

## Unbundling and desorption of semiflexible polymers

J. KIERFELD and R. LIPOWSKY

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung  
14424 Potsdam, Germany*

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**Abstract.** – A complete classification for unbundling transitions of two semiflexible polymers and for desorption transitions of such polymers at planar surfaces is presented. The interaction potentials can depend both on the polymer/polymer (or polymer/surface) separation and on the orientation of the polymers. Using analytical transfer matrix methods and scaling arguments, the order of the transitions and the corresponding critical exponents are obtained for all types of interaction potentials in arbitrary spatial dimension  $d = 1 + d_{\perp}$ . Our results are applicable to biopolymers or polyelectrolytes with large persistence lengths such as actin filaments, microtubules, or DNA.

*Introduction.* – Semiflexible polymers such as DNA or actin filaments have a large bending stiffness and, thus, a large persistence length,  $L_p$ . On scales which exceed  $L_p$ , the orientational order of the polymer segments decays exponentially, and the polymer effectively behaves as a flexible chain with the segment size set by  $L_p$ . In contrast, on length scales which are small compared to  $L_p$ , the bending energy of the semiflexible polymer plays an equally important role and strongly affects the behaviour of the polymer. The persistence lengths of the most prominent biopolymers range from 50 nm for DNA [1], to the  $\mu\text{m}$  range for actin [2–4] or even up to the mm range for microtubules [3].

Semiflexibility is also crucial for the bundling of such biopolymers and for their adsorption onto adhesive surfaces, as schematically shown in fig. 1. Important examples are bundles of F-actin which are crosslinked with various types of sticker molecules [5] and the adsorption of polyelectrolytes onto oppositely charged surfaces [6]. Unbundling and desorption transitions arise from the competition between the energy gained by binding to an attractive potential well and the associated loss of configurational entropy. As one increases the bending rigidity and, thus, the persistence length, this entropy loss is reduced and the polymers bundle and adsorb more easily. One case which is particularly interesting from an experimental point of view is the adsorption of semiflexible polymers onto planar substrates in three dimensions. Since the shape fluctuations parallel to such a substrate are not affected by the interaction potential between polymer and substrate, this case is equivalent to bundling in two dimensions.

For bundling (or adsorption), the potential of the polymer/polymer (or polymer/surface) interactions contains both an attractive potential well and a repulsive hard wall or rod. On the one hand, all potential wells which arise from intermolecular forces are short-ranged in the sense that they decay faster than  $1/|z|^{2/3}$  for large separations  $|z|$  of the interacting objects [7]. On the other hand, these attractive wells may not only depend on  $|z|$ , but also



Fig. 1 – Left: bundling of two semiflexible polymers. Right: adsorption of a semiflexible polymer onto a planar substrate.

on the orientation of the polymers. One example for the latter situation is provided by crosslinkers or stickers which bind with a preferred angle to the semiflexible polymers such as  $\alpha$ -actinin or fimbrin which crosslink F-actin [5].

For all of these potentials, the competition between bending energy and configurational entropy leads to an unbundling or desorption transition at a certain critical temperature (or potential depth). Our analytical solutions give explicit expressions for these transition points as well as for the critical exponents which characterize the corresponding critical behavior. Two exponents,  $\chi$  and  $\theta$  <sup>(1)</sup>, characterize the probability distribution of the polymers. Another critical exponent,  $\nu_{\parallel}$ , governs the longitudinal correlation length and the singular part of the free energy. This implies that  $\nu_{\parallel}$  determines the order of the transition provided  $\nu_{\parallel} \geq 1$ .

