

Adsorption transitions of polymers and crumpled membranes

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Adsorption transitions of polymers and crumpled membranes are studied for general substrate potentials in d -dimensional systems. Several regimes for the critical behavior are identified: (i) a weak-fluctuation regime for sufficiently long-ranged potentials which is well described by an ensemble of independent blobs; (ii) a complex intermediate fluctuation regime with infinite-order, second-order, and anomalous first-order transitions; and (iii) a strong-fluctuation regime for sufficiently short-ranged interactions which is characterized by *second-order* transitions with *universal* critical behavior.

I. INTRODUCTION

On large scales, polymers are crumpled (i.e., highly convoluted) as a result of thermal fluctuations. They then form random coils with a gyration radius R_G which grows as $R_G \sim N^\nu$ with the total length N of the polymer chain.¹ Recently, it has been realized that thermally excited crumpling can also occur for two-dimensional sheets of molecules such as fluid membranes in microemulsions² and tethered (or polymerized) membranes.³ For crumpled membranes, the gyration radius also scales as $R_G \sim N^\nu$ where N^2 is now the total area of the membrane.

Here, we consider crumpled polymers and membranes that are adsorbed onto a solid substrate or any other interface. Adsorbed polymers are important from a technological point of view since they can be used to stabilize colloidal suspensions. Likewise, in the context of biophysics, they serve as simple model systems for the macromolecules which are attached to the surfaces of cells and organelles. Adsorbed states of crumpled membranes represent a possible structure for the interface between a microemulsion and another thermodynamic phase.

We will study the dilute case in which the adsorbed polymers or membranes have no overlap and can be treated as independent. Furthermore, we focus on length scales which are small compared to the gyration radius R_G of a free polymer or membrane. The system may then undergo an *adsorption* (or *unbinding*) *transition* in which the adsorbed manifold unbinds from the substrate surface in a continuous or discontinuous fashion.

We show below that the *form* of the substrate potential acting on the polymer or membrane segment has important consequences for the nature of this transition and for its scaling properties. In real systems, the substrate potential contains short-ranged and long-ranged contributions such as electrostatic, van der Waals, or structural interactions. The latter interactions typically arise from the decay of short-range order within the solvent. If the *attractive* part of the potential is sufficiently strong, it will bind the polymer or membrane to the substrate surface. However, thermally excited shape fluctuations of the ad-

sorbed manifolds renormalize the substrate potential: quite generally, they act to reduce its attractive part and to enhance its repulsive part. At the transition temperature $T = T^*$ of the adsorption (or unbinding) transition, these shape fluctuations lead to a renormalized potential which is completely repulsive.

Three different scaling regimes for such transitions will be identified: (i) a *weak-fluctuation* (WFL) regime for sufficiently long-ranged substrate potentials⁴ where the adsorbed chain or membrane can undergo a *first-order* transition at a finite temperature $T = T^*$ but a *second-order* transition is only possible at $T^* = \infty$ or when the potential strength is decreased to zero; (ii) an *intermediate fluctuation* (IFL) regime characterized by a complex interplay of short-ranged and long-ranged potentials. This regime exhibits three subregimes including *anomalous* first-order transitions and transitions of *infinite* order governed by essential singularities; and (iii) a *strong-fluctuation* (SFL) regime for sufficiently short-ranged potentials. In this latter regime, the system undergoes a second-order transition at finite T^* which is characterized by *universal* critical behavior. First-order transitions, on the other hand, are impossible in the SFL regime as a result of the strong fluctuations.

Our derivation of these properties starts from a heuristic scaling picture in which the adsorbed polymer is viewed as a collection of independent blobs.⁵ We find that this intuitively appealing picture correctly identifies the various scaling regimes. As far as the critical behavior is concerned, the picture gives a reliable description in the WFL regime but fails in the IFL and in the SFL regimes. We also show how to extend the blob picture to crumpled membranes.

