

Unbinding Transitions of Semi-flexible Polymers.

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Abstract. – We consider a semi-flexible chain adsorbed on a wall by a constant external field, h , or a short-range surface potential, V_s . When the amplitude of h or V is decreased the system undergoes an unbinding transition; the properties of such transitions are studied here through various analytical and numerical methods (Flory approximation, scaling arguments, transfer matrix methods and Monte Carlo simulations). In particular, we obtain a general form for the entropy reduction («steric interactions») for constrained chains. The unbinding transition from an attractive V_s is shown to be discontinuous in the limit of very rigid chains.

Rigidity, or bending energy, has been shown to play an important role in the statistical behaviour of amphiphilic membranes and films [1]. In particular, if thermal fluctuations are governed by rigidity, the entropic repulsion between two such «semi-flexible» two-dimensional ($2d$) objects is effectively long-ranged [2]. This «steric» repulsion can in fact overcome the molecular attraction acting between membranes and give rise to an *unbinding transition* [3] at which membranes separate each from the other. In this letter, we shall study a similar phenomenon for *semi-flexible chains* (SFC). It is now well established that certain linear macromolecules such as polypeptides, DNA etc., have a large persistence length [4] (*i.e.* the correlation length of their orientation), and therefore the rigidity plays an important role in their statistical behaviour. For instance, it was shown [5] in recent experiments that the sequence-dependent stiffness of DNA can influence protein-DNA binding specificity. The steric repulsion between rigid macromolecules are now also being studied in DNA crystals [6]. Here we examine the adsorption and unbinding of SFCs from lines and surfaces. The connection of our results to the unbinding of $2d$ membranes is briefly discussed at the end of this paper.

A simple model describing a SFC consisting of N monomers of size $a = 1$ in the potential $V(\mathbf{r})$ can be introduced through the Hamiltonian

$$\beta \mathcal{H} = \sum_i \beta V(\mathbf{r}_i) - \kappa \sum_i \hat{n}_i \cdot \hat{n}_{i+1},$$

with unit «bond» vectors $\hat{n}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$ ($\beta = 1/k_B T$), and we put $k_B = 1$. κ plays the role of the persistence length [7]: it typically takes length κ to reverse the chain's orientation. We shall consider such a SFC in two different situations both leading to unbinding transitions.

In the first case the chain is held against a wall by an external field, h , thus $V(\mathbf{r}) = hz$: an unbinding transition then occurs as the field is reduced, *i.e.* when $h \rightarrow 0$: $\langle z \rangle \sim h^{-\lambda}$, where z is the distance from the wall and the brackets denote a thermal average. To understand this phenomenon, and in particular to calculate the value of the exponent λ it is sufficient to consider a SFC in a constrained geometry (*e.g.* between two hard walls spaced by L). Then one can evaluate the *constraining potential*, or the reduction in entropic free energy per monomer, $f_s(L)$. We find in general three nontrivial regimes for this potential: a «*self-avoiding regime*», where the excluded volume effects are important, a «*Gaussian regime*», where they are unimportant and a «*squashed regime*»⁽¹⁾, where essentially all segments of the chain are nearly parallel to the wall. In these three regimes one finds, respectively,

$$f_s(L) \sim \begin{cases} T\kappa^{1/3} L^{-1/\nu}, \\ T\kappa L^{-2}, \\ T\kappa^{-1/3} L^{-2/3}, \end{cases} \quad (1)$$

where ν is the radius of gyration exponent of a self-avoiding chain: $R_G \sim N^\nu$. The first regime disappears for spatial dimensionality $d \geq 4$ [4], while the second Gaussian one does not exist in $d = 2$ [8]. The corresponding unbinding exponents λ are obtained by simply minimizing⁽²⁾ $f_s(\langle z \rangle) + \langle z \rangle h$: $\lambda = \nu/(\nu + 1)$, $1/3$, $3/5$ in the three regimes, respectively. The result of eq. (1), obtained here through standard Flory-de Gennes type of arguments [4] and also confirmed through a numerical simulation of *tethered chains* in $2d$, can be viewed as a generalization of the fluctuation-induced, *steric interactions* for the case of *highly crumpled chains*.

