

Adsorption transition of a self-avoiding polymer chain onto a rigid rod

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 S1731

(<http://iopscience.iop.org/0953-8984/17/20/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 04:51

Please note that [terms and conditions apply](#).

Adsorption transition of a self-avoiding polymer chain onto a rigid rod

Andreas Hanke

Department of Physics, University of Texas at Brownsville, Brownsville, TX 78520, USA

E-mail: hanke@phys.utb.edu

Received 8 February 2005, in final form 23 March 2005

Published 6 May 2005

Online at stacks.iop.org/JPhysCM/17/S1731

Abstract

The subject of this work is the adsorption transition of a long flexible self-avoiding polymer chain onto a rigid thin rod. The rod is represented by a cylinder of radius R with a short-ranged attractive surface potential for the chain monomers. General scaling results are obtained by using renormalization group arguments in conjunction with available results for quantum field theories with curved boundaries (McAvity and Osborn 1993 *Nucl. Phys. B* **394** 728). Relevant critical exponents are identified and estimated using geometric arguments.

1. Introduction

Polymers and polymer solutions belong to the most intensively studied group of objects in condensed matter physics [1–3]. The adsorption of polymers on surfaces and interfaces is of special importance [4]. Adsorption of free polymers in solution on the container wall or other boundaries occurs in the presence of attractive interactions between the surface and the chain monomers. Examples of such interactions include Coulomb and van der Waals forces, and more specific molecular interactions. Coulomb forces are screened by counter-ions in the solution and can be tuned to some extent by adding salt to the solvent. Thus on changing the properties of the solvent an individual polymer chain can undergo a reversible transition from a freely floating, desorbed state to an adsorbed state in which the chain monomers are close to the surface on average. The adsorption of polymers on flat surfaces has been studied theoretically and experimentally, and is now well understood [1, 4–6]. Due to the importance to colloidal dispersions the interaction of polymers with spherical and rodlike particles has been studied as well [7–11]. The adsorption of flexible polymers on rodlike particles is relevant, for example, for gels [9], and for the binding of flexible polymers to relatively stiff biomolecules such as DNA [12]. Another class of polymer adsorption transitions involve two flexible self-avoiding but mutually attracting polymers which can form a bound, double-stranded, so-called ‘zipped’

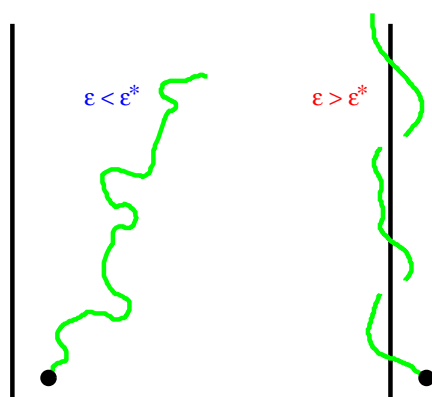


Figure 1. A long flexible self-avoiding polymer chain (green) adsorbs onto a thin elongated rod (black) if the adsorption energy per chain monomer \mathcal{E} is larger than the threshold value \mathcal{E}^* .

state. A prominent example of this kind of transition is the denaturation transition of double-stranded DNA [13, 14] which recently attracted considerable attention regarding its statistical mechanical properties and thermodynamic order [15–20] (for a recent review on the biophysics related to DNA topology, see [21]). The DNA denaturation transition is usually modelled in such a way that monomer i of one strand can only interact with monomer i of the other strand, reflecting the key–lock principle of natural, inhomogeneous DNA with its specific sequence of base pairs. Two-chain systems in which any monomer of one chain can interact with any monomer of the other chain include diblock copolymers, which consist of linear chains of N monomers of type A followed by N' monomers of type B , with different AA , BB , and AB interactions; systems of this kind have been intensively studied as well [22–27]. Recently it was found that self-avoiding mutually attracting diblock copolymers can adopt a zipped state in which the two components form a bound, double-stranded structure which however remains swollen and does not assume compact configurations. The zipped state is located between a swollen, unbound high-temperature state and a compact low-temperature state, separated by second-order and first-order phase transitions, respectively [28–30].

In this work we focus on the adsorption transition of a long flexible self-avoiding polymer chain onto a rigid thin elongated rod, as shown in figure 1. We assume that the rod is endowed with a short-ranged surface potential, or adsorption energy, \mathcal{E} , for the chain monomers; the more positive \mathcal{E} , the more attractive the interaction. Thus, on increasing \mathcal{E} from a low value, at some threshold value \mathcal{E}^* the chain is expected to undergo a transition from an unbound, free state to a bound state in which the overall gain in binding energy compensates the loss of configurational entropy. An interesting feature of this transition is the fact that it represents a true phase transition in the thermodynamic sense, the adsorbed state forming an elongated, aligned structure; see figure 1. In contrast, for a particle of finite size, a self-avoiding polymer chain cannot undergo a true adsorption phase transition due to steric constraints. The focus of the present work is on the former case. Since the polymer adsorption transition is characterized by large fluctuations we expect scaling and universal behaviour. We thus use the renormalization group to obtain general scaling results for the chain partition function. We also obtain estimates for relevant critical exponents by geometric arguments. Before we introduce and study our model in section 2 we recall some general ideas and concepts for later reference. In section 1.1 we discuss typical scaling arguments related to the polymer adsorption transition.

Since our work strongly relies on field-theoretical methods, in section 1.2 and the appendix we sketch the mapping of the polymer system onto the Ginzburg–Landau model.

1.1. General scaling behaviour

Consider the adsorption of a long flexible polymer chain onto an object \mathcal{S} . For the time being, this object can be a surface, a thin rod, another flexible polymer chain or any other extended manifold that allows for a thermodynamic adsorption phase transition. The quantity of interest is the partition function Z of the chain with one end fixed close to the object \mathcal{S} and the other end moving freely. Upon adjusting the system’s thermodynamic variables close to the adsorption transition point, only the number of chain monomers $N \gg 1$ and the adsorption energy $\mathcal{E} \approx \mathcal{E}^*$ remain as relevant parameters, where \mathcal{E}^* is the adsorption energy at the transition point. The partition function Z is expected to obey the scaling

$$Z(N, \mathcal{E}) \sim p^N N^{\gamma'-1} f[(\mathcal{E} - \mathcal{E}^*)N^\Phi] \tag{1}$$

where p is the lattice-dependent connectivity constant and γ', Φ are critical exponents. The scaling function $f(x)$ is regular at $x = 0$ since $Z(N, \mathcal{E})$ has no singularity for finite N and $\mathcal{E} \approx \mathcal{E}^*$. The exponent γ' thus characterizes the scaling of Z right at the transition point: $Z(N, \mathcal{E}^*) \sim p^N N^{\gamma'-1}$. Note that γ' is not necessarily equal to the critical exponent γ for an unbounded, free chain, for which $Z_{\text{free}}(N) \sim p^N N^{\gamma-1}$ (compare equation (56) in section 2.3, with γ_1 introduced in equation (52) and $L \sim N$). The exponent Φ is referred to as the crossover exponent. Since $-\mathcal{E}$ acts as a chemical potential for monomers close to \mathcal{S} , the number N_S of adsorbed monomers scales as

$$N_S \sim \frac{d}{d\mathcal{E}} \ln Z(N, \mathcal{E}). \tag{2}$$

Equation (1) implies three distinct scaling regimes for N_S .

- (i) $\mathcal{E} = \mathcal{E}^*$. Equations (1) and (2) yield

$$N_S \sim N^\Phi, \quad \mathcal{E} = \mathcal{E}^*, \quad N \rightarrow \infty. \tag{3}$$

For $0 < \Phi < 1$ this implies that N_S grows with N but the *fraction* of adsorbed monomers, N_S/N , vanishes for $N \rightarrow \infty$. For $\Phi = 1$, the behaviour $N_S \sim N$ at $\mathcal{E} = \mathcal{E}^*$ indicates that the adsorption transition is of first order.

