

# Surface phase transitions in polymer systems

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Self-avoiding walks, lattice trees, and related geometrical models provide a link between the physics of polymers and the study of critical phenomena. In particular, these models in the presence of a surface provide insight into surface adsorption in dilute polymer systems in a good solvent. The theme of this review is the influence of polymer structure (topology) on the critical properties of these models. Emphasis is placed on recent results by rigorous methods, scaling theory, and conformal covariance theory. Numerical results that may be used to test the predictions of scaling and conformal covariance theories are also summarized. Related topics such as the adsorption of directed polymers, the semidilute regime, the theta point and theta solvents, and percolation (polymer gels) are briefly discussed in the final section.

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## A. Motivation

It is well known that self-avoiding walks (SAWs) provide a model of linear polymers in a dilute, good solution

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(de Gennes, 1979a; Freed, 1987). The term “good solution” is used to imply that the attraction between the monomers and solvent molecules is greater than the monomer-monomer attraction. This may be modeled as an effective repulsive monomer-monomer interaction. The self-avoiding constraint is necessary to represent the excluded volume effect of the monomers forming the polymer chain. Self-avoiding walks also behave in a manner analogous to magnetic (and other) systems undergoing a second-order phase transition. This analogy may be formulated as a formal equivalence between SAWs and the  $n \rightarrow 0$  limit of an  $n$ -component spin model (Sec. I.C). The study of SAWs close to an impenetrable wall provides a model for the study of phase transitions in the presence of a surface and indicates that adsorbed polymers may provide experimental tests of our understanding of critical behavior of surfaces. The model of a SAW in contact with a surface is perhaps the best known example of a “geometrical” phase transition at a surface. Recently, other polymer structures such as stars, combs, and more intricate networks have also been studied subject to a variety of constraints. In this review we shall attempt to summarize the advances that have been made in this area of geometrical phase transitions at surfaces. We shall explore, in particular, the influence of polymer architecture on the configurational properties in a lattice and on the adsorption transition. Our focus will be on rigorous results (Sec. II), the application of scaling theory (Sec. III), and conformal covariance theory (Sec. IV). Numerical tests of the scaling theories and the predictions of conformal covariance theory are summarized in Sec. V. Although the emphasis of this work is on surface phase transitions in dilute polymer systems, related topics are briefly outlined in Sec. VI. Surface critical phenomena in magnetic systems are reviewed by Binder (1983). Although certain results of the application of the renormalization group are discussed, a detailed treatment of this technique is beyond the scope of this article. For a general description of the application of the renormalization group to polymers, we refer the reader to the book by Freed (1987). A general review of the renormalization group for systems with a surface has been given by Diehl (1986). The review by Duplantier (1989) describes the application of the renormalization group to general polymer networks (including those attached to

surfaces) and provides an interpretation in this context of the scaling theory described in Sec. III.

### B. Polymer structures and topologies

The ability of chemists to produce specific polymer structures (Roovers, Hadjichristidis, and Fetters, 1983; Roovers, Toporowski, and Martin, 1989) has generated interest in the properties of geometric models with a variety of topologies that retain the self-avoiding constraint. An example of such a structure is the star polymer formed by joining the terminal vertices of  $f$  linear polymers at a vertex of degree  $f$ . (See Fig. 1 for typical polymer structures.) Since we shall be interested in a large number of monomers in the polymer, represented by taking the limit  $N \rightarrow \infty$ , we specify our use of the following terms.

(i) A chain is a set of vertices of degree 2 connected in sequence by single edges and with terminal vertices of degree  $\neq 2$ , the number of vertices in the chain being  $O(N)$ . A chain with terminal vertices of degree 1 is a walk.

(ii) A leg is a chain with one terminal vertex of degree 1 and one terminal vertex of degree  $\geq 3$ .

(iii) A topology is any structure formed by joining chains at vertices of degree  $\geq 3$  and suppressing vertices of degree 2.

(iv) An  $f$  star is a topology of  $f$  legs with a single common (terminal) vertex of degree  $f$ .

(v) A tree is any topology with no loops. In considering the problem of lattice trees we shall consider the embeddings of all possible trees on a given lattice. This provides a model of branched polymers in a good, dilute solution. The problem of lattice animals, in which lattice embeddings of all possible graphs are considered, is believed to be in the same universality class as the lattice-tree problem. Site animals or trees are those in which nearest-neighbor vertices are considered to be connected by an edge and all such edges are part of the animal (tree). In bond animals or trees only the specified bonds or edges are part of the animal (tree).

(vi) A comb is a tree in which every vertex of degree

$\geq 3$  is of degree  $f$ . However, all the vertices of degree  $f$  are connected in sequence by a walk with no backsteps. An  $H$  comb is a comb with exactly two vertices of degree 3.

### C. Connection with critical phenomena

In the presence of a surface, the derivation of the formal relation between a self-avoiding-walk model and the  $n \rightarrow 0$  limit of an interacting-spin model follows that for the corresponding bulk problem. The weight given to surface contacts, modeling a surface interaction, corresponds to an enhanced (or degraded) nearest-neighbor interaction in the surface of the spin model. The Hamiltonian of the interacting spin systems is

$$-\beta H = \sum_{ij} K \vec{s}_i \cdot \vec{s}_j + \sum_{ij} K_1 \vec{s}_i \cdot \vec{s}_j, \quad (1)$$

where the second sum is performed over all nearest-neighbor pairs on the lattice such that both the site labeled by  $i$  and that labeled by  $j$  are on the surface and the first sum is performed over all other nearest-neighbor pairs on the lattice. We may choose the  $z=0$  plane as the surface and restrict all sites to be in the half space  $z \geq 0$ .

Following de Gennes (1979a, 1979b), we choose the normalization of the  $n$ -component spin vector to be

$$|\vec{s}_i|^2 = n \quad (2)$$

and note that the properties of the trace (i.e., integration over  $\vec{s}$  subject to this normalization) of a product of spin components  $s^\alpha s^\beta \dots$  may be obtained from the generating function  $g(\vec{k})$  defined by

$$i^m \frac{\partial^m g(\vec{k})}{\partial k^\alpha \dots \partial k^\omega} \Big|_{\vec{k}=0} = \text{Tr} s^\alpha s^\beta \dots s^\omega, \quad (3)$$

where

$$g(\vec{k}) = \text{Tr} \exp(-i\vec{k} \cdot \vec{s}). \quad (4)$$

The normalization of  $s$  then leads to

$$\nabla^2 g = \sum_\alpha \frac{\partial^2 g}{\partial k^\alpha \partial k^\alpha} = - \sum \text{Tr} s^{\alpha 2} \exp(i\vec{k} \cdot \vec{s}). \quad (5)$$

Performing the sum, we obtain

$$\nabla^2 g = -ng. \quad (6)$$

Since  $g(\vec{k})$  involves a trace over  $\vec{s}$ ,  $g$  depends only on  $k$ . Thus

$$\frac{\partial g}{\partial k^\alpha} = \frac{k^\alpha}{k} \frac{\partial g}{\partial k}, \quad (7)$$

$$\frac{\partial^2 g}{\partial k^\alpha \partial k^\alpha} = \frac{1}{k} \frac{\partial g}{\partial k} + \frac{k^{\alpha 2}}{k} \frac{\partial}{\partial k} \frac{1}{k} \frac{\partial g}{\partial k}, \quad (8)$$

$$\nabla^2 g = \frac{n-1}{k} \frac{\partial g}{\partial k} + \frac{\partial^2 g}{\partial k^2} = -ng. \quad (9)$$

The second-order differential equation is solved subject

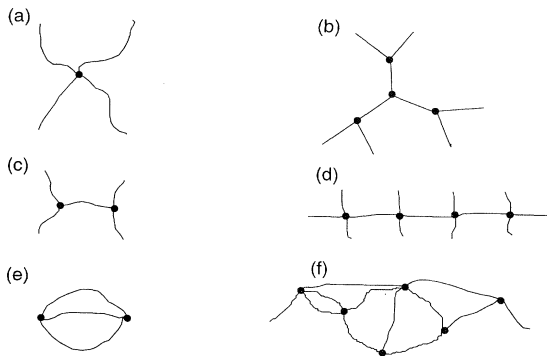


FIG. 1. Typical polymer structures: (a) a 4 star; (b) a tree; (c) an  $H$  comb; (d) a comb; (e) a watermelon; (f) a general topology with 5 cycles.

to the boundary conditions

$$g(k=0)=1, \quad (10)$$

$$\frac{\partial^2 g}{\partial k^{\alpha^2}}=1. \quad (11)$$

The second of these boundary conditions follows from the normalization of  $\vec{s}$  and the symmetry of the Hamiltonian. Taking the limit  $n \rightarrow 0$  and solving the second-order equation, we obtain

$$g(k)=1+k^2/2, \quad (12)$$

from which we conclude

$$\text{Tr} s^\alpha s^\beta = \delta_{\alpha\beta} \quad (13)$$

and that the trace of any other product of spin components is zero.

Consider now the correlation function

$$\langle s_i^\alpha s_j^\alpha \cdots s_k^\omega s_l^\omega \rangle = \frac{\text{Tr} s_i^\alpha s_j^\alpha \cdots s_k^\omega s_l^\omega \exp(-\beta H)}{\text{Tr} \exp(-\beta H)}, \quad (14)$$

in which the component labels  $\alpha \cdots \omega$  are assumed to be distinct. The right-hand side may then be expressed as a double expansion in the variables  $K$  and  $K_1$ . Each term in the expansion is evaluated in the limit  $n \rightarrow 0$  by applying the rules for the trace derived above. It can be verified that only products that may be graphically represented by a set of chains connecting pairwise those sites assigned the same component label in the argument of the correlation function have nonzero weight. Moreover, each such graph embedding on the lattice has weight 1. In particular,

$$\lim_{n \rightarrow 0} \langle s_i^\alpha s_j^\alpha \rangle = \sum_{n,m} C_{n,m} K^n K_1^m, \quad (15)$$

where  $C_{n,m}$  is the number of  $(n+m)$ -step self-avoiding walks with  $m$  steps in the surface connecting sites  $i$  and  $j$ .

The application of this formal equivalence to other polymer topologies follows from our interest only in the limit  $N \rightarrow \infty$ , since in this limit we may treat a group of  $f$  vertices of degree 1, which are maintained within a short distance of each other, as a single (renormalized) vertex of degree  $f$  (Duplantier, 1986; Ohno and Binder, 1988). Thus any topology may be generated by specifying the lattice site labels of the correlation function in a suitable way. For example, consider the correlation function

$$\langle s_1^\alpha s_2^\alpha s_3^\beta s_4^\beta s_5^\gamma s_6^\gamma \rangle \quad (16)$$

defined so that the sites labeled 1, 3, and 5 are all neighbors of a central site labeled 0. The coefficients appearing in the expansion of the correlation function will then simply be the number of 3 stars with a central vertex at site 0 and vertices of degree 1 at sites labeled 2, 4, and 6. Moreover, if label 0 is kept fixed and a sum performed over the labels 2, 4, and 6 (corresponding to a generalized susceptibility in the magnetic model), the resultant expansion is the generating function for the number of 3

stars embeddable on the lattice (apart from a trivial prefactor).

That all topologies may be related to the correlation functions of a single  $n \rightarrow 0$  model (for a given) lattice has an immediate corollary. If we assume that the generating function is divergent on a phase boundary  $(K, K_1)$ , this phase boundary is independent of the topology, since we do not expect it to depend on which correlation function we examine. We shall show in Sec. II that this result can be established rigorously. Moreover, the exponent describing the divergence of the mean-square distance between points in the structure (corresponding to the correlation length of the magnetic system) must be independent of topology, since our current understanding of second-order phase transitions requires that only a single diverging length scale appear at a second-order phase transition.

## II. EXACT RESULTS

### A. Random walks

In this subsection we remove the self-avoiding constraint from the walk, thus obtaining a model for which the surface critical properties may be calculated exactly. The approach used here follows that of De'Bell (1980a), in which the random-walk model provides an approximation for percolation in the low-density regime (see also De'Bell and Essam, 1981).

A random walk  $(\vec{r}_0, \vec{r}_1, \dots, \vec{r}_N)$  consists of an initial point  $\vec{r}_0$  and  $N$  steps determined by their end points  $\vec{r}_i$ :  $1 \leq i \leq N$ , such that  $\vec{r}_i$  is in the capture region of  $\vec{r}_{i-1}$  for all  $1 \leq i \leq N$ . Here we define the capture region of  $\vec{r}_i$  to be a  $d$ -dimensional hypercube of side  $2a$  centered on  $\vec{r}_i$ , thus allowing a continuum formulation of the problem. The corresponding lattice problem is obtained by restricting the  $\vec{r}_i$  to the lattice sites and assuming the capture region of  $\vec{r}_i$  to be the neighboring lattice sites.

In the bulk system with complete translational invariance, the generating function  $G(\vec{r}_0, \vec{r}_N)$ , for  $C_N(\vec{r}_0, \vec{r}_N)$ , the number of  $N$ -step walks from  $\vec{r}_0$  to  $\vec{r}_N$ , is defined by

$$G(\vec{r}_0, \vec{r}_N) = \sum_N C_N(\vec{r}_0, \vec{r}_N) \rho^N. \quad (17)$$

It is determined by

$$G(\vec{r}_0, \vec{r}_N) = \rho \gamma(\vec{r}_0, \vec{r}_N) + \rho \int \gamma(\vec{r}_0, \vec{r}_j) G(\vec{r}_j, \vec{r}_N) dr_j, \quad (18)$$

where  $\gamma$  is the indicator function defined by

$$\gamma(\vec{r}, \vec{r}') = \begin{cases} 1 & \text{if } \vec{r}' \text{ is in the capture region of } \vec{r} \\ 0 & \text{otherwise} \end{cases}. \quad (19)$$

The generating function for the total number of walks originating at  $\vec{r}_0$  is then

$$\begin{aligned} \chi(\vec{r}_0) &= \int G(\vec{r}_0, \vec{r}_N) dr_N, \\ &= \rho V + \rho \int \gamma(\vec{r}_0, \vec{r}_N) \chi(\vec{r}_j) dr_j, \end{aligned} \quad (20)$$

$$V = (2a)^d . \quad (21)$$

The translational invariance of the bulk system now gives

$$\chi(\vec{r}) = \chi_b = \rho V / (1 - \rho V) \quad (22)$$

or

$$\chi_b \sim (1 - \rho V)^{-\gamma} , \quad (23)$$

with the usual identification of the random-walk critical exponent  $\gamma = 1$ .

We now introduce a surface at  $z = 0$  by restricting the coordinates of  $\vec{r}_0$ ,  $\vec{r}_N$ , and  $\vec{r}_j$  in Eq. (18) to the half space  $z \geq 0$ . In addition, we allow the possibility of a  $z$ -dependent "density"  $\rho(z)$  such that

$$\rho(z) = \begin{cases} \rho, & z > a \\ \rho_1, & 0 < z < a . \end{cases} \quad (24)$$

In terms of the polymer this allows for an additional attractive or repulsive potential experienced by monomers close to the surface.

