)\right), \qquad (1)$$

where ρ is the particle density, k_B is Boltzmann's constant, T is the absolute temperature, and $\omega_k(\rho,a,b)$ is the work required to insert a particle having orientation k into the system at the density ρ. SPT is used to evaluate $\omega_k(\rho,a,b)$ by considering limiting cases of very large and very small sizes for the particle being added in orientation state k.[4] The procedure involves calculating the area excluded to a "scaled particle" of dimensions $\alpha a, \beta b$ by regular size particles in other orientational states. This function is

$$A_{kl}(\alpha,\beta)=ab(1+\alpha\beta)+|\sin\theta_{lk}|(\alpha a^2+\beta b^2)+|\cos\theta_{lk}|ab(\alpha+\beta), \qquad (2)$$

where θ_{lk} is the angle made by rods in states l and k. In SPT Eq. (2) is used to obtain a limiting form for $\omega_k(\rho,\alpha a,\beta b)$ for $\alpha,\beta\approx 0$:

$$\omega_k(0,0)=-k_BT\ln\left(1-\rho\sum_l \alpha_l A_{kl}(0,0)\right). \qquad (3)$$

For the other extreme, we expect that if the scaled rod is very large, then

$$\omega_k\approx P_{\mathrm{HC}}\alpha\beta ab, \qquad (4)$$

where P_{HC} is the hard-core pressure. The next step is to construct $\omega_k(\alpha,\beta)$ for all α,β (in particular $\alpha,\beta=1$) by assuming a polynomial form in α and β and matching coefficients. The result is, for $\alpha=\beta=1$,

$$\frac{G_{\mathrm{HC}}}{Nk_BT}=\ln\rho+\sum_k \alpha_k\ln\alpha_k-\ln(1-\rho ab)+\frac{\rho}{1-\rho ab}\left(\sum_{k,l}\alpha_k\alpha_l[(a^2+b^2)|\sin\theta_{lk}|+2ab|\cos\theta_{lk}|]\right)+(P_{\mathrm{HC}}/k_BT)ab. \qquad (5)$$

Any one of several techniques[3,4] may be utilized to eliminate P_{HC} and calculate the Helmholtz free energy, obtaining

$$F/Nk_BT=\ln\left(\frac{\rho}{1-\rho ab}\right)+\sum_k \alpha_k\ln\alpha_k-1+\frac{\frac{1}{2}\rho}{1-\rho ab}\sum_{k,l}\alpha_k\alpha_l[(a^2+b^2)|\sin\theta_{lk}|+2ab|\cos\theta_{lk}|]. \qquad (6)$$

The thermodynamic state of the system is determined by finding the occupation fractions $\{\alpha_k\}$ which minimize Eq. (6) at each fixed density. In the present problem there are often several sets of $\{\alpha_k\}$ which satisfy the minimization equations. In this case the set $\{\alpha_k\}_{\min}$ which represents the true physical state of the system is that for which Eq. (6) is an absolute minimum. At low densities this will be a set in which all the $\{\alpha_i\}$ are approximately equal to $1/M$ while at high densities most of the α_i should be zero. In some systems the $\{\alpha_i\}_{\min}$ will vary smoothly with the density for low to high density, while in other systems a first-order phase change may occur as the system switches from one set of $\{\alpha_i\}$ to another to maintain the absolute minimum in the free energy.

Generalizing the model, consider now a mixture of hard rods of varying length. That is, let b remain fixed but allow a to take on a set of discrete values. This model can be directly related to hydrocarbon chain packing in lipid bilayers where a large value of a is the result of conformational disorder by the chains. The principal types of disorder involve gauche rotations about carbon-carbon bonds which then tend to bend the chains away from an axis perpendicular to the bilayer plane. Viewed from the top of such a plane, the projections of a set of lipids in various conformational states would appear as rods of various sizes. Such a view is shown in Fig. 1. As the density of such a system is increased, conformational changes which increase the effective rod size in Fig. 1 become less likely. Thus, for this type of mixture the concentrations of various rod species are also order parameters which vary with density. In polymer chain statistics one often assigns statistical weights to various conformational states.[3] Here we consider mixtures of the type shown in Fig. 1, both with and without statistical weight factors. Other systems in which variable molecular size might be of interest include, for example, liquid crystals with n-CH_2 side chains.[6,7]

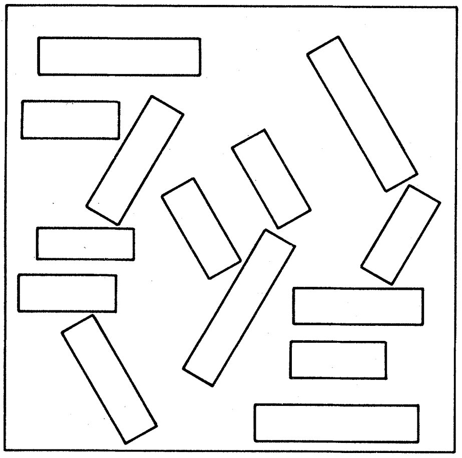

FIG. 1. Schematic drawing of a mixture of planar hard rods of varying area. For the biomembrane application of the theory, this is the top view of a lipid bilayer looking perpendicular to the bilayer plane.