Somewhat surprisingly, we find that the exponent  $\nu_{\parallel}$  is changed by the orientation dependence of the interaction potentials whereas this dependence does not affect the two exponents  $\chi$  and  $\theta$ . Therefore, two systems, which are characterized by the same values for the exponents  $\chi$  and  $\theta$ , may differ in the order of their transitions. One example is provided by desorption from a planar substrate which is *second* order if the interaction potential is independent of the polymer orientation, but *first* order if it is orientation-dependent. Different values for  $\nu_{\parallel}$  are also found for symmetric potential wells in the absence of hard walls. Furthermore, the hard-rod repulsion is argued to be *irrelevant* in  $d \geq 3$  dimensions.

Our analytical approach starts from the differential transfer matrix equation discussed previously in [8–10]. We study the corresponding eigenvalue equation for the localized ground state and derive a general integral expression for it. In order to obtain explicit solutions, we consider attractive potential wells with potential range  $\ell_a$  and determine the matching conditions at  $\ell_a$ . In the limit of *small*  $\ell_a$ , these matching conditions become analytically tractable and lead to two relations: the first relation determines the scaling form of the probability distribution and, thus, the critical exponents  $\chi$  and  $\theta$ ; the second relation determines the transition point and the critical exponent  $\nu_{\parallel}$ . Our results for the critical exponents are expected to apply to all short-ranged interaction potentials, *i.e.*, to all potentials which decay faster than  $1/|z|^{2/3}$  for large separations  $|z|$ .

*Model.* – We consider polymer chains (or long polymer segments) with bending rigidity  $\kappa$  and persistence length  $L_p = 2\kappa/T$ , where  $T$  is the temperature in energy units. These polymers have a contour length  $L_c$  which is comparable to or smaller than  $L_p$ . In this regime, the semiflexible polymer is oriented along one axis, say the  $x$ -axis as in fig. 1, and can be parameterized by displacements  $\mathbf{z}(x)$  perpendicular to the  $x$ -axis with  $0 < x < L$ , where  $L$  is the projected length of the polymer. We consider polymers in  $d = 1 + d_{\perp}$  dimensions for which  $\mathbf{z}$  is a  $d_{\perp}$ -dimensional vector. This parameterization is appropriate provided i) one does not focus on the properties of the polymer ends such as the distribution of the end-to-end distance [11] and ii) the longitudinal correlation length  $\xi_{\parallel}$  to be defined below is small compared to  $L_p$ .

<sup>(1)</sup>The exponent  $\chi$  was previously denoted by  $x$  or by  $\zeta_2$  and governs the contact probability which scales as  $1/\xi_{\parallel}^{\chi}$  with the longitudinal correlation length  $\xi_{\parallel}$ .

The conformations of the polymer are governed by the interplay between its bending energy  $\int_0^L dx \frac{1}{2} \kappa (\partial_x^2 \mathbf{z})^2$  and its potential energy  $\int_0^L dx V(\mathbf{z}(x))$ , where  $V(\mathbf{z}(x))$  contains an attractive potential well of range  $\ell_a$  which favours the straight configuration  $\mathbf{z}(x) = 0$ . The unbundling of a pair of semiflexible polymers interacting with the potential  $V(\mathbf{z}_1 - \mathbf{z}_2)$  is equivalent to the unbinding of a single polymer with relative coordinate  $\mathbf{z} = \mathbf{z}_1 - \mathbf{z}_2$  and effective  $\kappa = \kappa_1 \kappa_2 / (\kappa_1 + \kappa_2)$  from the external potential  $V(\mathbf{z}(x))$ .

We model the attractive part of the interaction potentials as spherical potential wells of radius  $\ell_a$ . Such binding potentials can arise from van der Waals forces, screened electrostatic interactions, and crosslinking molecules. In these cases, the potential range  $\ell_a$  is comparable to the polymer thickness, the Debye-Hückel screening length, and the size of the linker molecule, respectively. For van der Waals forces and for electrostatic interactions dominated by ion-ion interactions, the attractive potential does not depend on the orientation of the polymer segments. For crosslinker-mediated adhesion, on the other hand, such an orientation dependence arises if the linker molecules prefer to bind to polymer segments at a preferred angle as applies, *e.g.*, to the crosslinkers  $\alpha$ -actinin and fimbrin [5] which prefer to bind to F-actin at right angles. Therefore, we will consider generalized potential wells which depend on the tangent vector  $\mathbf{v} \equiv \partial_x \mathbf{z}$  and have the form

