RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 48, NUMBER 6 DECEMBER 1993

Vesicle adsorption on a plane: Scaling regimes and crossover phenomena

E. Orlandini,[1] A. L. Stella,[1] M. C. Tesi,[1] and F. Sullivan[2]
[1]*Dipartimento di Fisica and Sezione Istituto Nazionale di Fisica Nucleare di Bologna, Bologna, Italy*
[2]*Computing and Applied Mathematics Laboratory, National Institute of Standards and Technology,*
Gaithersburg, Maryland 20899
(Received 6 July 1992)

Lattice self-avoiding surfaces with spherical topology, rooted on a plane, are studied with Monte Carlo and scaling methods. As the adsorption energy increases, two transitions occur. The first is in the universality class of the special adsorption point for branched polymers. The adsorbed vesicle's interior changes from branched polymer to two-dimensional compact at a second multicritical point, beyond which the perimeter on the plane keeps a self-avoiding ring dimension. This point, in a class recently discovered for interacting ring polymers, does not exist for strictly two-dimensional vesicles.

PACS number(s): 61.41.+e, 64.70.−p, 68.45.−v

The stochastic geometry of random surfaces, conceived for example as topologically two-dimensional objects embedded in three-dimensional Euclidean space, is an issue of considerable current interest for both condensed-matter physics and field theory. Random surfaces model various physical objects, ranging from biological membranes to interfaces separating different phases [1]. The statistics of surfaces is also closely related to topics like string [2] and lattice gauge theories [3].

Among the various existing types of random surfaces, those constructed with elementary plaquettes of a regular lattice have played an important role since the very beginning of activity on the subject, especially through their close relation to lattice gauge theories [3]. These models are extensively studied also in connection with the physics of vesicles, i.e., closed membranes like those constituting red blood cells [1,4,5].

A vesicle can be described by a closed self-avoiding surface (SAS) built up with lattice plaquettes in such a way that neither overlaps nor intersections occur [6]. A closed SAS with spherical topology behaves as a branched polymer (BP) in the scaling limit, due to the dominance of thin ramified configurations [7,8]. Here we study adsorption on a plane of such a SAS.

Polymer adsorption is a subject of much interest from both fundamental and applied points of view [9,10]. In the determination of vesicles' shapes, the importance of adhesion has already been stressed [11]. In this Rapid Communication we provide the first systematic study of adsorption critical phenomena in $d=3$ for a model of a fluid, or hexatic vesicle. Besides identifying novel scaling regimes and multicritical phenomena peculiar to SAS, due to their three-dimensional (3D) nature even in the strongly adsorbed regime, we also establish interesting connections of some features of SAS adsorption with recently discussed polymer collapse phenomena [12] and vesicle models [5] in $d=2$.

Our model has a generating function

$$Z=\sum_{S}|S|^{x}K^{|S|}t^{N_a(S)}=\sum_{n,n_a}c_{n,n_a}n^{x}K^{n}t^{n_a}\ , \tag{1}$$

where the sum is over the SAS, S, with $|S|$ plaquettes all belonging to the $z\geq 0$ half-space of a cubic lattice. $N_a(S)$ is the number of plaquettes of S belonging to the $z=0$ plane. K is a plaquette fugacity, while t has the meaning of a Boltzmann factor associated with the contact of a plaquette with the plane. ($t>1$ implies attraction.) In Eq. (1) all S have a fixed plaquette on the plane, and c_{n,n_a} is the number of distinct S with $|S|=n$ and $N_a(S)=n_a$. The integer x is chosen big enough ($x=2,3$) to ensure that Z and grand-canonical averages of interest diverge at criticality [7].

Our Monte Carlo strategy is described in Ref. [7]. The main innovation is an oct-tree data structure that allows satisfactory control of the statistics, even when the model is very close to criticality ($|S|\sim 10^3$).

