

The Phase Transition in a One-Dimensional Lattice of Axisymmetric Bodies

Jerzy Szulga,¹ Wojbor A. Woyczynski,¹ Bernard Ycart,¹ and J. Adin Mann, Jr.²

Received June 9, 1986; revision received September 12, 1986

The partition function is studied for an array of axisymmetric, hard bodies (capped cylinders, etc.) with each fixed at the base on a regular one-dimensional lattice. It is shown that if a phase transition occurs in a system of n molecules, then it also occurs in a system of two molecules for the same value of the spacing parameter. With certain additional technical assumptions the converse is also true. Results are reported specifically for a system of thin, hard rods. Necessary and sufficient conditions are shown for a first-order transition to occur in the thermodynamic limit; there is only one transition and that happens when the spacing parameter is equal to the length of the rod. As expected, there is no phase transition when the rod is contracted to a point.

KEY WORDS: Phase transition; monomolecular film; one-dimensional lattice; partition function; thermodynamic limit.

1. INTRODUCTION

The behavior of monomolecular films (monolayers) spread at liquid–fluid interfaces and crystalline substrates has been intensively studied^(1–6) since the last century. Langmuir's experimental work in the early part of this century showed the existence of two-dimensional condensation phenomena of monolayers under compression. The model we develop in this paper can be used for monolayers either formed by adsorption onto solid surfaces or spread at the liquid/fluid interface. To be explicit, we will refer to spread monolayers⁽¹⁾ composed of long-chain amphiphatic molecules (containing both hydrophilic and hydrophobic groups), which may behave like cylin-

¹ Department of Mathematics and Statistics, Case Western Reserve University, Cleveland, Ohio 44106.

² Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106.

ders or ellipsoids of revolution. The phase behavior of monolayers of this type has been studied extensively; a liquid-gas transition and a liquid-expanded to liquid-condensed transition have been found experimentally.^(1,2) Of particular interest was the determination by Pallas⁽³⁾ that the liquid-expanded to liquid-condensed transition wherein both the molecular orientation and the monolayer density change was first order at least for pentadecanoic acid. The various theories that have been constructed to represent this transition are designed to predict higher order transitions. It is timely to investigate this problem again, keeping in mind that such transitions involve molecular orientation and can be first order.

Discussion of the relevant early theories using a thermodynamic approach is found in the monograph by Mayer and Mayer⁽⁴⁾; see also the fundamental papers by Kac *et al.*⁽⁵⁾ One should also consult the following articles and the literature quoted in Refs. 6–8 for discussions of various models for molecules and the concepts involved in phase transitions; Refs. 7 and 9 discuss rotating squares or thin rods; Ref. 10 discusses flexible molecules sitting on a planar lattice interacting according to the rules of the Brownian dynamics; and Ref. 11 discusses Gaussian ellipsoids. Although there exists a rich and deep theory of condensation phenomena, quantitative results are often derived by numerical methods.

In this paper we deal with finite systems of identical rigid molecules with their bases constrained to sites on a one-dimensional lattice (see Fig. 1). Their motion is restricted to swinging in the upper half-plane. The molecules are modeled by hard objects, with their nearest neighbor interac-

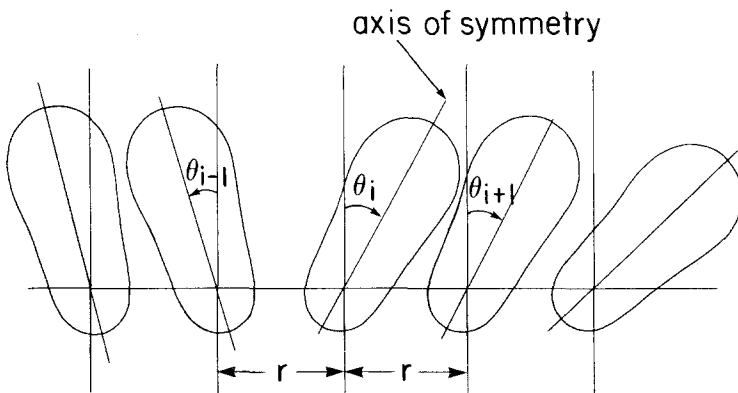


Fig. 1. The statistical mechanical system in which each particle is represented by a two-dimensional body with an axis of symmetry. The dynamics of the system is derived from rotational motions of particles in the upper half-plane ($-\pi/2 \leq \theta_j \leq \pi/2$) about sites of a one-dimensional lattice with spacing r .

tion governed by a hard core potential. We also take into account outside forces provided by the substrate or external sources. In the last section it is shown that these forces can strongly influence condensation phenomena. The principal thermodynamic quantities (such as the partition function, pressure, etc.) depend on many parameters (such as the temperature and other parameters determining the shape of the potential function), but we are mainly interested in their dependence on the lattice spacing r .

The partition function, even in the simplest case, is a numerically complicated object. We obtain exact formulas for the partition function, at least for certain domains of the parameter r . In particular, we have a simple way for deriving expressions for the partition function in the thermodynamic limit.

We define a phase transition to have occurred if the “pressure” ($\partial \log Q / \partial r$) takes infinite values at some concentration (value of $1/r$). We seek values of r where the partition function is nonanalytic.

We summarize the relevant equations of statistical thermodynamics used in this paper so as to establish notation. Consider a system of N particles with configuration $\bar{\theta} = (\theta_1, \dots, \theta_N) \in \Theta^N$, where $\Theta = [a, b]$.