$\chi(\vec{r})$  is now explicitly dependent on  $z$ , so that, for  $z > 2a$ ,

$$\chi(z) = \rho V + \rho(2a)^{d-1} \int_{z-a}^{z+a} \chi(z'') dz'' , \quad (25)$$

with the solution (De'Bell, 1980a; De'Bell and Essam, 1981)

$$\chi(z) = A \exp(-\lambda z) + \chi_b , \quad (26)$$

$$\lambda = 2\rho(2a)^{d-1} \sinh(a\lambda) . \quad (27)$$

The solution is of the same form at  $z = 0$  if the boundary condition

$$\rho \int_{-a}^a \chi(z') dz' - \rho_1 \int_0^a \chi(z') dz' = V(\rho_1 - 2\rho) / 2(2a)^{d-1} \quad (28)$$

is met. Hence

$$\chi(0) = \chi_b \frac{1 - \exp(-a\lambda) - \sinh(a\lambda)}{1 - \exp(-a\lambda) - 2(\rho/\rho_1)\sinh(a\lambda)} . \quad (29)$$

Writing  $\delta\rho = V^{-1} - \rho$  and noting that  $\lambda^2 \sim \delta\rho$  as  $\delta\rho \rightarrow 0$ , we obtain

$$\chi(0) \sim \delta\rho^{-1/2} \text{ as } \delta\rho \rightarrow 0 \text{ if } \rho_1 < 2\rho , \quad (30)$$

$$\chi(0) \sim \delta\rho^{-1} \text{ as } \delta\rho \rightarrow 0 \text{ if } \rho_1 = 2\rho . \quad (31)$$

This divergence of the generating function for walks with initial vertex in the surface as  $\delta\rho \rightarrow 0$ , with an exponent  $\gamma_1 = \frac{1}{2} < \gamma$  if  $\rho_1 < 2\rho$  and with an exponent  $\gamma_1 = \gamma = 1$  if  $\rho_1 = 2\rho$ , corresponds to the ordinary and special transitions, respectively, identified by Mills (1971) in the mean-field theory of magnetic systems. In polymer systems the ordinary transition may be regarded as the case in which the polymer, though attached to the surface, extends a large distance ( $\approx$  the radius of gyration of the polymer) into the solvent above the surface. In much of this review, this case is typified by the zero-surface-interaction case. The polymer transition corresponding

to the special transition is the adsorption transition (and is referred to as such in this review) at which the polymer collapses onto the surface.

If  $\rho_1 > 2\rho$ , the surface transition, defined by a divergence in  $\chi(0)$  while  $\chi_b$  remains finite, occurs when the denominator in Eq. (29) vanishes at  $\delta\rho = \delta\rho_c$ . In this case

$$\chi(0) \sim (\delta\rho_c - \delta\rho)^{-\gamma_1} \quad (32)$$

with  $\gamma_1 = 1$ . The value of  $\delta\rho_c$  in the region  $\delta\rho \approx 0$  varies as

$$\delta\rho_c \sim (\rho_1 - 2\rho)^2 . \quad (33)$$

In terms of the polymer system, the surface transition corresponds to a polymer that has adsorbed onto the surface due to the attractive potential experienced by monomers in the vicinity of the surface. Consequently, in this case, the monomers of the polymer are all within a "small" distance from the surface.

In the language of critical phenomena, the adsorption transition point is a bicritical point. We shall show that  $\chi(0)$  for the random walks can be written in terms of a crossover function with the expected scaling form for such a bicritical point (Sec. III).

Noting that if the adsorption transition point is approached along the line  $\rho_1 = 2\rho$  then  $\chi(0) = \chi_b$ , we define

$$\epsilon\delta\rho = (2/V - \rho_1) - 2\delta\rho \quad (34)$$

and expanding  $\chi(0)$  in powers of  $\epsilon\delta\rho$ , we obtain

$$\chi(0) = \chi_b \left[ 1 + \frac{\epsilon\delta\rho}{2\rho(\delta\rho)^{1/2}} \right] . \quad (35)$$

This then has the form

$$\chi(0) \sim x^{-\gamma_1} \Phi(y/x^\phi) , \quad (36)$$

where  $x = \delta\rho$  and  $y = \epsilon\delta\rho$  are the deviations from the scaling axes (see Sec. III).

The values of  $\gamma$  and  $\gamma_1$  found here for random walks are equivalent to the mean-field values of  $\gamma$  and  $\gamma_1$  for the corresponding susceptibilities in the  $n$ -vector model. Cardy (1983) has extended the mean-field theory to systems confined to a wedge by two surfaces meeting at an angle  $\alpha$ . At the ordinary transition the exponent describing the divergence of the generating function for walks with an initial vertex in the edge of the wedge is

$$\gamma(\alpha) = 1 - \pi/2\alpha . \quad (37)$$

This is a special case of the relationship between the wedge exponent  $\gamma(\alpha)$  and the surface exponent  $\gamma_1$ , which results from the assumption of conformal invariance at a phase transition, derived in Sec. III.

When the space is bounded by two infinite parallel  $(d-1)$ -dimensional planes, so that the walks are restricted to a slab of thickness  $L$ , the ordinary transition no longer occurs at  $\delta\rho = 0$  but at a critical value of  $\delta\rho$  that is

dependent on  $L$  (De'Bell, 1980a). In the limit of large  $L$ , this dependence has the form

$$\delta\rho_c \sim L^{-2}. \quad (38)$$

This is in accordance with general arguments for the critical point in slabs of finite thickness (Barber, 1983), which show that the shift in the critical point is given by

$$\delta\rho_c \sim L^{-1/\nu}, \quad (39)$$

where  $2\nu$  is the exponent for the divergence of the mean-square end-to-end distance in the  $d$ -dimensional bulk system. That is,

$$\begin{aligned} \langle R^2 \rangle &= \sum_{\vec{r}} (\vec{r} - \vec{r}')^2 G(\vec{r}, \vec{r}') / \chi_b \\ &\sim \delta\rho^{-2\nu}. \end{aligned} \quad (40)$$

The exponent  $\nu$  may easily be shown to be  $\nu = \frac{1}{2}$  for random walks.

## B. Self-avoiding walks

### 1. Configurational properties

When one considers a walk as a simple model of a linear polymer it is clear that the random walk ignores the physical characteristic that each monomer has an associated volume which may not be occupied by any other monomer. This may readily be incorporated into the model by associating with each step end  $\vec{r}_i$  an excluded volume  $\Omega(i)$  centered on  $\vec{r}_i$  and such that  $\Omega(i)$  is wholly within but does not fill the capture region of  $\vec{r}_i$ . In this subsection we take the walk to be defined on a simple hypercubic lattice so that  $\vec{r}_i$  must correspond to exactly one lattice site. The excluded volume  $\Omega(i)$  is the lattice site itself, and the remaining capture region is the set of neighboring sites. The walk is then constrained so that, for any pair ( $0 \leq i < j \leq N$ ),  $\vec{r}_j \notin \Omega(i)$ . This simple additional constraint generates a sufficiently difficult mathematical problem that few exact results are available for the resulting self-avoiding-walk (SAW) problem. For bulk SAWs, the existence of the limit

$$\lim_{N \rightarrow \infty} N^{-1} \ln C_N = \lim_{N \rightarrow \infty} N^{-1} \ln P_N = \kappa \quad (41)$$

has been proved (Hammersley, 1957). Here  $C_N$  denotes the number of SAWs with fixed  $\vec{r}_0$  and  $P_N$  denotes the number of polygons (SAWs with  $\vec{r}_N$  in the capture region of  $\vec{r}_0$ ) with fixed  $\vec{r}_0$ .  $\kappa$  is called the connective constant [note that some authors refer to  $\mu = \exp(\kappa)$  as the connective constant]. The techniques developed by Hammersley, Whittington, and others have been used to determine the behavior of the connective constant in a variety of restricted geometries. In the rest of this section, we illustrate the techniques and summarize some of the main results obtained.

For the problem of self-avoiding walks attached to a

surface (taken to be the  $z=0$  plane), we define  $C_N^1$  to be the number of  $N$ -step SAWs with fixed  $\vec{r}_0$  such that  $z_0=0$ , and  $C_N^{11}$  to be the number of  $N$ -step SAWs with fixed  $\vec{r}_0$  such that  $z_0=z_N=0$ . We shall now show that the limits for  $C_N^1$  and  $C_N^{11}$  corresponding to Eq. (41) exist and are equal to the bulk connective constant  $\kappa$  (Whittington, 1975, 1983).

To obtain this result, consider any polygon (weakly) embedded on the bulk lattice. Let  $z_i$  denote the  $z$  coordinate of the  $i$ th vertex in the polygon and define the integer  $q$  by

$$z_q = \min(z_i; 0 \leq i \leq N). \quad (42)$$

(If more than one possible choice of  $q$  exists we choose the smallest value.) Now translate the polygon vertically,

$$z_i \rightarrow z'_i = z_i - z_q \quad \text{for all } i \quad (43)$$

(leaving all other coordinates unchanged). On the hypercubic lattice one of the following cases must occur:

$$(i) \quad z_{q+1} = z_{q-1} = 0, \quad (44)$$

$$(ii) \quad z_{q+1} = 0, \quad z_{q-1} = 1, \quad (45)$$

$$(iii) \quad z_{q+1} = 1, \quad z_{q-1} = 0. \quad (46)$$

In cases (i) and (ii) the edge  $(q, q+1)$  is deleted, and in case (iii) the edge  $(q-1, q)$  is deleted to obtain a walk confined to the half space  $z \geq 0$  and with  $z_0 = z_N = 0$ . Polygons that differ by more than a vertical translation each generate a distinct walk in this way, and the normalization of  $P_N$  ensures that each distinct walk receives weight 1. Therefore

$$P_N \leq C_N^{11} \leq C_N^1 \leq C_N \quad (47)$$

and, using the bulk result [Eq. (41)], we obtain

$$\lim_{N \rightarrow \infty} N^{-1} \ln C_N^{11} = \lim_{N \rightarrow \infty} N^{-1} \ln C_N^1 = \kappa. \quad (48)$$

### 2. Interaction with a surface and surface adsorption

An important feature that arises in the adsorption problem is that the part of the SAW that lies in the surface must be taken into account. This means that any translation or body shift has to leave the configurations unchanged, not only with respect to the bulk, but also in the surface. Hammersley, Torrie, and Whittington (1982) studied the SAW model of a linear polymer interacting with a surface. They established that, if the monomers interact with the surface with energy  $\omega$ , there exists a critical value  $\omega_c$  at which the SAW undergoes a phase transition. Moreover, it can be shown that the transition is from  $d$ -dimensional to  $(d-1)$ -dimensional behavior. This result can be extended to more general polymer topologies for which it can be proved that the behavior of the limiting entropy per monomer is the same as for a SAW interacting with a surface (Zhao and Lookman, 1991a, 1991b; Whittington and Soteros, 1992).

We therefore outline the proof for the existence of the transition for SAWs defined on a  $d$ -dimensional Euclidean space with integer coordinates, where the surface is the hyperplane  $z=0$ . The idea behind the proof is the use of a simple "squeeze" law. We consider the number  $C_n(m)$  of SAWs in the  $d$ -dimensional lattice starting at the origin, with no vertex, with negative  $z$  coordinate and with  $m+1$  visits to the surface. The partition function is given by

$$Z_n(\omega) = \sum_{m=0}^n C_n(m) e^{\omega m} \quad (49)$$

and the reduced limiting free energy per monomer is

$$A(\omega) = \lim_{n \rightarrow \infty} \frac{1}{n} \ln Z_n(\omega). \quad (50)$$

The limit can be shown to exist for all  $\omega$ . Positive values of  $\omega$  correspond to an attractive interaction with the surface  $z=0$ . With  $\omega=0$ , we have

$$Z_n(0) = \sum_{m=0}^n C_n(m) = C_n^1. \quad (51)$$

For  $\omega \leq 0$ , since  $Z_n(\omega)$  is a monotone increasing function of  $\omega$ ,

$$Z_n(\omega) \leq C_n^1. \quad (52)$$

Clearly,

$$Z_n(\omega) \geq C_n(0). \quad (53)$$

Moreover,

$$C_n(0) = C_{n-1}^1 \quad (54)$$

if we remove the first step and translate the walk by unit distance in the negative  $x$  direction. Then

$$C_{n-1}^1 \leq Z_n(\omega) \leq C_n^1 \quad (55)$$

or

$$A(\omega) = \kappa_d \quad \forall \omega \leq 0, \quad (56)$$

where  $\kappa_d$  is the connective constant of the  $d$ -dimensional lattice. For  $\omega \geq 0$ ,

$$Z_n(\omega) \geq C_n(n) e^{\omega n}, \quad (57)$$

so that

$$A(\omega) \geq \lim_{n \rightarrow \infty} \frac{1}{n} \ln C_n(n) + \omega \quad (58)$$

or

$$A(\omega) \geq \kappa_{d-1} + \omega, \quad (59)$$

where  $\kappa_{d-1}$  is the connective constant of the  $(d-1)$ -dimensional lattice.

Thus  $A(\omega)$  has a constant value ( $=\kappa_d$ ) for all  $\omega \leq 0$ , but is greater than  $\kappa_d$  for  $\omega > \kappa_d - \kappa_{d-1}$  so that  $A(\omega)$  is nonanalytic at some value  $\omega_c$ . This means that there is a phase transition (the adsorption transition) from  $d$ -

dimensional to  $(d-1)$ -dimensional behavior in the model. In particular, Hammersley, Torrie, and Whittington (1982) showed that the limit

$$A(\omega) = \lim_{N \rightarrow \infty} A_N(\omega) \quad (60)$$

exists for all  $\omega$  and is bounded by

$$\max(\kappa, \kappa_{d-1} + \omega) \leq A(\omega) \leq \max(\kappa, \kappa + \omega). \quad (61)$$

Moreover, there exists a critical value of  $\omega$  defined by

$$\omega_c = \sup[\omega: A(\omega) = \kappa] \quad (62)$$

and bounded by

$$0 \leq \omega_c \leq \kappa - \kappa_{d-1}. \quad (63)$$

Physically, these results imply the existence of the ordinary, adsorption, and surface transitions for linear polymers modeled by SAWs (see Fig. 2). For  $\omega < \omega_c$ , the connective constant for a polymer attached to the surface retains the value for a polymer in the bulk solution. For  $\omega > \omega_c$ , the connective constant decreases and has a lower limit given by the connective constant for the corresponding  $(d-1)$ -dimensional bulk problem. The value of  $\omega_c$  then corresponds to the critical value of the attractive interaction of the monomers with the surface at which the surface adsorption transition occurs.

The crossover exponent  $\phi$  at  $\omega_c$  is defined by

$$A(\omega) - A(\omega_0) \sim (\omega - \omega_0)^{1/\phi}. \quad (64)$$

Zhao, Lookman, and De'Bell (1990) have used two variable Padé approximants to obtain precise estimates of  $\phi$  and  $\omega_c$  (Sec. V.C). It has been shown that SAWs confined to a wedge and interacting with a surface have the same reduced limiting entropy per monomer as a SAW interacting with a surface (Whittington and Soteros, 1990). The method outlined above can be applied to a variety of other geometrical constraints and polymer structures such as stars, combs, and other topologies (Sec. II.D).

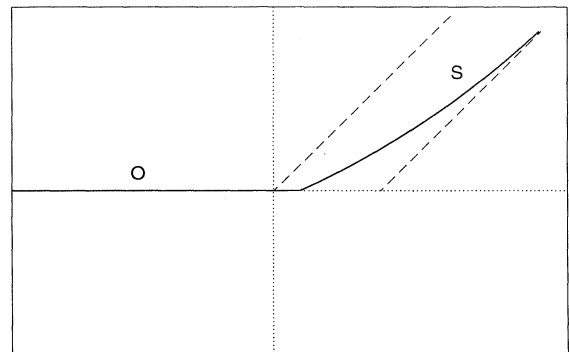


FIG. 2. The phase diagram for SAWs interacting with a surface, with O and S referring to the ordinary and surface transitions, respectively. The function  $A(\omega)$  is plotted against  $\omega$  and approaches the broken line  $\kappa_{d-1} + \omega$ . The other broken line is  $\kappa_d + \omega$ .

### C. SAWs in wedges and slabs

The problem of walks restricted to a wedge and terminally attached to the apex of the wedge may be generalized by considering walks that are restricted so that for each

$$\vec{r}_i = (r^1, r^2, \dots, r^d) \quad (65)$$

in the walk

$$r^1 \geq 0 \text{ and } 0 \leq r^j \leq f_j(r^1) \text{ for } 2 \leq j \leq d. \quad (66)$$

Denoting the number of  $N$ -step walks starting from the origin by  $C_N(f)$ , it may be shown (Hammersley and Whittington, 1985), that for any  $f$  such that

$$f_j(x) \rightarrow \infty \text{ as } x \rightarrow \infty \text{ for } 2 \leq j \leq d, \quad (67)$$

the limit

$$\lim_{N \rightarrow \infty} C_N(f) = \kappa \quad (68)$$

exists and is equal to the bulk connective constant.

This result is of considerable importance since it enables us to show that the connective constant for other structures, in many cases of interest, is equal to the bulk connective constant for SAWs (see Sec. II.D).