We estimate critical behaviors such as

$$c_n(t)=\sum_{n_a}c_{n,n_a}t^{n_a}t^{n_a}\underset{n\to\infty}{\sim}n^{-\theta_1}K_c(t)^{-n} \tag{2}$$

or

$$R(K,t)=\frac{\sum_{n}c_n n^{x}K^{n}R_n(t)}{Z}\underset{K\to K_c(t)-}{\sim}[K_c(t)-K]^{-\nu}\ , \tag{3}$$

where $R_n(t)$ is the canonical rms radius of gyration, with respect to the center of mass, of surfaces with $|S|=n$ and arbitrary $N_a(S)$. Equation (3) is also equivalent to $R_n(t)\sim n^{\nu}$, as $n\to\infty$. The different regimes of the adsorption process can be detected from the scaling

$$\langle n_a\rangle_n=\frac{\sum_{n_a}c_{n,n_a}n_a t^{n_a}}{c_n}\underset{n\to\infty}{\sim}n^{\phi}\ . \tag{4}$$

In the case of polymers one can distinguish three critical regimes [10]. By analogy we expect an ordinary regime in which t is not big enough to produce adsorption. Then, in Eq. (4), $\phi=0$ applies; because the surface grows as an essentially bulk object, K_c should have its bulk value, independent of t. In the adsorbed regime, by contrast, a finite fraction of plaquettes is adsorbed, and $\phi=1$. The adsorbed regime occurs for t above some threshold t_1; in this case, K_c becomes t dependent. In passing from ordinary to adsorbed regimes, exponents like ν and θ should also change. Indeed, $t=t_1$ marks a special multicritical point, at which ν still has its bulk value, but $\phi=\phi(t_1)$, the surface crossover exponent, with $0<\phi(t_1)<1$.

We verified that all this occurs in SAS adsorption. However, for SAS the adsorbed regime has a richer structure distinct from the polymer case.

The qualitative phase diagram in Fig. 1(a) summarizes our results for $t>t_1$ (see also Fig. 2). An extra fugacity W_3 controls the SAS volume in the same way as K controls the area. We normally operate at $W_3=1$, so W_3 is not included explicitly in the formulas. A critical surface sheet exists in the $W_3 \leq 1$ half-space and intersects the line $K=K_c(t)$ on the $W_3=1$ plane. The region $K<K_c(t)$; $W_3=1$ is a locus of first-order transitions. Two-dimensional BP critical behavior holds on the critical surface for $W_3<1$ and for $W_3=1$ with $t_1<t<t_2$. For $W_3=1$, at $t=t_2$ a multicritical point separates the BP regime from a line of criticality characterizing a vesicle with 2D compact interior for $t>t_2$.

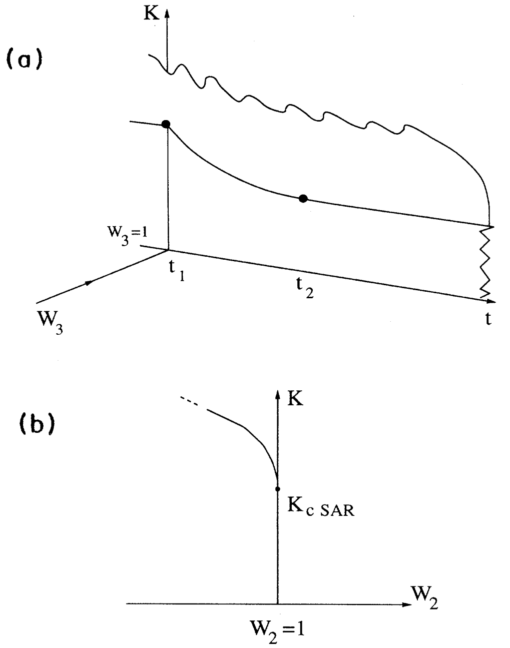

FIG. 1. Sketch of SAS phase diagram in the adsorbed region. (a) For $t<t_1$, K_c keeps the constant bulk value. (b) Phase diagram of 2D vesicle.