$$\begin{aligned} V_a(\mathbf{z}, \mathbf{v}) &= W \Phi_\Delta(\mathbf{v}) = G_\Delta \Phi_\Delta(\mathbf{v}) / c(d_\perp) \ell_a^{d_\perp} \quad \text{for } |\mathbf{z}| < \ell_a, \\ &= 0 \quad \text{for } |\mathbf{z}| > \ell_a \end{aligned} \quad (1)$$

with potential strength  $W \equiv G_\Delta / c(d_\perp) \ell_a^{d_\perp} < 0$ ,  $c(d_\perp) \equiv \pi^{d_\perp/2} / \Gamma(1 + d_\perp/2)$ , and the dimensionless function  $\Phi_\Delta(\mathbf{v})$ . This potential well attains the asymptotic form  $V_a(\mathbf{z}, \mathbf{v}) \approx G_\Delta \Phi_\Delta(\mathbf{v}) \delta(\mathbf{z})$  in the limit of small  $\ell_a$ . It will be convenient to consider a general class of functions  $\Phi_\Delta(\mathbf{v})$  which satisfy the homogeneity relation  $\Phi_\Delta(b\mathbf{v}) = b^{-d_\perp \Delta} \Phi_\Delta(\mathbf{v})$ . Orientation-independent interactions arising, *e.g.*, from electrostatic forces correspond to  $\Delta = 0$  and  $\Phi_0(\mathbf{v}) = 1$ ; linker molecules, which bind at right angles to *both* filaments, allow binding only for parallel polymer segments and correspond to  $\Delta = 1$  and  $\Phi_1(\mathbf{v}) = \delta(\mathbf{v})$ .

In order to study adsorption of semiflexible polymers on planar surfaces or to take the mutual avoidance of the polymers into account, we include a repulsive potential  $V_r(\mathbf{z})$  with  $V_r = \infty$  for  $|\mathbf{z}| < \ell_w$  with  $\ell_w < \ell_a$ . In  $d_\perp = 1$ , this is equivalent to a hard wall (or a half-space geometry) with  $z > 0$ ; in higher dimensions, the potential  $V = V_r$  excludes the polymer from a hard rod around  $|\mathbf{z}| = 0$ . In the following, we will study both purely attractive potentials  $V = V_a$  and potential wells in front of a hard wall or rod as described by  $V = V_a + V_r$ .

*Transfer matrix.* – It is convenient to measure all length scales in units of the persistence length  $L_p$  and all energies in units of  $T$ . Thus, we introduce the dimensionless quantities  $\bar{\mathbf{z}} = \mathbf{z}/L_p$ ,  $\bar{x} = x/L_p$ ,  $\bar{\mathbf{v}} = \mathbf{v}$  and  $\bar{V}(\bar{\mathbf{z}}, \bar{\mathbf{v}}) = L_p V(\bar{\mathbf{z}} L_p, \bar{\mathbf{v}}) / T$  (*e.g.*,  $\bar{\ell}_a = \ell_a / L_p$  and  $\bar{G}_\Delta = L_p^{1-d_\perp} G_\Delta / T$ ). In the following, we will use these dimensionless quantities but suppress the overbars for ease of notation. The restricted partition sum of a single semiflexible polymer is then given by

$$Z(\mathbf{z}, \mathbf{v}; L) = \int_{(\mathbf{0}, \mathbf{0}; \mathbf{0})}^{(\mathbf{z}, \mathbf{v}; L)} \mathcal{D} \mathbf{z}'(x) \exp \left[ - \int_0^L dx \left[ \frac{1}{4} (\partial_x^2 \mathbf{z}')^2 + V(\mathbf{z}', \partial_x \mathbf{z}') \right] \right], \quad (2)$$