- (ii) $\mathcal{E} < \mathcal{E}^*$. Equation (1) implies that the scaling behaviour of Z for $N \rightarrow \infty$ is governed by the behaviour of $f(x)$ for $x \rightarrow -\infty$, regardless of the precise value of \mathcal{E} . In this case \mathcal{S} is repulsive for the chain monomers and N_S stays finite even for $N \rightarrow \infty$.
- (iii) $\mathcal{E} > \mathcal{E}^*$. The chain adopts an adsorbed state and stays close to \mathcal{S} on average. Thus, $N_S \sim N$, which implies a *finite* fraction of adsorbed monomers for $N \rightarrow \infty$:

$$F(\mathcal{E}) \equiv \lim_{N \rightarrow \infty} \frac{N_S(N, \mathcal{E})}{N} > 0, \quad \mathcal{E} > \mathcal{E}^*. \tag{4}$$

To analyse the behaviour of $F(\mathcal{E})$ it is useful to consider the grand canonical ensemble. The partition function in the grand canonical ensemble, $\mathcal{X}(\mu, \mathcal{E})$, is related to $Z(N, \mathcal{E})$ by a Laplace transform:

$$\mathcal{X}(\mu, \mathcal{E}) = \int_0^\infty dN e^{-\mu N} Z(N, \mathcal{E}), \tag{5}$$

where μ is the chemical potential conjugate to N . Equation (5) is valid for $\mu > \mu_c$ with $\mu_c = \ln p$. One is allowed to set $p = 1$ for simplicity, so that $\mu_c = 0$. Equation (1) then implies the scaling behaviour

$$\mathcal{X}(\mu, \mathcal{E}) \sim \mu^{-\gamma'} g[(\mathcal{E} - \mathcal{E}^*)\mu^{-\Phi}], \quad \mu > 0. \tag{6}$$

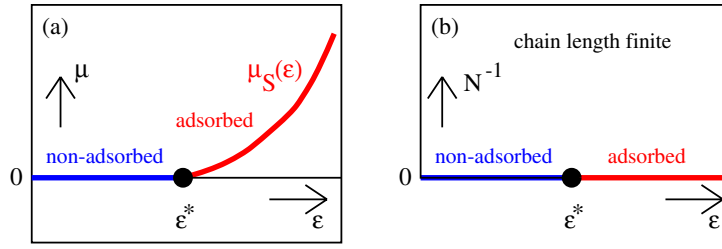


Figure 2. Typical phase diagrams for polymer adsorption in the (a) grand canonical ensemble (μ, \mathcal{E}) and (b) canonical ensemble (N, \mathcal{E}) . The manifold \mathcal{S} on which the polymer adsorbs can be any object which allows for an adsorbed thermodynamic state. For $N \rightarrow \infty$, the fraction of adsorbed monomers N_S/N vanishes for $\mathcal{E} < \mathcal{E}^*$ (blue lines) whereas it is finite for $\mathcal{E} > \mathcal{E}^*$ (red lines). The shape of the red line in (a) is given by the function $\mu_S(\mathcal{E})$ in equation (8). Compare figure 1.

By reasoning similar to that below equation (1) one finds that the scaling function $g(y)$ is regular at $y = 0$ and γ' characterizes the scaling of \mathcal{X} right at the transition point: $\mathcal{X}(\mu, \mathcal{E}^*) \sim \mu^{-\gamma'}$. On the other hand, we know that for $\mathcal{E} > \mathcal{E}^*$ the chain takes an adsorbed state form. For the grand canonical ensemble this implies, for given $\mathcal{E} > \mathcal{E}^*$, that $N_S \rightarrow \infty$ for $\mu \searrow \mu_S(\mathcal{E})$ with some $\mu_S(\mathcal{E}) > 0$. In this limit we thus expect the scaling behaviour $\mathcal{X}(\mu, \mathcal{E}) \sim (\mu - \mu_S)^{-\gamma_S}$ where γ_S is characteristic for the *adsorbed* state and *different* from γ' . For example, if \mathcal{S} is another flexible polymer chain, the adsorbed state forms a double-stranded structure which, as a whole, behaves like an unbounded, free, self-avoiding chain, which implies $\gamma_S = \gamma$ in this case [15]. Using equation (6) it follows that the scaling function $g(y)$ must have a singularity at some $y_S > 0$ of the form

$$g(y \nearrow y_S) \sim (y_S - y)^{-\gamma_S}. \quad (7)$$

The relation $(\mathcal{E} - \mathcal{E}^*)\mu_S^{-\Phi} = y_S$ determines the shape of the line $\mu_S(\mathcal{E})$ as

$$\mu_S(\mathcal{E}) \sim (\mathcal{E} - \mathcal{E}^*)^{1/\Phi}, \quad \mathcal{E} > \mathcal{E}^*. \quad (8)$$

Figure 2 shows typical phase diagrams for polymer adsorption in the grand canonical ensemble (fixed μ) and canonical ensemble (fixed N).

According to the above, for $\mathcal{E} > \mathcal{E}^*$, $\mathcal{X}(\mu, \mathcal{E})$ in equation (5) has a singularity for $\mu \searrow \mu_S(\mathcal{E}) > 0$, and $N (\geq N_S)$ diverges in this limit. This, in turn, implies

$$Z(N, \mathcal{E}) \sim \exp[\mu_S(\mathcal{E})N], \quad \mathcal{E} > \mathcal{E}^*, \quad N \rightarrow \infty. \quad (9)$$

Using equation (2) one finds

$$N_S \sim N \frac{d}{d\mathcal{E}} \mu_S(\mathcal{E}), \quad (10)$$

and thus, using equations (4) and (8),

$$F(\mathcal{E}) = \lim_{N \rightarrow \infty} \frac{N_S}{N} \sim \frac{d}{d\mathcal{E}} \mu_S(\mathcal{E}) \sim (\mathcal{E} - \mathcal{E}^*)^\kappa, \quad \mathcal{E} > \mathcal{E}^*, \quad (11)$$

where the exponent κ is related to the crossover exponent Φ in equation (3) by

$$\kappa = \frac{1 - \Phi}{\Phi}. \quad (12)$$

In particular, for $\Phi = 1$ the fraction $\lim_{N \rightarrow \infty} N_S/N$ jumps from zero for $\mathcal{E} < \mathcal{E}^*$ to a finite value for $\mathcal{E} > \mathcal{E}^*$, which is then independent of \mathcal{E} ; this corresponds to a first-order transition (compare case (i) above).

The scaling behaviours (3) and (11), (12) have been proven rigorously for the polymer adsorption transition on a *flat* surface [5, 6]. This system is closely related to the semi-infinite Ginzburg–Landau model—see [31–33] for reviews; the mapping of the polymer system on the Ginzburg–Landau model is discussed below. The scaling behaviours (3) and (11), (12) also hold reasonably well in a recent numerical study of the DNA denaturation transition [15].