We determined K_c as a function of t on the basis of both maximum likelihood methods for the behavior (2), and of fits of

$$\langle n \rangle = \sum_n c_n n^{1+x} K^n / Z \underset{K \to K_c}{\sim} -(1+x-\theta_1)/(K_c-K) \, ,$$

using runs at different K's [7]. Sampling frequency and statistical errors were determined with the criteria illustrated in Ref. [7]. For $t>1$ it is easy to prove the following inequalities:

$$K_c(1) t^{-1/2} \leq K_c(t) \leq t^{-1/2} \tag{5}$$

where $K_c(1)$ was already estimated [7]. For $t>6$ the upper bound in Eq. (5) almost matches the curve

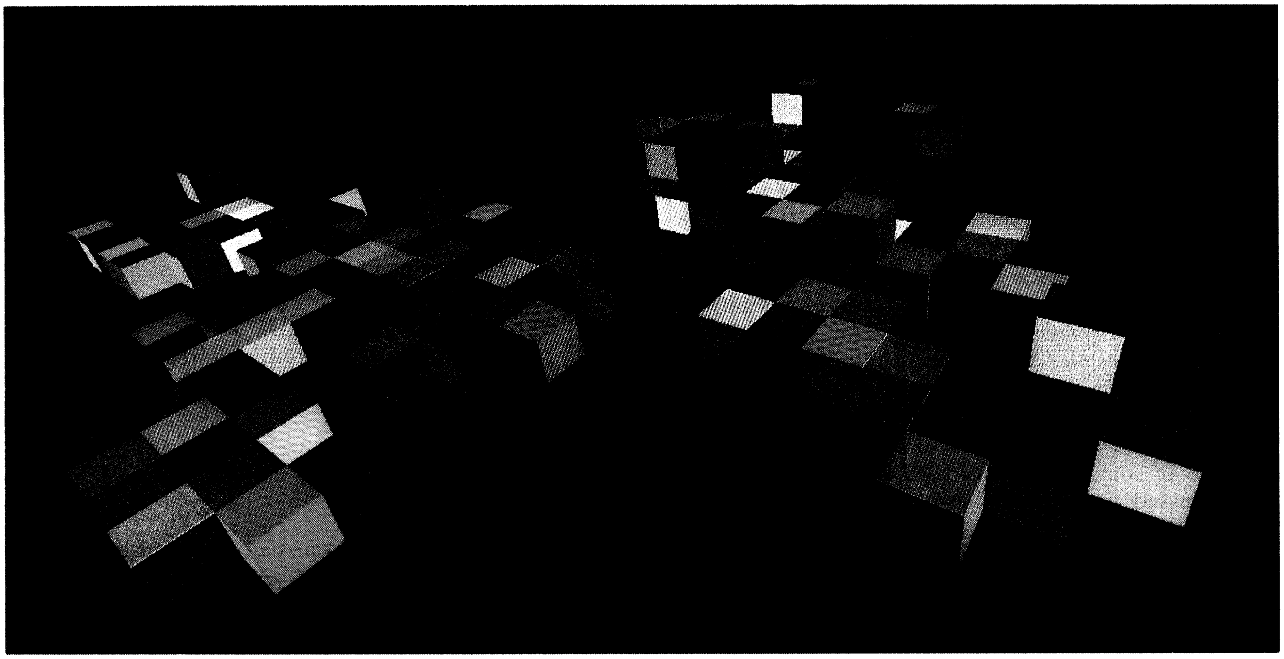

FIG. 2. Picture of a typical vesicle configuration in the adsorbed regime. Colors have no special meaning.

$K_c = K_c(t)$ as discussed below. Such a bound is obtained by considering that, for our vesicles, $n_a < n/2$. Thus, asymptotically, disk-like configurations, in which the surface "spreads" compactly on the plane, should dominate. In such configurations $n_a \sim n/2$ for $n \rightarrow \infty$.