The states of the above system are probability distributions on Θ^N that possess a density with respect to Lebesgue measure m on Θ^N ; the set of admissible states is

$$\sigma = \left\{ f: f \geq 0, f \in L^1(\Theta^N, m), \int f \, dm = 1 \right\}$$

A physical quantity of this system is any Borel function $G: \Theta^N \rightarrow R$. What is observable in state f is

$$E(f) = \int_{\Theta^N} G(\bar{\theta}) f(\bar{\theta}) \, dm(\bar{\theta})$$

The entropy of state f is given by

$$S(f) = - \int_{\Theta^N} f(\bar{\theta}) \log f(\bar{\theta}) \, dm(\bar{\theta})$$

and its maximum value for $f \in \sigma$ (corresponding to equilibrium of the system) is attained for

$$f_\beta(\bar{\theta}) = Q^{-1}(\beta) \exp[-\beta H(\bar{\theta})]$$

Here the partition function for the canonical ensemble depends on β and perhaps other parameters embedded in H and is defined by

$$Q(\beta) = \int_{\Theta^N} \exp[-\beta H(\bar{\theta})] \, dm(\bar{\theta})$$

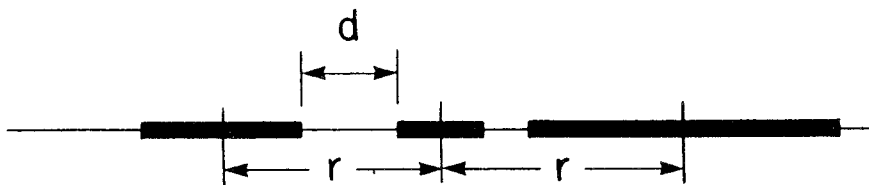


Fig. 2. The statistical mechanical system in which each particle is represented by its projection on a one-dimensional lattice. Mathematically the system reduces to the system of intervals of varying length with centers located at lattice points with spacing r . The interaction potential depends on the distance d .

where $H(\bar{\theta}) = T_e + V(\bar{\theta}) + V_0(\bar{\theta})$. Here T_e stands for the kinetic energy, V is the potential energy for the configuration, and V_0 is an external potential. For this ensemble, the Helmholtz free energy is $F = -kT \log Q$.

Experimentally, phase transitions are observed as “pathological” behavior of the free energy or its derivatives. As we have mentioned, this may involve the nonanalyticity of the partition function.

Section 2 contains a description of the model and Section 3 the thermodynamic considerations. Specific pair interactions are developed in Section 4. We conclude with a description of the phase transition for the system of thin rods.

The major conclusion is that the one-dimensional lattice of a monolayer of rods permits a phase transition. This result should be compared, first, with the results of Kac *et al.*,⁽⁵⁾ who prove that the system of hard balls with centers restricted to a one-dimensional line and exponential potentials exhibits no phase transition, and second, with the result of Casey and Runnels,⁽³⁾ who established that a one-dimensional system of hard squares on a lattice with a rotational degree of freedom will exhibit a phase transition as the lattice spacing is increased.

Our results have been obtained via purely analytic means, whereas other models (cf. Casey and Runnels⁽³⁾ and Mann⁽¹⁰⁾), although geometrically simple and involving a relatively small number of molecules, were only treated numerically, subject to limited computer resources.

Other chemical results are due to Onsager.⁽¹³⁾ The Onsager approach is to treat molecules in different positions as having different shapes. A typical (one-dimensional) example is shown in Fig. 2.

2. ONE-DIMENSIONAL LATTICE MODEL OF A SURFACTANT MONOLAYER

In this section we describe a simple one-dimensional model that mimics a change in both orientation and density with compression of a surfactant monolayer.

Suppose that each molecule is represented by a two-dimensional regular body (Fig. 1) with an axis of symmetry. The dynamics of a molecule is derived from rotational motion about a point on the axis of symmetry (called the head). The heads are tied down at lattice positions (see Fig. 1). A formalization of this model involves a Hamiltonian of the following form:

$$H(\bar{\theta}) = \sum_{i=1}^n \frac{1}{2} I_i \omega_i^2 + \sum_{i=1}^{n-1} U(\theta_i, \theta_{i+1}) + \tilde{U}(\theta_n, \theta_1) + \sum_{i=1}^n U_0(\theta_i) \quad (1)$$

where I_i is the moment of inertia, ω_i is the angular momentum, and θ_i determines the angle of tilt of the i th molecule (Fig. 1). It is convenient to take θ_i as the angle between the axis of symmetry of the i th molecule and the normal to the lattice line. The potential U_0 includes outside forces, in particular an influence of the substrate, the lattice in this case. The potential \tilde{U} accounts for the boundary of the lattice; periodic ($\tilde{U} = U$) and non-periodic versions of the model will be considered.

Only pairs of nearest neighbor interactions are considered. The potential U (or \tilde{U}) takes the value $+\infty$ if molecules overlap and is zero otherwise. The configuration space for a pair of molecules is a product of intervals $[-\pi/2, \pi/2] \times [-\pi/2, \pi/2]$. Therefore, we can find a set $C \subset [-\pi/2, \pi/2] \times [-\pi/2, \pi/2]$ that is symmetric with respect to the line $\theta_1 + \theta_2 = 0$ and such that

$$U(\theta_1, \theta_2) = +\infty I_C(\theta_1, \theta_2) \quad (2)$$

where I is the 0-1 indicator function of C (by convention, $+\infty \times 0 = 0$). Notice that C and U depend on additional parameters associated with a geometric structure of a molecule and its location on the lattice.

We remark that Eq. (2) is a special case of the Kihara potential, where molecular interaction works through the minimal distance between shells occupied by molecules (cf., e.g., Ref. 12, Chapter 4).