The second situation which we consider is the one in which a SFC is adsorbed on a wall by an attractive, *short-ranged* surface potential, V_s . An unbinding transition takes place when the attraction $|V_s|$ is decreased below some threshold V_0 ⁽³⁾. This transition is in general continuous, however, we find that in the limit of large rigidities κ it *becomes effectively of first order*. In fact this is an unusual situation in which a so-called special surface transition [10] (the unbinding transition in this case) becomes discontinuous. This result is demonstrated here both analytically and through the numerical study of a transfer matrix which also demonstrates *finite size scaling*.

We now address various issues underlying these results⁽⁴⁾. We first consider a SFC in a constrained geometry, *e.g.*, between two parallel walls. *Flory-de Gennes type of arguments* [4, 8] lead to seven different regimes for the behaviour of the chain, as illustrated in fig. 1. First consider N large, such that for unconstrained geometry ($L \gg R_G$) the self-avoidance is important [8]. This happens in the Flory approximation⁽⁵⁾ when $N > N^* \sim$

⁽¹⁾ This last «squashed regime» is the one usually considered in the problems of interacting chains or membranes: see, *e.g.*, ref. [3].

⁽²⁾ This corresponds to the so-called *complete unbinding* transitions of interfaces and membranes, see, *e.g.*, ref. [9].

⁽³⁾ This corresponds to the so-called *critical unbinding* transitions, see ref. [3] and footnote⁽²⁾.

⁽⁴⁾ Details of the calculations will be published elsewhere.

⁽⁵⁾ Note that for a nonself-avoiding SFC N^* is the size for which the average number of self-intersections is of order 1. For $d > 4$ N^* is infinite: the self-interactions are then irrelevant.

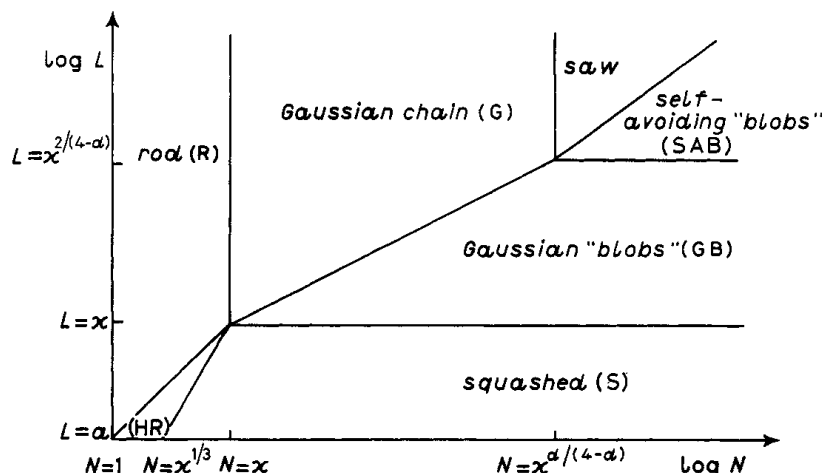


Fig. 1. – Different regimes for a SFC constrained between two walls for $2 \leq d \leq 4$. (HR denotes the hindered-rod regime.) Note that the transitions between regimes are not sharp; continuous crossovers occur in the vicinities of the lines indicated.

$\sim \chi^{d/(4-d)}$, the radius of gyration is then $R_G(N) \sim N^{\nu_F} \chi^{1/(d+2)}$, with $\nu_F = 3/(d+2)$. The constraints distort the coil when $L \leq R_G(N)$. The confined chain can be viewed [4] as a string of blobs of linear size L with N_b monomers per blob provided that $L \geq \chi$. For $L \geq R_G(N^*)$ the self-avoidance is important within each blob whereas for $L < R_G(N^*)$ the blobs are Gaussian. The confinement energy is T per blob [4], thus the free energy cost of confinement per monomer is T/N_b . For self-avoiding blobs, *i.e.* for $N_b \geq N^*$, $N_b \sim L^{1/\nu_F} \chi^{-1/3}$, whereas for Gaussian blobs $N_b \rightarrow L^2 \chi^{-1}$. This leads to the first two formulae of eq. (1). If the chain is constrained further to $L < \chi$ the blob picture does not hold. In this «squashed» regime one can estimate the $f_s(L)$, via an argument similar to that used for interfaces with surface tension [11]. The z component of \hat{n}_i , $v_i \equiv \hat{n}_i \cdot \hat{z}$, performs a random walk, and therefore $\langle |v_i - v_j| \rangle \sim (|i - j|/\chi)^{1/2}$ for $|i - j|$ small enough. The positions, $z_i = \sum_{j=1} v_j$, then fluctuate as $\langle |z_i - z_j| \rangle \sim |i - j|^{3/2} \chi^{-1/2}$. The density of collisions with the wall is thus of order $L^{-2/3} \chi^{-1/3}$. This leads to the last formula in eq. (1) under the assumption that the confinement = free energy is of order T per collision [12]. For smaller values of N , namely $\chi \leq N \leq N^*$, an unconstrained coil is Gaussian [8] (except in $2d$ where the regime disappears). On decreasing L such coils transform into strings of Gaussian blobs (at $L \sim R_G(N) \sim (N\chi)^{1/2}$) and finally enter the squashed regime (at $L \sim \chi$). For $N \leq \chi$ the free chain behaves like a rod of length N . The orientations of such rods are restricted for $L < N$. Furthermore, the squashed regime is entered for $L \leq N^{3/2} \chi^{-1/2}$ (see above).