where  $\mathbf{z} \equiv \mathbf{z}'(L)$  and  $\mathbf{v} \equiv \partial_x \mathbf{z}'(L)$  now denote the end points and end tangents of the chain. In the following, we will study (2) by transfer matrix methods. This leads to the differential equation [8, 9]

$$\partial_L Z = -\mathbf{v} \cdot \nabla_{\mathbf{z}} Z + \nabla_{\mathbf{v}}^2 Z - V(\mathbf{z}, \mathbf{v}) Z \quad (3)$$

with the boundary condition  $Z(\mathbf{z}, \mathbf{v}; 0) = \delta(\mathbf{z}) \delta(\mathbf{v})$ .

*Scaling behaviour.* – For  $V = 0$ , the solution of (3) has the scaling form

$$Z(\mathbf{z}, \mathbf{v}; L) = L^{-2d_{\perp}} \Omega_0\left(|\mathbf{z}|/L^{3/2}, |\mathbf{v}|/L^{1/2}, \vartheta\right), \quad (4)$$

where  $\vartheta$  is the angle enclosed by  $\mathbf{z}$  and  $\mathbf{v}$  (with  $\vartheta = 0, \pi$  for  $d_{\perp} = 1$ ). In this case, the shape function is given by  $\Omega_0(y, u, \vartheta) = (\frac{\sqrt{3}}{2\pi})^{d_{\perp}} \exp[-3y^2 + 3yu \cos \vartheta - u^2]$  [8, 10]. Expression (4) implies  $\langle |\mathbf{v}|^2 \rangle \sim L$  for the tangents and  $\langle |\mathbf{z}|^2 \rangle \sim L^3$  for the displacements.

If the polymer is bound to a sufficiently strong attractive potential, its partition function behaves as  $Z(\mathbf{z}, \mathbf{v}; L) \sim Z_E(\mathbf{z}, \mathbf{v}) \exp[-EL]$  for large system size  $L$ , where the ground state  $Z_E$  satisfies the eigenvalue equation

$$-EZ_E = -\mathbf{v} \cdot \nabla_{\mathbf{z}} Z_E + \nabla_{\mathbf{v}}^2 Z_E - V(\mathbf{z}, \mathbf{v}) Z_E \quad (5)$$

with ground-state energy  $E < 0$ . The normalization  $\int d^{d_{\perp}} \mathbf{z} \int d_{\perp}^d \mathbf{v} Z_E(\mathbf{z}, \mathbf{v})^2 = 1$  and the boundary condition for  $Z(\mathbf{z}, \mathbf{v}; 0)$  imply the asymptotic equality  $Z(\mathbf{z}, \mathbf{v}; L) \approx Z_E(\mathbf{z}, \mathbf{v}) Z_E(0, 0) \exp[-EL]$  for large  $L$ .

The attractive potential modifies the scaling result (4) in two ways: i) The system is now characterized by the longitudinal correlation length  $\xi_{\parallel} = 1/|E|$  parallel to the polymer which diverges upon approaching the unbinding transition at  $E = 0$ , and ii) the small-distance behaviour at  $z = 0$  is affected by the potential and we expect the more general scaling form

$$Z(\mathbf{z}, \mathbf{v}; L) = \xi_{\parallel}^{-\chi} |\mathbf{z}|^{\theta/2} \Omega\left(|\mathbf{z}|/\xi_{\parallel}^{3/2}, |\mathbf{v}|/|\mathbf{z}|^{1/3}, \vartheta\right) e^{-L/\xi_{\parallel}}, \quad (6)$$

where we used the relation  $\langle |\mathbf{v}|^2 \rangle \propto \langle |\mathbf{z}|^2 \rangle^{1/3}$  to reformulate the scaling in  $|\mathbf{z}|$ . Furthermore, we implicitly assumed a rotationally invariant potential  $V = V(|\mathbf{z}|, |\mathbf{v}|)$  for  $d_{\perp} > 1$ .