1.2. Mapping of the polymer system onto the Ginzburg–Landau model

According to Edwards’ continuous chain model we represent the configuration of a linear chain of length L by a curve $\mathbf{R}(s)$, parameterized by its arc length s , in D -dimensional space. The chain length L is proportional to the number of chain monomers N . In the presence of an external potential $V(\mathbf{r})$ the partition function of the chain is given by

$$Z^{(2)}(\mathbf{r}, \mathbf{r}'; L) = \int_{\mathbf{r}}^{\mathbf{r}'} \mathcal{D}\mathbf{R} \exp\left\{-\frac{1}{4} \int_0^L ds \left(\frac{d\mathbf{R}}{ds}\right)^2\right\} \exp\left\{-\int d^D r \left[V(\mathbf{r})\rho(\mathbf{r}) + \frac{u}{6}\rho^2(\mathbf{r})\right]\right\} \quad (13)$$

with the monomer density

$$\rho(\mathbf{r}) = \int_0^L ds \delta^D(\mathbf{r} - \mathbf{R}(s)). \quad (14)$$

The symbol $\int_{\mathbf{r}}^{\mathbf{r}'}$ $\mathcal{D}\mathbf{R}$ denotes functional integration over all chain configurations with the chain ends fixed at \mathbf{r} and \mathbf{r}' . The superscript ‘(2)’ on Z indicates that the chain is fixed at both ends. The coupling constant u of the $\rho^2(\mathbf{r})$ interaction characterizes the strength of the contact interaction between chain monomers: $u = 0$ describes a Gaussian random walk whereas $u > 0$ describes a self-avoiding chain. The case $u < 0$ is related to the polymer collapse transition to a compact state in a poor solvent [34, 35]; in this work we do not consider this collapse transition, and therefore exclude the case $u < 0$.

As first noticed by de Gennes [36], the polymer system can be mapped on the Ginzburg–Landau model of an n -component order parameter field $\vec{\Phi} = (\Phi_1, \dots, \Phi_n)$ in the limit $n \rightarrow 0$. It is worthwhile to note that this mapping not only works in perturbation theory but already at the level of the Hamiltonian in the Ginzburg–Landau model. The derivation, using a Gaussian transformation to linearize the $\rho^2(\mathbf{r})$ interaction in equation (13) [37], is left to the appendix. The result is

$$Z^{(2)}(\mathbf{r}, \mathbf{r}'; L) = \mathcal{L}_{t \rightarrow L} \lim_{n \rightarrow 0} \langle \Phi_1(\mathbf{r}) \Phi_1(\mathbf{r}') \rangle \quad (15)$$

where

$$\langle \Phi_1(\mathbf{r}) \Phi_1(\mathbf{r}') \rangle = \int \mathcal{D}\vec{\Phi} \Phi_1(\mathbf{r}) \Phi_1(\mathbf{r}') e^{-\mathcal{H}(\vec{\Phi})} \quad (16)$$

is the two-point correlation function in the Ginzburg–Landau model with the standard Hamiltonian [38, 39]

$$\mathcal{H}\{\vec{\Phi}\} = \int d^D r \left[\frac{1}{2} (\nabla \vec{\Phi})^2 + \frac{t}{2} \vec{\Phi}^2 + \frac{1}{2} V(\mathbf{r}) \vec{\Phi}^2 + \frac{u}{24} (\vec{\Phi}^2)^2 \right]. \quad (17)$$

The operation

$$\mathcal{L}_{t \rightarrow L} = \frac{1}{2\pi i} \int_C dt e^{tL} \quad (18)$$

acting on the correlation function in equation (15) is an inverse Laplace transform in which the integration path C in the complex t -plane is a parallel to the imaginary axis to the right of

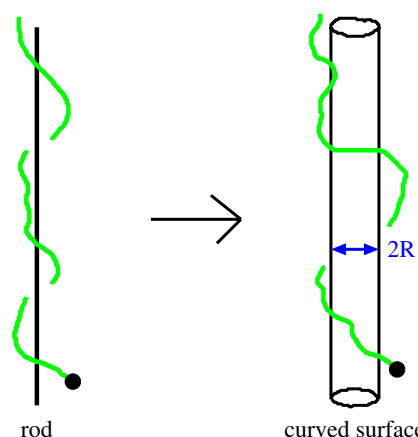


Figure 3. The rod is represented by a cylinder with finite radius R . This allows one to use available results for field theories with curved boundaries, but introduces the additional variable R into the problem. Compare figure 1.

all singularities. Equations (15)–(18) describe the statistics of the polymer chain in terms of properties of the near-critical ferromagnetic n -vector model in the limit $n \rightarrow 0$. In the context of the n -vector model, the parameter $t \sim T - T_c$ describes the deviation of the temperature T from the critical temperature T_c . The form of the interaction involving the potential $V(\mathbf{r})$ in equation (17) shows that the $O(n)$ -invariant scalar $\vec{\Phi}^2$ is related to the monomer density $\rho(\mathbf{r})$ of the polymer chain in equation (13). Thus, translated to the polymer system, the term $\vec{\Phi}^2 \cdot \vec{\Phi}^2$ is related to the contact interaction between chain monomers and t plays the role of a chemical potential for chain monomers in the bulk.

2. Polymer adsorption transition onto a rigid rod

The objective of this work is the study of the adsorption of a long flexible polymer chain onto a rigid thin rod. However, for the time being we model the rod as an infinitely elongated cylinder with small but finite radius R . The introduction of a finite cylinder radius R is necessary since the limit of a rod with zero radius turns out to be too singular for the present field-theoretical treatment; see figure 3 and the discussion below equation (29). On the other hand, the fact that the adsorption transition now takes place on a *surface*, albeit a curved one, allows us to take advantage of available results for field theories with curved boundaries [40]; see section 2.3 below. The chain of total length $L_0 \sim N$, where N is the number of chain monomers, is fixed with one end at the point \mathbf{r}_S on the cylinder surface S while the other end is moving freely. The cylinder surface is endowed with a short-ranged surface potential c_0 acting on the chain monomers, and it is understood that the chain monomers are excluded from the interior of the cylinder. The potential $V(\mathbf{r})$ in equation (13) is thus given by

$$V(\mathbf{r}) = c_0 \int_S dS' \delta^D(\mathbf{r} - \mathbf{r}'_S) \quad (19)$$

and $V(\mathbf{r}) = \infty$ if \mathbf{r} is located in the interior of the cylinder. By virtue of equation (15), the chain partition function is given by

$$Z(L_0) = \int_V d^D r' Z^{(2)}(\mathbf{r}_S, \mathbf{r}'; L_0) = \mathcal{L}_{t_0 \rightarrow L_0} \lim_{n \rightarrow 0} \chi(t_0). \quad (20)$$

The integration volume V is the outer space of the cylinder bounded by the cylinder surface S . On the right-hand side, $\chi(t_0) \equiv \chi(\mathbf{r}_S; t_0)$, where the *susceptibility* $\chi(\mathbf{r}; t_0)$ in the Ginzburg–Landau model is obtained by integrating the two-point correlation function, i.e.

$$\chi(\mathbf{r}; t_0) = \int_V d^D r' \langle \Phi_1(\mathbf{r}) \Phi_1(\mathbf{r}') \rangle, \quad (21)$$

in a Ginzburg–Landau-type field theory with Hamiltonian [31–33]

$$\mathcal{H}\{\Phi\} = \int_V d^D r \left[\frac{1}{2} (\nabla \vec{\Phi})^2 + \frac{t_0}{2} \vec{\Phi}^2 + \frac{u_0}{24} (\vec{\Phi}^2)^2 \right] + \int_S dS \frac{c_0}{2} \vec{\Phi}^2 \quad (22)$$

of an n -component order parameter field $\vec{\Phi} = (\Phi_1, \dots, \Phi_n)$. In the following we will understand $\chi(\mathbf{r}; t_0)$ as the chain partition function in the grand canonical ensemble, where t_0 is conjugate to L_0 (compare section 1.1 with $t_0 \sim \mu$, $L_0 \sim N$, and $c_0 \sim -\mathcal{E}$). The subscript ‘0’ on c_0, t_0, L_0, u_0 is used to distinguish these parameters from their renormalized counterparts that will be introduced below. If $\mathbf{r} = \mathbf{r}_S$ in $\chi(\mathbf{r}; t_0)$ we suppress the argument \mathbf{r}_S since χ does not depend of the choice of \mathbf{r}_S by symmetry; compare equation (20).