3. THERMODYNAMICS

The canonical partition functions associated with the Hamiltonian (1) are

$$Q_n = A^{-n} \int \cdots \int_{[-\pi/2, \pi/2]^n} \exp[-V(\bar{\theta})/kT] d\bar{\theta} \quad (3)$$

where $A = h/(2\pi kT)^{1/2}$, k and h being the Boltzmann and Planck constants, respectively. We consider only two boundary conditions: either $\tilde{U} = 0$ or

$\tilde{U} = U$. In the second case, which corresponds to periodic boundary conditions, a tilde will be used over the appropriate quantities. Denote

$$B_{i,j} = \{(\theta_1, \dots, \theta_n) : (\theta_i, \theta_j) \notin C\}$$

where C is the configuration set appearing in Eq. (2). In this notation

$$B_n = \bigcap_{i=1}^{n-1} B_{i,i+1} \quad (\tilde{B}_n = B_n \cap B_{n,1})$$

is the total configuration space for n particles. If we define $\varphi(\theta) = \exp[-U_0(\theta)/kT]$ and $A_1 = h/2\pi kT$, then we can rewrite (3) in the form

$$Q_n = A_1^{-n} \int_{B_n} \cdots \int \varphi(\theta_1) \cdots \varphi(\theta_n) d\bar{\theta} \quad (3a)$$

If $U_0 = u_0 \equiv \text{const}$, then

$$Q_n = (e^{-u_0/kT}/A_1)^n m(B_n) \quad (3b)$$

where m denotes the n -dimensional Lebesgue measure. The quantities \tilde{Q}_n and $m(\tilde{B}_n)$ can be obtained in a similar way with obvious modification due to periodicity. All principal thermodynamic functions can be derived from Q_n . The Helmholtz free energy is expressed by the equation $A_n = -kT \log Q_n$, and the one-dimensional analog of the three-dimensional pressure or two-dimensional surface tension is given by the equation $P_n = -kT(\partial \log Q_n/\partial r)$. We are interested in the limit behavior of the averages, in particular, of the average Helmholtz free energy per molecule

$$F = \lim_{n \rightarrow \infty} A_n/n = -kT \lim_{n \rightarrow \infty} \log Q_n^{1/n}$$

Here, the lattice spacing r is held constant as n goes to infinity.

A phase transition that occurs in the system we study corresponds to the existence of a lattice spacing $r_0 > 0$ such that $|p_n(r_0)| = \infty$.

A priori, the phase transition in a finite system may depend on the number of molecules, the boundary conditions of the model, and the form of the potential U_0 that represents outside forces, and its study is usually very complicated due to combinatorial reasons. In practice, the phase transition is often considered for the system in the thermodynamic limit (i.e., when $n \rightarrow \infty$). For example, general methods developed for nearest neighbor potential reduce the problem of evaluation of the free energy in the limit to the problem of finding the maximal eigenvalue for the linear

integral operator $\varphi \rightarrow \int \varphi(y) 1_C(x, y) dy$. The reduction means that the information about certain pair characteristics is sufficient to determine the behavior of the whole system (cf., e.g., the classic paper by Kac *et al.*⁽⁵⁾).

4. PAIR VERSUS n -PARTICLE PHASE TRANSITIONS

As observed at the end of Section 3, the information about pairs often suffices for the study of the whole system. In this section, we will show that for the potential considered in this paper, under certain additional restrictions, the phase transition for the system of n particles occurs if and only if the phase transition occurs for the system of two particles.

From here on we assume that the potential V_0 is bounded from below. Such a natural assumption excludes infinite outside attractive forces, and implies existence of a constant $K > 0$ such that

$$\varphi(\theta) = \exp[-U_0(\theta)] < K$$

for every $\theta \in [-\pi/2, \pi/2]$.

Proposition 1. If a phase transition occurs in a system of n molecules, then it also occurs in a system of two molecules for the same value of the spacing parameter.

Proof. Let r, r_0 be in the domain of the partition function Q_n . The increment of Q_n from r to r_0 can be decomposed as follows:

$$\begin{aligned} \Delta Q_n &\stackrel{\text{def}}{=} Q_n(r) - Q_n(r_0) \\ &= A_1^{-n} \int_{B_n(r) - B_n(r_0)} \cdots \int \varphi(\theta_1) \cdots \varphi(\theta_n) d\bar{\theta} \\ &= A_1^{-n} \left(\int_{B_n(r)} \cdots \int - \int_{B_n(r, r_0)} \cdots \int + \int_{B_n(r, r_0)} \cdots \int - \int_{B_n(r_0)} \cdots \int \right) \end{aligned}$$

where

$$B_n(r, r_0) = \{ \bar{\theta} : (\theta_1, \theta_2) \notin C(r_0), \dots, (\theta_{n-2}, \theta_{n-1}) \notin C(r_0), (\theta_{n-1}, \theta_n) \notin C(r) \}$$

One can check easily that

$$\begin{aligned} B_n(r) - B_n(r, r_0) &\subset B_{n-1}(r) - B_{n-1}(r_0) \\ B_n(r, r_0) - B_n(r_0) &\subset B_2(r) - B_2(r_0) \end{aligned}$$

