

## Phase Transitions in Systems of Grafted Rods

Zhong-Ying Chen,<sup>(a)</sup> Julian Talbot, and William M. Gelbart

*Department of Chemistry, University of California, Los Angeles, California 90024*

and

Avinoam Ben-Shaul

*Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel*

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Mobile rigid rods grafted on an interface are treated both by Onsager-type and Monte Carlo approaches. Symmetry arguments are presented which show that, unlike the case of hard rods in bulk, no orientational "standing-up" transition occurs: Attractive forces between rods are necessary for a discontinuous change in alignment. These conclusions are confirmed by Monte Carlo simulations and are discussed in the context of recent controversies concerning the "expanded" to "condensed" phase transition in adsorbed surfactant monolayers.

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The successive phase transitions observed in adsorbed surfactant monolayers, e.g., fatty acids on water, comprise one of the classic problems in physical chemistry.<sup>1</sup> Many statistical mechanical theories, including lattice packing<sup>2</sup> and Ising Hamiltonian<sup>3</sup> formulations, have been advanced in an effort to account for the orientational ordering transitions in these systems. Similarly, powerful new experimental techniques, notably fluorescence microscopy,<sup>4</sup> synchrotron x-ray scattering,<sup>5</sup> and second-harmonic generation,<sup>6</sup> have been successfully applied to explore microscopic structures in the regions of two-phase coexistence. Of particular interest has been the question of whether—at pressures intermediate between those characterizing the gas-liquid condensation and the fluid-solid ordering—a first-order transformation occurs from "expanded" to "condensed" liquid states. A great deal of controversy remains concerning the order parameters, and hence the molecular degrees of freedom, appropriate to a fundamental description of these phase transitions. Closely associated questions concern the presence and nature of orientational ordering (standing-up) transitions in physisorbed, small-molecule, monolayers (e.g., nitrogen on graphite<sup>7</sup>).

In an effort to clarify the above issues, we have treated the simpler, but intimately related, problem of hard, rigid rods which are grafted to a planar, impenetrable, surface. Hard here means that the particles interact with each other only through short-range repulsions; rigid describes the complete neglect of conformational flexibility; and grafted implies that each rod has one of its ends attached to the surface, even as it is mobile (i.e., free to translate). Halperin, Alexander, and Schechter<sup>8</sup> have considered this system within the second-virial approximation and have found that the orientational order increases continuously over the full range of density. They speculated that anisotropic adsorption at the surface, or attraction between rods, might be sufficient to give a

first-order transition. In the present Letter, employing both mean-field (symmetry) analyses and Monte Carlo simulations, we show that (1) unlike the situation *in bulk*, grafted hard rods do not undergo a fluid-fluid (orientational ordering) phase change; (2) attractions between particles *are* necessary for a first-order transition, whereas anisotropic adsorption alone is *not* sufficient; and (3), again unlike the fully 3D (bulk) case, attracting hard rods which are grafted to a surface appear not to undergo *successive* changes of state between gas-liquid and liquid-liquid (isotropic-nematic) uniaxial phases.

To expose most clearly our symmetry arguments, we use the Zwanzig approximation<sup>9</sup> according to which the rod orientations are restricted to lie along one of the space-fixed ( $x, y, z$ ) axes. With Onsager,<sup>10</sup> we write the dimensionless Helmholtz free energy per particle as

$$f \equiv \frac{F/N}{kT} = \sum_{i=x,y,z} p_i \ln p_i + \frac{\rho}{2} \sum_{i,j} p_i p_j V_{ij} + O(\rho^2). \quad (1)$$

Here  $p_i$  is the fraction of rods pointing along the  $i (=x, y, z)$  direction,  $\rho = N/A$  is the number density of rods, and  $V_{ij}$  is the second-virial coefficient—the pair excluded volume associated with hard rods having orientations  $i$  and  $j$ . From the Onsager and Zwanzig analyses<sup>9,10</sup> we know that spontaneous alignment in this system can be qualitatively accounted for by neglect of the  $O(\rho^2)$  terms: Accordingly, it is convenient here to consider only the two-body covolumes. For rods (rectangular parallelepipeds, say) of length  $a$  and width  $b$ , the  $V_{ij}$  matrix has the form

$$V = \begin{pmatrix} 4ab & (a+b)^2 & 2b(a+b) \\ (a+b)^2 & 4ab & 2b(a+b) \\ 2b(a+b) & 2b(a+b) & 4b^2 \end{pmatrix}. \quad (2)$$

