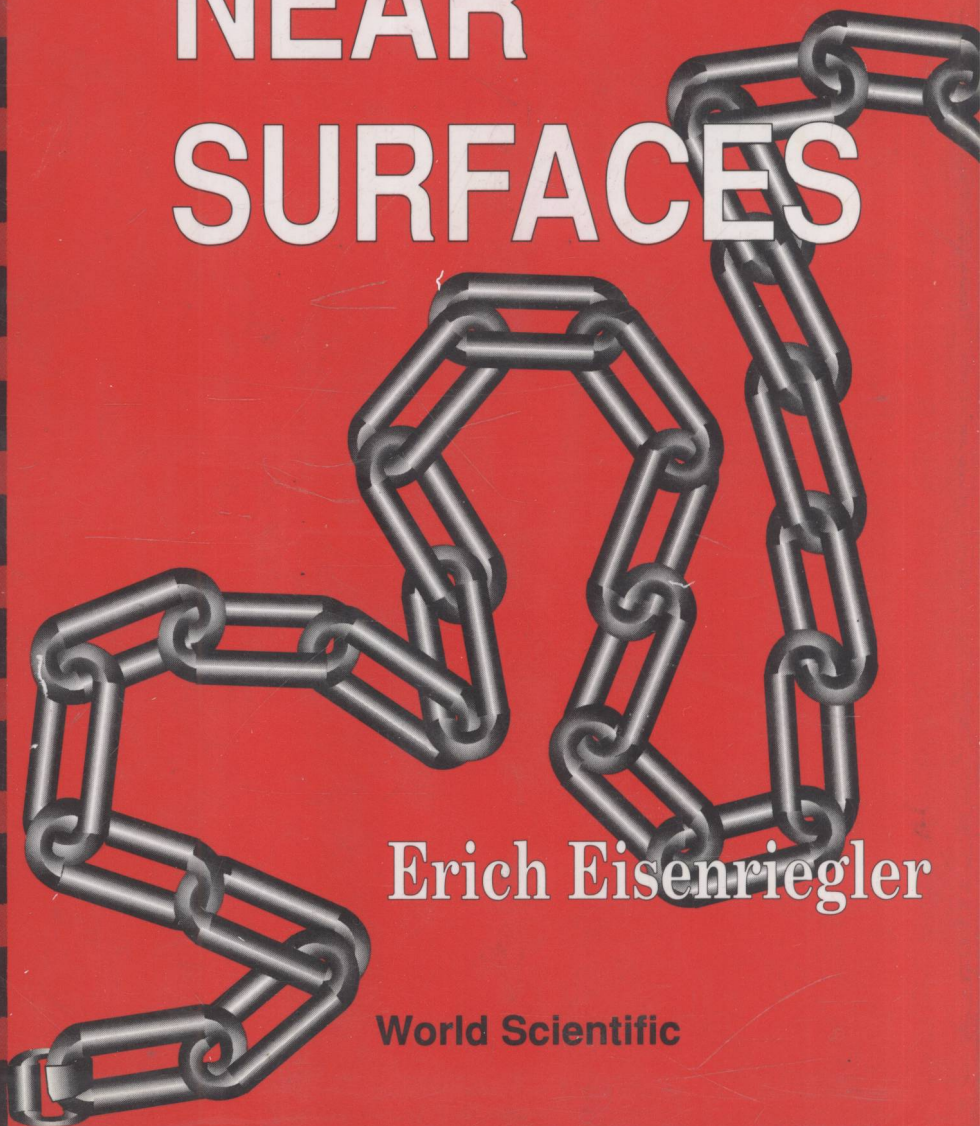


Conformation Properties and  
Relation to Critical Phenomena

# POLYMERS NEAR SURFACES



Erich Eisenriegler

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## **POLYMERS NEAR SURFACES**

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Conformation Properties and Relation to Critical Phenomena

# **POLYMERS NEAR SURFACES**

## Preface

This book is about surface effects in the conformation statistics of long flexible polymer chains in dilute solution. The effects are basic to an entire branch of polymer physics — ‘polymers near surfaces’ — which has considerable practical importance, with applications even in biology and technology. Another intriguing feature of these effects is their interdisciplinary character. A direct relation to surface effects in critical phenomena and field theory leads to cross-fertilization. In particular, considerable recent progress in the understanding of surface critical phenomena leads — via the above mentioned relation — to a number of new important insights into polymer behaviour. Properties discovered in critical field theories (or spin models in statistical mechanics) with a surface — such as the renormalization group, short distance expansions and conformal invariance — have their counterparts for polymers near a surface.