K_c is nearly constant and roughly equal to the bulk value, $K_c(1)$, for $t \leq t_1 = 1.43 \pm 0.03$, whereas a rather noticeable decrease sets in for $t > t_1$. An alternative way of locating the transition exploits the fact that the behavior of R_n should cross over from a ν value appropriate to bulk criticality to one appropriate to the adsorbed regime. So, the variation in estimated ν exponents signals the transition. This is better located by studying the trend of effective canonical ν determinations, ν_k, based on successively more asymptotic samplings, i.e., samplings cut at increasing maximum $n = k$. The ν_k variations as a function of t should become more and more sharp for $k \rightarrow \infty$, because finite-size round-off effects become progressively less pronounced. At the multicritical point marking the transition, the direction of approach of the ν_k's to the asymptotic values typically inverts itself, and the curves tend to intersect at ν values which approximate ν_1, the exponent of the multicritical point. Accurate determinations of ν_1 can be obtained by extrapolating, for increasing k, the intersections of $\nu_k(t)$ and $\nu_l(t)$, with, e.g., $l > k$. Extrapolations of the ν_k values for $t < t_1$ and $t > t_1$ lead, respectively, to $\nu = 0.506 \pm 0.008$ and 0.64 ± 0.01, fully consistent with what is expected for branched polymers in $d = 3$ ($\nu = \frac{1}{2}$ [13]) and $d = 2$ ($\nu = 0.6408 \pm 0.0003$ [14]). The ν values obtained from the intersections of the various curves are very close to 0.5 and extrapolation leads to $\nu(t_1) = 0.51 \pm 0.02$. This is consistent with a special adsorption point, for which the ν exponent is still the bulk one, as in the ordinary regime.

With the same procedure used to estimate K_c, we determined also the entropic exponent θ_1 as a function of t, although with larger uncertainties than for ν and ϕ. We obtained, respectively, $\theta_1^{\text{ord}} = \theta_1(t < t_1) = 1.4 \pm 0.1$ and $\theta_1^{\text{sp}} = \theta_1(t_1) = 0.3 \pm 0.2$. That θ_1^{ord} should equal the bulk value $\theta = \frac{3}{2}$ is expected for BP [15]. The crossover exponent $\phi(t_1)$ at the special point was determined by linear fitting of the behavior (4) on a log-log plot. This yielded $\phi(t_1) = 0.70 \pm 0.06$, quite consistent with the estimate $\phi = 0.68$ for branched polymers in Ref. [16]. Most recently [17] both θ_1^{sp} and ϕ were conjectured for BP by attempting an extension to semi-infinite geometry of field theory results of Ref. [13]. However, our ϕ, like that of Ref. [16], seems hardly compatible with the value $\phi = \frac{1}{2}$ produced there. For $t_1 < t < t_2$, with $t_2 = 6.0 \pm 0.3$, the adsorbed SAS behaves as a branched polymer in $d = 2$. Equation (2) holds there with $\theta_1 = 0.0 \pm 0.2$, which is consistent with the $d = 2$ bulk exponent [13], taking into account the shift by unity due to rooting with a $d = 2$ bulk.