Before we proceed with the renormalization of the model defined by equation (22) we review some cases in which results are available. To this end it is useful to consider not only a cylinder in $D = 3$ dimensions but bodies of more general shape. The ‘generalized cylinders’ have an infinitely extended axis of dimension $D - d$ and a curved surface with constant curvature radius R in the subspace of co-dimension d .¹ The axis can be the axis of an ordinary cylinder in three dimensions, for which $(d, D) = (2, 3)$, the mid-plane of a plate ($d = 1$), or the centre of a sphere ($d = D$). The explicit form of a ‘generalized cylinder’ is given by the set $\{\mathbf{r} = (\mathbf{r}_\perp, \mathbf{r}_\parallel) \in \mathbb{R}^d \times \mathbb{R}^{D-d}; |\mathbf{r}_\perp| \leq R\}$. Figure 4 shows some examples in the (d, D) -plane; compare also references [10, 41, 42].

2.1. Flat surface

First, consider the line $d = 1$ with D arbitrary in figure 4. Then, of course, equation (22) corresponds to the semi-infinite n -vector model bounded by a *flat* surface for which many results are available [31–33]. In particular, for the polymer case $n = 0$, the considerations of section 1.1 can be made explicit, proving equations (3) and (11), (12) [5, 6].

2.2. Gaussian model

Next, consider the line $D = 4$ with d arbitrary in figure 4. Since $D = 4$ is the upper critical dimension of the model in equation (22), this case corresponds to the Gaussian field theory and to Gaussian random walks, respectively. Both cases are described by $u_0 = 0$ in equation (22) and can be solved exactly by standard methods [10]. Thus, the susceptibility defined in equation (21), corresponding to the chain partition function in the grand canonical ensemble, is given by [10]

$$\chi(\mathbf{r}; t_0) = \frac{1}{t_0} \left[1 - \frac{\zeta_0 \rho^{-\alpha} K_\alpha(\rho \sqrt{\tau_0})}{\sqrt{\tau_0} K_{\alpha+1}(\sqrt{\tau_0}) + \zeta_0 K_\alpha(\sqrt{\tau_0})} \right] \quad (23)$$

¹ The co-dimension of an object of dimension D_{obj} in a space of dimension D is given by $D - D_{\text{obj}}$.

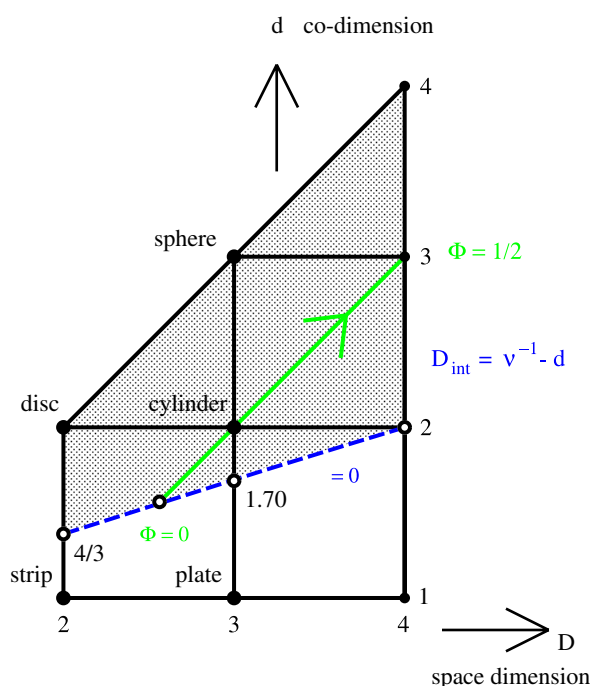


Figure 4. Diagram of ‘generalized cylinders’ which behave as relevant or irrelevant perturbations for long, flexible, self-avoiding polymer chains. The parameter $d \leq D$ characterizes the shape of the body and D is the space dimension. The point $(d, D) = (2, 2)$ corresponds to a disc for $D = 2$ and the points $(3, 3)$ to a sphere for $D = 3$. The point $(2, 3)$ corresponds to an infinitely elongated cylinder in $D = 3$ (in which we are ultimately interested). The line $D = 4$ indicates the upper critical dimension where the polymer chains behave like Gaussian random walks. The open circles and the dashed line (blue) indicate points (d, D) for which the dimension $D_{\text{int}} = \nu^{-1}(D) - d$ of intersection points of the body with an unbounded, free, self-avoiding random walk vanishes. For $D_{\text{int}} < 0$ the intersection probability is zero. In this sense, in the shaded region above the dashed line the body represents an irrelevant perturbation.

where $\rho = |\mathbf{r}_\perp|/R$ (so that $\rho = 1$ for $\mathbf{r} = \mathbf{r}_S$), $\zeta_0 = Rc_0$ and $\tau_0 = R^2 t_0$. The functions K_α and $K_{\alpha+1}$ are modified Bessel functions [43] with $\alpha = (d-2)/2$. From equation (23) one obtains the asymptotic behaviour right at the transition point:

$$N_S \sim N^\Phi, \quad \zeta_0 = \zeta_0^*, \quad N \rightarrow \infty, \quad (24)$$

with

$$\zeta_0^* = \begin{cases} 0, & d \leq 2 \\ -(d-2), & d > 2. \end{cases} \quad (25)$$

The crossover exponent Φ in equation (24) is given by [10]

$$\Phi = \frac{|d-2|}{2}, \quad 1 \leq d < 4, \quad d \neq 2, \quad (26)$$

$N_S \sim \ln N$ for $d = 2$, $N_S \sim N/\ln N$ for $d = 4$, and for $d > 4$ one finds $\Phi = 1$ corresponding to a first-order transition. For $\zeta_0 < \zeta_0^*$ the finite fraction of adsorbed monomers scales like

$$\lim_{N \rightarrow \infty} \frac{N_S}{N} \sim (\zeta_0^* - \zeta_0)^\kappa, \quad \zeta_0 < \zeta_0^*, \quad (27)$$

with the exponent [10]

$$\kappa = \frac{2 - |d - 2|}{|d - 2|}, \quad 1 \leq d < 4, \quad d \neq 2. \tag{28}$$

For $d = 2$ one finds

$$\lim_{N \rightarrow \infty} \frac{N_S}{N} \sim e^{-2/|\zeta_0|}, \quad \zeta_0 < 0, \quad d = 2, \tag{29}$$

which formally corresponds to $\kappa = \infty$. For $d = 4$ one finds $\lim_{N \rightarrow \infty} N_S/N \sim -1/\ln(\zeta_0^* - \zeta_0)$ while for $d > 4$ the fraction tends to a finite value, which reflects the fact that in this case the transition is of first order. Equations (24)–(29) are to be compared with equations (3)–(12) in section 1.1, where the variable $\zeta_0^* - \zeta_0$ here corresponds to $\mathcal{E} - \mathcal{E}^*$ there. In particular, for given $\zeta_0 < \zeta_0^*$ the chain partition function $\chi(t_0)$ exhibits a singularity for $t_0 \searrow t_S(\zeta_0)$ where the function $t_S(\zeta_0)$ is determined by an analysis of the zero of the denominator in equation (23) [10]. The values of the exponents Φ and κ in equations (26) and (28) obey the scaling relation $\kappa = (1 - \Phi)/\Phi$ from equation (12). Note that for $d > 2$ the limit $R \rightarrow 0$ yields merely the trivial bulk result $\chi(\mathbf{r}; t_0) = 1/t_0$, and hence no phase transition for $d > 2$. Thus, in the present treatment it is necessary to keep the cylinder radius R finite even though the results for Φ and κ do not depend on R .