The main purpose of the book is to give a self-contained introduction into these rather recent developments as well as to their applications to polymer physics. A number of interesting properties such as grafted-chain behavior and density profiles of solutions are discussed in detail for the three basic surface states (nonadsorbed, adsorbed and adsorption threshold) and for different types of interactions (ideal, good solvent, theta solvent) in bulk. Open chains as well as ring polymers are considered. The results are obtained in terms of universal power law exponents, amplitude ratios and scaling functions. Crossover between different types of behavior is also discussed. The attempt to keep a balance between the necessary theoretical foundation and interesting applications is at the expense of completeness. Some of the omitted topics are briefly reviewed in a final chapter.

The book is addressed to both students and research workers with an interest in either polymer physics, statistical mechanics, critical phenomena or field theory. A general background in statistical mechanics is assumed.

Most of what I know about surface critical behavior I learnt through collaborating with T. W. Burkhardt and H. W. Diehl. To them I wish to express my warmest thanks. I am strongly indebted to K. Binder for stimulating my interest in polymers and to H. Wagner for pointing out the relevance of field theory methods in critical phenomena and for the support which enabled the close contact with his Munich group. I am also grateful to R. Bausch, S. Dietrich, H. K. Janssen, K. Kremer, R. Lipowsky, L. Schäfer, and P. Upton for enlightening discussions. The book originates from a number of graduate courses and lecture series which I have given at the universities of Aachen, Düsseldorf, Frankfurt and Munich. I would like to thank the audiences for questions and remarks.

Finally, I would like to express my sincere appreciation to C. Glowacki, Ch. Hake and C. Müller for the excellent typing of the manuscript.

Conformation Properties and Relation to Critical Phenomena

# **POLYMERS NEAR SURFACES**

# Contents

Preface	v
1. Introduction	1
1.1. The Critical Behavior of Polymers Near Surfaces	3
2. Ideal Chain on a One-dimensional Lattice	11
2.1. Infinite Space	11
2.2. Semi-infinite Space	15
2.2.1. No surface adsorption energy	15
2.2.2. Influence of surface adsorption energy	17
3. Ideal Chain — Continuum Description	24
3.1. Gaussian Chain in Infinite Space Subject to an External Potential	24
3.2. Continuous Chain in Half Space	30
3.3. Long Chains Near the Compensation Point	41
3.4. Adsorption of (Ideal) Ring Polymers	52
4. Conformations of a Real Chain in Infinite Homogeneous Space	54
4.1. Cluster Expansion	55
4.2. Rules for Cluster Expansion of Laplace Transformed Chain Partition Function	62
4.3. Problems with the Continuum Limit and Different Types of Regularization	64
4.4. Relation to Field Theory	66
4.5. Field Theory and Critical Behavior	72
4.5.1. Phenomenology	72
4.5.2. Renormalization	80
4.5.3. Renormalization-group equations	100

4.6. Renormalization and Renormalization-group Equations for Polymer Quantities	104
4.7. Ring Polymers, Open Chains with Close Ends and Short Distance Expansions	115
4.7.1. Partition function of a ring polymer	116
4.7.2. Open chain with close ends	117
4.7.3. Operator short distance expansion	119
4.7.4. Renormalization flow for the short distance function $E_{\varphi^2; \varphi, \varphi}$ and open chains with close ends revisited	133
Appendix 4A. Low Order Diagrams, Their Divergent Subintegrations and Final Divergencies	135
Appendix 4B. Evaluation of the Amplitude Ratio $\langle R_G^2 \rangle / \langle R^2 \rangle$	144
5. Polymer Chain in Good Solvent; Conformations Near a Boundary	149
5.1. Cluster Expansion and Mapping to Field Theory for a Chain in Half Space	150
5.2. Renormalization Flow Near the Adsorption Threshold: Choice of Hamiltonian	156
5.3. Renormalization for Good Solvents	163
5.4. Renormalization Group Equations (RGE's) for Polymer Quantities	178
5.5. Excluded Volume Effects in Polymer Adsorption	182
5.5.1. Chain with one end fixed at a distance $z_A$ from surface; partition function $\mathcal{Z}_L(z_A; \hat{b}_2)$ at $c = c_{\text{ads}}$	183
5.5.2. Free end distribution of surface grafted chain	190
5.5.3. Monomer density for a dilute monodisperse solution of chains at $c = c_{\text{ads}}$	192
5.5.4. Ring polymer at adsorption point	194
5.5.5. Monomer density near a grafted end	197
5.5.6. Crossover to adsorbed state	199
5.6. Polymer near a Pure Hard Wall and Threshold to Nonadsorbed Crossover	203
5.6.1. Renormalization and SDE's of the $c = +\infty$ theory	204
5.6.2. Polymer properties near a pure hard wall: partition function $\mathcal{Z}_L^{(\infty)}(z_A)$ of a chain with one end fixed, monomer density $\sim \langle m(r) \rangle_{\text{DS}}^{(\infty)}$ of a dilute solution and partition function $\mathcal{Z}_{0010}^{(\infty)}(z)$ of a ring polymer with one monomer fixed	208
5.6.3. Chain with one end fixed close to a hard wall: layered distributions $\mathcal{Z}_\lambda^{(\infty)}$ for the free end position and $\langle m^\lambda \rangle^{(\infty)}$ for the monomer number	212