Proving the existence of the corresponding limit for walks confined between two parallel  $(d-1)$ -dimensional planes illustrates many of the techniques required to obtain the exact results described in this and the next subsection. The required result for walks restricted to a slab of thickness  $L$  is obtained by noting that a limit may be obtained for a subset of the possible walks (Whittington, 1983). Let  $\mathcal{C}_N(L, z_0)$  be the set of  $N$ -step walks beginning at an origin with  $z$  coordinate  $z_0$  and let  $\mathcal{D}_N(L, z_0)$  be the subset of  $\mathcal{C}_N(L, z_0)$  such that

$$y_0 \leq y_i \leq y_N, \quad (69)$$

where  $y$  is a chosen coordinate not equal to  $z$ . The subset of  $\mathcal{D}_N(L, 0)$  that have  $z_N = 0$  is denoted by  $\mathcal{B}_N(L)$ . A member of  $\mathcal{B}_N(L)$  and a member of  $\mathcal{B}_M(L)$  can be combined by translating the initial vertex of the  $M$ -step walk to coincide with the final vertex of the  $N$ -step walk. If  $B_N$  is the number of walks in the  $\mathcal{B}_N(L)$  we have

$$B_{N+M} \geq B_N B_M, \quad (70)$$

and since  $B_N$  is bounded above by  $(2d)^N$  we have

$$0 < \lim_{N \rightarrow \infty} \ln B_N(L) = \kappa(L) \leq \ln(2d). \quad (71)$$

Any member of  $\mathcal{D}_N(L, z_0)$  can be converted to a member of  $\mathcal{B}_N(L)$  by adding  $L+2$  edges at each end of the walk (Whittington, 1983) using the procedure illustrated in Fig. 3(b). A member of  $\mathcal{C}_N(L, z_0)$  can be converted to a member of  $\mathcal{D}_N(L, z_0)$  by an unfolding transformation [Fig. 3(a)]. This transformation consists of selecting the smallest integer  $q$  such that

$$y_q = \min(y_i) \quad (72)$$

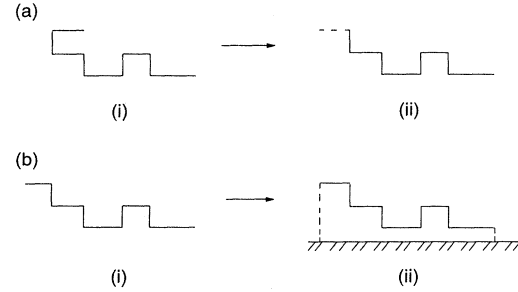


FIG. 3. Conversion of walks from one subset to another: (a) a member of  $\mathcal{C}$  (i) is converted to a member of  $\mathcal{D}$  (ii) by an unfolding transformation; (b) a walk (i) belonging to the subset  $\mathcal{D}$  is converted to a member (ii) of  $\mathcal{B}$ .

and reflecting the vertices labeled by  $1, \dots, q-1$  in the plane  $y = y_q$ . By iterating this procedure and similar reflections in the plane

$$y = y_q = \max(y_i) \quad (73)$$

one generates a member of  $\mathcal{D}_N(L, z_0)$ . Since it is known that there exists a constant  $\varphi$  such that not more than  $\exp(\varphi N^{1/2})$  members of  $\mathcal{C}_N(L, z_0)$  generate the same member of  $\mathcal{D}_N(L, z_0)$  by this transformation, if  $C_N(L)$  and  $D_N(L)$  denote the number of walks in  $\mathcal{C}_N(L, z_0)$  and  $\mathcal{D}_N(L, z_0)$ , respectively,

$$D_N(L) \leq C_N(L) \leq D_N(L) \exp(\varphi N^{1/2}). \quad (74)$$

From the relationship between the members of  $\mathcal{D}_N(L, z_0)$  and  $\mathcal{B}_N(L)$

$$B_N(L) \leq D_N(L) \leq B_{N+2L+4}(L). \quad (75)$$

Therefore we have the limit

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln C_N(L) = \kappa(L). \quad (76)$$

Using Kesten's pattern theorem (Kesten, 1963), one can show (Hammersley and Whittington, 1985) that  $\kappa(L) < \kappa$  and as  $L \rightarrow \infty$ ,  $\kappa(L) \rightarrow \kappa$ . This provides a useful guideline when performing numerical calculations for finite slabs.

### D. Stars and other topologies

#### 1. Configurational properties

In this section we examine the influence of polymer architecture and geometrical constraints on the connective constant  $\kappa$ , which is also the limiting entropy per monomer of the polymer.

Consider a star with  $f$  legs, each containing  $N$  edges, embedded in the bulk in such a way that its central vertex is at a chosen origin. The space may be divided into  $f$  equal wedges which meet at the origin. Let  $D_N(f)$  be the number of possible embeddings if each leg of the star is restricted to one of the wedges, so that each leg is a

SAW restricted to a wedge. We then have

$$D_N(f) \leq C_N(f) \leq (C_N)^f \quad (77)$$

and using Eqs. (41) and (68)

$$\lim_{N \rightarrow \infty} 1/N \ln C_N(f) = f\kappa, \quad (78)$$

where  $\kappa$  is the self-avoiding-walk connective constant (Wilkinson, Gaunt, Lipson, and Whittington, 1986). That the corresponding limit for  $f$  stars attached to a surface or the edge of a wedge is also  $\kappa$  follows in exactly the same way, since the space can again be divided into  $f$  wedges (Whittington, 1987). A similar result for trees (topologies with no closed loops) of fixed topology can be obtained by an inductive argument. We assume here that each chain in the tree has  $N$  edges. Let  $\mathcal{T}$  denote the topology of the tree. A branch point is a vertex of degree  $\geq 3$ . We choose one vertex to be fixed at the origin. Then from the vertex at the origin to any branch point there is a single path involving no backsteps. Choose any branch point such that dividing the tree at this vertex results in a tree of topology  $\mathcal{T}'$  and an  $f$  star ( $f+1$  being the degree of the chosen vertex), only the chosen vertex being common to both the tree  $\mathcal{T}'$  and the  $f$  star. Now locate the chosen vertex at the origin and draw a  $(d-1)$ -dimensional plane  $x=0$ . Consider embeddings of  $\mathcal{T}$  such that members of  $\mathcal{T}'$  are restricted to  $x > 0$  (except the vertex at the origin) and members of the  $f$  star are restricted to the space  $x \leq 0$ . Then

$$D_N(\mathcal{T}')D_N(f) \leq C_N(\mathcal{T}) \leq (C_N)^b, \quad (79)$$

where  $D_N(\mathcal{T}')$  and  $D_N(f)$  are the restricted number of embeddings for  $\mathcal{T}'$  and the  $f$  star, respectively, and  $b$  is the number of chains in  $\mathcal{T}$ . Since any tree may be constructed by a concatenation of stars and SAWs, it follows that

$$\lim_{N \rightarrow \infty} \frac{1}{n} \ln C_N(\mathcal{T}) = b\kappa. \quad (80)$$

(This result is valid for trees embedded in the bulk or attached to a surface or wedge edge. In the case of a surface or wedge, the plane  $x=0$  must be parallel to the surface or wedge edge and each embedding must be combined with a translation perpendicular to this plane so that a specified vertex is in the surface or edge.)

Stars embedded in a slab, infinite in  $d-1$  dimensions and of finite thickness  $L$ , have been considered by Chee and Whittington (1987). They conclude that in three or more dimensions the limit

$$\lim_{N \rightarrow \infty} N^{-1} \ln C_N(f) = \kappa(L, f) \quad (81)$$

is independent of  $f$ , but in two dimensions the limit depends on  $f$  (Chee and Whittington, 1987; see also Soteros and Whittington, 1989).

For lattice animals, which may be regarded as models of branched polymers with general topology, the limiting value of the number of lattice animals of  $N$  vertices contained in a wedge of angle  $\alpha$  obeys

$$\lim_{N \rightarrow \infty} N^{-1} \ln a_N = \kappa_\alpha, \quad (82)$$

where  $\kappa_\alpha$  is independent of the wedge angle and equal to the corresponding bulk limit (Whittington and Soteros, 1990).

For a polymer network  $g_n(c, n_3, \dots, n_{2d})$ , defined on a  $d$ -dimensional hypercubic lattice where the topology is specified in terms of  $c$  cycles,  $n_3$  vertices of degree 3,  $\dots$ ,  $n_{2d}$  vertices of degree  $2d$ , Gaunt, Lipson, Torrie, Whittington, and Wilkinson (1984) have shown that, for such networks with total length  $N$ , the connective constant is the same as that for SAWs. Zhao and Lookman (1991b) have considered such specified topologies confined to one side of a surface and have shown that  $\kappa$  is again the same as walks for uniform networks.

In conclusion, we see that a polymer network has the same connective constant as a SAW in the infinite bulk, but there are interesting differences in behavior depending on the geometrical constraints used to confine the polymer.

## 2. Critical exponents

The influence of topology on the critical exponent  $\gamma_t$  of polymer networks with the self-avoiding constraint has been previously investigated (Gaunt *et al.*, 1984; Duplantier, 1986). The results of scaling and renormalization theory hold for the uniform or "pseudouniform" network for which the number of monomers in each of the chains is expected to be of  $O(N)$ . Few rigorous results exist for uniform networks. For nonuniform networks, Zhao and Lookman (1992a) have proved that, for the case of simple networks with cut edges (Fig. 4), the subdominant exponent  $\gamma_t$  satisfies the conjecture  $\gamma_t = \gamma + b - 1$  (Gaunt *et al.*, 1984), where  $b$  is the number of cut edges. A cut edge of a graph is one which, if deleted, disconnects the graph. They also consider the exponent  $\nu_t$ , characterizing the divergence of the mean-square end-to-end dis-

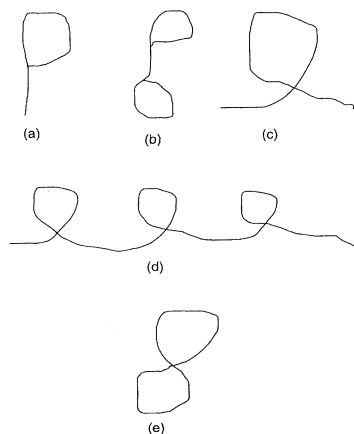


FIG. 4. Examples of simple topologies: (a) tadpole, (b) dumbbell, (c) twin-tailed tadpole, (d) 3-twin-tailed tadpole, (e) figure eight.



tance of a chain within the network, and prove that it is equal to  $\nu$ , the self-avoiding exponent. Similar results for the subdominant exponents hold for the half-space problem if these topologies have their initial, or both initial and terminal, vertices attached to the surface. Consequently the scaling relations involving the bulk and surface exponents ( $\gamma - \gamma_1$  and  $\gamma - \gamma_{11}$ ) are the same as for SAWs, a result that was previously conjectured only for uniform networks (see Sec. III.B). Moreover, by assigning an interaction energy to a nearest-neighbor contact, one can prove that the collapse transition for these topologies is the same as that for SAWs (Sec. VI.C). For the figure-eight topology (which does not have a cut edge), the subdominant exponent  $\epsilon$  is equal to  $\alpha$ , the exponent for polygons and the collapse transition is the same as that for polygons. The asymptotic forms  $p_n \sim n^{\alpha-2} e^{n\kappa}$  and  $\epsilon_n \sim n^{\epsilon-1} e^{n\kappa}$  are assumed for the number of polygons and figure eights, respectively.

The study of such networks is also related to the problem of lattice trails, which are random walks on a lattice in which edges are not allowed to overlap. Zhao and Lookman (1992b) show that for trails in a hypercubic lattice with  $c$  cycles (a  $c$  trail),  $\gamma_c = \gamma + c$  and  $\nu_c = \nu$ .

### 3. Interaction with a surface

For a general polymer network attached to a surface and in a number of restricted geometries, Duplantier and Saleur (1986) have conjectured the dependence of the critical exponent  $\gamma$  on polymer topology (Sec. IV.C). Ohno and Binder (1988) have rederived the scaling theory for a polymer network by using the equivalence between the generating function for the number of configurations and the correlation function for the classical  $n$ -vector model in the limit  $n \rightarrow 0$ . It is of interest to examine the effects of an interaction between an adsorption surface and such polymer networks and to determine how adsorption depends on the polymer architecture. As introduced in Sec. II.D.1, the general polymer network may be represented by  $g_n(c, n_3, \dots, n_{2d})$ . Using Euler's law of edges, we have

$$2c = 2 - n_1 + \sum_{i=3}^{2d} (i-2)n_i \quad (83)$$

and

$$2\kappa = n_1 + \sum_{i=3}^{2d} in_i, \quad (84)$$

where  $n_i$  is the number of vertices with degree  $i$  and  $K$  is the number of chains connecting the branch points of degree  $i$ . Each of the chains is an  $n$ -step SAW. The vertices of degree 2 are suppressed, since they do not affect the topology. The case  $c=0$  refers to treelike structures in general. More than one topology can have the same set of values for  $\{c, n_3, n_4, \dots, n_{2d}\}$  (Fig. 5). The values  $\{c, n_3, n_4, \dots, n_{2d}\}$  therefore do not specify a unique topology, since the connectivity is not uniquely determined.

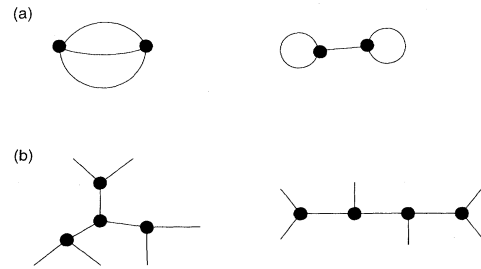


FIG. 5. Examples of topologies with the same  $\{c, n_3, n_4, \dots, n_{2d}\}$ : (a) a  $\theta$  graph and a dumbbell with  $\{2, 2, 0, 0, \dots\}$ ; (b) a tree and a comb with  $\{0, 4, 0, 0, \dots, 0\}$ .

However, for certain values of  $\{c, n_3, n_4, \dots, n_{2d}\}$  unique topologies are obtained. For example,  $n_f=1$ ,  $n_i=0$  for  $f \neq i$  refers to an  $f$  star, while  $n_3=2$ ,  $n_i=0$ ,  $i \geq 4$  refers to an  $H$  comb. The topology contains  $Kn$  edges, since each of the  $K$  chains is an  $n$ -step SAW. We denote by  $g_{Kn,m}$  the number of networks with a total of  $m$  edges in the surface  $x_1=0$ . The generating function is then defined by

$$G_n(c, n_3, \dots, n_{2d}, \omega) = \sum_{m=0}^{Kn} g_{Kn,m} e^{m\omega}. \quad (85)$$

Zhao and Lookman (1991b) and Soteros (1992) have shown that for  $d > 2$

$$\lim_{n \rightarrow \infty} \frac{1}{Kn} \ln G_n(c, n_3, \dots, n_{2d}, \omega) = A(\omega), \quad (86)$$

where  $A(\omega)$  is the reduced free energy of SAWs in terms of the number of edges in the surface. For  $d=2$  and for topologies with cut edges, the free energy is not the same as for SAWs (Whittington and Soteros, 1992; Soteros, 1992). However, it can be shown that the transition point and crossover behavior are the same (Zhao, 1992). The particular case of a  $k$  loop in which  $n_k=2$ ,  $k > 2$ ,  $n_i=0$ ,  $i \neq k$  is considered in detail in Zhao and Lookman (1991a). The results also imply that the connective constant  $\kappa$  for nonuniform networks is the same as for SAWs, since the uniform case provides a lower bound.

In summary, the specified polymer topology has the same reduced free energy and hence critical point and crossover behavior as that for SAWs interacting with a surface, either penetrable or impenetrable. There thus appears to be a universality in the free energy brought about by a surface interaction. Moreover, it is known that  $\phi = 1 - \nu$  for the penetrable surface problem (i.e., when the polymer is able to cross the surface; Diehl, 1986). Since the above requires that  $\phi$  be the same for all fixed topologies,  $\nu$  is also the same as for SAWs, a result generally assumed in scaling arguments.