Most interesting here is the clear indication from the ν analysis that for $t = t_2$ a new multicritical phenomenon occurs, which shows a crossover of ν from $d = 2$ BP, to $d = 2$ compact value $\nu = \frac{1}{2}$. This further transition is the mechanism through which the system adapts itself to the expected asymptotic dominance of compact, disk-like configurations. For a strongly adsorbed vesicle the most important configurations involve no plaquette reaching higher than the $z = 1$ plane. Thus, the SAS projection on the plane could behave like a 2D vesicle without holes, controlled by effective fugacities $W_2 = K^2 t$ and K for enclosed plaquettes and perimeter steps, respectively. For 2D vesicles the phase diagram is reported in Fig. 1(b). The critical behavior is known to be BP as long as $W_2 < 1$ [5]. At $W_2 = 1$ the vesicle is critical with compact area and self-avoiding ring (SAR) perimeter for $K = K_{c\text{SAR}} = 0.3790\ldots$, while it has first-order droplet singularities for $K < K_{c\text{SAR}}$ [5]. We find $K_c^2(t_2)t_2 = 0.94 \pm 0.06$ and an effective W_2 extremely close to, but never exceeding, unity for $t > t_2$, consistent with Eq. (5). In spite of these coincidences, however, the line $K = K_c(t)$, $t > t_2$ *is not* a first-order line. Indeed, we verified that the volume and projected area of our SAS keep becoming critical with $\nu \sim \frac{1}{2}$ as $K \rightarrow K_c(t)-$ from t_2 up to $t \sim 9.0$, at least. A second-order transition is also indicated by an analysis of fluctuations of the above quantities.

For 2D vesicles the compact area critical behavior is realized only at one point, $W_2 = 1$, $K = K_{c\text{SAR}}$, of the critical line, and crossover to BP is not controlled by an additional multicritical point. For adsorbed SAS, on the contrary, the effective ν_k's for both volume and projected area extrapolate to a multicritical $\nu(t_2) = 0.54 \pm 0.03$. A full elucidation of the nature of the point at t_2 is a challenging issue, bearing also on polymer statistics problems. For sure this point has features expected for a BP Θ point. However, $\nu(t_2)$, even if barely compatible with a recent numerical estimate at the BP Θ point in $d = 2$ ($\nu = 0.509 \pm 0.003$ [18]), could be inconsistent with the latest conjectured exact value $\nu = \frac{1}{2}$ [19]. Thus, the multicritical point displayed by SAS in the adsorbed regime could well belong to a new universality class, different from that of the $d = 2$ BP Θ point studied in Refs. [18] and [19]. This is also suggested by the circumstance that in Ref. [19] such a Θ point has been mapped into the point $W_2 = 1$, $K = K_{c\text{SAR}}$ of 2D vesicles.

A further indication of the richness of SAS and of the intriguing nature of the multicritical point at t_2 is given by the behavior of the vesicle's perimeter on the adsorbing plane. As perimeter we consider the subset of surface plaquettes perpendicular to such a plane. Clearly such perimeters can in principle have self-intersections and disconnections, but we expect them to be irrelevant in the strongly adsorbed regime. Indeed, the average canonical radius, R_{p,n_p}, for perimeters with n_p plaquettes, behaves as $R_{p,n_p} \underset{n_p \rightarrow \infty}{\sim} n_p^{\nu_p}$. The extrapolated value is $\nu_p = 0.64 \pm 0.02$ in a wide portion of the (t_1, t_2) interval, fully consistent with the adsorbed SAS behaving as a 2D BP. For $t > t_2$ the $\nu_{p,k}$ exponents extrapolate to $\nu_p = 0.74 + -0.02$ in a wide range up to $t \sim 9.0$. This ν_p is consistent with the perimeter having SAR critical behavior along the line $t > t_2$, $K = K_c(t)$. Indeed, we know that the 2D SAR's are dense objects [20]; so, the results for the perimeter are compatible with the behaviors of volume and area discussed above.

Intersections of $\nu_{p,k}$ curves are consistent with the above location of t_2, and their extrapolation gives $\nu_p(t_2)=0.66\pm0.03$ as the multicritical exponent, a further indication that the present crossover from the BP to SAR perimeter is not the one of 2D vesicles. In the context of $d=2$ polymer statistics, a similar SAR-BP crossover has been discussed most recently for ringlike structures [12]. In that case the transition is driven by suitable attractive interactions which lead the ring to stick onto itself to form a sort of highly ramified double structure. Although with a different physical mechanism, due to adsorption, the same transition takes place here for the vesicle's perimeter. Our estimate of $\nu_p(t_2)$ supports the possibility that the multicritical point found for the SAS profile belongs to the universality class of the SAR-BP collapse discussed in Ref. [12] ($\nu=0.66\pm0.03$).