The scaling form (6) depends on the two exponents  $\chi$  and  $\theta$ , which are not independent but related by a normalization condition which gives  $\chi = 2d_{\perp} + 3\theta/2$  for  $\chi > 0$ . The latter relation was first derived in [8] for  $d_{\perp} = 1$ . For  $2d_{\perp} + 3\theta/2 < 0$ , the main contributions in the normalization integral come from small scales, which implies  $\chi = 0$  and thus the more general exponent relation  $\chi = \max(2d_{\perp} + \frac{3}{2}\theta, 0)$ . The dominance of small scales for  $2d_{\perp} + 3\theta/2 < 0$  and  $\chi = 0$  indicates that a finite fraction of polymer segments remains bound at the transition point, which is analogous to the behavior of strings in  $d \geq 1 + 4$  dimensions [12].

*Potential well in 1 + 1 dimensions.* – We first consider a purely attractive potential  $V = V_a$  as defined in (1) in 1 + 1 dimensions. We start from a matching procedure at the boundary of the potential well, *i.e.*, at  $|z| = \ell_a$ , from which we determine the ground state  $Z_E$  of the eigenvalue equation (5). In the exterior region  $|z| > \ell_a$ , where  $V$  vanishes, the ground state has the form

$$Z_E(z, v) = \int d\alpha \Theta(\alpha z) A_E(\alpha) e^{-\alpha z} \psi_{\alpha, E}(v), \quad (7)$$

where  $\Theta(y)$  is the Heaviside step function. The function  $\psi_{\alpha, E}(v)$  fulfills the eigenvalue equation  $(\alpha v + \partial_v^2) \psi_{\alpha, E} = -E \psi_{\alpha, E}$  and has the form

$$\psi_{\alpha, E}(v) = \psi_{-\alpha, E}(-v) = \alpha^{-1/6} Ai\left[-\alpha^{1/3} v - \frac{E}{\alpha^{2/3}}\right] \quad \text{for } \alpha > 0, \quad (8)$$

where  $Ai(x)$  denotes the Airy function [13]. In order to determine the coefficient function  $A_E(\alpha)$ , we integrate over the interior region  $|z| < \ell_a$  on both sides of (5), which leads to the matching condition

$$v(Z_E(\ell_a, v) - Z_E(-\ell_a, v)) \approx -G_{\Delta} \Phi_{\Delta}(v) \frac{1}{2} (Z_E(\ell_a, v) + Z_E(-\ell_a, v)) \quad (9)$$

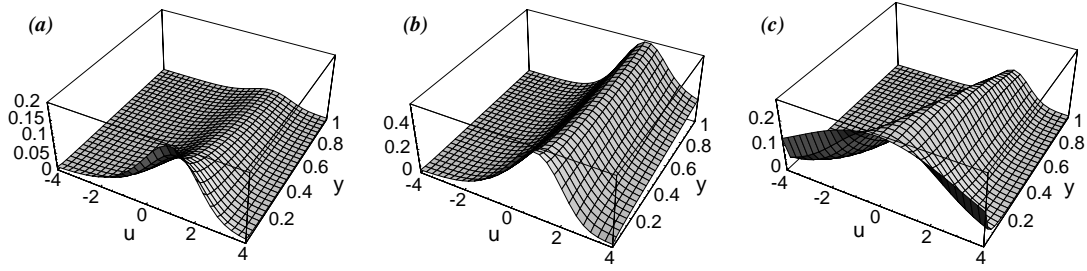


Fig. 2 – Shape functions  $\Omega(y, u)$  in 1+1 dimensions: (a), (b), and (c) exhibit the functional dependence as given by the expressions (12), (14), and (4) corresponding to interactions potentials  $V = V_a$ ,  $V = V_a + V_r$  and  $V = 0$ , respectively.