Therefore

$$\begin{aligned} \left| \frac{\Delta Q_n}{r-r_0} \right| &\leq \frac{A_1^{-n}}{|r-r_0|} \left[\left| \int_{B_{n-1}(r)-B_{n-1}(r_0)} \cdots \int \varphi(\theta_1) \cdots \varphi(\theta_n) d\bar{\theta} \right| \right. \\ &\quad \left. + \left| \int_{B_2(r)-B_2(r_0)} \cdots \int \varphi(\theta_1) \cdots \varphi(\theta_n) d\bar{\theta} \right| \right] \\ &\leq \frac{K}{A_1} \left| \frac{\Delta \theta_{n-1}}{r-r_0} \right| + \left(\frac{K}{A_1} \right)^{n-2} \left| \frac{\Delta Q_2}{r-r_0} \right| \\ &\leq (n-1) \left(\frac{K}{A_1} \right)^{n-2} \left| \frac{\Delta Q_2}{r-r_0} \right| \end{aligned}$$

the last inequality following by induction. The above estimate immediately yields the following implications:

$$\left| \frac{dQ_n}{dr}(r_0) \right| = \infty \rightarrow \left| \frac{dQ_2}{dr}(r_0) \right| = \infty$$

which ends the proof of Proposition 1 in the case $\tilde{U}=0$. In the periodic case ($\tilde{U}=U$), we proceed in a similar way to get the following inequality:

$$\left| \frac{\Delta \tilde{Q}_n}{\Delta r} \right| \leq n \left(\frac{K}{A_1} \right)^{n-2} \left| \frac{\Delta Q_2}{\Delta r} \right| = \frac{n}{2} \left(\frac{K}{A_1} \right)^{n-2} \left| \frac{\Delta \tilde{Q}_2}{\Delta r} \right|$$

since $Q_2(r) = \frac{1}{2} + \frac{1}{2}\tilde{Q}_2(r)$. ■

For the nonperiodic model and under additional technical assumptions the implication converse to the one contained in Proposition 1 also holds true.

Suppose that R is a set of the spacing parameters r such that

- (a) $C(r)$ is a decreasing set-valued function on R [i.e., $C(r) \subset C(r')$ whenever $r \geq r'$, $r, r' \in R$].
- (b) $u = u(r) = \text{def } \max\{\theta: (\theta, -\theta) \notin C\} > 0, r \in R\}$ (cf. Fig. 3).

Condition (a) has an obvious physical interpretation: the higher the concentration, the more restricted the configuration space becomes. Property (b) excludes certain pathological situations. For instance, it may happen that for certain values of parameter r only finitely many molecules are allowed in the system, and the passage to the thermodynamic limit becomes meaningless. These comments are well illustrated by the example of a curiously behaving system of quarter-circles swinging around the circles' centers [cf. Figs. 4a and 4b, the latter representing $C(r)$].

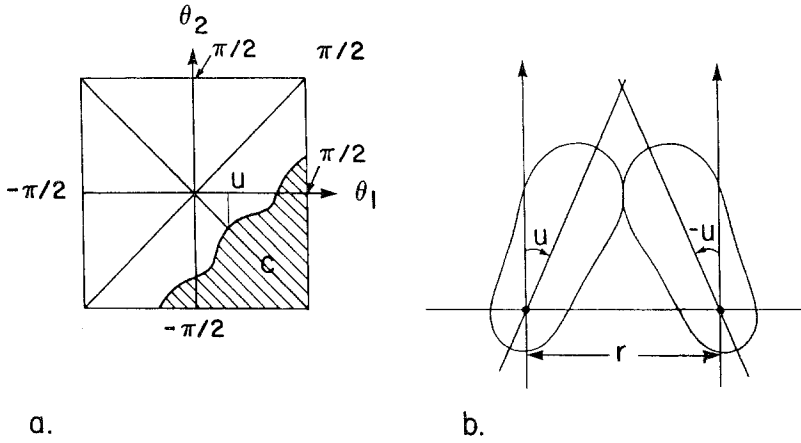


Fig. 3. Configuration space for pair interactions. (a) $C = C(r)$ represents the excluded configurations of angles θ_1, θ_2 describing positions of neighboring particles. (b) The angle $u = u(r) = \max\{\theta: (\theta, -\theta) \notin C\}$ corresponds to the maximal symmetric permissible tilt of neighboring particles.

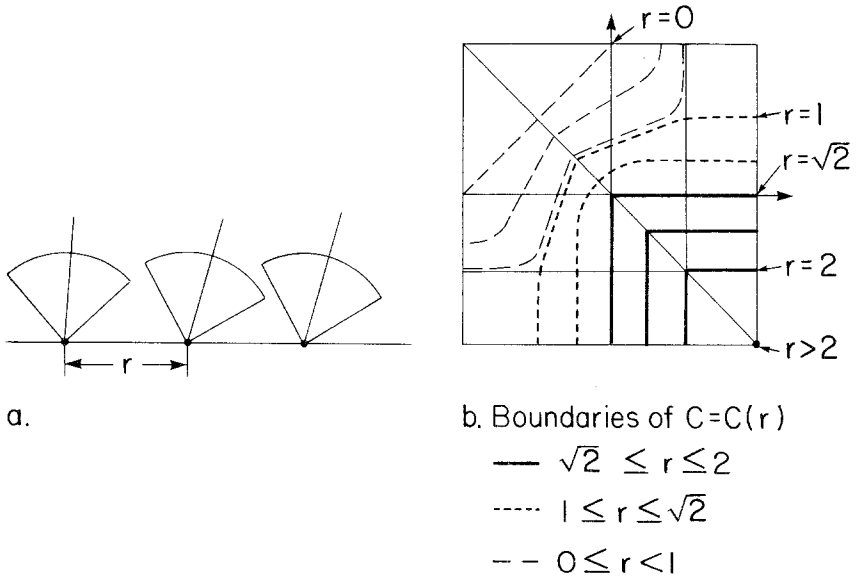


Fig. 4. The curious behavior of quarter-circle particles. (a) The thermodynamic limit is meaningless for $r \leq 1$ since in this case only a finite number of particles is allowed in the system. (b) The shapes of regions of excluded configurations change abruptly for values of the spacing parameter r equal to 0, 1, $\sqrt{2}$, 2.

Proposition 2. Suppose that R and $C(r)$, $r \in R$, satisfy conditions (a) and (b). Then if a phase transition occurs in a system of two molecules, then it also occurs in a system of n molecules for the same value of the spacing parameter.