II. INDEPENDENT BLOB PICTURE FOR POLYMERS

Consider a linear or branched polymer chain which is adsorbed onto a $(d - 1)$ -dimensional surface (with $d \geq 2$) and which forms a layer of thickness l . It will be useful to view this layer as a string of blobs which have a linear size $\sim l$. On scales small compared to l , the chain should not feel the constraint arising from the external potential

and thus should crumple as if it were free.⁵ Then, a blob will contain N_l monomers with

$$l/a \sim N_l^\nu \text{ for } l \gg a, \quad (1)$$

where a is the microscopic persistence length. Furthermore, one may assume that the correlations between different blobs are destroyed by the external potential.⁵ Then, the chain with N monomers can be viewed as a string of $\sim N/N_l$ independent blobs. The elastic free energy stored within each blob should be $\sim T$ as suggested by the equipartition theorem. Therefore the elastic free energy F_{el} of the whole chain should scale as

$$F_{el} \sim T(N/N_l) \sim NT(a/l)^{1/\nu}. \quad (2)$$

This represents the loss of entropy resulting from the confinement; it acts to thicken the blobs and, thus, to reduce the overall entropy loss. However, thicker blobs have a larger potential energy F_{pot} arising from the substrate potential per monomer $U(z)$ where z measures the distance from the substrate surface. This energy is

$$F_{pot} = N \langle U(z) \rangle \sim NU(l). \quad (3)$$

Now, one can attempt to determine l in a self-consistent way by minimization of

$$f(l) \equiv (F_{el} + F_{pot})/N \simeq T(a/l)^{1/\nu} + U(l). \quad (4)$$

Note that $T(a/l)^{1/\nu}$ is the entropy loss *per monomer*. It turns out that this heuristic procedure correctly identifies the three scaling regimes for $U(z)$ even though it does *not* yield the correct critical behavior in two of the three regimes. Indeed, the superposition ansatz in (4) immediately leads to the following classification: (i) the WFL regime characterized by⁴

$$|U(l)| \gg 1/l^{1/\nu} \text{ for large } l. \quad (5)$$

In this regime, the entropy gain from crumbling cannot compete with the substrate potential $U(l)$ for large l ; (ii) IFL regime with

$$|U(l)| \sim 1/l^{1/\nu} \text{ for large } l. \quad (6)$$

Now, the shape of $f(l)$ in (4) crucially depends on the amplitude W of $U(l) \approx -W/l^{1/\nu}$. For $W < 0$, the superposition can lead to a first-order transition in the presence of a short-ranged attractive part. In addition, a second-order transition is also found when W is decreased from large positive values. It will be shown below that this regime does indeed exhibit rather complex critical behavior; and (iii) the SFL regime with

$$|U(l)| \ll 1/l^{1/\nu} \text{ for large } l. \quad (7)$$

In this case, the minimization procedure leads to a first-order transition at finite T^* if $U(z)$ contains a sufficiently strong attractive part. There is indeed a transition at finite T^* but it is of second order as will be shown in the following.

III. ADSORPTION OF IDEAL CHAINS

Now, we will confirm the above scaling regimes for the case of an ideal chain with $\nu = \frac{1}{2}$. The configuration of the chain will be described by $\mathbf{r}(s) = (\mathbf{x}(s), z(s))$ where $\mathbf{x} = (x_1, \dots, x_{d-1})$ and z are coordinates parallel and perpendicular to the substrate surface, and s labels the sequence of monomers. In the continuum limit, the chain is then governed by the effective Hamiltonian

$$\mathcal{H}\{\mathbf{r}\} = \int_0^{Na} ds a^{-1} \left[\frac{1}{2} T \left(\frac{d\mathbf{x}}{ds} \right)^2 + \frac{1}{2} T \left(\frac{dz}{ds} \right)^2 + U(z) \right]. \quad (8)$$

As before, $U(z)$ is the potential energy of one monomer at distance z from the surface. The statistical properties which follow from the Boltzmann factor $\exp(-\mathcal{H}/T)$ can be obtained *exactly* for this case since the \mathbf{x} and z coordinate decouple. Thus the \mathbf{x} coordinate describes an ideal and free chain in $d-1$ dimensions while the behavior of the z coordinate can be determined via transfer-matrix methods. One must then solve a Schrödinger-type equation of the form

$$\left[-\frac{1}{2} a^2 T \frac{\partial^2}{\partial z^2} + U(z) \right] \phi_n(z) = E_n \phi_n(z). \quad (9)$$