### E. Lattice animals

Lattice animals and trees have been considered as models of branched polymers with excluded volume, and

the techniques used to handle the animal problem are closely related to techniques in the theory of self-avoiding walks (Hammersley, 1957; Kesten, 1963). Lattice animals are closely related to percolation clusters, although the associated weights are different in the two problems (Kesten, 1982). The results available on configurational properties have been reviewed by Whittington and Soteros (1990). If  $a_n$  and  $A_n$  are the number of bond and site animals with  $n$  vertices, and  $t_n$  and  $T_n$  are the number of bond and site trees with  $n$  vertices, then the limits

$$\lambda = \lim_{n \rightarrow \infty} a_n^{1/n}, \quad (87)$$

$$\Lambda = \lim_{n \rightarrow \infty} A_n^{1/n}, \quad (88)$$

$$\lambda_0 = \lim_{n \rightarrow \infty} t_n^{1/n}, \quad (89)$$

$$\Lambda_0 = \lim_{n \rightarrow \infty} T_n^{1/n} \quad (90)$$

can be established. Moreover,

$$\Lambda_0 < \Lambda < \lambda_0 < \lambda. \quad (91)$$

For lattice animals confined in a wedge of angle  $\alpha$ , Whittington and Soteros (1990) show that

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln a_N = \lambda_\alpha, \quad (92)$$

where  $\lambda_\alpha$  is independent of the wedge angle and equal to the corresponding bulk limit.

It is believed that

$$a_n \sim \lambda^n n^{-\theta}, \quad n \rightarrow \infty, \quad (93)$$

where  $\theta$  is the subdominant exponent. Similarly, for trees it is expected that

$$t_n \sim \lambda^n n^{-\theta_0}. \quad (94)$$

Renormalization-group arguments and numerical results (Lubensky and Isaacson, 1979; Gaunt *et al.*, 1982) suggest that  $\theta = \theta_0$ . A connection between lattice animals with cyclomatic index  $c$  and trees was provided by Soteros and Whittington (1988), who proved that

$$\theta_c = \theta_0 - c. \quad (95)$$

The adsorption transition for lattice trees has recently been considered by Lookman, Zhao, and De'Bell (1991), who, following the arguments of Hammersley, Torrie, and Whittington (1982) for walks, established the existence of a transition. Estimates of the critical point, based on an exact enumeration study, have also been given.

If the asymptotic form for the number of lattice trees rooted to the surface,  $nC_n$ , is assumed to be

$$C_n \sim \lambda^n n^{-\theta_1}, \quad n \rightarrow \infty, \quad (96)$$

where  $\theta_1$  is the critical exponent describing the subdominant behavior, De'Bell, Lookman, and Zhao (1991) have

proved that the result

$$\theta_1 = \theta + 1 \quad (97)$$

is valid for all dimensions  $d \geq 2$ . To obtain this result, we note that

$$nC_n \geq t_n, \quad (98)$$

since we can always generate a one-rooted tree by allowing the surface to approach the unrooted bulk tree from below and rooting the tree at the vertex that the surface first touches. However, in some cases more than one vertex can touch the surface in this way. On the other hand, a subset of the bulk embeddings will result in rooted surface embeddings in which only one vertex (the root) is in the surface.

We therefore have

$$t_{n+1} \geq (n+1)C_{n+1,1}, \quad (99)$$

where  $C_{n+1,1}$  indicates the number of embeddings in which only the root is in the surface. Moreover,

$$(n+1)C_{n+1,1} = nC_n, \quad (100)$$

since from any tree of  $n$  vertices rooted in the surface we may generate a tree of  $n+1$  vertices by displacing the surface by one lattice layer. The additional vertex is then placed in the new surface directly below the previous root and an additional edge is added adjacent to the previous root and the new root in the new surface. Hence we have the bounds

$$t_{n+1} \geq nC_n \geq t_n \quad (101)$$

and, assuming  $t_n \sim \lambda^n n^{-\theta}$ ,  $n \rightarrow \infty$ , the required result follows.

Zhao and Lookman (1992a) have recently studied two lattice models for  $c$  animals. The models are (a)  $c$  animals with an interaction energy  $\alpha$  between nearest-neighbor pairs of vertices and (b)  $c$  animals as in (a) but with an additional interaction energy  $\omega$  between the vertices of the animal and an adsorption surface. By assuming that the partition functions satisfy

$$A_n(c, \alpha) \sim n^{-\theta_c(\alpha)} \lambda_c^n(\alpha) \quad (102)$$

and

$$A_n(c, \alpha, \omega) \sim n^{-\theta_c(\alpha, \omega)} \lambda_c^n(\alpha, \omega) \quad (103)$$

as  $n \rightarrow \infty$  with  $c$  fixed, they show that

$$\theta_c(\alpha) = \theta_0(\alpha) - c \quad \text{for } -\infty < \alpha < \infty \quad (104)$$

and

$$\theta_c(\alpha, \omega) = \theta_0(\alpha, \omega) - c \quad \text{for } -\infty < \alpha, \omega < \infty, \quad (105)$$

where  $\theta_0(\alpha)$  and  $\theta_0(\alpha, \omega)$  are the corresponding exponents for trees. The result  $\theta_c(\omega) = \theta_0(\omega) - c$  was previously obtained by Zhao and Lookman (1991c). These results are generalizations of the bulk result  $\theta_c = \theta_0 - c$ .

The irrelevance of cycles on the properties of lattice

animals has been considered previously using renormalization-group methods (Lubensky and Isaacson, 1979, Family, 1980). Zhao, Wu, and Lookman (1992) have recently proved the result  $\nu_c = \nu_0$ , where  $\nu_c$  is the exponent characterizing the mean-square radius of gyration of lattice bond  $c$  animals with cyclomatic index  $c$  and  $\nu_0$  is the exponent for lattice bond trees. The proof makes use of a pattern theorem for lattice animals (Madras, 1988).

### III. SCALING THEORY

#### A. Self-avoiding walks

While the subdominant behavior of  $C_N$  as  $N \rightarrow \infty$  has not been determined rigorously, it is widely supposed that for SAWs in the bulk

$$C_N \sim \exp(N_\kappa) N^{\gamma-1}, \quad (106)$$

and we therefore expect the generating function for SAWs to exhibit critical behavior of the form

$$G(p) = \sum_N C_N p^N \sim (p_c - p)^{-\gamma}, \quad (107)$$

where

$$p_c = \exp(-\kappa). \quad (108)$$

Consider SAWs confined to the half space  $z \geq 0$  which interact with the surface in the way described in Sec. II.B. The generating function is then

$$G_1(p, \omega) = \sum_{N,t} C_{N,t} p^N \exp(t\omega) = \sum_{N,t} C_{N,t} p^N p_1^t. \quad (109)$$

If a subdominant form, similar to that for bulk walks, is assumed,

$$A_N(\omega) \sim \exp[\kappa(\omega)N] N^{\gamma(\omega)-1}, \quad (110)$$

this combined with the results of Sec. II.B implies that  $G_1(p, \omega)$  will diverge at the bulk critical point  $p_c = \exp(-\kappa)$  for all  $\omega \leq \omega_c$ . However, for  $\omega > \omega_c$  the divergence occurs at  $p(\omega) \leq p_c$ . Thus the SAW problem is expected to exhibit ordinary, adsorption, and surface transitions as found in the random-walk case (Sec. II.A).

Renormalization-group arguments (Kremer, 1983; Diehl, 1986) indicate that there is a single value of  $\gamma(\omega)$  for each of these transitions as follows:

$$\text{ordinary } \omega < \omega_c, \quad \gamma(\omega) = \gamma_1, \quad (111)$$

$$\text{adsorption } \omega = \omega_c, \quad \gamma(\omega) = \gamma_1^{ad}, \quad (112)$$

$$\text{surface } \omega > \omega_c, \quad \gamma(\omega) = \gamma_1^s. \quad (113)$$

Moreover, these arguments show that  $\gamma_1^s$  is equal to the value of  $\gamma$  for a  $(d-1)$ -dimensional system.

It is necessary to make further assumptions in order to determine relationships between the local surface exponents and bulk exponents for the ordinary and adsorption transitions. Scaling theory assumes the generating

functions to be generalized homogeneous functions of their arguments (Binder, 1983). This assumption allows a set of relationships to be derived such that for the ordinary transition, if any one local exponent is known, the remaining local exponents may be obtained from this and the bulk exponents. In this and the following two subsections we deal principally with the ordinary transition and therefore set  $p_1 = p$ , deferring a discussion of the special transition to Sec. III.D.

In Sec. III.B we shall show that a set of relationships between bulk and surface polymer exponents may be obtained from geometric arguments. These arguments assume that there is a single diverging length scale  $\xi$ , which characterizes the critical behavior and which diverges in the same manner as the average distance between vertices in a chain. That is,

$$\xi \sim (p_c - p)^{-\nu}. \quad (114)$$

As an example, we consider how the amplitude of the generating function  $\chi(z)$  for SAWs with initial vertex fixed at a perpendicular distance  $z$  from the surface depends on  $z$ . In the limit of large  $N$  we expect  $C_N(z)$ , the number of  $N$ -step walks with initial vertex distance  $z$  from the surface, to have the following properties:

$$C_N(z) \sim A(z) \mu^N N^{\gamma_1-1} \quad \text{for } z \ll \xi, \quad (115)$$

$$C_N(z) \sim A \mu^N N^{\gamma-1} \quad \text{for } z \gg \xi. \quad (116)$$

Since  $A(z)$  is dimensionless,  $A(z) = A(z/\xi)$ , and therefore

$$A(z) \sim (z/\xi)^{(\gamma-\gamma_1)/\nu}. \quad (117)$$

Hence

$$\chi(z) \sim z^{(\gamma-\gamma_1)/\nu} \quad \text{for } z \ll \xi, \quad p \rightarrow p_c. \quad (118)$$

Consider now the global surface function

$$\chi_s = \sum_z (\chi - \chi(z)). \quad (119)$$

Assuming that the contribution from SAWs with end-to-end distance  $> \xi$  may be neglected, we have

$$\chi_s = \xi \chi - \sum_{z=0}^{\xi} \chi(z). \quad (120)$$

Substituting Eq. (118) for  $\chi(z)$  in the sum, we find

$$\chi_s \sim (p_c - p)^{-\gamma_s} \quad (121)$$

with

$$\gamma_s = \gamma + \nu. \quad (122)$$

Thus the global surface exponent  $\gamma_s$  is completely determined in terms of the bulk critical exponents. However, some caution is necessary since Eq. (118) is valid only if  $z \ll \xi$ . It has recently been pointed out that the correction term resulting from summing over the region  $z \approx \xi$  in the construction of  $\chi_s$  may make the determination of

TABLE I. Examples of scaling relations obtained from the geometric scaling arguments given in the text ( $f$  denotes an  $f$  star,  $H$  denotes an  $H$  comb, and  $G$  denotes a general topology having  $L$  loops and  $B$  surface bridges).

$\gamma = 2\sigma_1 + 1$	$\gamma(H) = 2\gamma(3) - \gamma$
$\gamma_1 = \sigma_1 + \sigma'_1 + 1$	$\gamma_1(H) = 2\gamma(3) + \gamma_1 - 2\gamma$
$\gamma_{11} = 2\gamma_1 - \gamma - \nu$	$\gamma_{11}(H) = 2\gamma(3) + \gamma_{11} - 2\gamma$
$\gamma_2 = \sigma'_2 + 2\sigma_1 + 1$	$\gamma_3(H) = \gamma(3) + \gamma_3(3) - \gamma$
$\gamma_{21} = \gamma_2 + \gamma_{11} - \gamma_1$	$\gamma_{33}(H) = 2\gamma_3(3) - \gamma - \nu$
$\gamma(f) = \sigma_f + f\sigma_1 + 1$	$\gamma \dots (G) = \sum_i n_i \sigma_i - \sum_i n'_i \sigma'_i - L d\nu - B\nu$
$\gamma_f(f) = \sigma'_f + f\sigma_1 + 1$	$\gamma_1(G) - \gamma_{11}(G) = \gamma - \gamma_1 + \nu$
$\gamma_1(f) = \gamma(f) + \gamma_{11} - \gamma_1 + \nu$	
$\gamma_{11}(f) = \gamma(f) + \gamma_{11} - \gamma$	

the leading exponent difficult (De'Bell, Lookman, and Whittington, 1990).

**B. Geometric derivation of scaling theory**

We now demonstrate the derivation of scaling relations between the local surface exponents and the bulk exponents. The geometric derivation given here is that developed by Duplantier (1988) and provides considerable insight into the underlying reasons for the scaling relations between the critical exponents of different polymer topologies and different arrangements of surface-attached polymers. Typical scaling relations derived in this way are listed in Table I, and some corresponding surface attached configurations are illustrated in Fig. 6.

Begin by considering SAWs embedded in the bulk, for which we expect

$$C_N(1) \sim \mu^N N^{\gamma(1)-1} . \tag{123}$$

The argument of  $C_N$  and  $\gamma$  indicates that the SAW is to be considered a 1 star. We write

$$\gamma(1) - 1 = 2\sigma_1 , \tag{124}$$

that is, with each vertex of degree 1 we associate a  $\sigma_1$ .

By analogy, the asymptotic behavior of  $f$  stars with  $N$  vertices in each leg is expected to be

$$C_{N,f} \sim \mu^{fN} N^{\gamma(f)-1} . \tag{125}$$

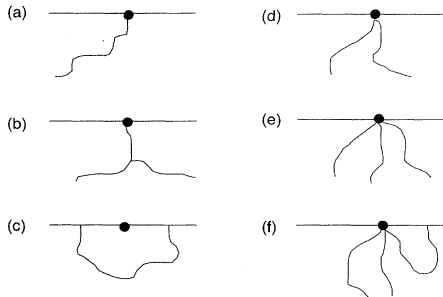


FIG. 6. Some surface-attached configurations. The configurations contribute to the following exponents: (a)  $\gamma_1$ , (b)  $\gamma_1(3)$ , (c)  $\gamma_{11}$ , (d)  $\gamma_2$ , (e)  $\gamma_3(3)$ , (f)  $\gamma_{13}(3)$ .

We therefore write

$$\gamma(f) - 1 = \sigma_f + f\sigma_1 . \tag{126}$$

Thus with the central vertex of degree  $f$  there is associated a  $\sigma_f$ , which may be determined from the properties of the  $f$  star.

Notice that a 2 star is also a SAW, and therefore we require

$$\sigma_2 + 2\sigma_1 = 2\sigma_1 , \tag{127}$$

that is,

$$\sigma_2 = 0 . \tag{128}$$

The utility of this approach becomes apparent if we consider the exponent of a more complex topology. For example, an  $H$  comb may be constructed by bringing together two 3 stars in such a way that two vertices of degree 1 are replaced by a vertex of degree 2. Assuming the asymptotic behavior of the number of  $H$  combs with  $N$  edges in each chain to be

$$C^N(H) \sim \mu^{5N} N^{\gamma(H)-1} , \tag{129}$$

we have

$$\gamma(H) - 1 = 2\sigma_3 + 4\sigma_1 = 2[\gamma(3) - 1] - [\gamma(1) - 1] , \tag{130}$$

$$\gamma(H) = 2\gamma(3) - \gamma(1) . \tag{131}$$

Therefore no additional information, other than that available from the 3 stars and SAWs, is required to evaluate  $\gamma(H)$ . Similarly, the critical exponent for any fixed topology  $\mathcal{G}$  may be constructed from the exponents for  $f$  stars.

To clarify, this remarkable property may be thought of as a consequence of our assumption that vertices separated by a distance of  $O(\xi)$  are distinct and do not interfere with each other, while vertices at closer distances must be grouped into a single renormalized vertex.

Topologies that contain loops require special attention. To see this, consider any chain in a fixed topology. Choose one of the terminal vertices to be fixed and consider an arbitrarily chosen vertex  $i$  of degree 2 in the chain  $N'$  steps from the fixed terminal vertex and such that  $N - N' = O(1)$ . Note that in general this vertex  $i$  can occupy any site in a volume of  $O(\xi^d)$ . We therefore

expect the number of configurations to contain a corresponding factor of  $N^{d\nu}$ . However, if the chain closes a loop by connecting to a terminal vertex that is already fixed (embedded), the sites available to site  $i$  occupy a region of  $O(1)$ . As the  $\sigma_f$ 's are generated from stars, they are generated for structures with chains in which one of the ends is "free" during embedding. Consequently, when forming the exponent for a general topology, we must subtract a term  $d\nu$  for each chain that closes a loop (and therefore for each loop).