Adsorbed SAS's thus give rise to a much richer scenario than 2D vesicles [Figs. 1(a) and 1(b)]. This includes a new multicritical point connected to both BP Θ collapse and to the SAR-BP transition for the perimeter. Our analysis suggests that the study of properly defined external perimeters for standard models of BP Θ collapse could be quite interesting.

The multicritical point at t_2 and the second-order line for $t>t_2$ can be understood by considering the difference between the strongly adsorbed SAS, which is still a 3D object, and a strictly 2D vesicle living on the plane. For SAS a volume fugacity W_3 can be switched on, together with the effective area fugacity. W_3 is expected to act as a W_2 fugacity in Fig. 1(b), as far as the adsorbed SAS projected area is concerned. Monte Carlo tests confirm that as soon as $W_3<1$ ramification is favored and 2D BP behavior is established. At the same time, it is easy to conclude that $W_3=1$ and $K<K_c(t)$ is a first-order surface, since the SAS increases suddenly to infinity as soon as $W_3>1$ [5]. Thus, intersecting the phase diagram in Fig. 1(a) with a generic plane $t=\text{const}>t_2$ we obtain a realization of the phase diagram of 2D vesicles [Fig. 1(b)]. This does not depend on the particular plane considered, consistently with the above conclusions concerning the nature of the critical line for $t>t_2$.

This work was supported by NATO Grant No. 86/0782 and by Consorzio Interuniversitario Nazionale per la Fisica della Materia, Unità du Padova. The authors acknowledge J. R. Banavar, T. L. Einstein, and S. G. Whittington for criticism and useful discussions, D. Dobkin for providing the graphical Salem software, and I. Beichl for invaluable help in the computational work.

---

[1] See, e.g., contributions to *Statistical Mechanics of Membranes and Interfaces,* edited by D. R. Nelson, T. Piran, and S. Weinberg (World Scientific, Singapore, 1989).

[2] A. M. Polyakov, *Gauge Fields and Strings* (Harwood Academic, New York, 1982).

[3] J. M. Drouffe and C. Itzykson, Phys. Rep. **38C**, 133 (1979).

[4] S. Leibler, R. R. P. Singh, and M. E. Fisher, Phys. Rev. Lett. **59**, 1989 (1987).

[5] M. E. Fisher, A. J. Guttmann, S. G. Whittington, J. Phys. A **24**, 3095 (1991); J. R. Banavar, A. Maritan, and A. L. Stella, Phys. Rev. A **43**, 5752 (1991); Science **252**, 825 (1991).

[6] This means that each lattice plaquette can enter only once to form the SAS, and each lattice edge belongs either to two, or to zero SAS plaquettes.

[7] J. O'Connell, F. Sullivan, D. Libes, E. Orlandini, M. C. Tesi, A. L. Stella, and T. L. Einstein, J. Phys. A **24**, 4619 (1991).

[8] U. Glaus and T. L. Einstein, J. Phys. A **20**, L105 (1987). See also U. Glaus, J. Stat. Phys. **50**, 1141 (1988), for earlier and related results.

[9] P. G. de Gennes, Adv. Coll. Interface Soc. **27**, 189 (1987).

[10] K. Binder, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8, p. 1.

[11] R. Lipowsky, Nature **349**, 475 (1991).

[12] E. Orlandini, F. Seno, A. L. Stella, and M. C. Tesi, Phys. Rev. Lett. **68**, 488 (1992).

[13] G. Parisi and N. Sourlas, Phys. Rev. Lett. **46**, 871 (1981).

[14] B. Derrida and L. De Seze, J. Phys. (Paris) **43**, 475 (1982); B. Derrida and D. Stauffer, J. Phys. (Paris) **46**, 1623 (1985).