Proof. Let $r, r_0 \in R$ be such that $r > r_0$ and put $u_0 = u(r_0)$. Then

$$\begin{aligned} & \{\bar{\theta}: \theta_1 \in [-u_0, u_0], \dots, \theta_{n-2} \in [-u_0, u_0], \\ & (\theta_{n-1}, \theta_n) \in C(r_0) - C(r), \theta_{n-1} + \theta_n \geq 0\} \\ & \subset \{\bar{\theta}: \theta_1 \in [-u_0, u_0], \dots, \theta_{n-2} \in [-u_0, u_0], \\ & \theta_{n-1} \geq -u_0, (\theta_{n-1}, \theta_n) \in C(r_0) - C(r)\} \\ & \subset \{\bar{\theta}: (\theta_1, \theta_2) \notin C(r_0), \dots, (\theta_{n-2}, \theta_{n-1}) \notin C(r_0), \\ & (\theta_{n-1}, \theta_n) \notin C(r) - C(r_0)\} \stackrel{\text{df}}{=} D \end{aligned}$$

Now, using the same decomposition as in the proof of Proposition 1, we have that

$$\begin{aligned} \Delta\theta_n &= \theta_n(r) - \theta_n(r_0) \geq A_1^{-n} \left[\int_{B_n(r, r_0)} \dots \int - \int_{B_n(r_0)} \dots \int \right] \\ & \geq A_1^{-n} \int_D \dots \int \varphi(\theta_1) \dots \varphi(\theta_n) d\bar{\theta} \\ & \geq A_1^{-n} \left[\int_{-u_0}^{u_0} \varphi(\theta) d\theta \right]^{n-2} \int \int_{\substack{C(r_0) - C(r) \\ \theta_{n-1} + \theta_n \geq 0}} \varphi(\theta_{n-1}) \varphi(\theta_n) d\theta_{n-1} d\theta_n \\ & = \frac{1}{2} A_1^{-n} \left[\int_{-u_0}^{u_0} \varphi(\theta) d\theta \right]^{n-2} [Q_2(r) - Q_2(r_0)] \end{aligned} \quad (4)$$

which proves the implication

$$\left| \frac{dQ_2}{dr} \right| = \infty \rightarrow \left| \frac{dQ_n}{dr} \right| = \infty. \quad \blacksquare$$

Remark 1. The method applied in the proof of Proposition 2 does not work in the periodic case. However, even in this case we can obtain the following version of the estimate (4):

$$\bar{\theta}_n(r) - \bar{\theta}_n(r_0) \geq A_1^{-n} \left[\int_{-u_0}^{u_0} \varphi(\theta) d\theta \right]^{n-2} [Q_2^*(r) - Q_2^*(r_0)] \quad (5)$$

where $r > r_0$, and where Q_n^* is the partition function restricted to the set

$$C^* \stackrel{\text{df}}{=} \{(\theta_1, \theta_2) \in C: \theta_1 \geq 0, \theta_2 \leq 0\} \quad (6)$$

(cf. Fig. 6). This version will be used later to solve the phase transition problem in a special case.

5. EXPLICIT FORMULAS FOR PARTITION FUNCTIONS

In the previous section a qualitative comparison between the behavior of n - and two-element systems was provided. However, for certain values of the spacing parameter r , it is possible to obtain an explicit functional relation between partition functions Q_n and Q_2 .

Let us define

$$\rho = \int_{-\pi/2}^{\pi/2} \varphi(\theta) d\theta, \quad c = c(r) \stackrel{\text{df}}{=} \rho^2 - A_1^2 Q_2 = \int \int_C \varphi(\theta_1) \varphi(\theta_2) d\theta_1 d\theta_2 \quad (7)$$

Theorem 1. Suppose that $C \subset [0, \pi/2] \times [-\pi/2, 0]$. Then

$$Q_n = A_2^{-n} \frac{(1+a)^{n+1} - (1-a)^{n+1}}{2a}$$

and for periodic boundary conditions

$$\tilde{Q}_n = A_2^{-n} [(1+a)^n + (1-a)^n]$$

where $A_2 = 2A_1/\rho$ and $a = (1 - 4c/\rho^2)^{1/2}$.

Proof. Using the notation of Section 3, let us denote

$$A_{i,j} = [-\pi/2, \pi/2]^n - B_{i,j}$$

$$A_n = A_{1,2} \cup \cdots \cup A_{n-1,n}$$

and

$$\tilde{A}_n = A_{1,2} \cup \cdots \cup A_{n-1,n} \cup A_{n,1}$$

where $n \geq 2$, and, by definition, $A_1 = \emptyset$.

For $n \geq 3$, using the fact that $A_{n-2,n-1} \cap A_{n-1,n} = \emptyset$, we obtain that

$$\begin{aligned} a_n &\stackrel{\text{df}}{=} \int \cdots \int_{A_n} \varphi(\theta_1) \cdots \varphi(\theta_n) d\bar{\theta} \\ &= \left(\int \int_{A_{1,2} \cup \cdots \cup A_{n-2,n-1}} + \int \cdots \int_{A_{n-1,n}} - \int \int_{(A_{1,2} \cup \cdots \cup A_{n-2,n-1}) \cap A_{n-1,n}} \right) \\ &\quad \times \varphi(\theta_1) \cdots \varphi(\theta_n) d\bar{\theta} \\ &= \rho a_{n-1} + \rho^{n-2} a_2 - a_2 a_{n-2} \end{aligned}$$

If we define

$$b_n \stackrel{\text{df}}{=} A_1^n \theta_n = \rho^n - a_n \quad (8)$$

then we get

$$\rho^n - b_n = \rho(\rho^{n-1} - b_{n-1}) + \rho^{n-2}a_2 - a_2(\rho^{n-2} - b_{n-2})$$

A straightforward computation shows that

$$b_n = \rho b_{n-1} - c b_{n-2}, \quad n = 3, 4, \dots$$

Therefore, for the reduced quantities $b_n^* = b_n/\rho^n$, we obtain the following recurrence formula:

$$b_n^* = b_{n-1}^* - c^* b_{n-2}^* \quad (9)$$

with $b_1^* = 1$, $b_2^* = 1 - c^*$, $c^* = c/\rho^2$.