5.6.4. Threshold-nonadsorbed crossover	218
5.7. Is the Short Range Model Realistic?	222
Appendix 5A. Short Distance (SD) Expansions Near Adsorption Threshold (Special Transition)	228
Appendix 5B. Short Distance Expansions for a Pure Hard Wall ( $c = +\infty$ )	234
Appendix 5C. Ward Identity (WI) for a Pure Hard Wall ( $c = +\infty$ )	242
6. $\Theta$ -polymers Near a Boundary	250
6.1. $\Theta$ -polymer in Bulk	250
6.2. Hamiltonian for Adsorption and Renormalization Group Equations for Polymer Partition Functions	254
6.3. Renormalization Flow and Behavior of $\Theta$ -polymers at the Adsorption Point	263
6.4. $\Theta$ -polymer Near a Pure Hard Wall	272
Appendix 6A. Surface Renormalization Factors for Adsorption Threshold	276
Appendix 6B. Logarithmic Corrections for a $\Theta$ Chain in the Bulk	283
7. Polymer in Two-dimensional Half Space Bounded by a Line	287
7.1. The $n$ -vector Model	287
7.2. Conformal Invariance of Unbounded Critical Systems	297
7.2.1. Coordinate transformations and the stress tensor	297
7.2.2. The Virasoro algebra	311
7.2.3. Conformal charge and Casimir effect	315
7.2.4. Degenerate fields	319
7.2.5. Fusion rules	327
7.2.6. Four point functions of degenerate fields	332
7.2.7. Self avoiding ring polymers in unbounded two-dimensional space	343
7.3. Conformal Invariance of Semi-infinite Critical Systems and Polymers Near Surfaces	346
7.3.1. Coordinate transformations and stress tensor in half space	346
7.3.2. Consequences of special conformal invariance	349
7.3.3. Correlation functions in the half plane for degenerate fields	353
7.3.4. Energy correlations in the $n$ -vector model	361
7.3.5. Self avoiding polymers near surfaces: crossover exponent for adsorption and ring polymers near a pure hard wall	364
7.3.6. Other surface exponents for polymers	366

Appendix 7A. Conformal Invariance and Real Space Renormalization	372
Appendix 7B. Special Conformal Invariance, Form of Primary Correlation Functions and Structure Constants in Short Distance Expansions	378
Appendix 7C. Stress Tensor for a Gaussian Field Theory with $d > 2$ in Unbounded Bulk and Half-Space	384
8. Further Interesting Topics	390
8.1. Collapse and Adsorption	390
8.2. Overlapping Chains	391
8.3. Other Geometries	392
8.4. Branched Polymers Near a Surface	393
8.5. Polymers Near a Dirty Wall	394
References	397
Index	407

## Introduction

Polymers near surfaces is a field which has fascinated physicists and chemists now for nearly half a century, with respect to both basic and applied research.

One of the attractive features is the interdisciplinary character of the field. Possible applications range even to technology and biology. Polymers attached to colloid particles lead to 'steric' stabilization of the colloid which can be of importance, e.g. for producing paints (NAPPER (1989)). The exterior of red blood cells is covered with macromolecules (glykocalix) which act as a protection layer and control the interaction with other cells and with the walls of blood vessels (ABERTS *et al.* (1983)). On the side of basic research, one of the main challenges is the proper theoretical treatment of polymer conformation statistics in the presence of a surface. Here there are strong relations to probability theory, diffusion problems and—in particular—to critical phenomena of magnetic (spin) systems and Landau-Ginzburg type field theories.