For the 3D (bulk) case, on the other hand,  $V$  is fully

symmetric, with all diagonal elements equal to one another, and similarly for the off-diagonal ones. This is because the isotropy of space can only distinguish between parallel and perpendicular pairs, whereas in the grafted case the excluded area depends on whether the pair of rods lie normal to or within the planar surface. It is precisely this symmetry difference which accounts for the contrasting phase-transition behaviors in the bulk and grafted systems.

More explicitly, writing  $p_x = p_y = \frac{1}{3} + \Delta$  and  $p_z = \frac{1}{3} - 2\Delta$ , substituting for  $V_{ij}$  from (2), and expanding Eq. (1) in powers of the orientational order parameter  $\Delta$ , we have

$$f = f_0(\bar{\rho}) + (\bar{\rho}K)\Delta + (9 + \bar{\rho}L)\Delta^2 + 9\Delta^3 + \frac{81}{2}\Delta^4 + \dots + O(\rho^2). \quad (3)$$

Here  $\bar{\rho} = b^2\rho$  is the (dimensionless) density, and  $K \equiv \frac{2}{3}(\chi+5)(\chi-1)$  and  $L \equiv (\chi-1)^2$ , with  $\chi \equiv a/b (> 1)$  the axial ratio of a rod. From the positivity of both  $K$  and  $L$ , it follows immediately that the  $\Delta_{\min}$  minimizing  $f$  is nonzero, no matter how small the density ( $\Delta_{\min} \rightarrow 0$  only as  $\rho \rightarrow 0$ ), i.e., there is no isotropic phase; and there is no inflection point in  $f$  vs  $\Delta$ , and hence only one minimum.  $\Delta_{\min}$  simply increases continuously as the density is raised. By contrast, in the bulk situation, the symmetry of  $V$  results in a vanishing coefficient ( $K \equiv 0$ ) for the linear term in  $\Delta$ , and in a  $\Delta^2$  coefficient (free-energy curvature) which changes from positive to negative for sufficiently large  $\rho$ . This leads to the well-known first-order orientational ordering transition in 3D systems of hard rods.<sup>9,10</sup> In the grafted case, on the other hand, attractions between rods are necessary to give the transition.

Including both anisotropic adsorption and interparticle attractions, and treating the latter in mean-field approximation, we obtain<sup>11</sup> a free energy of the form (3), but with  $\bar{\rho}K \rightarrow \bar{\rho}K - 2\epsilon$  and  $L \rightarrow L - 3A$ . Here  $\epsilon$  is the adsorption energy (in units of kT) that a rod gains by lying on the surface (relative to its standing normal).  $A > 0$  is a dimensionless measure of the anisotropy in the average pair attraction between rods. It arises from the mean-field terms  $\frac{1}{2}\bar{\rho}\sum_i p_i p_j E_{ij}$ , with  $E_{ij}$  having the form  $-(I + A\delta_{ij})$ : Note that  $I (> 0)$  makes no contribution to the  $\Delta$ -dependent terms in  $f$ . Hence  $A$  measures the mean energy lowering for parallel configurations. Since  $\epsilon$  appears only in the linear term in  $\Delta$ , it follows that orientational-dependent adsorption energy alone cannot bring about a phase transition. The anisotropic attraction  $A$  enters into the free-energy curvature ( $\Delta^2$  coefficient), however, and hence suffices to introduce (at high enough density) a second minimum in  $f$  vs  $\Delta$ .