The extension of the SPT formalism to such mixtures is straightforward. The resulting free energy has the form

$$\frac{F}{Nk_BT}=\sum_i \alpha_i \ln\alpha_i - \sum_i \alpha_i \ln\omega_i + \ln\left[\rho\Big/\left(1-\rho\sum_i \alpha_i a_i b_i\right)\right] - 1$$
$$+\left[\tfrac{1}{2}\rho\Big/\left(1-\rho\sum_i \alpha_i a_i b_i\right)\right] \sum_{k,l} \alpha_k\alpha_l\{[b_k b_l + a_k a_l\,|\sin\theta_{kl}| + (a_k b_l + a_l b_k)\,|\cos\theta_{kl}|]\}, \tag{7}$$

where the sets $\{a_k\}$ and $\{b_k\}$ are the allowed values of the long- and short-rod dimensions, respectively, and the ω_i are statistical weights for each state i. In Eq. (7) the α_k represents not only orientation but area class. That is, if there are six allowed orientations and five allowed values of a_k, then there are 30 members of the set $\{\alpha_k\}$ (in this paper we use $b_k = b$, fixed).

As a final consideration we introduce an attractive potential energy to our system. Since exact inclusion of van der Waals forces in complex molecular systems presents insurmountable difficulties, we use the following semiempirical potential:

$$V_{\text{att}} = -C(A - A_0)^{-1.5}, \tag{8}$$

where C and A_0 are constants and A is the molecular area. A_0 is chosen so that Eq. (8) is not singular for accessible values of A. This function was used in Ref. 3 as a semiempirical attractive potential energy for the oriented hydrocarbon chains in lipid bilayers, and the results were in good agreement with experiment. For this reason the potential is used again here although it is not consistent in the statistical-mechanical sense[8] since

$$N^{-1}V_{\text{att}} \neq \rho\, \partial V_{\text{att}}/\partial\rho. \tag{9}$$

As long as V_{att} is a function of the form $(A - A_0)^\sigma$, it cannot satisfy Eq. (9). However, we found in constructing the semiempirical model of Ref. 3 that models with functions of the form $V_{\text{att}} \sim (A)^\sigma$

do not agree nearly as well with experiment for lipid bilayers, even when $\sigma=-1$ [satisfying (9)].

Minimization of Eq. (7) or Eqs. (7) plus (8) over such a large set of variables is a difficult and time-consuming chore. The computer program we use is STEPIT, written by Chandler of the Oklahoma State University computer science department, and has proved reliable and accurate for all cases considered. The introduction of additional degrees of freedom to the system might be expected to lead to more complex phase behavior since we have order parameters which correspond to orientation and to the lengths of the rods. In the next section we discuss the properties of the various models considered above.

RESULTS AND DISCUSSION

The properties of simple systems (rods of one size only with six possible orientations) are similar to those discussed by Cotter[9] for three-dimensional systems. At certain critical densities the rods spontaneously order themselves, exhibiting a weak first-order phase transition. In Figs. 2 and 3 are pressure-density plots for systems of 8×5 and 10×4 rectangles, respectively, with 6 orientational degrees of freedom. The phase transition is characterized by the van der Waals loop in the isotherm. The dashed lines on part of the loop show portions for which numerical results are, due to the steep slope, very difficult to obtain. The horizontal line is placed over the loops using the Maxwell equal-area rule. The low-density phase has $\alpha_i=\frac{1}{6}$ for $i=1\cdots6$, representing random orientation, while in the high-density phase a large fraction of the rods are in one of three equivalent parallel orientations. As the density is increased to the close packing density, this fraction increases to one. In Table I the properties of the systems of Figs. 2 and 3 are listed. The transitions are quite similar to those found in three-dimensional spherocylindrical and other rodlike systems.[9-12] The packing fractions associated with the two phases are close to those of Cotter[9] for three-dimensional unrestricted orientation models at common length: breadth ratios, while they are larger than those of Ref. 9 when orientations are restricted to the X, Y, and Z axes.