This last relation which is often termed the 'polymer-magnet analogy' offers a very powerful approach to investigate the conformation statistics of long flexible polymers near surfaces. The analogy was first pointed out (DE GENNES (1976)) soon after the discovery of the polymer-magnet analogy for translational invariant systems (DE GENNES (1972)). In order to put it to use, it is necessary, of course, to have a sufficient understanding of critical spin systems with a surface. This has been achieved only within the last decade, notably via the renormalization group (BINDER (1983), DIEHL (1986)) or by exploiting the 'conformal invariance' of critical phenomena (CARDY 1984)). Here it is appropriate to point out the importance of the polymer-magnet analogy. The far reaching insights for critical systems with a surface such as (a) the renormalization group, (b) the so-called 'short distance expansions' and

(c) implications of conformal invariance, are understood best and were discovered first for field theories or magnetic spin systems. The reason is the locality of these systems as we shall see. The analogy allows transfer of (a)–(c) to polymer systems where the interactions are nonlocal (in the monomer label along the chain).

It is the purpose of this monograph to introduce these rather recent developments and to show how they can be applied to the discovery and investigation of interesting physical properties of polymers near surfaces. An effort is made to present this introduction in a self contained form, i.e. assuming only basic knowledge in statistical mechanics. On the other hand formal proofs will often be avoided in favour of plausibility arguments and explicit studies of instructive examples. As for the physical effects considered, no attempt is made for completeness. Rather we shall concentrate on the simplest situations and explicitly consider these in detail. The hope is that in this way the reader will become familiar with the structure and machinery of the approaches to such an extent that she or he can apply them to other interesting physical problems in the field. The situations which will be considered are characterized by the following properties:

- (i) The macromolecules have the form of linear chains which are either open (with two ends) or closed (ring polymer). Thus we shall not consider branched polymers or polymer networks.
- (ii) Only single chains or dilute solutions are investigated where overlap between chains is unimportant.
- (iii) Interactions between monomers and between a monomer and the surface are short ranged. We shall exclude charged systems such as polyelectrolytes but allow for the van der Waals interaction.
- (iv) Bulk and surface interactions are assumed homogeneous in the bulk and along the surface, respectively. We shall not consider disorder.
- (v) Only a half space geometry with a single, infinite, plane surface will be discussed, i.e. we do not consider more complicated geometries like slits or tubes.

It should be stressed that (i)–(v) only characterize the simplest physical situations and by no means imply limitations for a successful use of the relation between polymers and critical phenomena. Rather there exist interesting situations outside (i)–(v) where the analogy can be applied. Some of these are briefly mentioned in Chapter 8.

### 1.1. The Critical Behavior of Polymers Near Surfaces

Long flexible polymers—and low concentrated solutions thereof—show critical behavior such as universality<sup>a</sup> and scaling.<sup>a</sup> For translationally invariant situations, i.e. without a surface, this is amply described in the excellent monographs by DE GENNES (1979) and by DES CLOIZEAUX and JANNINK (1987). Here a brief overview is given about the different types of critical behavior which may arise for polymers near a surface, and only the simple situations defined above are considered. This will also serve as a guide to the rest of the monograph.

One of the most important properties of critical phenomena is universality. This means that close enough to the critical point there exist certain 'universal' properties which are independent of most of the details of the system. Consider first a single polymer chain in infinite space without a surface. The critical behavior arises if the number  $N$  of monomers (repeat units) in the chain becomes large and the critical point is  $N = \infty$ . One universal property is the exponent  $\nu$  of the power law  $\sim N^\nu$  which describes the growth of the mean end-to-end distance  $R$  of the open chain with  $N$ . Another one is the ratio  $R_G^2/R^2$  where  $R_G^2$  is the mean square radius of gyration (second moment of the mass distribution of the monomers around their center of mass). For  $N$  large enough these two—and other universal properties—are independent of 'most details'. E. g. for polymers modelled by a random walk on a lattice the universal properties are independent of the lattice structure (the same for a simple cubic lattice or a diamond lattice, for example). One finds the same values for these properties even if the polymer is modelled by a succession of linked rods with equal length which are either freely rotating in space or where successive ones have to form a given fixed angle. These and certain other polymer models belong to the 'universality class' of random walk generated, or 'ideal', polymer chains. Each of its representatives shows the same values for the universal properties if  $N$  is large enough.