Specifically one can show that, for any  $\epsilon$ , a first-order transition appears for  $A > \{[99K/(1+72\epsilon)] + (L/3)\} \equiv A^*$ . This is seen in Fig. 1 where the parameter space associated with  $A$  and  $\epsilon$  (the two dimensionless energies

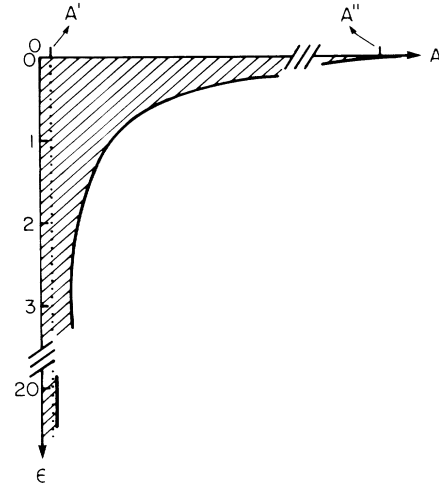


FIG. 1. Phase diagram in  $A, \epsilon$  space. For all  $A, \epsilon$  pairs above the solid curve (i.e., in the shaded region) no "standing-up" transition occurs with increase in density. The asymptote  $A'$  and intercept  $A''$  depend on axial ratio:  $A' \equiv A^*(\epsilon = \infty) = L/3$ , and  $A''(\epsilon = 0) = 99K + L/3$ . Note the change in scale for both  $\epsilon$  and  $A$  axes.

appearing in the problem) is divided by the curve  $A = A^*(\epsilon)$  into complementary regions where a phase transition does and does not occur. That is, for any  $A, \epsilon$  lying below this curve, an increase in density ( $\rho$ ) results in a first-order jump in orientational order ( $\Delta$ ); on the curve,  $\Delta$  grows continuously with density. Note then that anisotropic adsorption is neither sufficient nor necessary:  $A^*$  remains finite even as  $\epsilon \rightarrow 0$ . Nevertheless, from the approximately inverse relationship between  $A^*$  and  $\epsilon$ , we see that  $\epsilon > 0$  does serve to raise the critical temperature ( $\sim 1/A^*$ ) for the orientational ordering transition.

The above behavior has been confirmed by Monte Carlo calculations in which we simulate hard spherocylinders grafted to a plane. Apart from the constraint that one end of each rod is required to stay on the surface, the particles are free to translate and rotate, as long as no rods overlap each other or penetrate the plane. In addition to the hard-core repulsions, the spherocylinders attract one another according to the dispersive form  $-CP_2(\cos\theta_{ij})/r_{ij}^6$  where  $\theta_{ij}$  and  $r_{ij}$  are the angle between long axes and the distance between grafted ends, respectively;  $P_2(x) = (3x^2 - 1)/2$  is the second Legendre polynomial. The dimensionless quantity  $\tilde{C} \equiv C/kTb^6$ , with  $b$  the rod diameter, corresponds roughly to  $A$  in the mean-field model. The (one-body) anisotropic adsorption energy is written as  $\epsilon e^{-a\cos^2\theta_i}$ , with  $a$  chosen large enough so that  $\epsilon$  is essentially the energy gained as a particle lies down ( $\theta_i = \pi/2$ ). Our Monte Carlo simulations were carried out in both the  $(N, A, T)$  and  $(N, P, T)$  ensembles, in a square cell with periodic boundary conditions. Each trial move consists of a combined translation