Finally, we note that the adsorption of a Gaussian chain onto a rigid rod is equivalent to the denaturation transition of two *flexible* Gaussian chains A and B if monomer s of chain A can only interact with monomer s of chain B . This corresponds to an interaction of the form $\sim \int_0^{L_0} ds \delta[\mathbf{R}_A(s) - \mathbf{R}_B(s)]$ in the partition function (13). It is easy to see that the system of two flexible Gaussian chains with the above interaction can be mapped onto the system of one flexible Gaussian chain interacting with a rigid rod, using the transformation [15, 17]

$$\mathbf{R}(s) = \mathbf{R}_A(s) - \mathbf{R}_B(s), \quad \mathbf{R}_{CM}(s) = \frac{1}{2} [\mathbf{R}_A(s) + \mathbf{R}_B(s)]. \tag{30}$$

For Gaussian chains (and only for Gaussian chains) the degrees of freedom described by the centre of mass (CM) coordinates $\mathbf{R}_{CM}(s)$ and the relative coordinates $\mathbf{R}(s)$ decouple from each other. The relative coordinates $\mathbf{R}(s)$ describe a Gaussian chain which interacts with the origin at $\mathbf{R} = 0$ in the d -dimensional subspace, while the degrees of freedom of the remaining $D - d$ dimensions are unbounded and independent of the degrees of freedom of the d -dimensional subspace. By virtue of this mapping, the above results (24)–(29) have also been obtained in [15].

2.3. Renormalization of the field theory bounded by the curved cylinder surface

We now turn to the renormalization of the n -vector model defined by equation (22). The objective is to determine the scaling behaviour of the renormalized chain partition function $\chi_{\text{ren}}(R, t, c)$ in the grand canonical ensemble in terms of the cylinder radius R and renormalized parameters t (conjugate to the renormalized chain length L) and c . The n -vector model in equation (22) can be dimensionally regularized and renormalized by minimal subtraction of poles in $\varepsilon = 4 - D$. The renormalizations of the bulk field $\vec{\Phi}(\mathbf{r})$, $\mathbf{r} \in V$, and the bulk parameters t_0, u_0 have the same form as in the unbounded case, and are given by [38, 39, 32] (we follow the convention of [32])

$$\vec{\Phi} = Z_\Phi^{1/2} \vec{\Phi}_{\text{ren}} \tag{31}$$

$$t_0 = \mu^2 Z_t t + t_b \tag{32}$$

$$u_0 = \mu^\varepsilon 2^D \pi^{D/2} Z_u u. \tag{33}$$

The parameters $\vec{\Phi}_{\text{ren}}, t, u$ are renormalized counterparts of the bare parameters $\vec{\Phi}, t_0, u_0$ in equation (22). In a regularization scheme using a large momentum cut-off Λ , the bulk

renormalization factors Z_Φ , Z_t , Z_u absorb divergencies logarithmic in Λ , corresponding to poles in ε in dimensional regularization. The parameter t_b absorbs divergencies quadratic in Λ and describes the shift of the critical temperature T_c of the n -vector model due to fluctuations. In dimensional regularization, $t_b = 0$, and [38, 39, 32]

$$Z_\Phi = 1 - \frac{n+2}{36\varepsilon}u^2 + \mathcal{O}(u^3) \quad (34)$$

$$Z_t Z_\Phi = 1 + \frac{n+2}{3\varepsilon}u + \left[\frac{(n+2)(n+5)}{9\varepsilon^2} - \frac{n+2}{6\varepsilon} \right] u^2 + \mathcal{O}(u^3) \quad (35)$$

$$Z_u = 1 + \frac{n+8}{3\varepsilon}u + \left[\frac{(n+8)^2}{9\varepsilon^2} - \frac{3n+14}{6\varepsilon} \right] u^2 + \mathcal{O}(u^3). \quad (36)$$

The presence of the cylinder surface S requires, in addition, renormalization of the surface field $\vec{\Phi}|_S = \vec{\Phi}(\mathbf{r})$, $\mathbf{r} \in S$, and of the surface parameter c_0 in equation (22). For a *flat* surface these additional renormalizations are given by [44, 45, 32]

$$\vec{\Phi}|_S = (Z_\Phi Z_1)^{1/2} (\vec{\Phi}|_S)_{\text{ren}} = Z_1^{1/2} \vec{\Phi}_{\text{ren}}|_S \quad (37)$$

$$c_0 = \mu Z_c c + c_{\text{sp}} \quad (38)$$

defining the renormalized surface field $(\vec{\Phi}|_S)_{\text{ren}}$ and surface parameter c . The new renormalization factors Z_1 and Z_c absorb divergencies logarithmic in Λ which occur at a flat surface, corresponding to poles in ε in dimensional regularization. The parameter c_{sp} absorbs divergencies linear in Λ and describes the shift of the multicritical point due to fluctuations (compare figure 2, $-c \sim \mathcal{E}$). In dimensional regularization, $c_{\text{sp}} = 0$, and Z_1 and Z_c are given by [44, 45, 32]

$$Z_1 = 1 + \frac{n+2}{3\varepsilon}u + \left[\frac{(n+2)(n+5)}{9\varepsilon^2} - \frac{n+2}{3\varepsilon} \right] u^2 + \mathcal{O}(u^3) \quad (39)$$

$$Z_c = 1 + \frac{n+2}{3\varepsilon}u + \left[\frac{(n+2)(n+5)}{9\varepsilon^2} + \frac{n+2}{36\varepsilon}(1 - 4\pi^2) \right] u^2 + \mathcal{O}(u^3). \quad (40)$$

Equations (37) and (38) hold for a flat surface. As shown by McAvity and Osborn [40], the required renormalizations become modified if the surface S is curved, like in the present case. While the renormalization of the surface field $(\vec{\Phi}|_S)_{\text{ren}}$ remains unchanged, the renormalization of the surface parameter c_0 requires an additional, additive term that depends on the mean curvature [40]:

$$c_0 = \mu Z_c c + \frac{d-1}{R} \mathcal{C}(u, \varepsilon) \quad (41)$$

or, with $\zeta_0 = Rc_0$ and $\zeta = \mu Rc$,

$$\zeta_0 = Z_c \zeta + (d-1) \mathcal{C}(u, \varepsilon). \quad (42)$$

Z_c is the same renormalization factor as in equation (38) for a flat surface and $\mathcal{C}(u, \varepsilon)$ to second order in u can be deduced from [40]:

$$\mathcal{C}(u, \varepsilon) = \frac{n+2}{9} \left\{ \frac{u}{\varepsilon} + \left[\frac{n+5}{3\varepsilon^2} + \frac{n+1-4\pi^2}{12\varepsilon} \right] u^2 \right\} + \mathcal{O}(u^3). \quad (43)$$