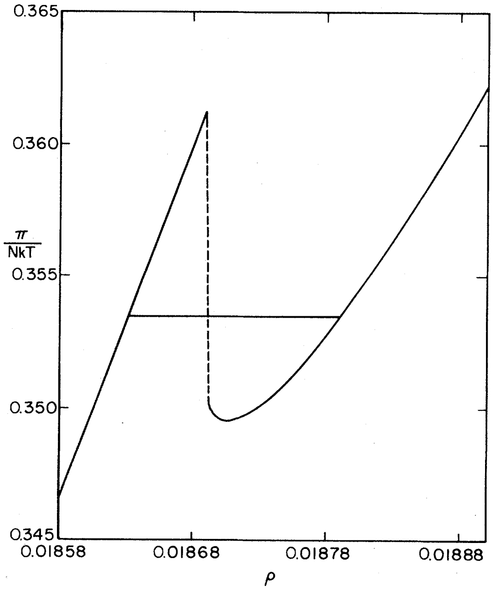

FIG. 2. Pressure (π)-density (ρ) plot for a system of rectangular 5×8 (arbitrary units) rods. The dashed line represents a region in which the slope was too steep to obtain accurate numerical results.

The properties of models with variable molecular shape are given in Table I also, and shown in Fig. 4. When only hard-core repulsions are considered, the systems exhibit a single-phase transition, just as the simpler systems do. As the density of the system increases the α_k corresponding to larger values of the molecular area gradually decrease. All orientational states remain equally populated, however, until the phase-transition density is reached. In the high-density phase nearly all rods are parallel and have the smallest possible area. When statistically weighted states are considered, results are qualitatively the same except that, due to larger ω_i, some of the intermediate area states contain a proportionately larger fraction of the molecules. Table I lists the results of our computation, along with the values assigned to a and the weights ω_i. The transition pressures and entropies are smaller, and the densities are somewhat larger than the simpler systems discussed earlier. This may re-

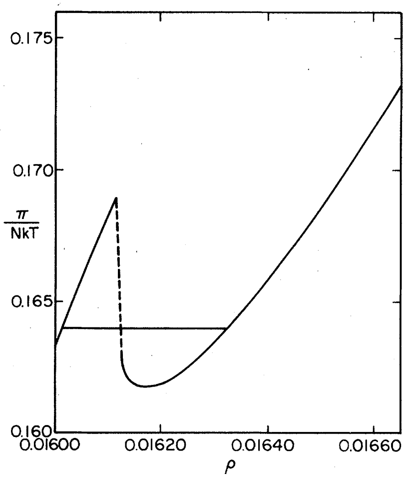

FIG. 3. π-ρ plot for a system of 4×10 (arbitrary units) rectangular rods.

TABLE I. Parameters for the 2-dimensional hard-rod transitions: π_t = transition pressure, ρ_a = anisotropic phase density, ρ_i = isotropic phase density, $\Delta S/Nk$ = relative entropy change.

Rectangle size	π_t/Nk	ρ_a [a]	ρ_i [a]	$\Delta S/Nk_B$ (eu)
5 × 8		(0.751 6)	(0.745 2)	
	0.354	0.018 79	0.018 63	0.159
4 × 10		(0.653 2)	(0.640 8)	
	0.164	0.016 33	0.016 02	0.194
Mixture (no weights) [b]	0.135	0.020 95	0.021 15	0.061
Mixture (with weights) [b]	0.103	0.018 73	0.018 60	0.038

[a] Packing fractions are given in parentheses for the single-component cases.

[b] For mixtures $b=5$ and $a=8.16$, 9.78, 9.52, 10.38, or 11.42, chosen to match areas in the lipid bilayer problem. Weights are also chosen by considering lipid chain conformations and have the values 1, 20, 192, 676, and 192 for the various respective values of a_K (Ref. 3).

flect the fact that disordered systems having varying shapes may be able to pack more efficiently than disordered systems having no conformational freedom.

When an attractive potential energy term is added, we compute pressure (π)-area (A) isotherms such as those shown in Fig. 5. For sufficiently low temperature or large C [Eq. (8)], we find a double van der Waals loop in a mixture model with no statistical weights. The large loop corresponds to the phase transition from a low to a high density, while the smaller loop is an orientational phase change from randomly aligned molecules to molecules aligned parallel. The larger transition is accompanied by a large reduction in the number of molecules in large-area conformations. The small transition involves very little conformational change. Application of the Maxwell area rule to the lower isotherm of Fig. 5 eradicates the small transition. However, while the large transition disappears at a critical point (near the upper curve in Fig. 5), the small transition