in the limit of small  $\ell_a$ . We now insert the integral representation (7) for  $Z_E$  which leads, after some computation, to two relations. The first relation gives the explicit expression

$$A_E(\alpha) = \mathcal{N}_E \psi_{\alpha, E}(0) \tag{10}$$

for the coefficient function  $A_E(\alpha)$ , where  $\mathcal{N}_E$  is an  $\alpha$ -independent normalization constant. This relation determines the distribution  $Z_E(z, v)$  via (7) which is found to be *independent* of  $\Phi_\Delta(v)$ . The normalization condition for  $Z_E$  leads to  $\mathcal{N}_E \sim 1/\ln^{1/2}(1/\ell_a|E|^{3/2})$ . In this way, we *derive* the scaling form (6) for the partition sum of the polymer with exponents

$$\theta_a = -4/3 \quad \text{and} \quad \chi_a = 0 \text{ (log)}, \tag{11}$$

and the shape function

$$\Omega_a(y, u) \propto \int_0^\infty d\alpha \exp[-\alpha] \alpha^{-1/3} Ai \left[ \left( \frac{y}{\alpha} \right)^{2/3} \right] Ai \left[ -u\alpha^{1/3} + \left( \frac{y}{\alpha} \right)^{2/3} \right] \tag{12}$$

as plotted in fig. 2. Apart from the logarithmic singularity, the exponents as given by (11) have been obtained previously by field-theoretic methods [10].

The matching condition (9) leads to a second implicit relation  $E = E(G_\Delta)$  between the ground-state energy  $E$  and the strength  $G_\Delta$  of the potential in (1). This relation determines the transition point and, thus, the critical potential depth  $G_{\Delta, c}$  for binding via the implicit equation  $0 = E(G_{\Delta, c})$ . In contrast to the result for the segment distribution, the relation  $E = E(G_\Delta)$  is non-universal in the sense that it depends on  $\Delta$  and, thus, on the potential function  $\Phi_\Delta(v)$ .

The critical potential depth  $G_{\Delta, c}$  is found to behave as  $|G_{\Delta, c}| \approx |g_{\Delta, c}| \ell_a^{(1+\Delta)/3}$  for small potential range  $\ell_a$  with  $|g_{0, c}| = 1/\Gamma(1/3) Ai[0]$  for  $\Delta = 0$  and  $|g_{1, c}| = 1/\Gamma(2/3) Ai^2[0]$  for  $\Delta = 1$ . Furthermore, an expansion around  $G_\Delta = G_{\Delta, c}$  and  $E = 0$  determines the exponent  $\nu_\parallel$  for the longitudinal correlation length  $\xi_\parallel$  which diverges as  $\xi_\parallel \propto |g_\Delta - g_{\Delta, c}|^{-\nu_\parallel} \sim |t|^{-\nu_\parallel}$ , where  $t$  is the reduced temperature (note that the rescaled potential strength  $G_\Delta \sim 1/T^2$ ). This gives  $1/\nu_\parallel = \min((1 + \Delta)/2, 1)$  for the correlation length exponent; for  $\Delta = 0$ , this implies  $\nu_\parallel = 2$ . For  $\Delta = 1$ , one has  $\xi_\parallel \sim |\log t|/t$  and  $\nu_\parallel = 1 + \log$ . The free energy of the polymer is given by the ground-state energy  $f = E \sim 1/\xi_\parallel$  and we find a *second-order* delocalization transition for  $0 \leq \Delta \leq 1$ .

*Potential well with hard wall in 1 + 1 dimensions.* – Next, we consider an attractive potential well in front of a hard wall as described by  $V = V_a + V_r$  in 1 + 1 dimensions. Outside of the well, *i.e.*, for  $z > \ell_a$ , the ground state  $Z_E$  can again be written as in (7), and the coefficient function  $A_E(\alpha)$  can again be determined by the corresponding matching condition. The additional boundary conditions  $Z_E(0, v) = 0$  for  $v > 0$ , which is imposed by the hard wall at  $z = 0$ , can be incorporated by eigenfunctions  $\phi_{\alpha, E}(v)$  which have been explicitly determined in ref. [14] for  $V = V_r$ , *i.e.*, in the absence of the potential well.