To proceed, we consider the two-point correlation function

$$\langle \Phi_1(\mathbf{r}_S) \Phi_1(\mathbf{r}') \rangle = G(\mathbf{r}_S, \mathbf{r}', R; t_0, \zeta_0, u_0), \quad (44)$$

where \mathbf{r}_S is located on the cylinder surface S and $\mathbf{r}' \in V$. From G , the chain partition function $\chi(R, t_0, \zeta_0, u_0)$ follows by an integration over \mathbf{r}' —see equation (21); by symmetry, χ does

not depend on \mathbf{r}_S . The renormalization group (RG) equation for the renormalized counterpart G_{ren} of G follows in the standard way, using the relation

$$G_{\text{ren}}(\mathbf{r}_S, \mathbf{r}', R; t, \zeta, u; \mu) = Z_\Phi^{-1} Z_1^{-1/2} G(\mathbf{r}_S, \mathbf{r}', R; t_0, \zeta_0, u_0) \quad (45)$$

and the fact that G does not depend on μ : $\mu \partial_\mu G|_{\mu=0} = 0$. This leads to the RG equation

$$\left[\mathcal{D}_\mu + \eta_\Phi + \frac{1}{2} \eta_1 + \mu \frac{\partial \zeta}{\partial \mu} \Big|_{\mu=0} \partial_\zeta \right] G_{\text{ren}} = 0 \quad (46)$$

where we have used the abbreviation

$$\mathcal{D}_\mu = \mu \partial_\mu |_{\mu=0} + \beta(u) \partial_u - (2 + \eta_t) t \partial_t \quad (47)$$

with

$$\beta(u) = \mu \partial_\mu u |_{\mu=0} \quad (48)$$

and the exponent functions $\eta_i(u) = \mu \partial_\mu \ln Z_i |_{\mu=0}$ with $i = \Phi, 1, t$. The new feature of the RG equation (46) generated by the surface curvature is the function

$$\mu \frac{\partial \zeta}{\partial \mu} \Big|_{\mu=0} = -\eta_c \left[\zeta + \frac{d-1}{3} + \frac{n(d-1)}{18} u + O(u^2) \right] \quad (49)$$

where

$$\eta_c(u) = \mu \partial_\mu \ln Z_c |_{\mu=0} = -\frac{n+2}{3} u + \frac{n+2}{18} (4\pi^2 - 1) u^2 + O(u^3) \quad (50)$$

is the exponent function for c corresponding to a *flat* surface, with Z_c from equation (40) [32]. A necessary condition for the two-point function G to be scale invariant (SI) is that the right-hand side of equation (49) vanishes, which is the case for $u = 0$ (Gaussian model) or if ζ takes the value for which the square bracket in equation (49) vanishes:

$$\zeta = \zeta_{\text{SI}} \equiv -\frac{d-1}{3} + O(u). \quad (51)$$

Note that the value of ζ_{SI} to leading order in u , $\zeta_{\text{SI}} = -(d-1)/3$, is *different* from the value ζ_0^* in equation (25) corresponding to the onset of the adsorption transition in the Gaussian model. It is also interesting to note that for a sphere, corresponding to $d = D = 4 - \varepsilon$, the value of ζ_{SI} to leading order in u , $\zeta_{\text{SI}} = -1$, coincides with the value $\zeta_{\text{CI}} = -(d-2)/2$ for which the Gaussian two-point correlation function at $t_0 = 0$ is conformal invariant (CI) [46, 47]. However, within the Φ^4 -model the special value ζ_{SI} is already fixed by scale invariance, whereas in the Gaussian model the value ζ_{CI} is only fixed if one requires conformal invariance.

By solving the RG equation (46) for the two-point function in the standard way using characteristics and integrating over \mathbf{r}' , one derives the general scaling behaviour of the chain partition function in the grand canonical ensemble:

$$\chi_{\text{ren}}(R, t, \zeta, u; \mu) \sim t^{-\gamma_1} \Theta(\alpha \mu R t^\nu, \beta \Delta \zeta t^{\nu - \Phi_{\text{nat}}}) \quad (52)$$

where

$$\Delta \zeta = \zeta - \zeta_{\text{SI}} \quad (53)$$

with ζ_{SI} from equation (51). The exponent $\nu = (2 + \eta_t^*)^{-1}$ is a bulk critical exponent, while $\Phi_{\text{nat}} = \nu(1 + \eta_c^*)$ (the crossover exponent) and $\gamma_1 = \nu(2 - \eta_\Phi^* - \eta_1^*/2)$ are critical exponents associated with a *flat* surface [32]. The exponent functions $\eta_i(u)$ for $i = t, c, \Phi, 1$ are defined below equation (48) and in equation (50). The values η_i^* are the values of the exponent functions at the fixed point u^* . The constants α and β in equation (52) are nonuniversal prefactors, while the function $\Theta(x, y)$ is a universal scaling function.

Equation (52) is in line with the Gaussian model (where $\nu = \Phi_{\text{flat}} = 1/2$ and $\gamma_1 = 1$):

$$\chi(R, t_0, \zeta_0) \sim t_0^{-1} \Theta_0(R t_0^{1/2}, \zeta_0), \quad \text{Gaussian model}; \quad (54)$$

compare equation (23). Finally, equation (52) can be compared with the corresponding behaviour for a flat surface:

$$\chi_{\text{ren}}(t, c, u; \mu) \sim t^{-\gamma_1} \Theta_{\text{flat}}(\beta' c t^{-\Phi_{\text{flat}}}), \quad \text{flat surface}. \quad (55)$$

Note that this limit can be obtained from equation (52) by rewriting the second scaling argument as $\Delta\zeta t^{\nu-\Phi_{\text{flat}}} = R t^\nu \cdot \Delta c t^{-\Phi_{\text{flat}}}$. Equation (55) then follows as the limit $R \rightarrow \infty$ of the scaling form $\chi_{\text{ren}} \sim t^{-\gamma_1} \tilde{\Theta}(\alpha' \mu R t^\nu, \beta' \Delta c t^{-\Phi_{\text{flat}}})$, where $\Delta c = c + O(1/R)$.

Let us come back to equation (52). According to recent estimates one has $\Phi_{\text{flat}} = 0.518$ [48] and $\nu = 0.588$ [39] for $n = 0$ in $D = 3$ so that the exponent $\nu - \Phi_{\text{flat}}$ in equation (52) is small but positive. From a naive point of view this would imply that the scaling variable $\Delta\zeta$ in the second scaling argument of Θ is *irrelevant* and could be omitted from the outset; however, one should keep in mind that the radius R in the first scaling argument is also irrelevant in principle. Now, the relevant question is whether the scaling function $\Theta(x, y)$ exhibits a singularity on a certain subset of (x, y) , corresponding to the polymer adsorption transition; compare the related discussion below equation (6) and below equation (29). In fact, we expect this singularity to occur for $y = y_S(x) < 0$, where now $y_S(x)$ is a function of the first scaling variable $x = \alpha \mu R t^\nu$. Note that the scaling function $\Theta_0(x, y)$ in equation (54), corresponding to the Gaussian model, does indeed exhibit this kind of singularity; compare section 2.2. Thus, in the present description, the adsorption transition is characterized by a balance of the two irrelevant variables $\Delta\zeta$ and R . In this sense the scaling variable $\Delta\zeta$ can be considered as a dangerously irrelevant variable.

Finally we note that equation (52) implies a corresponding scaling form of the chain partition function with fixed chain length L :

$$Z_{\text{ren}}(R, L, \zeta, u; \mu) \sim L^{\gamma_1-1} \Psi(\tilde{\alpha} \mu R L^{-\nu}, \tilde{\beta} \Delta\zeta L^{-(\nu-\Phi_{\text{flat}})}), \quad (56)$$

with (different) nonuniversal prefactors $\tilde{\alpha}$ and $\tilde{\beta}$ and a universal scaling function Ψ . From equations (52) and (56) the number of adsorbed monomers N_S for $\Delta\zeta = 0$ and the finite fraction of adsorbed monomers N_S/N for $\Delta\zeta < 0$ can be derived as outlined in section 1.1 in principle. However, the thin rod limit $R \rightarrow 0$ corresponds to singular limits of the scaling functions Θ and Ψ which are rather difficult to obtain. At least it is easy to see that the exponents Φ and κ defined in equations (3) and (11) are *universal*, using the fact that Θ and Ψ are universal scaling functions. To proceed, in the next section we use a different method to obtain estimates for the exponents Φ and κ for a cylinder for $D = 3$.