By a standard procedure, the solutions of (9) can be obtained by introducing the characteristic equation associated with (9):

$$x^2 = x - c^*$$

Its roots are equal to $x_1 = (1 + a)/2$, $x_2 = (1 - a)/2$, where $a = (1 - 4c^*)^{1/2}$, and the solution of (9) is given by the formula

$$b_n^* = \alpha x_1^n + \beta x_2^n$$

The coefficients α and β are easily determined from the system of two linear equations obtained from (9) for $n = 1$ and $n = 2$:

$$\alpha = (1 + a)/2a, \quad \beta = -(1 - a)/2a$$

So, finally, we have that

$$\theta_n = A_1^{-n} b_n = \frac{A_1^{-n} \rho^n (1 + a)^{n+1} - (1 - a)^{n+1}}{2^n \cdot 2a}$$

which proves the first formula of Theorem 1. To obtain the second formula, it suffices to observe that

$$A_1^n \tilde{\theta}_n = b_n - c b_{n-2}$$

and substitute the b_n computed above. ■

Corollary 1. We have that

$$\theta_n = \Phi_n(c) = \Psi_n(\theta_2) \quad [\tilde{\theta} = \tilde{\Phi}_n(c) = \tilde{\Psi}_n(\tilde{\theta}_2)]$$

where $\Phi_n, \Psi_n (\tilde{\Phi}_n, \tilde{\Psi}_n)$ are polynomials of degree $[(n+1)/2]$, and, in particular, θ_n depends smoothly on θ_2 .

Corollary 2. Under the assumption of Theorem 1, we obtain the following formula for the average energy per molecule in the thermodynamic limit:

$$\tilde{F} = F = -kT \lim_{n \rightarrow \infty} \log Q_n^{1/n} = -kT \{ \log A_2^{-1} + \log [1 + (1 - 4c/\rho^2)^{1/2}] \}$$

Therefore

$$\begin{aligned} P \stackrel{\text{df}}{=} \frac{\partial F}{\partial r} &= kT \frac{2 \partial c / \partial r}{(\rho^2 - 4c)^{1/2} [\rho + (\rho^2 - 4c)^{1/2}]} \\ &= - \frac{h^2}{2\pi^2 kT} \frac{\partial \theta_2 / \partial r}{(\rho^2 - 4c)^{1/2} [\rho + (\rho^2 - 4c)^{1/2}]} \end{aligned}$$

which indicates that the system in the thermodynamic limit exhibits a phase transition at r_0 if and only if the two-element system does so [provided $c(r_0) \neq \rho^2/4$].

Remark 1. The assumption $c(r_0) \neq \rho^2/4$ is essential above. Consider, for instance, the model introduced on Fig. 4, with an additional condition $U_0 = 0$. In this case $\rho = \pi^2$ [cf. (7)] and for $2^{1/2} \leq r \leq 2$, we have that

$$c(r) = (\frac{1}{4}\pi + \arccos \frac{1}{2}r)^2$$

Hence $\rho^2 - 4c(2^{1/2}) = 0$, but $c'(2^{1/2}) = \pi/2^{1/2} \neq 0$.

The system exhibits the phase transition in the thermodynamic limit at $r_0 = 2^{1/2}$, although the corresponding system of two elements does not.

Remark 2. Theorem 1 holds under the formal assumption that $C(r) \subset [0, \pi/2] \times [-\pi/2, 0]$ for $r \geq r_{\min}$. The intuitive physical interpretation of r_{\min} is clear: r_{\min} is the minimum spacing of molecules that excludes simultaneous interaction of more than two molecules (cf. Fig. 5).

6. PHASE TRANSITION FOR THE SYSTEM OF THIN RODS

In this section we find the specific value of the spacing parameter r for which the phase transition occurs in the system of thin rods pictured in Fig. 5d. We assume, without loss of generality, that the rods are of length 1. In this case the set C is symmetric with respect to the line $x + y = 0$ and its

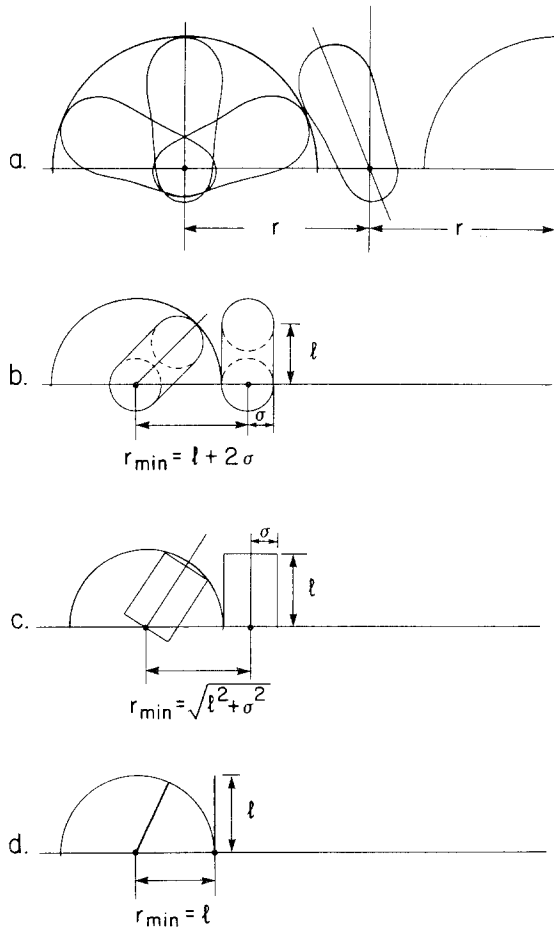
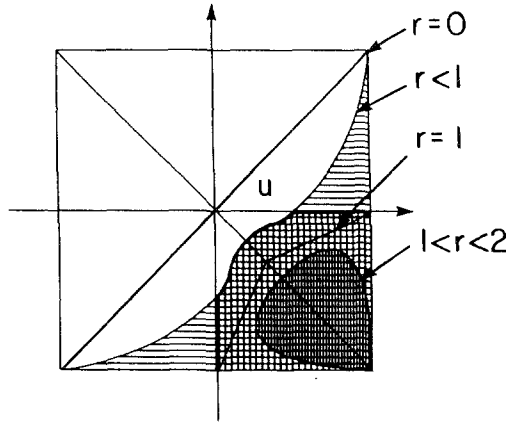