The scaling properties of the adsorbed chain follow from the ground state $\phi_0(z)$ and its energy E_0 . This problem is, in fact, identical with the unbinding of a one-dimensional interface for wetting in $d=2$. In the latter case, a *complete classification* of the critical behavior has been obtained.⁶ This classification can now be applied to the adsorption transition of ideal chains in *any* dimension $d \geq 2$. One then finds that the three scaling regimes are correctly given by (5) and (6). Furthermore, one finds the following critical behavior: (i) in the WFL regime, the exact critical behavior is identical with the behavior obtained from the superposition ansatz (4). As an example, consider the potential $U(z) = Gz$ for $z > 0$ (arising, e.g., from gravity). Then, the average thickness \bar{l} of the adsorbed polymer scales as $\bar{l}/a \sim (T/aG)^\psi$ with $\psi = \frac{1}{3}$. The chain may also undergo a first-order transition where l jumps from a finite value to infinity (for an infinite chain with $N = \infty$) if $U(z)$ contains an attractive short-ranged part and a repulsive long-ranged part; (ii) in the IFL regime with $U(z) \approx -W/z^2$, one has three different subregimes (A), (B), and (C). In subregime (A), the chain undergoes an adsorption transition of infinite order, and the average thickness behaves as

$$\bar{l} \sim \exp(\text{const}/\sqrt{T^* - T}) \text{ with } T^* = 8W/a^2. \quad (10)$$

In subregime (B) with $-\frac{3}{4} \leq 2W/a^2 T \leq \frac{1}{4}$, one has

$$\bar{l} \sim (T^* - T)^{-\psi} \text{ with } \psi = (1 - 8W/a^2 T)^{-1/2}. \quad (11)$$

Finally, for $2W/a^2 T < -\frac{3}{4}$, one enters subregime (C). Then, the transition becomes first order in the sense that the first derivative of the free energy is discontinuous but the density profile $P(z)$ is *scale invariant* since $P(z) \sim z^{-\mu}$ for large z with $\mu = (1 - 8W/a^2 T)^{1/2} - 1$; and (iii) in the

SFL regime, there are *no* first-order transitions since the polymer “tunnels” through any potential barrier but only second-order transitions with the *universal* critical exponent $\psi=1$ as follows from (11) for $W=0$.

IV. ADSORPTION OF SELF-AVOIDING (SA) CHAINS

For self-avoiding (SA) chains, the exponent ν depends on d : $\nu=\nu(d)$. For *linear* chains, one has $\nu(2)=\frac{3}{4}$ and $\nu(3)\approx\frac{3}{5}$ as obtained from a Flory argument;¹ for *branched* chains, $\nu(2)\approx 0.61$ and $\nu(3)\approx\frac{1}{2}$.⁷ In general, the independent blob picture should give the correct behavior in the WFL regime as defined in (5). Consider, e.g., the potential, $U(z)=Gz$. Then, minimization of (4) leads to

$$\bar{l}/a \sim (T/aG)^\psi \quad \text{with } \psi = \nu/(1+\nu). \quad (12)$$

It then follows that $\bar{l}/a \sim 1/g^{3/7}$ with $g \equiv aG/T$ for linear SA chains in $d=2$ since $\nu=\frac{3}{4}$.

As shown in Fig. 1, this relation is well confirmed by Monte Carlo (MC) simulations. These MC data have been obtained for chains which consist of a linear sequence of N disks. These disks have diameter c and their centers are connected by linear bonds of length $a > c$. The SA constraint is embodied by the requirement that disks are not allowed to overlap. For comparison, Fig. 1 also shows MC data for ideal chains (with $c=0$); in this case, one has $\bar{l}/a \sim 1/g^{1/3}$ as mentioned. *Finite-size effects* set in once $\bar{l}/a \sim R_G/a \sim N^\nu$. For $\bar{l} \gtrsim R_G$, the chains behave as a single particle in an external potential. This implies $\bar{l}/a \sim 1/gN$ for the example considered here which is visible in Fig. 1 for small values of g and SA chains with $N=40$ or 80. (The corresponding data for ideal chains have been omitted.)