In order to check these simple arguments we have performed a Monte Carlo simulation of a SFC in $2d$, subject to a constraining field h (see⁽⁴⁾). We used a «tethered-chain» model (*e.g.*, described in ref. [13]) with the bending Hamiltonian, and N varying up to 100. Figure 2 shows some results of such simulations. For small χ and large N one finds in fact both the (self-avoiding) coil and blobs regimes characterized by $\lambda = 1$ and $\nu/(\nu+1)$, respectively (we find the values 0.97 ± 0.05 and 0.425 ± 0.015). Note that the scaling plot in fig. 2a) does not show the squashed regime since here we put $\chi = 0$ (see fig. 1). For large χ this squashed regime characterized by $\lambda = 3/5$ is clearly seen already for $N = 50$ (we find the value 0.59 ± 0.01). Figure 2b) also shows the freely rotating and hindered rod regimes.

We now turn to the problem of surface adsorption of SFCs for general d and short-range surface potentials. We first neglect the self-interactions. Any configuration of the chain consists of alternating segments in and out of the surface potential. Such a situation can be

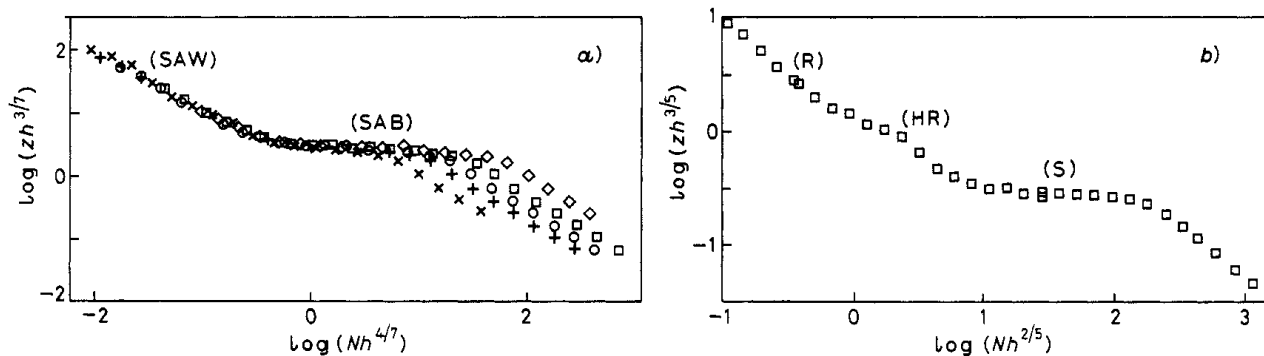


Fig. 2. – Results of Monte Carlo simulations for a SFC in $d=2$. The abbreviations for different regimes correspond to those in fig. 1. An additional large- h regime, with $\langle z \rangle \sim h^{-1}$ is entered when h becomes large. a) \times $N=10$, \times $N=20$, \times $N=30$, \times $N=50$, \times $N=100$, \times $N=2000$, b) $N=50$, \times $N=2000$.

treated using generating-function techniques [14]. An important quantity is the partition function Z_l of a segment of length l out of the surface potential whose ends are at the wall [14]. For large l this function behaves as $Z_l \sim \exp[-\beta l f_0] l^{-\psi}$, where f_0 is the free energy per monomer in the absence of the wall. The nature of the unbinding transition is determined by ψ : for $1 < \psi < 2$ the transition is *continuous* with critical exponents determined by ψ [14], whereas for $\psi > 2$ the transition is *first order*. We shall show now that in the limit of large κ the transition is indeed first order with $\psi \geq 9/4$.