Fig. 5. For various shapes of particles the minimum spacing r_{\min} is evaluated that still permits free swinging of one of the neighboring particles. In particular, for spacings $r \geq r_{\min}$, the exclusion region $C(r)$ is contained in the quadrant $[0, \pi/2] \times [-\pi/2, 0]$.

boundaries are given by the sides of the square $[-\pi/2, \pi/2] \times [-\pi/2, \pi/2]$ and the curve

$$\sin(x - y) = \begin{cases} r \cos y, & u \leq x \leq \pi/2, & x + y \geq 0 \\ r \cos x, & -\pi/2 \leq y \leq -u, & x + y \leq 0 \end{cases} \quad (10)$$

where $\sin u = r/2$. We show some sample regions $C(r)$ in Fig. 6. As far as the outside potential U_0 is concerned, we assume that it depends only on the average distance of the rod from the substrate, i.e., U_0 is a function of



- $C(r)$ for $r, 0 < r < 1$
- $C^*(r)$ for this r
- $C(r) = C^*(r)$ for $r, 1 \leq r < 2$

Fig. 6. Exclusion regions $C = C(r)$ for the system of thin rods depend on the spacing r . The shape of the regions changes abruptly as r crosses the value 1. The angle $u = u(r) = \max\{\theta: (\theta, -\theta) \notin C\}$ corresponding to the maximal symmetric permissible tilt of neighboring particles is here equal to $u(r) = \arcsin(r/2)$.

$\xi = \cos \theta$; $\varphi(\theta) = \psi(\xi)$ for a certain function ψ . For the purpose of this section we assume that $\psi(1) = \varphi(0) \neq 0$ and that ψ is continuous in a neighborhood of 1. Also, recall that the conditions imposed on φ in Section 4 imply that φ is bounded from above by a constant K .

Theorem 2. For the system of thin rods described above, the phase transition occurs at $r_0 = r_{\min} = 1$ if and only if

$$\int_0^a \frac{\psi(\xi)}{\xi} d\xi = \infty$$

for some $a > 0$. Moreover, $r_0 = 1$ corresponds to the only possible phase transition in the above system.

Proof. In view of Propositions 1 and 2 and Remark 1, it suffices to prove the following implications:

- (i) If $dc/dr(1) = \infty$, then for every $a > 0$ (or, equivalently, for some $a > 0$) $\int_0^a \psi(\xi)/\xi d\xi = \infty$.
- (ii) If there exists an $a > 0$ such that $\int_0^a \psi(\xi)/\xi d\xi = \infty$, then $dc^*/dr(1) = \infty$.

A simple reformulation of (10) gives the following formula for the boundary curve of C contained in the triangle $x + y \geq 0$:

$$y = y(x, r) = \arctan \frac{\sin x - r}{\cos x} \quad (11)$$

where $u \leq x \leq \pi/2$. Hence

$$\frac{\partial y}{\partial r} = \frac{-\cos x}{1 - 2r \sin x + r^2}$$

Since in our case [cf. (7)]

$$c = c(r) = 2 \int_{u(r)}^{\pi/2} g(x, r) dx$$

where

$$u(r) = \arcsin(r/2)$$

$$g(x, r) = \psi(\cos x) \int_{-x}^{y(x, r)} \psi(\cos y) dy$$

we have

$$c^*(r) = c(r) - 2 \int_{v(r)}^{\pi/2} g^*(x, r) dx$$

where

$$v(r) = \arcsin \min(r, 1)$$

$$g^*(x, r) = \psi(\cos x) \int_0^{y(x, r)} \psi(\cos y) dy$$

(cf. Fig. 6). Clearly $c(r) = c^*(r)$ for $r \geq 1$. Since $g(u(r), r) = g(v(r), r) = 0$, the corresponding derivatives take the form

$$\begin{aligned} \frac{dc}{dr} &= 2 \int_{u(r)}^{\pi/2} \psi(\cos x) \psi(\cos y(x, r)) \frac{\partial y(x, r)}{\partial r} dx \\ \frac{dc^*}{d\tau} &= 2 \int_{u(r)}^{v(r)} \psi(\cos x) \psi(\cos y(x, r)) \frac{\partial y(x, r)}{\partial r} dx \end{aligned}$$