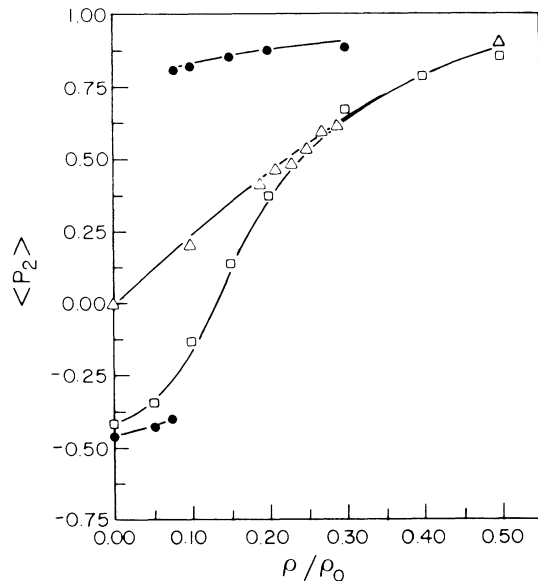


FIG. 2. Monte Carlo results for the orientational order parameter,  $\langle P_2 \rangle$ , as a function of density for grafted spherocylinders ( $N=100$ ). The density is measured relative to that of closest packing,  $\rho_0=2/\sqrt{3}b^2$ , where  $b$  is the diameter of the spherocylinder. All curves are for an axial ratio of  $\chi=4$ . Triangles: pure hard core ( $\tilde{C}=0$ ,  $\epsilon=0$ ). Squares: ( $\tilde{C}=4$ ,  $\epsilon=4$ ,  $\alpha=8$ ). Circles: ( $\tilde{C}=8$ ,  $\epsilon=5$ ,  $\alpha=10$ ). The lines are drawn as a guide only.

plus rotation, with the ratio of the maximum of each adjusted so that translation and reorientation contribute equally to the probability that a move is rejected. The orientational order parameter,  $\langle P_2(\cos\theta) \rangle$ , showed little dependence on system size (we used  $N=100$  and  $N=196$ ). All state points were equilibrated for at least  $\frac{1}{2} \times 10^6$  configurations (attempted moves), followed by a production phase of at least  $10^6$  configurations (up to  $10^7$  near the transition) during which the averages were evaluated. Full details of the simulations will be reported elsewhere.<sup>11</sup> Here we simply show in Fig. 2 some orientational order parameter versus density results for particles of axial ratio 4, for different interaction potentials. Note that no transition occurs for anisotropies as small as  $\tilde{C} \approx 4 \approx \epsilon$ , whereas a large discontinuity—from essentially lying-down to standing-up rods—appears for slightly stronger attraction ( $\tilde{C}=8$ ) and adsorption ( $\epsilon=5$ ).

The existence of an orientational phase transition in the presence of strong enough attractions raises the question of whether one should expect *two*, successive transitions between fluid states, the first corresponding to a gas-liquid-like condensation and the second to a liquid-liquid-crystal-type ordering. This is, of course, precisely what one sees in the familiar 3D, bulk, system. But in this latter case, as we have already stressed, the lowest-density (gas) phase has no long-range order. According-

ly, the condensation corresponds “simply” to a jump in density; it is only at the second transition that orientational ordering appears. In the grafted case, on the other hand, the symmetry-breaking effect of the interface couples  $\tilde{\rho}$  and  $\Delta$  at *all* densities: Hence we see a phase transition in which both order parameters jump from one nonzero value to another.

Generalizing our mean field theory to include all powers of  $\tilde{\rho}$  in the  $\Delta$ -independent free energy  $f_0$ , we still find only one orientational phase transition. More explicitly, the common tangent constructions involve *either* a van der Waals loop on a single branch (for small anisotropies), *or* (for large enough  $\chi$ ,  $A$ , and  $\epsilon$ ) a jump from one branch to another which preempts this loop. Hence it appears that attractions between grafted rods have given rise to only *one* fluid-fluid transition in which both  $\tilde{\rho}$  and  $\Delta$  jump from nonzero to larger values. The *two*, successive, first-order coexistences observed in adsorbed surfactant monolayers<sup>4,5</sup> must arise from coupling to other degrees of freedom and/or the interplay with lower symmetry states. Possibilities of the first type include the conformational flexibility explicitly suppressed in the rigid-rod theory, or different pair interaction length scales associated with polar (ionic) head groups. A mechanism involving new symmetry, on the other hand, appears as soon as one allows for *biaxial* states. A numerical analysis of our Onsager-Zwanzig-Landau order-parameter theory then shows that two successive orientational transitions *can* occur—the intermediate state being biaxial—and that *either* adsorption *or* anisotropic attraction is sufficient.<sup>12</sup> Similar behavior is observed in the Monte Carlo calculations, for sufficiently large values of  $\epsilon$ . In this limit there are enough rods in the plane of the surface so that a biaxial orientational ordering arises<sup>13</sup> at intermediate densities, although less pronounced than in the mean-field analysis. These points, as well as a full discussion of the corresponding Monte Carlo simulations, and analogies with various lattice-gas and Potts models, will be represented in a separate paper.<sup>11</sup>

(a)Present address: Center of Statistical Mechanics, Department of Physics, University of Texas, Austin, TX 78712.

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