Let us consider the Boltzmann weight $f_l(\mathbf{r}, \hat{n})$ of a SFC with l monomers whose end is at \mathbf{r} with «bond» orientation \hat{n} . For large κ when the chain is near the wall the dominant configurations have \mathbf{n} almost parallel to the wall; one can then rescale the z -direction, introducing $\tilde{v} = \hat{n} \cdot \hat{z} \kappa^{1/2}$ and $\tilde{z} = \mathbf{r} \cdot \hat{z} \kappa^{1/2}$. In the limit $\kappa \rightarrow \infty$ the Fokker-Planck equation [15] can be written as

$$\frac{\partial f_l}{\partial l} = \frac{\partial^2 f_l}{\partial \tilde{v}^2} - \tilde{v} \frac{\partial f_l}{\partial \tilde{z}} - \beta V(\tilde{z}) f_l. \quad (2)$$

(Note that with the above rescaling the limit $\kappa \rightarrow \infty$ *does not* correspond to the trivial problem of a strictly rigid rod.) On imposing the constraints that the SFC does not cross the wall we expect scaling of the form

$$f_l(\tilde{z}, \tilde{v}) \approx \frac{\tilde{z}^\alpha}{l^\psi} g\left(\frac{\tilde{z}}{l^{3/2}}, \frac{\tilde{v}}{l^{1/2}}\right), \quad (3)$$

for large l . The scaling function $g(x, y)$ drops rapidly for $x \gg 1$ or $y \gg 1$ and $g(x, 0) = O(1)$ for $x \rightarrow 0$. In the limit $x \ll 1$ and $y \ll 1$ one can show that $g(x, y) \approx h_\alpha(y^3/x)$, where h_α satisfies Kummer's confluent hypergeometrical equation [16]. The boundary conditions of no chains coming out of the wall ($f_l(0, \tilde{v}) = 0$ for $\tilde{v} > 0$) and that $I \equiv \int d\tilde{v} d\tilde{z} f_l$ is finite imply $\alpha = 1/6$. For this solution $I \sim 1/l^{\psi-9/4}$ and since this integral cannot increase with l , we obtain $\psi \geq 9/4$.

In order to test these arguments we have studied numerically a $2d$ lattice model based on the transfer matrix equation

$$f_{l+1}(\tilde{z}, \tilde{v}) = [0.5f_l(\tilde{z}-\tilde{v}, \tilde{v}) + 0.25f_l(\tilde{z}-\tilde{v}-1, \tilde{v}+1) + 0.25f_l(\tilde{z}-\tilde{v}+1, \tilde{v}-1)] \exp[-V(\tilde{z})], \quad (4)$$

with the initial condition $f_{l=1}(1, 0) = 1$. The potential $V(\tilde{z})$ consists here of two hard walls at 0 and L and an attractive part at $\tilde{z} = 1$: $V(1) = -V_s$. The system are of finite size L in the \tilde{z}