Now, the implication (i) follows immediately from the estimate

$$\left| \frac{dc}{dr} \right| \leq K_a + K'_a \int_0^a \frac{\psi(\xi)}{\xi} d\xi \quad (12)$$

where r is sufficiently close to 1 and K_a, K'_a are constants depending only on a . The estimate is obtained as follows: by the boundedness assumption imposed on the function ψ and in view of the inequality

$$1 - 2r \sin x + r^2 \geq 1 - \sin x, \quad 0 \leq x \leq \pi/2, \quad r > 0$$

we get that

$$\begin{aligned} \left| \frac{dc}{dr} \right| &\leq 2K \int_{u(r)}^{\pi/2} \frac{\cos x \psi(\cos x)}{1 - \sin x} dx \\ &= 2K \int_{r/2}^1 \frac{\psi((1-s^2)^{1/2})}{1-s} ds \\ &\leq 2K \int_{r/2}^b \frac{\psi((1-s^2)^{1/2})}{1-s} ds + 2K \int_b^1 \frac{\psi((1-s^2)^{1/2})}{1-s} ds \end{aligned}$$

for each $b, r/2 < b < 1$. Now,

$$\int_b^1 \frac{\psi((1-s^2)^{1/2})}{1-s} ds \leq \frac{2}{b} \int_b^1 \frac{\psi((1-s^2)^{1/2})}{1-s^2} s ds = \frac{2}{b} \int_0^a \frac{\psi(\xi)}{\xi} d\xi$$

where $a = (1 - b^2)^{1/2}$ and

$$\int_{r/2}^b \frac{\psi((1-s^2)^{1/2})}{1-s} ds \leq K \int_{r/2}^b \frac{ds}{1-s} = K \log \frac{1-r/2}{1-b} \leq K \log \frac{1-\delta/2}{1-b}$$

for $r > \delta$ ($\delta < 1$). The above two inequalities give (12) with

$$K_a = 2K^2 \log[(1 - \delta/2)/(1 - b)] \text{ and } K'_a = 4K/b$$

To obtain implication (ii), notice that the continuity assumption imposed on ψ yields the existence of a constant $K' > 0$, a number $w \in (u, \pi/2)$, and of a $\delta > 0$ such that $\psi(\cos y(x, r)) > K'$, for $r > \delta$ and $x > w$. Therefore, setting $\sin w = b$ and $\hat{r} = \min(r, 1)$, we get that

$$\begin{aligned} \left| \frac{dc^*}{dr} \right| &\geq K' \int_w^{v(r)} \frac{\cos x \psi(\cos x)}{1 - 2r \sin x + r^2} dx \\ &= K' \int_b^{\hat{r}} \frac{\psi((1-s^2)^{1/2})}{1-s} ds \geq \frac{1}{5} K' \int_b^{\hat{r}} \frac{\psi((1-s^2)^{1/2})}{1-s} ds \end{aligned}$$

since, for $s \leq \hat{r} \leq 2$, $1 - 2rs + r^2 \leq 5(1 - s)$. Furthermore,

$$\int_b^{\hat{r}} \frac{\psi((1-s^2)^{1/2})}{1-s} ds \geq \int_b^{\hat{r}} \frac{\psi((1-s^2)^{1/2})}{1-s^2} s ds = \int_{(1-\hat{r}^2)^{1/2}}^{(1-b^2)^{1/2}} \frac{\psi(\xi)}{\xi} d\xi$$

so that, for each $r > \delta$ and $a < (1 - b^2)^{1/2} = \cos w$,

$$\left| \frac{dc^*}{dr} \right| \geq \frac{K'}{5} \int_{(1-r^2)^{1/2}}^a \frac{\psi(\xi)}{\xi} d\xi$$

Taking $r \rightarrow 1$, the implication (ii) follows.

Corollary 3. Let $u_0 = -\log a_0 = \text{const}$. Then the phase transition occurs in the system of thin rods at $r_0 = 1$. Moreover, a straightforward computation shows that

$$\frac{dc}{dr} = -a_0 \frac{\log(1-r)^2}{2r}$$

and

$$\frac{dc^*}{dr} = \begin{cases} -a_0 \frac{\log(1-r)^2}{2r} & \text{for } r < 1 \\ -a_0 \frac{\log(1-r)^2}{2r} & \text{for } r > 1 \end{cases}$$

The above formulas permit computation of the one-dimensional pressure after substitution in the formula in Corollary 2.

Corollary 4. If $U_0 = \infty \cdot I_{(0, \xi_0)}$, then the system of thin rods will exhibit no phase transition.

ACKNOWLEDGMENT

Support by the Office of Naval Research under their SRO grant to Case Western Reserve University is acknowledged with gratitude.

REFERENCES

1. G. L. Gaines, Jr., *Insoluble Monolayers at Liquid-Gas Interfaces* (Interscience, New York, 1966).
2. A. W. Adamson, *Physical Chemistry of Surfaces*, 4th ed. (Wiley-Interscience, New York, 1982).
3. N. R. Pallas, Ph.D. Dissertation, Clarkson College of Technology [available from University Microfilms, Ann Arbor, MI]; S. R. Middleton and B. A. Pethica, *J. Chem. Soc. Faraday Symp.* **16**:109 (1981).
4. J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940).
5. M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* **4**:216 (1963).
6. C. Domb and M. S. Green (eds.), *Phase Transitions and Critical Phenomena*, Vol. 1-6 (Academic Press, London, 1972).

7. A. Fulinski and L. Longa, *J. Stat. Phys.* **21**:635 (1973).
8. G. W. Milton and M. E. Fisher, *J. Stat. Phys.* **32**:413 (1983).
9. L. M. Casey and L. K. Runnels, *J. Chem. Phys.* **51**:5070 (1969).
10. J. A. Mann, Jr., *Langmuir* **1**:11 (1985).
11. B. J. Berne and P. Pechukas, *J. Chem. Phys.* **56**:4213 (1972).
12. M. Reed and K. E. Gubbins, *Applied Statistical Mechanics* (McGraw-Hill, New York, 1973).
13. L. Onsager, *Ann. N. Y. Acad. Sci.* **51**:627 (1949).