[15] K. De'Bell, T. Lookman, and D. Zhao, Phys. Rev. A **44**, 1390 (1991). Here, as in Ref. [17], θ_1 is defined as our θ_1 plus unity. At least in the ordinary case, we find this somewhat misleading, because it incorrectly suggests that unrooting from the plane lowers by unity the power-law exponent in Eq. (2).

[16] P. M. Lam and K. Binder, J. Phys. A **21**, L405 (1988).

[17] H. K. Janssen and A. Lyssy, J. Phys. A **25**, L697 (1992).

[18] B. Derrida and H. Herrmann, J. Phys. (Paris) **44**, 1365 (1983).

[19] C. Vanderzande, Phys. Rev. Lett. **70**, 3595 (1993).

[20] B. Duplantier, Phys. Rev. Lett. **64**, L93 (1990). See also Refs. [4] and [5].

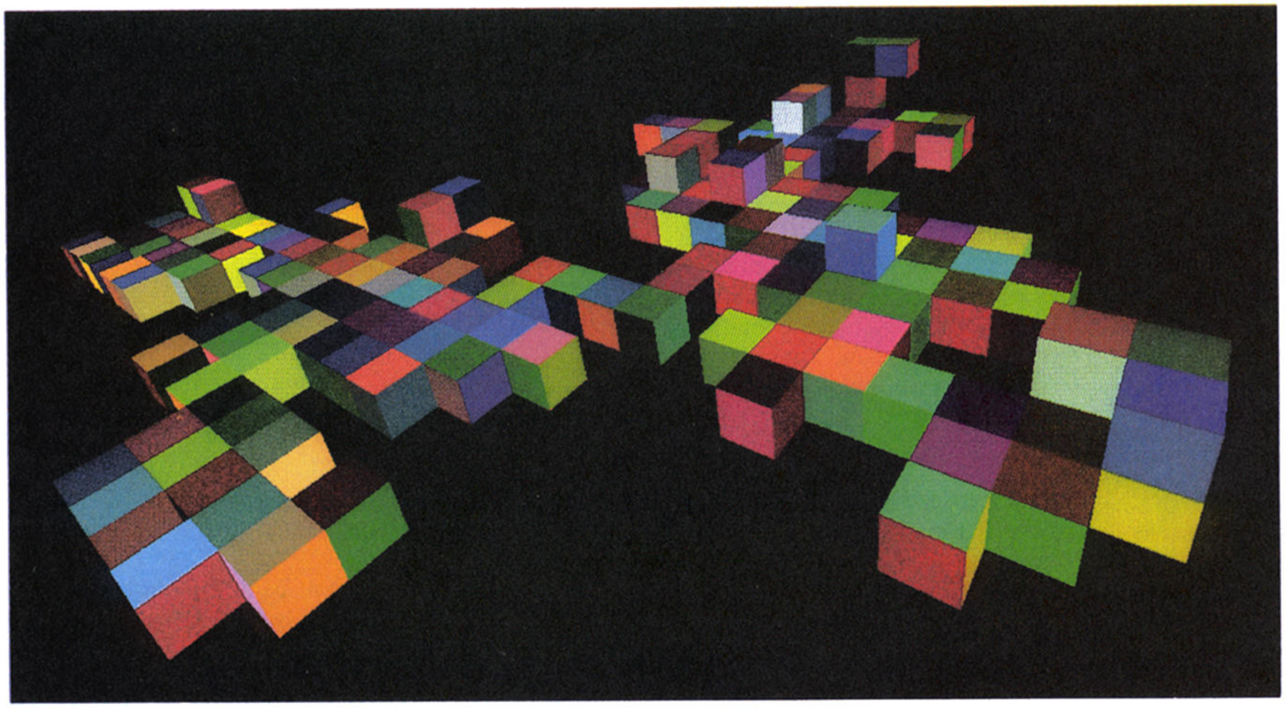

FIG. 2. Picture of a typical vesicle configuration in the adsorbed regime. Colors have no special meaning.