In this way, we derive again the scaling form (6) for the partition sum of the polymer. The critical exponents now have the values

$$\theta_{a,r} = -5/3 \quad \text{and} \quad \chi_{a,r} = \max(-1/2, 0) = 0 \quad (13)$$

and the shape function is given by

$$\Omega_{a,r}(y, u) \propto \int_0^\infty d\alpha \exp[-\alpha] \alpha^{-1/6} \exp\left[-\frac{2}{3}\frac{y}{\alpha}\right] Ai\left[-u\alpha^{1/3} + \left(\frac{y}{\alpha}\right)^{2/3}\right], \quad (14)$$

where we have used the asymptotic behavior  $\phi_{\alpha, E}(v) \approx \pi^{-1}(3v)^{1/2} \exp[-2E^{3/2}/3\alpha]$  of the eigenfunctions for  $0 < \alpha^{1/3}v \ll 1$  as obtained in [14]. As in the absence of the repulsive wall, the shape function  $\Omega$  is again independent of  $\Delta$ , which reflects the  $v$ -dependence of the binding potential; for  $E = 0$  it reduces to the special case treated in ref. [8]. The matching condition leads again to a second relation from which we obtain the critical binding strength  $|G_{\Delta,c}| \sim \ell_a^{(1+\Delta)/3}$  in the limit of small  $\ell_a$ . For  $\Delta > 0$ , non-singular terms dominate in the expansion of the free energy  $f = E(G_\Delta)$  around  $G_\Delta = G_{\Delta,c}$ , and the transition is *first* order with  $\nu_{\parallel} = 1$ , whereas it becomes *second* order with  $\nu_{\parallel} = 1 + \log$  for  $\Delta = 0$ . As in the case of strings in  $d \geq 1 + 4$  dimensions [12], these first-order unbinding transitions are peculiar, however, since the correlation length  $\xi_{\parallel} = 1/|E|$  diverges upon approaching the transition at  $E = 0$ , and polymer fluctuations exhibit scaling properties determined by the shape function  $\Omega(0, u)$ .

*Unbundling in 1 +  $d_{\perp}$  dimensions.* – For  $1 + d_{\perp} > 2$ , the solution of (5) depends on the angle  $\vartheta$  between  $\mathbf{z}$  and  $\mathbf{v}$  as in (6), which considerably complicates the analytical treatment. Progress can be made via two approximations in terms of the scaling variable  $u \equiv |\mathbf{v}|/|\mathbf{z}|^{1/3}$ : i) the large- $u$  approximation which leads to  $Z_E(|\mathbf{z}|, |\mathbf{v}|, \vartheta) \propto \delta(\vartheta)$ , *i.e.*, to a distribution which is localized around  $\vartheta = 0$ ; and ii) the small- $u$  approximation which leads to a spherically symmetric ground state  $Z_E(|\mathbf{z}|, |\mathbf{v}|, \vartheta) = Z_E(|\mathbf{z}|, |\mathbf{v}|, 0)$ . For both approximations, we can construct solutions using analogous procedures as for  $d_{\perp} = 1$ . First, a solution in the region  $|\mathbf{z}| > \ell_a$  is constructed and integration over the small sphere  $|\mathbf{z}| < \ell_a$  on both sides of (5) gives matching conditions which determine the corresponding coefficient functions.