Hence the exponent for a topology  $\mathcal{G}$  with  $L$  independent loops (cycles) will be

$$\gamma(\mathcal{G}) - 1 = \sum_i n_i \sigma_i - L d\nu, \quad (132)$$

where  $n_i$  is the number of vertices of degree  $i$  in  $\mathcal{G}$ . In particular, we obtain the well-known hyperscaling relation for the polygon exponent  $\alpha$ , that is,

$$2 - \alpha = d\nu. \quad (133)$$

The extension to polymers attached to a surface is straightforward. For each vertex of degree  $i$  attached to the surface we introduce a  $\sigma'_i$  (and note that  $\sigma'_2$  is not necessarily 0). All of the required  $\sigma'_i$  may be obtained by studying  $f$  stars attached to the surface by the vertex of degree  $f$ . A correction, similar to that required for loops, is necessary if there exists a surface bridge, that is, an independent pathway which begins and ends on the surface. Other monomers in the bridge are restricted to a region  $\ll \xi$  in a direction perpendicular to the surface. Consequently a term  $-\nu$  in the exponent must be introduced for each such bridge.

Thus, for a topology  $\mathcal{G}$  attached to the surface by one or more vertices, the critical exponent is

$$\gamma(\mathcal{G}) = \sum_i n_i \sigma_i + \sum_i n'_i \sigma'_i - L d\nu - B\nu, \quad (134)$$

where  $n'_i$  is the number of vertices of degree  $i$  embedded in the surface,  $n_i$  is the number embedded in the bulk, and  $B$  is the number of surface bridges. In addition to showing that the exponents for any topology may be obtained from those for SAWs and stars, Eqs. (132) and (134) allow us to obtain scaling relations between local surface and bulk exponents. For example, denoting by  $\gamma_{11}$  the exponent for walks attached to the surface by both the initial and final vertex, we immediately obtain the well-known scaling relation

$$\gamma + \nu = 2\gamma_1 - \gamma_{11}. \quad (135)$$

If we denote by  $\gamma(\mathcal{G}, n_i)$  the exponent for a topology  $\mathcal{G}$  attached to the surface by  $n_i$  vertices of degree 1, then

$$\gamma(\mathcal{G}, n_1) - \gamma(\mathcal{G}, n_2) \quad (136)$$

is independent of the topology  $\mathcal{G}$  (De'Bell, Lookman, and Whittington, 1990). This is a fascinating result, since it provides a set of numbers that are independent of topology. Tests of this independence would provide strong evidence in support of or against the scaling hypothesis.

Other differences that depend on the number and type of vertices embedded in the surface, but that are independent of  $\mathcal{G}$ , are easily obtained. The difference in two exponents expresses the asymptotic behavior of the ratio of the number of configurations for a topology  $\mathcal{G}$  with  $n_1$  and  $n_2$  legs attached to the surface. In particular, if  $n_1 = 0$  and  $n_2 = 1$ , this is

$$\gamma - \gamma_1, \quad (137)$$

which may be obtained from the self-avoiding walk series. More generally, if the chosen topology  $\mathcal{G}$  is connected to the surface by  $n$  legs, the difference between the bulk and surface exponents can be expressed as

$$\gamma(\mathcal{G}) - \gamma_n(\mathcal{G}) = n(\gamma - \gamma_1) + (n - 1)\nu. \quad (138)$$

The above scaling relations can also be derived from the direct renormalization approach (Duplantier, 1986; Duplantier and Saleur, 1986).

In the above discussion we have assumed that  $G$  is uniform in that all chains in the network contain  $O(N)$  monomers. However, Zhao and Lookman (1992a) have recently proved that, for nonuniform simple topologies, the scaling relations  $\gamma - \gamma_1$  and  $\gamma - \gamma_{11}$  are also independent of  $G$ . That is, they have the same value as the self-avoiding walk (Sec. II.D.2). It would be interesting to explore whether this result is generally true for nonuniform networks.

The exponents  $\gamma_G$  and  $\gamma'_G$ , for a directed network in bulk and one attached to a surface, respectively, may be obtained rigorously through an interesting connection between the directed connected polymer network in two dimensions and the problem of  $N$  random walkers or "vicious walkers," whose paths do not cross (Fisher, 1984; Duplantier, 1989; Zhao, Lookman, and Essam, 1992). A directed polymer chain may be represented by the  $t$ -step trajectory of a lock-step random walker in a one-dimensional lattice, who, at each tick of a clock, moves one step to the left or one step to the right. The  $N$  chains then correspond to the  $N$  vicious walkers, and asymptotic formulae may be obtained for the number  $N$  of vicious walkers. The topology of a connected polymer network  $G$ , consisting of  $F$  uniform interacting chains, is specified by  $n_f$ , the number of  $f$ -leg vertices connecting  $f$  chains, and  $L$ , the number of loops. These quantities satisfy

$$2N = \sum_{f \geq 1} f n_f, \quad (139)$$

$$L = \sum_{f \geq 1} \frac{1}{2}(f - 2)n_f + 1. \quad (140)$$

We consider connected networks of fully directed chains in which each link has a positive component parallel to some chosen direction. In the semi-infinite system this direction is parallel to the surface. At an  $f$ -leg vertex of such a network, chains flowing in and chains emanating from it are totally independent of each other. In other words, we can decompose an  $f$ -leg vertex into an  $f_1$ -leg vertex and an  $f_2$ -leg vertex with  $f_1 + f_2 = f$ . Each of them would be expected to make its own contribution

to the critical exponents.

It can be shown that the total number of configurations  $W_n(t)$  of a network  $G$  in which all chains have length  $t$  has the asymptotic form

$$W_N(t) \approx C 2^{Nt} \gamma_G^{-1}. \quad (141)$$

If we let  $\bar{n}_f$  be the total number of both incoming and outgoing  $f$ -leg fans in the bulk, then it can be shown (Zhao, Lookman, and Essam, 1992) that the critical exponent  $\gamma_G$  is given by

$$\gamma_G - 1 = -\frac{1}{2}L - \frac{1}{4} \sum_f \bar{n}_f f (f-1). \quad (142)$$

Thus, for a  $p$ -star polymer,  $L=0$ ,  $f_1=p$ ,  $f_2=1$  for  $i=2, \dots, p+1$ , and hence  $\gamma_G - 1 = -\frac{1}{4}p(p-1)$ , in agreement with Fisher [1984, Eq. (4.2)]. Similarly, for a  $p$  watermelon,  $L=p-1$ ,  $f_1^1=f_2^2=p$ , and  $\gamma_G = -1 = -\frac{1}{2}(p^2-1)$  [cf. Fisher, 1984, Eq. (4.3)].

Similarly, the configurations of a network  $G$  in which  $V_s$  of the vertices are fixed near a surface may be identified as the problem of vicious random walkers in the presence of an adsorbing wall (Forrester, 1990). It can be shown that

$$\begin{aligned} \gamma'_G - 1 = & -\frac{1}{2}(L + V_s - 1) - \frac{1}{4} \sum_f \bar{n}_f f (f-1) \\ & - \frac{1}{2} \sum_f \bar{n}'_f f^2, \end{aligned} \quad (143)$$

---


$$F = F_b + F_s, \quad (146)$$

$$F_b(\xi, \{\vec{h}(f)\}) = \xi^{-d} \Phi(\{h(f)^\alpha / \xi^{\Delta_f/\nu}\}), \quad (147)$$

$$F_s(\xi, \{\vec{h}(f)\}, \{\vec{h}'(f)\}) = \xi^{-(d-1)} \Phi_s(\{h(f)^\alpha / \xi^{\Delta_f/\nu}\}, \{h'(f) / \xi^{\Delta'_f/\nu}\}). \quad (148)$$

(A prime indicates that a quantity refers only to vertices embedded in the surface.)

$F_s$  is the surface free energy. The scaling relations derived in Sec. III.B may now be obtained by considering appropriate derivatives of  $F$  and identifying

$$\sigma_i = \Delta_i \quad (149)$$

and

$$\sigma'_i = \Delta'_i + \nu. \quad (150)$$

The corrections of  $-d\nu$  and  $\nu$  for loops and surface bridges, respectively, arise from restrictions on the sites that are to be summed over in the present formulation.

The geometric derivation of the scaling laws for polymer networks, described in Sec. III.B, provides considerable insight into the physics of the polymer network. However, it should be emphasized that this approach contains several assumptions. Within the geometric picture, the principal assumption is that "starlike" vertices (vertices of degree 1 or  $\geq 3$ ) have an associated exponent  $\sigma_f$  which is independent of the precise structure of the

where  $\bar{n}'_f$  is the total number of both incoming and outgoing  $f$ -leg fans in the surface. Thus, for a  $p$  star in which the vertex of degree  $p$  is embedded in the surface,  $\gamma'_G - 1 = -\frac{1}{2}p^2$  [cf. Forrester, 1989, Eq. (31)] and for the  $p$  watermelon  $\gamma'_G - 1 = -(3p^2 + p - 2)/4$  [Forrester, 1989, Eq. (28)].

### C. The scaling function

The scaling theory of Sec. III.B may be reformulated in terms of a generalized homogeneous function (Ohno and Binder, 1988) by exploiting the equivalence with the  $n \rightarrow 0$  limit of the  $n$ -vector model. A correlation function, of the type introduced in Sec. I.B, may be written as a derivative of the free energy, that is,

$$\langle s_i^\alpha s_j^\alpha \dots \rangle = \frac{\partial^m F}{\partial h_i^\alpha \partial h_j^\alpha \dots} \quad (144)$$

with

$$F = \ln \text{Tr} \exp(-\beta H). \quad (145)$$

In the magnetic system the  $h_i^\alpha$  is the  $\alpha$  component of the local magnetic field, and the derivative is to be evaluated in the limit of zero external field. If we associate with each renormalized vertex of degree  $f$  a local external field  $\vec{h}(f)$ , then the scaling hypothesis asserts that the free energy may be written as

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chains attached to the vertex and independent of the topology of the network. This is also the underlying assumption when writing the free energy in the scaling form given above [Eqs. (146), (147), (148)]. This assumption is closely linked to our restriction to networks in which all chains have  $O(N)$  steps in them (Sec. I.B). For such networks, we expect the star vertices (typically) to be separated by a distance  $O(\xi)$  which tends to infinity as  $N$  becomes large. However, if networks in which some chains have  $o(N)$  steps in them are considered, the assumption of an independent exponent associated with each starlike vertex may no longer be valid. Indeed, in line with the arguments in Sec. I.C it might be expected that the effect of two vertices separated by such a chain is that of a (composite) vertex of higher degree.

The foundation for this underlying assumption has been carefully considered by Schäfer, von Ferber, Lehr, and Duplantier (1992), who analyzed the corresponding renormalization-group theory. Although it is not strictly necessary for the work of Schäfer, von Ferber, Lehr, and Duplantier, it is convenient to think of the polymer network as the limiting case ( $n \rightarrow 0$ ) of a more general class

of field theories. The assumption that the  $\sigma_f$ 's are independent of the network structure is equivalent to the assumption that the correlation functions for the composite operators (associated with the starlike vertices) of the field theory are multiplicatively renormalizable.

Schäfer, von Ferber, Lehr, and Duplantier conclude that this assumption is valid in the polymer ( $n \rightarrow 0$ ) case when only long chains are allowed (although not in the more general case). However, if short chains are allowed, additional additive renormalizations are required, invalidating the assumption of independent  $\sigma_f$ 's in such cases. Therefore the conclusions of Schäfer, von Ferber, Lehr, and Duplantier validate the intuitive arguments for the scaling theory of Sec. III.B.

#### D. The adsorption transition

The scaling theory developed so far is appropriate to the ordinary transition, which is characterized by the divergence of the length  $\xi$  with an exponent equal to the bulk exponent  $\nu$ . Much of this scaling theory can also be applied to the adsorption transition, where the length  $\xi$  is again expected to diverge with its bulk exponent (Kremer, 1983; Diehl, 1986). However, in the language of critical phenomena, the adsorption transition occurs at a bicritical point. In Sec. II.A we saw that, for random walks attached to a surface, the generating function has the scaling form

$$\chi(0) \sim x^{-\gamma_1^{ad}} \Phi(y/x^\phi), \quad (151)$$

$$x = (p_c - p), \quad (152)$$

and  $y$  is a linear combination of  $(p_c - p)$  and  $(p_1^{sp} - p_1)$ .

This form is expected to remain valid for any bicritical point (Pfeuty, Jasnow, and Fisher, 1974). Thus two exponents are required to characterize the special transition point.

The physical meaning of  $\phi$  for polymer solutions is best seen in a picture developed by de Gennes (1981), who identifies three regions of the system according to distance from an adsorbing surface,

$$\text{proximal } z \ll \xi,$$

$$\text{central } z \approx \xi,$$

$$\text{distal } z \gg \xi.$$

Within this picture, the dependence of the monomer density in the proximal region is expected to be a singular function of the distance from the surface (Eisenriegler, Kremer, and Binder, 1982), as indicated by Eq. (155) below. In terms of the polymer, it is information about this singular behavior which is provided by the crossover exponent  $\phi$ . Following de Gennes and Pincus (1983), we consider a single polymer chain adsorbed on the surface and assume that for each monomer on the surface there is an additional energy  $-kT\delta$ . To make contact with our scaling theory of bicritical points, we assume that

$$\xi \sim aN^\nu \Phi(N^\phi \delta). \quad (153)$$

The thickness of an adsorbed polymer chain, measured parallel to the surface will then be

$$D \sim \xi(\text{adsorbed}) \sim a\delta^{-\nu/\phi} W(N^\phi \delta). \quad (154)$$

Assume that, due to the presence of the surface, the monomers have a concentration profile

$$c(z) = c_s (a/z)^m V(z/D), \quad (155)$$

where  $m$  is to be determined. The change in the free energy due to the surface is

$$\frac{F - F_0}{kT} = -s\delta + B(a/D)^{1/\nu}. \quad (156)$$

The last term is a confinement energy, which can be determined up to the constant  $B$  by requiring that the change in entropy be extensive (de Gennes, 1979b, 1981). The fraction of monomers in contact with the surface  $s$  is given by

$$s = ac_s \int_0^\infty c(z) dz = (a/D)^{1-m}. \quad (157)$$

Minimizing  $F$  with respect to  $D$  we obtain

$$\delta \sim (a/D)^{m-1+1/\nu}. \quad (158)$$

Comparing this and the previous relation between  $\delta$  and  $D$ , we get

$$m = 1 - \frac{1-\phi}{\nu}. \quad (159)$$

## IV. CONFORMAL COVARIANCE

### A. Angular dependence of the generating functions

The assumed scaling form for the free energy and correlation functions derived from it are closely related to the assumption of scale covariance of the correlation functions at the critical point. In particular, all of the scaling relations between exponents can be derived from the application of renormalization group theory. Recently, it has been shown that considerable information about the nature of the correlation functions results from the assumption that the critical correlation functions are covariant under a conformal transformation of the space in which they are embedded. The application of conformal covariance theory to critical phenomena has been reviewed by Cardy (1987) where a detailed account may be found. Here we demonstrate the application of this technique to the surface problem by a derivation of the angular dependence of the SAW generating functions given by Cardy (1984).

Consider a two-dimensional system restricted to the half space  $y \geq 0$ . Let  $G(\vec{r}; \vec{r}') = G(z_1, z_1^*; z_2, z_2^*)$  be the generating function for SAWs with initial vertex at  $\vec{r}$  and final vertex at  $\vec{r}'$ . The plane  $z = x + iy$ ,  $z^* = x - iy$  is a continuum and the assumption of conformal covariance

is written

$$G(z_1, z_1^*; z_2, z_2^*) = |w'(z_1)|^b |w'(z_2)|^b G(w_1, w_1^*; w_2, w_2^*) \quad (160)$$

where  $z \rightarrow w(z)$  is any conformal transformation,  $|w'(z)|$  is the Jacobian of the transformation.