The SFL regime contains all potentials with $|U(z)| \ll 1/z^{1/\nu}$, see (7). Therefore a potential of finite range with $U(z)=0$ for $z > z_0$ belongs to this regime. For such a potential, the adsorption transition of *linear* SA chains has been identified with the so-called special tran-

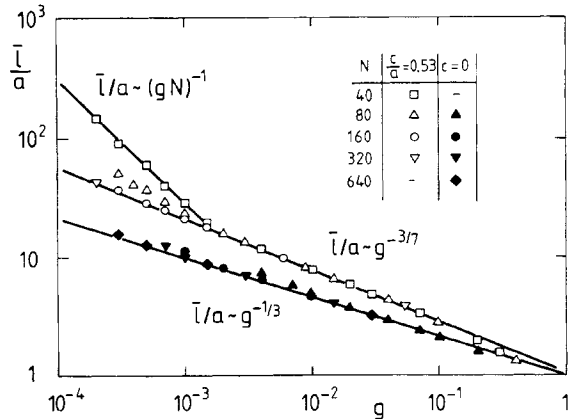


FIG. 1. Average thickness \bar{l} of adsorbed polymer in an external potential $U(z)=Gz$ as a function of $g \equiv aG/T$. The white and black data points correspond to self-avoiding and ideal chains, respectively.

sition of the semi-infinite n -vector model in the limit $n \rightarrow 0$.⁸ One then finds $\bar{l} \sim (T^* - T)^{-\psi}$ with $\psi = \nu/\varphi$ where φ is the crossover exponent at the special transition. Using the known results for ν and φ ,^{9,10} one obtains $\psi=1$ for $d \geq 4$, $\psi \approx 1 + (4-d)/4$ for small $4-d$, and $\psi = \frac{3}{2}$ for $d=2$; linear interpolation then gives $\psi \approx \frac{5}{4}$ for $d=3$. For *branched* SA chains in $d=3$, recent MC simulations gave the crossover exponent $\varphi \approx 0.71$.¹¹ This leads to $\bar{l} \sim (T^* - T)^{-\psi}$ with $\psi = \nu/\varphi \approx 0.5/0.71 \approx 0.70$.

The general classification scheme presented here implies that these values for ψ apply to the *whole* SFL regime for linear or branched SA chains. In particular, they apply to SA chains in $d=3$ in the presence of a realistic *van der Waals* potential with $U(z) \approx -W/z^3$ for large z .

V. ADSORPTION OF CRUMPLED MEMBRANES

Membranes are two-dimensional (2D) sheets which form spontaneously in solutions of amphiphilic molecules. Examples are monolayers of surfactant and bilayers of lipid molecules. Such a monolayer or bilayer often has a finite persistence length ξ_p .² Then, the membrane will exhibit orientational order (i.e., its normal vectors will be correlated) on length scales $\ll \xi_p$ but will be orientationally disordered and crumpled on length scales $\gg \xi_p$. Since we will focus on crumpled states, the membranes considered here are taken to consist of segments (or monomers) with area $a^2 \sim \xi_p^2$.

Now, consider a crumpled membrane which is adsorbed onto a $(d-1)$ -dimensional surface (with $d \geq 3$) and forms a layer of thickness l . In close analogy with the case of polymers, we will take the adsorbed layer to consist of independent blobs which have a linear extension $\sim l$. Each blob will now contain N_l^2 segments (or monomers) with $l/a \sim N_l^\nu$, and its elastic free energy will again be $\sim T$. Then, a membrane with a total number of N^2 segments contains $(N/N_l)^2$ blobs and, thus, has an elastic free energy $F_{el} \approx T(N/N_l)^2 \sim N^2 T (a/l)^{2/\nu}$. The substrate potential, on the other hand, leads to the free-energy contribution $F_{pot} = N^2 \langle U(z) \rangle \sim N^2 U(l)$. Therefore the free energy *per membrane segment* can be estimated by

$$f(l) \equiv (F_{el} + F_{pot})/N^2 \sim T(a/l)^{2/\nu} + U(l). \quad (13)$$

Now, the classification as given by (5)–(7), which has been obtained for polymers, carries over to crumpled membranes provided (i) we replace ν with $\nu/2$, and (ii) we use the ν value appropriate for membranes. In this way, we can also determine the behavior in the WFL regime of crumpled membranes. For example, $U(z)=Gz$ leads to $\bar{l} \sim (T/aG)^\psi$ for large T or small G with $\psi = \nu/(2+\nu)$.