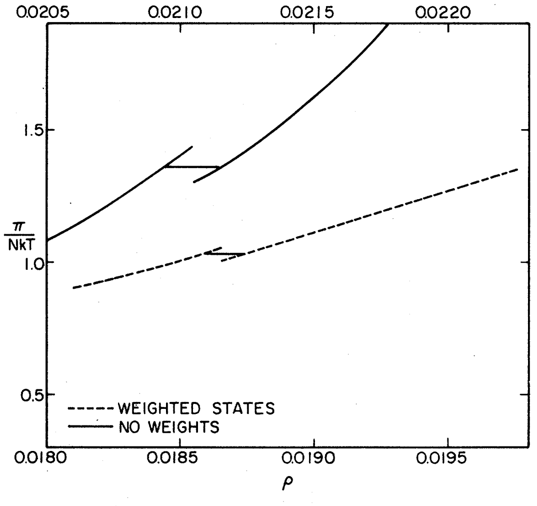

FIG. 4. π-ρ plots for the two types of hard-rod mixtures considered. The upper scale describes the system in which no statistical weights were utilized. The horizontal lines in both isotherms are obtained by the Maxwell equal-area rule. These isotherms appear flatter than those of Figs. 2 and 3, but this is largely due to a difference in scale.

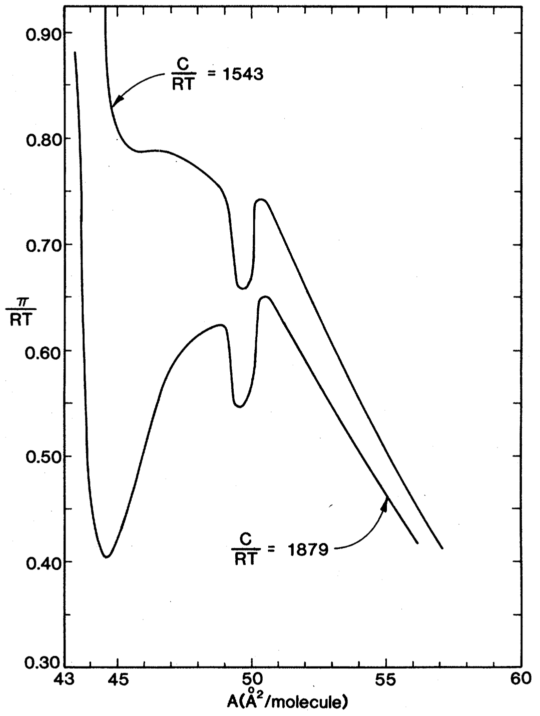

FIG. 5. π-A plots for hard-rod mixtures with an attractive potential energy for two values of C/RT, where C is the constant in Eq. (8) and $A_0=38.0$. The values for the molecular shape parameters are given in Table I. R is the gas constant Nk_B.

does not, so that the system *always* exhibits at least one transition. Very near the critical point of the large transition, the system has two transitions as the two sets of van der Waals loops are separated.

In summary, two-dimensional mixtures of hard rods have several interesting properties, at least when modeled by scaled particle theory. For simple systems the results described above are similar to those found for three-dimensional hard-rod systems by several different theoretical methods.[9-12] The use of the SPT to describe systems of large molecules with varying conformational shapes has a wide variety of potential applications in liquid crystal and biological physics. The unusual phase changes described here represent a sampling of the types of results one may expect if the methods described here and in Refs. 5 and 6 are applied to these problems. One must always keep in mind, however, that the SPT is inexact and not well understood. The only independent checks on its validity are for simple systems such as hard spheres. However, the checks for hard spheres show the theory to be remarkably successful so it is natural to extend it to systems such as those considered here to study its predictions.

ACKNOWLEDGMENT

This work was supported in part by NSF Grant No. PCM 76-20679.

---

[1] E. Helfand, H. L. Frish, and J. L. Lebowitz, J. Chem. Phys. 34, 1037 (1961).

[2] R. Jacobs, B. Hudson, and H. C. Andersen, Proc. Natl. Acad. Sci. U.S.A. 72, 3993 (1975).

[3] H. L. Scott and W. H. Cheng, Biophys. J. 28, 117 (1979).

[4] M. A. Cotter and D. C. Wacker, Phys. Rev. A 18, 2669 (1978).

[5] M. A. Cotter and D. C. Wacker, Phys. Rev. A 18, 2676 (1978).

[6] S. Marčelja, J. Chem. Phys. 60, 3599 (1974).

[7] W. H. de Jeu, J. van der Veen, and W. S. A. Goossens, Solid State Commun. 12, 405 (1973).

[8] M. A. Cotter, J. Chem. Phys. 67, 4268 (1977).

[9] M. A. Cotter, Phys. Rev. A 10, 625 (1974).

[10] M. A. Cotter, Mol. Cryst. Liq. Cryst. 35, 33 (1976).

[11] J. P. Straley, Mol. Cryst. Liq. Cryst. 22, 333 (1973).

[12] R. Alben, Mol. Cryst. Liq. Cryst. 13, 193 (1971).