Following Cardy (1984), we consider the special conformal transformation

$$\bar{r}'/r'^2 = \bar{r}/r^2 + \bar{a}, \quad (161)$$

which maps hyperspheres into hyperspheres.  $\bar{a}$  must be chosen parallel to the surface in order to maintain

$$G(x_1 - x_2, y_1, y_2) = (1 - 4\epsilon x_1)^b (1 - 4\epsilon x_2)^b G(x'_1 - x'_2, y'_1, y'_2). \quad (166)$$

Expanding the right-hand side to  $O(\epsilon)$  and writing  $u = x_1 - x_2$ , we obtain

$$[u(x_1 + x_2) - y_1^2 + y_2^2] \frac{\partial G}{\partial u} + [(x_1 + x_2) + u] y_1 \frac{\partial G}{\partial y_1} + [(x_1 + x_2) - u] y_2 \frac{\partial G}{\partial y_2} + 2b(x_1 + x_2)G = 0. \quad (167)$$

Since  $G$  does not depend on  $(x_1 + x_2)$ , we may separate this into two equations,

$$u \frac{\partial G}{\partial u} + y_1 \frac{\partial G}{\partial y_1} + y_2 \frac{\partial G}{\partial y_2} + 2bG = 0, \quad (168)$$

$$(y_2^2 - y_1^2) \frac{\partial G}{\partial u} + u \left[ y_1 \frac{\partial G}{\partial y_1} - y_2 \frac{\partial G}{\partial y_2} \right] = 0. \quad (169)$$

The first of these requires that  $G$  have the scaling form

$$G(u, y_1, y_2) = u^{-2b} \psi(y_1/u, y_2/u). \quad (170)$$

Substituting this form into the second equation and writing  $\xi_1 = y_1/u$  and  $\xi_2 = y_2/u$ , we obtain an equation for  $\psi$ ,

$$[1 + \xi_1^2 + \xi_2^2] \xi_1 \partial \psi / \partial \xi_1 - [1 - \xi_1^2 + \xi_2^2] \xi_2 \partial \psi / \partial \xi_2 = 2bu^{-2} \psi. \quad (171)$$

We shall restrict ourselves to the case in which  $|u| = |x_1 - x_2|$  is large. The term on the right-hand side may then be replaced by zero, and the resulting homogeneous equation has a solution

$$\psi(\xi_1, \xi_2) = \psi' \frac{[1 + \xi_1^2 + \xi_2^2]}{\xi_1 \xi_2} \quad (172)$$

and

$$G(u, y_1, y_2) = u^{-2b} \psi' \frac{[u^2 + y_1^2 + y_2^2]}{y_1 y_2}. \quad (173)$$

Consider now the case in which the initial and final vertices of the walk are restricted to be close to the surface [ $y_1 = O(1)$ ,  $y_2 = O(1)$ , and the separation between them,  $u$ , is large]. We then expect

$$G(u, y_1, y_2) \sim u^{-\eta_{\parallel}}. \quad (174)$$

Comparison with Eq. (173) then determines the behavior of  $\psi'(x)$  for large values of its argument:

$$\psi'(x) \sim x^{(\eta - \eta_{\parallel})/2}. \quad (175)$$

translational invariance. Let

$$\bar{a} = (\epsilon, 0) \quad \text{with } \epsilon \rightarrow 0; \quad (162)$$

then to order  $\epsilon$

$$x' = x - \epsilon(x^2 - y^2), \quad (163)$$

$$y' = y - \epsilon(2xy), \quad (164)$$

and the Jacobian is

$$1 - 4\epsilon x + O(\epsilon^2). \quad (165)$$

Therefore from the basic assumption we have

Similarly, if only the initial vertex is restricted to be close to the surface [ $y_1 = O(1)$ ] and  $y_2 = R \cos \theta$  and  $u = R \sin \theta$  with  $R$  large, we expect

$$G(R, \theta) \sim R^{-\eta_{\perp}}. \quad (176)$$

This determines the large- $x$  behavior of  $\psi'(x)$ ,

$$\psi'(x) \sim x^{\eta - \eta_{\perp}}. \quad (177)$$

Comparison of Eqs. (175) and (177) provides us with the result

$$2\eta_{\perp} = \eta + \eta_{\parallel}. \quad (178)$$

This result may be obtained from scaling theory alone (Binder, 1983). However, conformal covariance theory also determines the angular dependence of  $G(R, \theta)$ . From Eq. (175) we obtain

$$\psi(R, \theta) \propto (\cos \theta)^{-\eta + \eta_{\perp}}. \quad (179)$$



**B. Application to wedges and slabs**

Conformal covariance also provides a relationship between the surface exponents and the wedge exponents if we note that the wedge coordinates are related to those of the half space by the conformal transformation

$$w = z^{\alpha/\pi} \tag{180}$$

(where  $\alpha$  is the wedge angle). Then

$$G(z_1, z_1^*; z_2, z_2^*) = |z_1^{\alpha/\pi-1}|^b |z_2^{\alpha/\pi-1}|^b \times G(w_1, w_1^*; w_2, w_2^*) . \tag{181}$$

Consider now the behavior of  $G(w_1, w_1^*; w_2, w_2^*)$  as  $w_1$  is kept fixed near the origin [ $w_1 = O(1)$ ] and the real and imaginary parts of  $w_2$  become large. This corresponds to  $z_1$  fixed near the surface and real and imaginary parts of  $z_2$  becoming large in the half space. Therefore

$$G(w_1, w_1^*; w_2, w_2^*) \sim |w_2|^{-\eta(\alpha)} \tag{182}$$

with

$$\eta(\alpha) = \eta/2 + \pi\eta_{\parallel}/(2\alpha) . \tag{183}$$

Similarly, the properties of the generating function for walks in a slab of finite thickness  $L$ , with periodic boundary conditions, may be related to those in the bulk through the transformation

$$w = (2\pi/L)\ln z . \tag{184}$$

The generating function for walks in a slab (at the bulk critical point) is found to be

$$G(x_1, y_1; x_2, y_2) \propto (2\pi/L)^{2\eta} [ 2 \cosh(2\pi x_{12}/L) - 2 \cos(2\pi y_{12}/L) ]^{-\eta} , \tag{185}$$

$$x_{12} = x_1 - x_2; \quad y_{12} = y_1 - y_2 . \tag{186}$$

**C. Exact results in two dimensions**

The general forms for the generating functions obtained above may be extended to  $d > 2$ . For  $d = 2$ , as a result of the correspondence between the set of conformal transformations and the set of analytic functions, conformal covariance theory is particularly powerful and leads to the conclusion that any given exponent must be one of a set of identifiable rational fractions. Before summarizing the results obtained for two-dimensional systems, we write down the relations between the exponents used in this section ( $\eta$ , etc.) and those used in previous sections ( $\gamma$ ,  $\nu$ , etc.) and generalize  $G$  so that the appropriate exponents for the  $f$  stars may be derived (Duplantier, 1988).

Let  $G_f(\vec{r}, \vec{r}')$  be the generating function for structures consisting of  $f$  self-avoiding chains with a common initial vertex at  $\vec{r}$  and a common final vertex at  $\vec{r}'$  but otherwise

nonintersecting. This structure is represented by the watermelon graph of Fig. 1 in the case of  $f = 3$ . In the bulk we expect

$$G_{W(f)}(\vec{r}, \vec{r}') \sim |\vec{r} - \vec{r}'|^{-2x_f} , \tag{187}$$

$$\chi_{W(f)} = \int_{\vec{r}} G_{W(f)}(\vec{r}, \vec{r}') , \tag{188}$$

where  $W(f)$  denotes the watermelon with two vertices of degree  $f$ .

In keeping with our previous scaling arguments (Sec. III.A), we restrict the integration to a sphere of radius  $\xi$  to obtain

$$\chi_{W(f)} \sim \xi^{d-2x_f} , \tag{189}$$

$$\gamma(W(f)) = \nu(d-2x_f) . \tag{190}$$

In the formulation of the problem given by Duplantier and Saleur (1986), the watermelons are quasi-polydisperse [i.e., the number of monomers in each chain is allowed to fluctuate but, in accordance with the discussion in Sec. III.C, the number in each chain must remain  $O(N)$ ]. This gives rise to an additional factor of  $N^{(f-1)}$  in the number of configurations. Allowing for this,  $\gamma(W(f))$  may also be written in terms of  $\sigma_f$ , that is,

$$\gamma(W(f)) = 2\sigma_f + 1 - (f-1)d\nu + (f-1) . \tag{191}$$

The third term is the subtraction required for the  $(f-1)$  loops, and the fourth term allows for the polydisperse nature of the watermelons. Comparing the two forms for  $\gamma(W(f))$ , we obtain

$$\sigma_f = \frac{d\nu-1}{2} f - x_f \nu . \tag{192}$$

Similarly, if  $\vec{r}$  and  $\vec{r}'$  denote points in the surface,

$$G'_f(\vec{r}, \vec{r}') \sim |\vec{r} - \vec{r}'|^{-2x'_f} . \tag{193}$$

Integrating over a region of surface of radius  $\xi$  and again allowing for the polydispersity, we obtain

$$\sigma'_f = \frac{d\nu-1}{2} f - x'_f \nu . \tag{194}$$

Having established the relationship between the  $x_f$  used here ( $\eta$  and  $\eta_{\parallel}$  being special cases of these) and the exponents introduced in previous sections, we continue with the predictions for the  $x_f$  in two dimensions obtained by conformal covariance theory. The essential step in obtaining these exponents is the identification of the operators of the conformal theory with those of the Virasoro algebra (Cardy, 1987). This allows all of the exponents to be identified with the zeros of the Kac determinant,

$$h_{p,q} = \frac{(3p-2q)^2-1}{24} . \tag{195}$$

In particular, the exponents  $\gamma$  and  $\nu$  for bulk self-avoiding walks are obtained by making the identification (Cardy, 1987)

$$x_1 = 2h_{1/2,0}, \quad (196)$$

$$x_2 = 2h_{1,0} \quad (197)$$

( $\nu$  is obtained by requiring that  $\sigma_2 = 0$ ).

Duplantier and Saleur (1986) have proposed the extension to bulk  $f$  stars, that is,

$$x_f = 2h_{f/2,0}. \quad (198)$$

Similarly, the exponents for topologies attached to a surface are obtained from the identification (Duplantier and Saleur, 1986)

$$x'_f = h_{f,1,1}. \quad (199)$$

Typical values of the exponents derived from these identifications are listed in Table II.

Duplantier (1987) has also studied the ordinary transition in dense polymers in which the monomers occupy a finite fraction of the lattice sites. He identifies this model with the low-temperature regime of the  $n \rightarrow 0$  limit of the  $n$ -vector model and determines that

$$x_f = 2h_{0,f/2}, \quad (200)$$

$$x'_f = h_{1,f+1} \quad (201)$$

for dense polymers.

The above identification thus allows predictions of the exact critical exponents for two-dimensional systems. A small caveat must be added. The Kac determinant results are known to be valid for theories with unitarity. In general,  $h_{p,q}$  is of the form

$$h_{p,q} = \frac{[p(m+1) - mq]^2 - 1}{4m(m+1)}, \quad (202)$$

where for a unitary theory  $m$  is an integer  $m \geq 3$  and  $p$  and  $q$  are integers and belong to the minimal block (Cardy, 1987)

$$1 \leq q \leq p \leq m. \quad (203)$$

The values of  $m = 2$ ,  $p$ , and  $q$  for polymer models do not correspond to a unitary theory, and  $p$  and  $q$  are not restricted to integer values in the minimal block. The precise role of unitarity in the application of conformal theories to critical phenomena appears to be an open question.

TABLE II. Typical values of the exponents in two dimensions obtained from the conformal covariance theory.

$x_1 = \frac{5}{48}$	$\sigma_1 = \frac{33}{192}$	$\gamma = \frac{43}{32}$
$x_2 = \frac{2}{3}$	$\sigma_2 = 0$	$\nu = \frac{3}{4}$
$x_3 = \frac{77}{48}$	$\sigma_3 = -\frac{29}{64}$	$\gamma(3) = \frac{17}{16}$
$x'_1 = \frac{15}{24}$	$\sigma'_1 = -\frac{7}{32}$	$\gamma_1 = \frac{61}{64}$
$x'_2 = 2$	$\sigma'_2 = -1$	$\gamma_2 = \frac{11}{32}$
$x'_3 = \frac{99}{24}$	$\sigma'_3 = -\frac{75}{32}$	$\gamma_3(3) = -\frac{53}{64}$
		$\gamma(G) - \gamma_1(G) = \frac{25}{64}$
		$\gamma(G) - \gamma_{11}(G) = \frac{49}{32}$

## V. NUMERICAL RESULTS

### A. Self-avoiding walks

Self-avoiding walks terminally attached to a lattice surface have been extensively studied by numerical techniques, including series-expansion analysis of exact enumeration data, Monte Carlo simulation, and transfer matrix methods. As well as providing results which may be directly compared with experimental results, such techniques provide important tests of the results summarized in Secs. III and IV.

The numerical values obtained for various critical exponents are summarized in Table III. The predicted exact values obtained from conformal covariance theory are consistent with the numerical values in two dimensions. In three dimensions, such predictions of the exact results are not available. However, the numerical results may be used to test the surface scaling relations. The scaling relation

$$\gamma + \nu = 2\gamma_1 - \gamma_{11} \quad (204)$$

is consistent with the numerical results in both two and three dimensions. Verification of the scaling relation

$$\gamma_s = \gamma + \nu \quad (205)$$

has proved more elusive.

De'Bell and Jan (1989) have tested the expected dependence of the number of SAW configurations on the distance  $z$  of the fixed-terminal vertex from the surface. They concluded that their results were consistent with the form

$$C_N^{(1)}(z) = \mu^N N^{\gamma_1} \mathcal{C}(z/\xi) \quad (206)$$

for

$$a \ll z \ll \xi, \quad (207)$$

but this analysis is difficult because of the restricted range of  $z$  available.

As noted in Sec. III, if it is assumed that  $C_N^{(1)}$  has this form throughout the range of the sum

$$C_N^s = \sum_z C_N - C_N^{(1)}(z) \quad (208)$$

for  $z < \xi$ , and if the contribution from the upper end of the sum is neglected, the scaling relation [Eq. (205)] immediately follows. However, De'Bell, Lookman, and Whittington (1990) have recently pointed out that the region

$$\xi - \varpi < z < \xi + \varpi, \quad (209)$$

where

$$\varpi = o(\xi) \quad (210)$$

may be expected to give rise to a term

$$C_N^\varpi \sim \mu^N N^{\gamma-1} \quad (211)$$

TABLE III. Numerical results for self-avoiding walks attached to a surface.

	$d=2$	$d=3$
$\gamma$	$1.34361 \pm 0.00013^a$	$1.162 \pm 0.002^a$ $1.160 \pm 0.004^b$ $1.162 \pm 0.001^c$
$\nu$	$0.7500 \pm 0.0013^d$	$0.592 \pm 0.002^a$ $0.588 \pm 0.001^b$ $0.592 \pm 0.002^c$
$\gamma_1$	$0.9549^{+0.0011^c}_{-0.0015}$ $0.953 \pm 0.006^f$	$0.676 \pm 0.009^f$ $0.718 \pm 0.008 + 136\Delta x_c^g$ $0.70 \pm 0.02^h$ $0.675 - 0.680^i$
$\gamma_{11}$	$-0.19 \pm 0.02^d$	$-0.4 \pm 0.3^f$
$\gamma - \gamma_1$	$0.393 \pm 0.006^j$	$0.468 \pm 0.002^d$
$\gamma - \gamma_{11}$	$1.56 \pm 0.06^j$ $1.53 \pm 0.04^k$	$1.515 \pm 0.015^d$
$\gamma_{11} + 2\nu$	$1.323 \pm 0.013^l$	
$\gamma_s$	$1.81 \pm 0.02^m$	$2.10 \pm 0.01^m$
$\gamma_s - \gamma$	$0.75 \pm 0.03^n$	$0.60 \pm 0.01^d$

<sup>a</sup>Guttman, 1987.  
<sup>b</sup>LeGuillou and Zinn-Justin, 1985.  
<sup>c</sup>Lookman and De'Bell, 1987.  
<sup>d</sup>De'Bell, Lookman, and Whittington, 1990.  
<sup>e</sup>Rappaport, 1985.  
<sup>f</sup>Guttman and Torrie, 1984.  
<sup>g</sup>De'Bell and Lookman, 1985b  $\Delta x_c$  represents the change in  $x_c$  from its central estimate of 0.0995.  
<sup>h</sup>Ishinabe and Whittington, 1981.  
<sup>i</sup>Eisenriegler, Kremer, and Binder, 1982.  
<sup>j</sup>De'Bell, Lookman, and Whittington, 1990 square lattice, Baker-Hunter analysis.  
<sup>k</sup>Seno and Stella, 1988b.  
<sup>l</sup>De'Bell and Lookman, 1985b.  
<sup>m</sup>Whittington, Torrie, and Guttman, 1980.  
<sup>n</sup>De'Bell, Lookman, and Whittington, 1990, square lattice, ratio analysis of modified series.

in the sum. Expressing this in terms of the generating function

$$G^s = \sum_N C_N^s p^N, \tag{212}$$

we expect  $G^s$  to have a dominant singularity with exponent  $\gamma + \nu$  and a confluence with exponent  $\gamma$ . De'Bell, Lookman, and Whittington (1990) concluded that their results were consistent with the scaling relation if this confluence was explicitly taken into account.