2.4. Estimates for the exponents Φ and κ by using the additivity of co-dimensions

In this section we obtain estimates for the exponents Φ and κ for a cylinder for $D = 3$ introduced in equations (3) and (11) by means of an interpolation procedure between two known cases. Firstly, in the Gaussian model one has $\Phi = 1/2$ for $d = 3$, see equation (26), corresponding to the point $(d, D) = (3, 4)$ in figure 4. Likewise, $\kappa = 1$ from the scaling relation $\kappa = (1 - \Phi)/\Phi$, or from equation (28), for $(d, D) = (3, 4)$. Secondly, one has $\Phi = 0$ on the whole line $\nu^{-1}(D) - d = 0$ in figure 4. This result can be obtained by using the *co-dimension additivity theorem*, stating that the co-dimension of the intersection points of two objects of dimensions D_1 and D_2 is given by the sum of their co-dimensions: $D - D_{\text{int}} = (D - D_1) + (D - D_2)$, i.e.,

$$D_{\text{int}} = D_1 + D_2 - D. \quad (57)$$

For example, two-dimensional surfaces generically intersect along curves for $D = 3$ ($D_{\text{int}} = 2+2-3 = 1$) and only at isolated points for $D = 4$ ($D_{\text{int}} = 0$). Equation (57) is also expected to hold if one or both objects are fractal. In the present case, one object is a self-avoiding random walk with fractal (Hausdorff) dimension ν^{-1} and the other one is a ‘generalized cylinder’ with co-dimension d (see figure 4); the dimension of intersection points of these two objects is thus given by

$$D_{\text{int}} = \nu^{-1}(D) - d. \quad (58)$$

In figure 4, the line $D_{\text{int}} = 0$ as a function of d and D is shown as the blue dashed line. An unbounded, free, self-avoiding random walk does not intersect with ‘generalized cylinders’ located above the dashed line, apart from in exceptional cases. In this sense, ‘generalized cylinders’ above the dashed line are irrelevant perturbations for a free, self-avoiding random walk. Now, ‘generalized cylinders’ located right on the line $D_{\text{int}} = 0$ correspond to marginal cases: an unbounded, free, self-avoiding random walk *does* intersect with ‘generalized cylinders’ located on the dashed line, but only at isolated points. We thus expect that the number of intersecting monomers N_S grows with N for $N \rightarrow \infty$, but only logarithmically, i.e., $N_S \sim \ln N$, which implies $\Phi = 0$; compare the case $d = 2$ for the Gaussian model discussed in section 2.2, and compare the case $\mathcal{E} = \mathcal{E}^*$ with $\Phi = 0$ in section 1. It should be noted that this argument only applies to *unperturbed* random walks, and does not make any statement for walks that interact with the body.

Thus, the values of the exponent Φ at the end points of the green line in figure 4 are available. This can be used to obtain an estimate for Φ for an ordinary cylinder for $D = 3$ as follows. The shape of the dashed line in figure 4 is known quite accurately by means of the ε -expansion of $\nu(D)$ in conjunction with the exact value $\nu = 3/4$ for $n = 0$ in $D = 2$ [38, 39]. Thus, one may estimate Φ for a cylinder for $D = 3$, located at the point $(d, D) = (2, 3)$ in figure 4, by means of a linear interpolation between the known values at the end points of the green line; compare [41, 42]. In this way we find for a cylinder for $D = 3$ the estimates, using equation (12),

$$\Phi \simeq \frac{1}{6}, \quad \kappa = \frac{1 - \Phi}{\Phi} \simeq 5. \quad (59)$$

Since these exponents are universal and do not depend on the cylinder radius R , they are also expected to hold for a rigid rod with vanishing radius, or for a line of lattice sites in a numerical simulation of this system.

3. Conclusion

We have investigated the adsorption transition of a long flexible self-avoiding polymer chain onto a rigid thin rod by field-theoretical methods. The rod is endowed with a short-ranged adsorption energy \mathcal{E} for the chain monomers so that, on increasing \mathcal{E} , at some threshold value \mathcal{E}^* the chain undergoes a transition from an unbound state to a bound state, as shown in figure 1. The main results and remaining questions are summarized below.

- (1) By means of general scaling arguments we obtained the scaling relation (12) for the exponents Φ and κ defined in equations (3) and (11), and the phase diagrams shown in figure 2 in terms of the number of chain monomers N , the chemical potential μ conjugate to N and the adsorption energy \mathcal{E} .
- (2) By representing the rod by a cylinder of finite radius R we were able to use available results for field theories with curved boundaries [40]; see figure 3. By using renormalization group arguments, we derived the scaling behaviour of the chain partition function in the grand

canonical ensemble, equation (52), and in the canonical ensemble, equation (56), where $L \sim N$ and $t \sim \mu$. Notable features of the scaling results are the distinct form of the scaling variable $\zeta \propto Rc$, where c is related to the surface potential for chain monomers, and the curvature-induced shift of ζ in equation (53) with ζ_{SI} from equation (51). It also follows that the exponents Φ and κ introduced in equations (3) and (11) are universal.

- (3) Because the cylinder radius R enters the scaling functions Θ and Ψ in equations (52) and (56) explicitly it is difficult to obtain the universal exponents Φ and κ directly from them. Therefore we used the co-dimension additivity theorem in conjunction with an interpolation procedure, as shown in figure 4, to obtain the estimates for Φ and κ in equation (59). The checking of these exponents and the scaling relation (12) is a possible starting point for numerical simulations of this system.
- (4) It would be interesting to introduce new methods to derive the exponents Φ and κ , possibly avoiding the introduction of a finite cylinder radius R from the outset.
- (5) It would also be interesting to explain the relation between ζ_0^* and ζ_{SI} discussed below equation (51).

Acknowledgment

I would like to thank C v Ferber for useful correspondence.

Appendix. Mapping of the polymer system on the n -vector model

The $\rho^2(\mathbf{r})$ interaction in equation (13) can be linearized by means of a Gaussian transformation [37, 2]. This procedure makes use of the Gaussian integral

$$\int \mathcal{D}X \exp\left[-\frac{1}{2}X^T A X + b^T X\right] = \left(\det \frac{A}{2\pi}\right)^{-1/2} \exp\left[\frac{1}{2}b^T A^{-1}b\right] \quad (\text{A.1})$$

where X is a vector with discrete or continuous indices and the symmetric matrix A must have a positive definite real part. Using $X(\mathbf{r}) \propto i\sigma(\mathbf{r})$ with purely imaginary $\sigma(\mathbf{r})$, the matrix $A(\mathbf{r}, \mathbf{r}') = \frac{3}{u}\delta(\mathbf{r} - \mathbf{r}')$ and $b(\mathbf{r}) = i\rho(\mathbf{r})$, one finds

$$\exp\left\{-\frac{u}{6} \int d^D r \rho^2(\mathbf{r})\right\} = \int \mathcal{D}\sigma \exp\left[\frac{3}{2u} \int d^D r \sigma^2(\mathbf{r}) - \int d^D r \sigma(\mathbf{r})\rho(\mathbf{r})\right]. \quad (\text{A.2})$$

Note that A is positive definite due to our assumption $u > 0$. Inserting (A.2) in (13) yields

$$\begin{aligned} Z^{(2)}(\mathbf{r}, \mathbf{r}'; L) &= \int \mathcal{D}\sigma \exp\left[\frac{3}{2u} \int d^D r \sigma^2(\mathbf{r})\right] \\ &\times \int_{\mathbf{r}}^{\mathbf{r}'} \mathcal{D}\mathbf{R} \exp\left\{-\frac{1}{4} \int_0^L ds \left(\frac{d\mathbf{R}}{ds}\right)^2 - \int d^D r [V(\mathbf{r}) + \sigma(\mathbf{r})]\rho(\mathbf{r})\right\}. \end{aligned} \quad (\text{A.3})$$