For  $V = V_a$ , *i.e.*, without a hard rod, both approximations lead to the scaling form (6) with exponents  $\theta_a = 4(1 - 2d_{\perp})/3$  and  $\chi_a = \max(2(1 - d_{\perp}), 0)$ . As for  $d_{\perp} = 1$ , we find that these exponents are universal and do not depend on  $\Delta$ . It is interesting to note that the so-called necklace model [15] leads to the same values for  $\theta_a$  and  $\chi_a$  if one determines the contact probability for tangential contacts with the partition sum of the free polymer as given by (4). The latter values are also obtained using the field-theoretic methods in [10].

The correlation length exponent  $\nu_{\parallel}$ , on the other hand, is again found to depend on  $\Delta$ . Both the small- $u$  approximation and the necklace model lead to  $1/\nu_{\parallel} = \min((3d_{\perp} - 2 + d_{\perp}\Delta)/2, 1)$  which implies a second- (or higher-) order transition for  $\nu_{\parallel} > 1$  and a first-order transition for  $0 < \nu_{\parallel} < 1$ . For  $d_{\perp} = 2$ , the physically most interesting case, this implies  $\nu_{\parallel} = 1$  and a *first*-order unbundling transition in agreement with the Monte Carlo simulations

in [10]. The critical binding strength behaves as  $|G_{\Delta,c}| \sim \ell_a^{(3d_{\perp}-2+d_{\perp}\Delta)/3}$  for small  $\ell_a$ . When expressed in terms of the original potential depth  $W$  as defined in (1), this implies the critical depth  $|W_c| \sim (T/L_p)(L_p/\ell_a)^{(2-d_{\perp}\Delta)/3}$ . For  $\Delta = 0$ , this agrees with a two-state model as in [16] when the loss of entropy is estimated by  $\sim (T/L_p)(L_p/\ell_a)^{2/3}$  [17].

Finally, we want to argue that the hard-rod potential  $V = V_r$  is irrelevant in  $d \geq 1 + 2$  dimensions. This is expected from the large- $u$  approximation for  $V = V_a$  which leads to the shape function  $\Omega_a(0, u, \vartheta) \sim \exp[-u^3/9]$  at the transition point with  $u = |v|/|z|^{1/3}$  as before. In  $d = 1 + 1$ , essentially the same behavior of  $\Omega_a(0, u)$  is found for  $V = V_a + V_r$ , *i.e.*, for a potential well in the *presence* of a hard wall, whereas  $\Omega_a(0, u)$  decays as an inverse power in  $u$  for  $V = V_a$ . Thus, the insertion of the hard rod in  $d \geq 1 + 2$  should not change the critical behavior of the polymers, and the critical exponents given above should also apply for  $V = V_a + V_r$ . We have confirmed this expectation by Monte Carlo simulations in  $d = 1 + 2$  dimensions as will be described elsewhere. For strings in  $1 + d_{\perp}$  dimensions, the hard rod becomes irrelevant precisely in  $d = 1 + 2$  dimensions as follows by extending the results of [12].

*Conclusion.* – We have studied unbundling and desorption transitions of semiflexible polymers by analytical methods starting from the differential transfer matrix equation (5) for the ground state. We considered attractive potential wells, which can depend on the polymer orientation as described by the function  $G_{\Delta}\Phi_{\Delta}(v)$ , see (1), with scaling index  $0 \leq \Delta \leq 1$ . The distribution functions for the polymer displacements and orientations are shown to have the scaling form (6) and to be *independent* of  $\Delta$ . In contrast, the critical exponent  $\nu_{\parallel}$  for the longitudinal correlation length  $\xi_{\parallel}$  is found to depend explicitly on  $\Delta$ . This leads to a singular part of the free energy  $\sim 1/\xi_{\parallel}$  which determines the order of the transition provided  $\nu_{\parallel} \geq 1$ . Therefore, two potentials which differ in  $\Delta$  can lead to transitions of different order even though the distribution functions have the same scaling form. This happens in  $d = 1 + 1$  dimensions in the presence of a hard wall which is equivalent to the experimentally accessible case of desorption transitions from a planar substrate in  $d = 1 + 2$  dimensions.

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