For an *ideal tethered* membrane which can intersect itself, one has a marginal case with $\nu=0$ and $R_G^2 \sim a^2 \ln(N)$. In the presence of a substrate potential, $U(z)$, the membrane configurations are governed by the effective Hamiltonian

$$\mathcal{H}\{\mathbf{r}\} = \int_0^{Na} ds a^{-1} \int_0^{Na} dt a^{-1} \left[\frac{1}{2} T (\nabla \mathbf{x})^2 + \frac{1}{2} T (\nabla z)^2 + U(z) \right] \quad (14)$$

for the coordinate $\mathbf{r}=(\mathbf{x}(s,t),z(s,t))$ of the crumpled membrane, and $\nabla\equiv(\partial/\partial s,\partial/\partial t)$. In this case, the \mathbf{x} and z coordinate decouple again, and the z -dependent part becomes equivalent to the unbinding of a two-dimensional interface for wetting in $d=3$. Now, fluctuations of the z coordinate are found to be irrelevant for all potentials $U(z)$ which decay as a power of $1/z$ for large z . On the other hand, for $U(z)\sim\exp(-z/z_0)$ and sufficiently small z_0 , linear renormalization schemes give a finite value of T^* and $\bar{l}\sim 1/(T^*-T)$.

For a SA *tethered* membrane, a Flory-type argument gives the value $\nu=\nu_{\text{tet}}\simeq\frac{4}{5}$ in $d=3$, whereas recent computer simulations indicate $\nu=1$.³ It then follows from (13) that the overall loss of entropy per membrane segment scales as $\sim 1/l^{2/\nu}$ with $2/\nu\simeq\frac{5}{2}$ or $2/\nu=2$. This implies that a realistic van der Waals potential, $U(z)\sim 1/z^3$, again belongs to the SFL regime for which we expect a second-order adsorption transition with *universal* critical exponent ψ .

A strong-fluctuation regime has also been identified for the unbinding of interfaces and of oriented membranes, i.e., for wetting and adhesion transitions.¹² In this case, the fluctuations lead to an elastic free energy which scales as $\sim 1/l^\tau$ with the mean separation l of the interfaces or membranes. Furthermore, a functional renormalization group predicts that, in the SFL regime, ψ is a unique function of τ . Therefore the unbinding of 1D interfaces and of 2D fluid membranes should be characterized by the same value $\psi=1$ since $\tau=2$ holds in both cases. We speculate that such a property also applies to the unbinding of crumpled objects considered here. For polymers with $\tau=1/\nu\simeq(d+2)/3$ for $d\leq 4$, one has $\psi\simeq 2-d/4\simeq(10-3\tau)/4$.

For an ideal or a SA *fluid* membrane, the value of ν is not known at present. It seems plausible that ideal fluid

membranes also have $\nu=0$ since fluid membranes are more flexible than tethered ones. Self-avoidance in $d=3$ implies the bound $\nu>\frac{2}{3}$. One interesting possibility is that fluid membranes also become uncrumpled as a result of self-avoidance.

VI. SUMMARY AND OUTLOOK

In summary, a simple picture of independent blobs leads to the identification of several scaling regimes for the adsorption of polymers and crumpled membranes.¹³ The WFL regime contains all substrate potentials $U(z)$ which are sufficiently long ranged and satisfy $|U(z)|\gg 1/z^{d_{\parallel}/\nu}$ with $d_{\parallel}=1$ and 2 for polymers and membranes, respectively. In this regime, the scaling properties are governed by the *large* blobs, and the simple superposition ansatz (4) or (13) gives the correct critical behavior. In the IFL regime with $|U(z)|\sim 1/z^{d_{\parallel}/\nu}$ and in the SFL regime with $|U(z)|\ll 1/z^{d_{\parallel}/\nu}$, the behavior of the large blobs is strongly renormalized by the behavior of smaller blobs: one has a problem with many length scales, and the critical behavior at the adsorption transition *cannot* be obtained from the superposition ansatz (4) or (13).

For ideal chains with $\nu=\frac{1}{2}$, the critical behavior has been obtained exactly for all regimes: it is found to be universal within the SFL regime but to be highly nonuniversal within the IFL regime. We predict that this distinction holds in general even though the critical exponent ψ for the adsorbate thickness \bar{l} is not known in many cases. In particular, no precise estimate of ψ is presently available for the IFL and the SFL regimes of crumpled membranes. This remains a challenge for the future.

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⁴If the substrate potential contains a long-ranged repulsive part, one may distinguish a mean-field (MF) regime from the WFL regime. In the MF regime, the size of the blobs is small compared to the mean distance of the polymer from the substrate.

⁵Similar arguments have been applied to the stretching of polymers and to the confinement of polymers in pores; see Ref. 1.

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