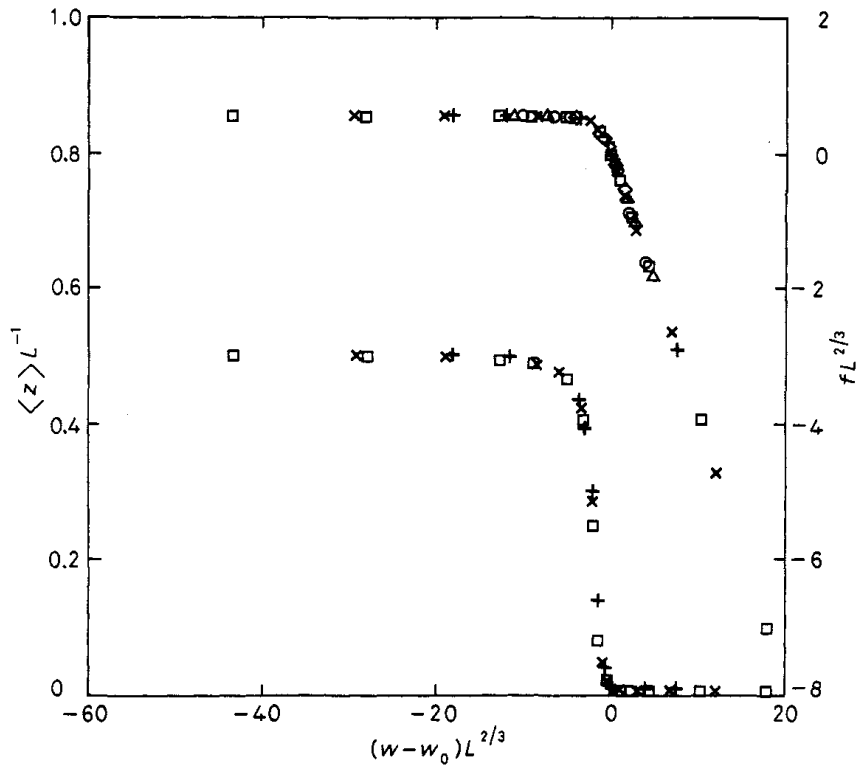


Fig. 3. – Results of transfer matrix calculations for the free energy per monomer, f , and the mean distance, $\langle z \rangle$, from an attractive wall. The transition happens at $w_0 \equiv \exp[-V_0] = 1.567 \pm 0.002$. $\diamond L = 41$, $\circ L = 75$, $\triangle L = 91$, $+ L = 181$, $\times L = 371$, $\square L = 671$.

direction (L varies from 41 to 671). From the scaling described above this is similar to taking chains of finite lengths $l \sim L^{2/3}$. The usual finite size scaling for first-order transitions [17] then has scaling variables $\langle z \rangle L^{-1}$, $(V_s - V_0)L^{2/3}$ and $fL^{2/3}$, where f is the free energy per monomer. Figure 3 shows that such finite size scaling is obeyed, demonstrating that the transition is first order. Moreover, we have directly measured within this model, and found $\psi \approx 5/2$. We also checked that $I \sim 1/l^{\psi-9/4} \sim l^{1/4}$.

For finite κ , and any d , this first-order transition crosses over to a continuous unbinding transition. In the necklace model, which still applies provided that there is no self-interaction, the Z_l decays as $1/l^\psi$ only for lengths shorter than the persistence length κ . For larger scales the chain behaves as a Gaussian random walk and Z_l decays as $1/l^{3/2}$ [14]. This causes the crossover to happen when the correlation length $\xi_{||}$ along the chain in the bound phase becomes of order κ . (When the transition is first order $\xi_{||} \sim (V_s - V_0)^{-1}$.) The resulting continuous transition is in the same universality class as (1 + 1)-dimensional wetting [18]. In the presence of self-interactions one expects to find a so-called polymer special transition [10, 19]. For $d = 2$ the crossover is directly from the first-order behaviour described above to this special transition (at $\xi_{||} \sim \kappa$), whereas for $d > 2$ there are actually two crossovers with an intermediate Gaussian regime for $\kappa \leq \xi_{||} \leq N^*$. These crossovers correspond precisely to the three regimes listed in eq. (1).

For $2d$ membranes we also expect a variety of regimes for unbinding. In contrast to SFCs there is no Gaussian regime for $d = 3$, since $2d$ membranes cannot avoid colliding. For fluid membranes the persistence length, ξ_x , is always finite [20]. One should thus have a crossover, analogous to that discussed above, from a squashed regime (studied in ref. [3]) to a self-avoiding-surface regime at lengths $\sim \xi_x$. In the latter regime the «blobs» are thought to have the statistics of branched polymers [21]. For polymerized (tethered) membranes, on

the other hand, a crumpling transition occurs as κ is decreased [22]. Thus there will be one universal unbinding behaviour in the rigid phase [23] and another one in the crumpled phase [24]. If the crumpling transition is continuous we expect a *third universality class* for the unbinding of such critical membranes.

Further work is clearly needed to understand fully all unbinding behaviours of semi-flexible chains and surfaces. We hope that the simple ideas presented here will stimulate new experimental studies of the adsorption and interactions of macromolecules and membranes.

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