As described in Sec. III, conformal covariance theory predicts the angular dependence of the correlation function for self-avoiding walks terminally attached to a surface. Cardy and Redner (1984) have tested these predictions numerically and obtained results fully consistent with the predictions.

The dependence of the exponent  $\gamma(\alpha)$  for SAWs confined to a wedge of angle  $\alpha$  on the wedge angle has been investigated by analysis of exact enumeration data by Cardy and Redner (1984), Guttman and Torrie (1984), and De'Bell and Lookman (1985a). Again, the re-

sults are fully consistent with conformal covariance theory. [Indeed, Guttman and Torrie (1984) were able to predict correctly the exact relation between  $\gamma(\alpha)$  and  $\alpha$  from their numerical results.]

### B. Other problems

The numerical results available for testing the predictions for other fixed topologies attached to a surface are much more restricted. The properties of  $f$  stars confined to a two-dimensional wedge have been investigated by Colby, Gaunt, Torrie, and Whittington (1987) using exact enumeration and Monte Carlo methods. The results, although restricted to  $f=2$  and  $f=3$ , are in excellent agreement with the predicted values (Table IV).

Gaunt and Colby (1990) have generated Monte Carlo data for  $f$  stars in a variety of three-dimensional wedges. They considered the effect of  $f$  on the exponent  $\gamma_f(f)$  if the star is attached to the apex of the wedge by its central vertex. Noting that for a half-space (semi-infinite system) both the conformal covariance results in two dimensions (Duplantier and Saleur, 1986) and the epsilon expansion results to  $O(\epsilon)$  (Ohno and Binder, 1988) for  $\gamma_f(f)$  are quadratic in  $f$ , Gaunt and Colby (1990) fitted their results to a quadratic function. The numerical results were well fitted by

$$\gamma_f(f) = 1.0513 - 0.27263f - 0.07571f^2. \tag{213}$$

If a cubic term is added to the fitted function the coefficient of this term is  $O(10^{-4})$ .

For lattice trees attached to a surface,  $\theta_1$  is given in terms of the bulk exponent by the exact result (see Sec. II.D.3)

$$\theta_1 = \theta + 1, \tag{214}$$

a result first indicated for two-dimensional systems by an analysis of exact enumeration data (De'Bell and Lookman, 1985c).

De'Bell and Lookman (1985a) have investigated the properties of lattice trees confined to a two-dimensional wedge. They found that for large wedge angles  $\alpha$  the exponents approximately obey the relation

$$\theta(\alpha) = 1 + \frac{\pi}{\alpha}. \tag{215}$$

However, at smaller angles the results significantly devi-

TABLE IV. Exponents for stars attached to a surface and in a wedge of angle  $\alpha$  in two dimensions (Colby, Gaunt, Torrie, and Whittington, 1987).

	Attached to a surface	In a wedge
$\gamma_2$	$0.35 \pm 0.05$	Wedge angle $\alpha = 2\pi/3$
$\gamma_1(3)$	$0.68 \pm 0.05$	$\gamma_2$ $-0.40 \pm 0.05$
$\gamma_3(3)$	$-0.82 \pm 0.05$	Wedge angle $\alpha = \pi/2$
		$\gamma_2$ $-1.15 \pm 0.05$

ate from this and do not obey a linear relation in  $(1/\alpha)$ . A similar analysis of lattice trees confined to the surface of a cone has recently been performed by Miller and De'Bell (1991), who have also discussed the constraints on a conformal theory for lattice trees and concluded that a linear relation in  $1/\alpha$  is a necessary feature of such a theory. Unfortunately, the analysis of the data for small values of  $\alpha$  is difficult, as the numerical estimates are in general less well behaved than for larger angles. Nonetheless, the numerical results appear to be strong evidence against conformal covariance of the lattice tree generating functions.

### C. The adsorption transition

A numerical analysis of the adsorption transition is inherently a two-variable problem. In particular, we expect the generating function to have the scaling form

$$G(p, p_1) = \sum_{n,m} C_{n,m} p^n p_1^m \sim (p_c - p)^{-\gamma_{ad}}. \quad (216)$$

As  $p_c$  is known to a high precision from analysis of the corresponding bulk problem, the analysis of the adsorption transition reduces to a determination of  $\gamma_{ad}$ ,  $\phi$ , and  $p_{1c}$ . Estimates of these values are given in Table V.

In two dimensions, Guim and Burkhardt (1989) used transfer-matrix techniques to determine these quantities. They were able to identify the values of the surface scaling dimensions in the corresponding conformal covariance analysis (see also Burkhardt, Eisenriegler, and Guim, 1989). They conjectured that the appropriate identification for the adsorption transition is

$$p'_f = h_{f+1,3}. \quad (217)$$

The crossover exponent  $\phi$  is not dependent on  $f$  but is obtained by noting that the surface thermal (or energy) scaling index is

$$p'_1 = d - 1 - p'_2 = \frac{2}{3}. \quad (218)$$

The exponent  $\phi$  is then the ratio of  $p'_1$  and  $p_1 = 1/\nu$ . This leads to the predicted exact results for SAWs in two dimensions,

$$\gamma_{ad} = 93/64, \quad \phi = \frac{1}{2}. \quad (219)$$

It is, perhaps, noteworthy that  $\phi$  has its random-walk value in two dimensions. It is not clear if this is fortuitous or if it is connected to the one-dimensional nature of the surface. Numerical results for  $\phi$  in three dimensions (Table V) indicate that it is a little higher than the random-walk value.

Recently, Janssen and Lyssy (1992) have used the supersymmetric connection between lattice animals and the Yang-Lee edge singularity to obtain an exact value for the crossover exponent in three dimensions. They conclude that

$$\phi = \frac{1}{2}. \quad (220)$$

Lookman, Zhao, and De'Bell (1991) have also attempted to analyze the adsorption transition in lattice trees by studying exact enumeration data for the square, triangular, and simple cubic lattices. Unfortunately, the results obtained by a partial differential approximant analysis of the data are not well converged, and only tentative estimates of  $p_{1c}$  were obtained.

## VI. OTHER PROBLEMS

### A. Adsorption of directed polymers

The problem of a directed polymer interacting with a surface has been far more tractable by analytic means than the undirected case (Privman and Svaric, 1989). The standard approach used is to write the generating

TABLE V. Critical-point and exponent estimates for the adsorption transition in the square (SQ), triangular (T), and simple cubic (SC) lattices. Site and bond refer to the counting of surface contacts by the number of surface sites and number of surface bonds the walk is embedded on, respectively.

Lattice	$x_c$	$y_c/x_c = \exp(\omega_c)$	$\gamma_{ad}$	$\phi$
SQ (bond)	0.379 05 <sup>a</sup>	2.06±0.10 <sup>b</sup> 2.041±0.002 <sup>c</sup> 2.01 <sup>d</sup>	1.45±0.05 <sup>b</sup> 1.454±0.004 <sup>e</sup>	0.50±0.09 <sup>b</sup> 0.501±0.003 <sup>c</sup> 0.55±0.01 <sup>e</sup>
SQ (site)	0.379 05 <sup>a</sup>	1.82±0.03 <sup>b</sup> 1.80±0.02 <sup>f</sup>	1.40±0.05 <sup>b</sup>	0.52±0.03 <sup>b</sup>
T (bond)	0.240 92 <sup>a</sup>	2.85±0.07 <sup>b</sup>	1.4±0.1 <sup>b</sup>	0.50±0.01 <sup>b</sup>
SC (bond)	0.213 5 <sup>a</sup>	1.47±0.02 <sup>b</sup> 1.45 <sup>g</sup>	1.55±0.15 <sup>b</sup> 1.44 <sup>g</sup>	0.54±0.07 <sup>b</sup> 0.59 <sup>g</sup>

<sup>a</sup>Guttman, 1987.

<sup>b</sup>Zhao, Lookman, and De'Bell, 1990.

<sup>c</sup>Guim and Burkhardt, 1989.

<sup>d</sup>Ishinabe, 1982.

<sup>e</sup>Kremer, 1983.

<sup>f</sup>Hammersley, Torrie, and Whittington, 1982.

<sup>g</sup>Eisenriegler, 1982.

function in terms of a transfer matrix such that the singularity in the generating function corresponding to the critical fugacity occurs when the largest eigenvalue of the transfer matrix is unity. Hence the approach is not rigorous in the sense of the results of Sec. II.B for SAWs.

Consider a directed polymer on a strip of width  $N$  (Fig. 7). The polymer is directed in that steps in the negative  $x$  direction are forbidden. The position of the polymer is given by specifying the numbers  $i, n_i$ . Attraction to the substrate can be modeled by assigning an energy  $K$  to each column in which  $n_i = 1$  or  $N$ . Nearest-neighbor interactions between monomers are introduced through an attractive energy  $J$  between bonds that occupy the same row in adjacent columns. The generating function can be written as

$$G = \sum_{\text{walks}} \omega^L \kappa^n \tau^n,$$

where  $\omega$  is the monomer fugacity,  $\kappa = e^{-K/k_B T}$ ,  $\tau = e^{-J/k_B T}$ ,  $L$  counts the total number of monomers,  $i$  the number of monomers lying in the surface, and  $n$  the number of nearest-neighbor interactions.

$G$  can be written in terms of a transfer matrix and the critical fugacity  $\omega^*$  is calculated through finite size approximations for a strip of width  $N$ . For the case in which there are no monomer-monomer interactions,  $\tau = 1$ , Privman, Forgacs, and Frisch (1988) found an adsorption transition at  $\omega^* = \sqrt{2} - 1$ ,  $\kappa^* = 1 + 1/\sqrt{2}$ . Veal, Yeomans, and Jug (1990) calculated the phase diagram on a semi-infinite square lattice with monomer-monomer interactions included. They found evidence suggesting that the adsorption transition is second order when the unbound polymer is extended but first order when collapsed. Recently, Binder, Owczarek, Veal, and Yeomans (1990) and Foster (1990) have obtained additional analytic results for the phase diagram. Bouchaud and Vanimènius (1989) have found agreement with the phase dia-

gram based on a real-space renormalization-group calculation for the three-dimensional Sierpinski gasket. Forgacs and Semak (1991) have studied the adsorption using a restricted solid-on-solid (RSOS) model in two dimensions. They found that the system does not exhibit a collapse or chain-folding transition. Although the RSOS model gives the same results as the solid-on-solid (SOS) model for universal properties, imposing the restriction on the SOS model appears to wash out the collapse transition

### B. Semidilute regime

So far we have considered only the limit of dilute systems in which the individual polymer molecules may be treated as isolated. In the semidilute and dense regimes the interactions between different polymer molecules can no longer be neglected.

In the semidilute regime the polymer molecules interact via the excluded volume effect; however, the concentration of monomers remains small (i.e., the fraction of lattice sites occupied by the polymers  $\rightarrow 0$ ). The degree to which this excluded volume effect changes the configurational properties of the polymers can be seen by studying  $C_{N,f}$ , the number of configurations for  $f$  structures when their centers are brought within distance  $r$  of each other. The use of scaling theory follows from the introduction of proximity exponents (des Cloizeaux, 1980). We shall illustrate this for linear polymers only, as the extension to other structures is straightforward (Duplantier, 1988).

We define the proximity exponent  $\theta_f$  for  $f$  chains, each of  $N$  edges, such that the initial vertex of each is within distance  $r$  of the initial vertices of the other chains by

$$\lim_{r/\xi \rightarrow 0} \frac{C_{N,f}}{(C_N)^f} \sim (r/\xi)^{\theta_f}. \tag{221}$$

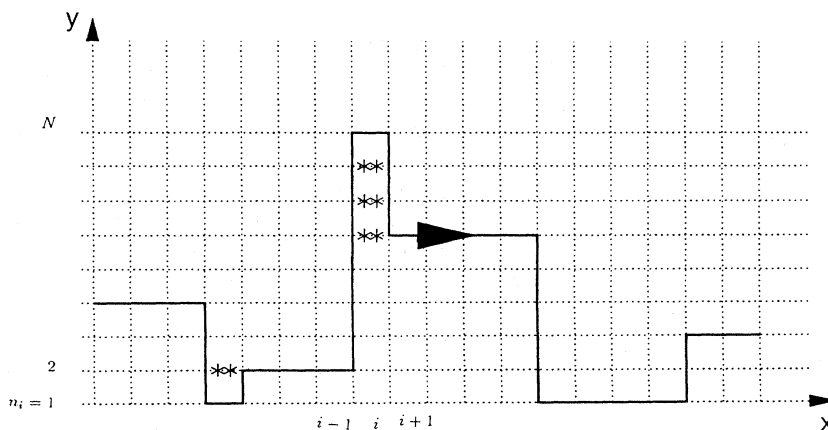


FIG. 7. A polymer directed in the positive  $x$  direction on a strip of width  $N$ . Nearest-neighbor interactions between monomers are represented by  $**$ .

However, following the previous scaling arguments of Sec. III.B, in this limit the  $f$  initial vertices may be treated as a single renormalized vertex and we obtain

$$\frac{C_{N,f}}{(C_N)^f} \sim N^{\gamma(f)-1+f\gamma+f} \xi^{[f-1-f\gamma+\gamma(f)]/\nu}, \quad (222)$$

$$\theta_f = [f\gamma - \gamma(f) - f + 1]/\nu. \quad (223)$$

Similarly, if we consider  $f$  chains each attached to the surface by its initial vertex and such that the initial vertices are within distance  $r$ , we may define the corresponding surface proximity exponent (for the ordinary transition) by

$$\lim_{r/\xi \rightarrow 0} \frac{C'_{N,f}}{(C_N)^f} \sim (r/\xi)^{\theta'_f} \quad (224)$$

with

$$\theta'_f = f\gamma_1 + 1 - \gamma_1(f) - f. \quad (225)$$

The theory of adsorbed polymers in the proximal region (Sec. III.E) may be extended to the semidilute regime (de Gennes and Pincus, 1983). In the proximal region the monomer concentration profile is assumed to be

$$c(z) \approx c_s (a/z)^m V(z/D), \quad (226)$$

and in the central region we have

$$\xi/a \sim c^\omega \quad (227)$$

with

$$\omega = \nu/(d\nu - 1). \quad (228)$$

To ensure a smooth crossover from the proximal to the central region, we assume

$$V(z/D) \sim |D/z|^b. \quad (229)$$

For large  $z$  we have

$$c_s \sim (a/D)^b \quad (230)$$

and

$$b + m = \omega^{-1}. \quad (231)$$

Using the available three-dimensional values of  $m$  and  $\omega$  in the single-chain case, one obtains

$$b \approx 1. \quad (232)$$

The change in the free energy/unit area is

$$\Gamma - \Gamma_0 = -kT\delta c_s a^{-2} + \Delta\Gamma, \quad (233)$$

where  $\Delta\Gamma$  is the change in the free energy due to the distortion of the concentration profile. Following de Gennes (1979b), this is written as a change in the osmotic pressure over a region of thickness  $D$ , that is,

$$\Delta F \approx kT \int_0^D (\xi(c))^{-3} dz \propto kT/D^2. \quad (234)$$

After minimizing the change in the free energy, we obtain

$$\frac{\Gamma - \Gamma_0}{\delta} \sim \delta^{b/(2-b)}. \quad (235)$$

The above analysis is valid for the attractive regime  $-\delta > 0$ ,  $D \ll \xi_b$ , where  $\xi_b$  is the bulk end-to-end distance of the polymer. Eisenriegler (1983) has used the mapping of the polymer model onto a spin model in both the dilute and semidilute cases to examine the behavior in the various possible limits (e.g.,  $\xi_b \gg D$ ). A theoretical discussion of a number of possible ways of observing the adsorption transition has been given by Eisenriegler (1984). Using the mapping to a spin system, Eisenriegler was able to calculate the universal amplitude ratios to order  $\epsilon$  ( $=4-d$ ) for surface-tension experiments.