The $\rho^2(\mathbf{r})$ interaction in equation (13) has been replaced by the interaction of $\rho(\mathbf{r})$ with an external, fluctuating potential $\sigma(\mathbf{r})$. The second line of equation (A.3) can be interpreted as the path integral representation of the evolution operator $\langle \mathbf{r}' | e^{-L\hat{H}} | \mathbf{r} \rangle$ in imaginary time s of a quantum mechanical particle with Hamiltonian $\hat{H} = -\Delta + V(\mathbf{r}) + \sigma(\mathbf{r})$. The Laplace transform of this evolution operator with respect to L yields the resolvent

$$\int_0^\infty dL e^{-tL} \langle \mathbf{r}' | e^{-L\hat{H}} | \mathbf{r} \rangle = \langle \mathbf{r}' | \frac{1}{-\Delta + t + V(\mathbf{r}) + \sigma(\mathbf{r})} | \mathbf{r} \rangle. \quad (\text{A.4})$$

The resolvent can be represented in the standard way by the two-point correlation function of an n -component field $\vec{\Phi} = (\Phi_1, \dots, \Phi_n)$ in the limit $n \rightarrow 0$. The result is

$$Z^{(2)}(\mathbf{r}, \mathbf{r}'; L) = \int \mathcal{D}\sigma \exp\left[\frac{3}{2u} \int d^D r \sigma^2(\mathbf{r})\right] \mathcal{L}_{t \rightarrow L} \lim_{n \rightarrow 0} \int \mathcal{D}\vec{\Phi} \Phi_1(\mathbf{r}) \Phi_1(\mathbf{r}') e^{-S(\vec{\Phi})} \quad (\text{A.5})$$

with the action

$$S\{\vec{\Phi}\} = \int d^D r \left[\frac{1}{2} (\nabla \vec{\Phi})^2 + \frac{t}{2} \vec{\Phi}^2 + \frac{1}{2} [\sigma(\mathbf{r}) + V(\mathbf{r})] \vec{\Phi}^2 \right]. \quad (\text{A.6})$$

The Gaussian integration in equation (A.5) can be carried out using equation (A.1) with the same $X(\mathbf{r}) \propto i\sigma(\mathbf{r})$ and matrix $A(\mathbf{r}, \mathbf{r}') = \frac{3}{u} \delta(\mathbf{r} - \mathbf{r}')$ as before, and now $b(\mathbf{r}) = \frac{i}{2} \vec{\Phi}^2(\mathbf{r})$. This leads to equations (15)–(17).

References

- [1] de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [2] des Cloizeaux J and Jannink G 1990 *Polymers in Solution: Their Modelling and Structure* (Oxford: Clarendon)
- [3] Schäfer L 1999 *Excluded Volume Effects in Polymer Solutions, as Explained by the Renormalization Group* (Berlin: Springer)
- [4] Fleer G, Cohen-Stuart M, Scheutjens J, Cosgrove T and Vincent B 1993 *Polymers at Interfaces* (London: Chapman and Hall)
- [5] Eisenriegler E, Kremer K and Binder K 1982 *J. Chem. Phys.* **77** 6296
- [6] Eisenriegler E 1993 *Polymers Near Surfaces* (Singapore: World Scientific)
- [7] Napper D H 1989 *Polymeric Stabilization of Colloidal Dispersions* (London: Academic)
- [8] Buitenhuis J, Donselaar L N, Buining P A, Stroobants A and Lekkerkerker H N 1995 *J. Colloid Interface Sci.* **175** 46
- [9] Piculell L, Viebke C and Linse P 1995 *J. Phys. Chem.* **99** 17423
- [10] Eisenriegler E, Hanke A and Dietrich S 1996 *Phys. Rev. E* **54** 1134
- [11] Nowicki W 2002 *Macromolecules* **35** 1424
- [12] Alberts B, Johnson A, Lewis J, Raff M, Roberts K and Walter P 2002 *Molecular Biology of the Cell* 4th edn (New York: Garland)
- [13] Poland D and Scheraga H A 1970 *Theory of Helix–Coil Transitions in Biopolymers* (New York: Academic)
- [14] Wartell R M and Benight A S 1985 *Phys. Rep.* **126** 67
- [15] Causo M S, Coluzzi B and Grassberger P 2000 *Phys. Rev. E* **62** 3958
- [16] Kafri Y, Mukamel D and Peliti L 2000 *Phys. Rev. Lett.* **85** 4988
- [17] Garel T, Monthus C and Orland H 2001 *Europhys. Lett.* **55** 132
- [18] Carlon E, Orlandini E and Stella A L 2002 *Phys. Rev. Lett.* **88** 198101
- [19] Richard C and Guttmann A J 2004 *J. Stat. Phys.* **115** 925
- [20] Schäfer L 2005 Can finite size effects in the Poland–Scheraga model explain simulations of a simple model for DNA denaturation? *Preprint cond-mat/0502668*
- [21] Metzler R and Hanke A 2005 Knots, bubbles, unwinding, and breathing: probing the topology of DNA and other biomolecules *Handbook of Theoretical and Computational Nanotechnology* ed M Rieth and W Schommers, at press
- [22] Joanny J F, Leibler L and Ball R 1984 *J. Chem. Phys.* **81** 4640
- [23] Schäfer L and Kappeler C 1985 *J. Physique* **46** 1853
- [24] Schäfer L and Kappeler C 1990 *Colloid Polym. Sci.* **268** 995
- [25] Schäfer L, Lehr U and Kappeler C 1991 *J. Physique I* **1** 211
- [26] von Ferber C and Holovatch Y 1997 *Phys. Rev. E* **56** 6370
- [27] Vanderzande C 1998 *Lattice Models of Polymers* (Cambridge: Cambridge University Press)
- [28] Orlandini E, Seno F and Stella A L 2000 *Phys. Rev. Lett.* **84** 294
- [29] Baiesi M, Carlon E, Orlandini E and Stella A L 2001 *Phys. Rev. E* **63** 041801
- [30] Kumar S, Giri D and Bhattacharjee S M 2004 Force induced triple point for interacting polymers *Preprint cond-mat/0407261*
- [31] Binder K 1983 *Phase Transitions and Critical Phenomena* vol 8, ed C Domb and J L Lebowitz (London: Academic) p 1
- [32] Diehl H W 1986 *Phase Transitions and Critical Phenomena* vol 10, ed C Domb and J L Lebowitz (London: Academic) p 75

-
- [33] Diehl H W 1997 *Int. J. Mod. Phys. B* **11** 3503
 - [34] de Gennes P G 1975 *J. Physique* **36** L55
 - [35] Duplantier B 1982 *J. Physique* **43** 991
 - [36] de Gennes P G 1972 *Phys. Lett. A* **38** 339
 - [37] des Cloizeaux J 1975 *J. Physique* **36** 281
 - [38] Amit D J 1984 *Field Theory, the Renormalization Group, and Critical Phenomena* 2nd edn (Singapore: World Scientific)
 - [39] Zinn-Justin J 2002 *Quantum Field Theory and Critical Phenomena* 4th edn (Oxford: Clarendon)
 - [40] McAvity D M and Osborn H 1993 *Nucl. Phys. B* **394** 728
 - [41] Hanke A and Dietrich S 1999 *Phys. Rev. E* **59** 5081
 - [42] Hanke A 2000 *Phys. Rev. Lett.* **84** 2180
 - [43] Abramowitz M and Stegun I A 1972 *Handbook of Mathematical Functions* (New York: Dover)
 - [44] Diehl H W and Dietrich S 1981 *Phys. Rev. B* **24** 2878
 - [45] Diehl H W and Dietrich S 1983 *Z. Phys. B* **50** 117
 - [46] Eisenriegler E and Ritschel U 1995 *Phys. Rev. B* **51** 13717
 - [47] Eisenriegler E, private communication
 - [48] Diehl H W and Shpot M 1994 *Phys. Rev. Lett.* **73** 3431