Since surface tension may be measured directly (di Meglio *et al.*, 1983; Ober *et al.*, 1983), this provides a means of experimentally investigating surface adsorption in dilute solutions. An initial experimental investigation of the adsorption transition using surface-tension measurements has been reported by di Meglio and Taupin (1989). They studied polydimethylsiloxane (PDMS) in three different solvents (hexane, heptane, and octane). Precision is difficult to obtain since the results involve taking the difference of two surface-tension measurements. However, di Meglio and Taupin (1989) were able to obtain approximate values of the temperature at which the adsorption transition occurs for each of the PDMS/solvent systems considered.

The de Gennes scaling theory has also been extended to nonequilibrium systems (nonsaturation coverage of the surface) by Rossi and Pincus (1989).

### C. The theta point

In a poor solvent the monomer-solvent repulsion (or, equivalently, monomer-monomer attraction) leads to the collapse of the monomer into an object that is compact compared with the swollen molecules which occur in a good solvent. While there is an extensive literature on the collapse transition at the theta point, which separates the swollen and compact regimes, we review here only the results for linear polymers attached to a surface.

Seno and Stella (1988a) have numerically estimated the exponents  $\gamma_{1t}$  and  $\gamma_{11t}$  [corresponding to  $\gamma_1$  and  $\gamma_{11}$  for the ordinary (swollen) SAWs] for SAWs at the theta point, attached to the surface of a square lattice, as well as the corresponding bulk exponents (Seno and Stella, 1988b). Chang, Meirovitch, and Shapir (1990) have numerically estimated the corresponding values of  $\gamma_{1t}$  and  $\gamma_{11t}$  for lattice trails (walks in which a site may be visited more than once but a lattice edge may be used as a step only once at most). These numerical values are summarized in Table VI.

Duplantier and Saleur (1987a) previously used conformal covariance arguments to predict the exact exponent values for this problem in two dimensions. Alternative values were obtained by Vanderzande (1988). However, the values predicted by Duplantier and Saleur are valid

TABLE VI. Exponents for the theta point in two dimensions.

(a) Bulk			
	$\gamma_t$	$\nu_t$	$\phi_t$
a	$\frac{8}{7} \approx 1.143$	$\frac{4}{7} \approx 0.571$	$\frac{3}{7} \approx 0.43$
b	$\frac{15}{14} \approx 1.07$	$\frac{4}{7} \approx 0.571$	$\frac{3}{7} \approx 0.43$
c	$1.10 \pm 0.04$	$0.570 \pm 0.015$	$0.52 \pm 0.07$
d	$1.133 \pm 0.024$	$0.569 \pm 0.008$	$\approx 0.71$
(b) Ordinary transition			
	$\gamma_{1t}$	$\gamma_{11t}$	
a	$\frac{8}{7} \approx 1.143$	$\frac{4}{7} \approx 0.571$	
b	$\frac{15}{28} \approx 0.53$	$-\frac{4}{7} \approx -0.57$	
e	$\frac{4}{7} \approx 0.571$	$-\frac{4}{7} \approx -0.571$	
c	$0.57 \pm 0.08$	$-0.53 \pm 0.10$	
d	$0.634 \pm 0.025$	$-0.44 \pm 0.02$	
f	$0.573 \pm 0.002$	$-0.55 \pm 0.05$	
(c) Adsorption transition			
	$\gamma_{1t}^{ad}$	$\gamma_{11t}^{ad}$	$\phi$
e	$\frac{8}{7} \approx 1.143$	$\frac{4}{7} \approx 0.571$	$\frac{8}{21} \approx 0.381$
f	$1.14 \pm 0.02$	$0.57 \pm 0.03$	$0.4 \pm 0.05$
g	$1.11 \pm 0.04$		$0.41 \pm 0.03$

<sup>a</sup>Duplantier and Saleur, 1987 ( $\theta'$  point).

<sup>b</sup>Vanderzande, 1988.

<sup>c</sup>Seno and Stella, 1988a, 1988b.

<sup>d</sup>H. Meirovitch and H. A. Lim, 1989; Chang, Meirovitch, and Shapir, 1990 (Lattice trails).

<sup>e</sup>Vanderzande, Stella, and Seno, 1991 (exact  $\theta'$  point).

<sup>f</sup>Foster, Orlandini, and Tesi, 1992.

<sup>g</sup>Vanderzande, Stella, and Seno, 1991 (series expansion  $\theta'$  point).

for the  $\theta'$  model. In this problem, only a subset of the walks that occur in the  $\theta$ -point problem are considered. Values predicted by the theories of Duplantier and Saleur (1987a) and Vanderzande (1988) for the bulk exponent  $\gamma_t$  are numerically quite close, and the numerical value obtained by Seno and Stella (1988b) cannot distinguish them. However, the surface exponents are quite different, and the numerical results are consistent with the Vanderzande values but not with the Duplantier and Saleur values (see Table VI). The differences between the numerical values obtained for the theta-point polymer at the ordinary transition and the predictions of Duplantier and Saleur has led to controversy concerning the universality of the  $\theta$ - and  $\theta'$ -point systems (Duplantier and Saleur, 1989, Seno, Stella, and Vanderzande, 1989). This controversy seems to have been resolved by recent work. Vanderzande, Stella, and Seno (1991) have used the relationship between the walks considered in the  $\theta'$  problem and walks on the hull of a percolation cluster (on the honeycomb lattice) to argue that the  $\theta'$  system with zero (explicit) surface interaction is, in fact, at the special transition point due to an effective surface-monomer interaction generated by the construction of the model. Consequently the values of the exponents given by Duplantier and Saleur apply to the theta-point system at the special transition. Further numerical work (Vander-

zande, Stella and Seno, 1991; Foster, Orlandini, and Tesi, 1992) is consistent with this explanation and with the universality of the  $\theta$ - and  $\theta'$ -point models (see Table VI). The universality class of lattice trails at the theta point appears to be an open question (see Chang, Meirovitch, and Shapir, 1990 and Vanderzande, Stella, and Seno, 1991).

In the language of critical phenomena, a polymer at the theta point is a system at a tricritical point (Stephen, 1975; DeGennes, 1979), which may be studied experimentally by light scattering techniques (Perynski, Adam, and Delsanti, 1982; Duplantier, Jannink, and Des Cloizeaux, 1986). Thus surface-attached polymers at the theta point offer an opportunity to study tricritical behavior in the presence of a surface. Renormalization-group theory (Wang, 1987; Eisenriegler and Diehl, 1988) predicts that such a system in three dimensions will exhibit random-walk critical exponents and that logarithmic corrections to the leading exponents will be present. (In the language of the renormalization group, the upper critical dimension of a tricritical system is  $d=3$ ). Van Dieren and Kremer (1987) have performed a Monte Carlo study of a polymer at the theta point near an attracting surface. They find that consistent values of the adsorption transition temperature and the crossover exponent  $\phi$  are obtained only if the predicted logarithmic

corrections (Wang, 1987) are included in the analysis. The model considered by van Dieren and Kremer (1987) and Wang (1987) approximates the surface-attached polymer at the theta point by a nonreversing random walk which is self-avoiding only in the immediate vicinity of the surface. A more general discussion, including the role played by various parameters of the model, has been given by Eisenriegler and Diehl (1988).

#### D. Poor solvents

For polymers in a  $\theta$  (poor) solvent, the polymer may be treated within a "mean-field" approximation due to the compact nature of the polymers. A formalism built on this approach (see, for example, Hong and Noolandi, 1983) allows the details of the interactions (monomer-monomer, solvent-monomer) specific to a particular polymer/solvent system to be built into the model. For example, Whitmore and Noolandi (1990) have modeled block copolymers, near the theta transition, in which one block has a surface affinity and so adsorbs onto the surface while the other block has no surface affinity and so tends to dangle into the solution. Their results for specific polymer systems may be compared directly with experiments such as surface force experiments on polymer brushes (e.g., Hu and Granick, 1990; Taunton *et al.*, 1990).

The rich structure of the surface-adsorbed phases of triblock copolymers due to self assembly has been investigated by Balazs and Lewandowski (1990) by computer simulation.

#### E. Percolation

The percolation problem is of interest in the study of polymers as it provides a model of gelation (for a comparison of experimental results on gels and the predictions of percolation theory see Patton *et al.*, 1989; for a review of percolation theory see Essam, 1980).

We may describe the problem of percolation at a surface in terms of a lattice occupying the half space  $z \geq 0$ . Bonds in the lattice are open with probability  $p$  (and closed with probability  $1-p$ ) except in the surface, where the probability that a bond is open is  $p_1$ . Two lattice sites  $i$  and  $j$  are said to be connected if there exists a walk from  $i$  to  $j$  involving nearest-neighbor steps on open bonds. A mutually connected set of sites forms a cluster. The generating function for clusters with  $s$  sites of which  $s_1$  are embedded in the surface is

$$\sum_{N,m} C_{s,s_1}(p,p_1) \exp(-hs - h_1 s_1) . \quad (236)$$

There exists a critical value of  $p$  at which the mean cluster size diverges, and we define the critical exponents  $\gamma$ ,  $\gamma_1$ , and  $\gamma_{11}$  by

$$\chi \sim (p_c - p)^{-\gamma} , \quad (237)$$

$$\chi_1 \sim (p_c - p)^{-\gamma_1} , \quad (238)$$

$$\chi_{11} \sim (p_c - p)^{-\gamma_{11}} , \quad (239)$$

where  $\chi$  is the mean cluster size in the bulk,  $\chi_1$  is the mean cluster size for clusters attached to the surface, and  $\chi_{11}$  is the mean number of surface sites in a cluster attached to the surface.

The problem of percolation at a surface has been studied by mean-field theory (Theumann, 1979; De'Bell and Essam, 1981), which predicts the existence of ordinary, adsorption, and surface transitions. However, real-space renormalization-group (De'Bell, 1979, 1980b) and series-expansion analysis (De'Bell and Essam, 1980) results indicate that the adsorption and surface transitions do not occur in two dimensions but do occur in three dimensions. The scaling relations derived for SAWs at the ordinary transition are also expected to be valid for percolation theory (De'Bell, 1980b), in particular,

$$\gamma + \nu = 2\gamma_1 - \gamma_{11} , \quad (240)$$

where  $\nu$  is the exponent describing the divergence of the connectedness length  $\xi$  (i.e., the root-mean-square distance between connected sites).

An interesting aspect of the percolation problem is that the critical exponents may be related to the fractal dimension of the infinite cluster that occurs at  $p_c$  (Leath, 1976; Stanley, 1977). The bulk fractal dimension  $d_f$  is defined by

$$M(b) \propto b^{d_f} , \quad (241)$$

where  $M_b$  is the number of sites belonging to the infinite cluster and contained within a box of side  $b$  centered on the cluster. The surface fractal dimension  $d_s$  is defined by

$$M_1(b) \propto b^{d_s} , \quad (242)$$

where  $M_1(b)$  is the number of surface sites belonging to the infinite cluster, contained in a surface area of side  $b$ .

For a Euclidean object,

$$(d_f - 1) - d_s = 0 . \quad (243)$$

However, for the percolation problem this difference is, in general, not zero and can be related to the critical exponents (De'Bell and Lookman, 1986), that is,

$$(d_f - 1) - d_s = (\gamma - \gamma_1) / \nu . \quad (244)$$

[Christou and Stinchcombe (1986) have given an equivalent relation in terms of the bulk and surface percolation probability exponents.]

The significance of this result is that it gives a direct geometrical interpretation to the difference between the exponent  $\gamma_1$ , which characterizes the divergence of surface clusters, and its bulk counterpart. Since  $(d_f - 1) - d_s > 0$  for percolation, the surface of a polymer gel may be expected to be a relatively open structure. To visualize this, consider a percolating cluster (or the equivalent polymer gel) grown in the bulk. Now cut through the percolation cluster with a surface so that parts of the cluster below the surface fall away. The above relation implies that sufficient parts of the cluster



above the surface will become disconnected from the main cluster and fall away to significantly alter the structure of the cluster (gel) near the surface.

Estimates of  $(d_f - 1) - d_s$  have been obtained in two and three dimensions by estimating the exponents on the right-hand side of Eq. (244) from an analysis of exact enumeration data (De'Bell and Lookman, 1986) and by direct estimates of the differences in the surface and bulk fractal dimensions from Monte Carlo simulations (Lookman and De'Bell, 1992). In two dimensions, when conformal covariance theory was applied to the  $n \rightarrow 0$  limit of a Potts model the prediction (Cardy, 1984) was

$$(d_f - 1) - d_s = 11/48, \quad d = 2. \quad (245)$$

The numerical results are completely consistent with this value. In three dimensions, the numerical analyses give

$$(d_f - 1) - d_s = 0.52 \pm 0.09, \quad \text{Series, } d = 3, \quad (246)$$

$$(d_f - 1) - d_s = 0.34 \pm 0.04 \text{ Monte Carlo, } d = 3. \quad (247)$$

The series result is based on a relatively small number of terms and, as such, the error estimate represents only the apparent convergence in the analysis. Therefore we consider the Monte Carlo estimate to be more reliable.

## VII. SUMMARY

The general principles of polymers attached to surfaces in dilute good solution and related surface critical phenomena are well understood as a result of rigorous methods and scaling and conformal theories, supplemented by numerical work, as described above. However, several problems remain outstanding. These include a thorough verification, by numerical methods, of the scaling theory for general topologies. Verifying that combinations of exponents such as  $\gamma_1(\mathcal{G}) - \gamma_{11}(\mathcal{G})$  are indeed independent of the topology  $\mathcal{G}$  would provide an exhaustive test of the theory. In practice, this is difficult because each chain must contain  $O(N)$  vertices. Further work on nonuniform networks is needed to explore whether the combinations of exponents are also independent of topology. There is an outstanding need for experimental results for dilute systems in areas such as the adsorption transition, perhaps using the methods described by di Meglio and Taupin (1989). The incorporation of system-specific features, such as monomer-monomer and monomer-solvent interactions in copolymers, into models of dilute good solvent systems remains an area in which there is much work to be done. Finally, we have not discussed in this review the dynamics of polymer adsorption. Relatively few results are available for this problem. However, some computer studies have been performed (Balazs and Lewandowski, 1990; Frantz and Granich, 1991) and we refer the interested reader to these.

*Note added.* After submission of this article, the authors received a preprint of the article by E. Orlandini, A. L. Stella, M. C. Tesi, and F. Sullivan (1992, "Vesicle

adsorption on a plane: new scaling regimes and cross-over phenomena"). In this work the value of the cross-over exponent at the adsorption transition for self-avoiding surfaces with spherical topology is found to be

$$\phi = 0.70 \pm 0.06.$$

This problem is expected to be in the same universality class as that of lattice trees (branched polymers). However, the value of  $\phi$  obtained is not compatible with the value obtained by Janssen and Lyssy (1992).

*Note added in proof.* Recently I. Chang and H. Meirovitch [Phys. Rev. Lett. **69**, 2232 (1992)] studied the surface adsorption transition of both SAWs and lattice trails at the theta point. Their results are consistent with the universality of SAWs and lattice trails at the theta point but inconsistent with the universality of  $\theta$  and  $\theta'$  models. This differs significantly with other recent work on these problems (see Sec. VI.C).

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