However, real polymers do not, in general, belong to the above universality class. One reason is the 'excluded volume interaction', i.e. a short range repulsive interaction between any two monomers of the chain which arises physically from the hard core part in the monomer pair interaction. This may be either modelled by a self avoiding walk on the lattice, i.e. only chain conformations are allowed where every lattice site is visited not more than

<sup>a</sup>These concepts are explained below.

once, or by attaching in the rod model a sphere (with radius smaller than half the rod length) around each link between successive rods and allowing only those conformations where no sphere overlaps another one. These models show numbers for  $\nu$  and  $R_G^2/R^2$  which are different from those in the ideal polymer class. However, they are the same for the two excluded volume models mentioned above. The radius  $\rho$  of the sphere in the above rod model can even be varied continuously. For all  $\rho > 0$ , the above numbers—and those of other universal properties—remain the same, i.e. the models all belong to the ‘excluded volume universality class’.

One may wonder how this last property can be reconciled with the different (ideal chain) numbers which arise for  $\rho = 0$ . The reason is that for  $\rho$  small but non-zero, the asymptotic ( $N \rightarrow \infty$ ) values are reached for very large  $N$  only. For large but not very large  $N$ , one finds a behavior of  $R$  and  $R_G$  consistent with the ideal chain class in this case. The behavior ‘crosses over’ to the excluded volume class only for very large  $N$ . One may thus say that the excluded volume class is more stable (against perturbing interactions) than the ideal chain class. While the former holds for a whole continuum ( $\rho > 0$ ) of  $\rho$ -values, the latter is realized only for one particular value,  $\rho = 0$ .

It is customary to call critical behavior where, in addition to the normal critical condition  $N \rightarrow \infty$ , another condition—such as  $\rho = 0$ —has to be met, a ‘multicritical’ behavior. Thus the ideal chain class is an example of multicritical behavior while the excluded volume class is ‘normal critical’.

In a real polymer chain the monomer pair interaction typically shows ‘Morse-type’ behavior, i.e. hard core repulsion (excluded volume interaction) at small separations followed by a region of attraction at slightly larger separations. In a lattice model these two effects could be described by a self avoiding walk where an energy  $E$  is gained for each pair of occupied nearest neighbor points on the lattice, for points which are not direct successors along the chain. For this more realistic situation one also finds a multicritical point. If the (reduced) energy gain  $E/k_B T$  is not large enough,  $E/k_B T < \vartheta$ , the chain is in the excluded volume class, i.e. the universal quantities such as  $\nu$  or  $R_G^2/R^2$  have the same values as for the self avoiding walk  $E = 0$ . For large energy gain (or low temperature)  $E/k_B T > \vartheta$ , the chain is in a collapsed state, it occupies a mean volume proportional to  $N$ , and  $\nu$  simply equals  $1/d$  with  $d$  the dimension of space. These two types of behavior are separated by a multicritical point  $E/k_B T = \vartheta$  which is called the ‘theta point’. Here the exponent  $\nu$  has a value  $\nu_\theta$  which is different from both the value  $1/d$  in the collapsed state and the excluded volume value  $\nu = \nu_{EV}$ . The theta point states of different models also

constitute a universality class but are less stable than those of the collapsed or excluded volume states. For example, the values  $\nu = \nu_\theta$  in the above lattice model and in a corresponding model with freely rotating rods are the same.

Now we turn to polymers near surfaces. Typically the surface is (i) impenetrable to monomers and may (ii) exert short range forces on the monomers.<sup>b</sup> In any of the above lattice models these properties can be easily taken care of by restricting the lattice to a half space bounded by the surface and by assigning an energy gain  $\mathcal{E}$  to each occupied surface site.

To understand the implications of (i) and (ii), it is instructive to consider a chain which is fixed ('grafted') to a surface point at one end and to observe the mean number  $N_1$  of other chain-monomers which happen to be located in the surface (number of 'surface contacts'). For  $\mathcal{E}=0$  the only property of the surface is its impenetrability; it acts as a 'pure hard wall' on the monomers. This has a repulsive effect, due to entropic reasons. It decreases the number  $N_1$  of surface contacts with respect to the corresponding number  $\tilde{N}_1$  for a chain in infinite space. Here  $\tilde{N}_1$  is the number of contacts or intersections with a plane (which is only mathematical) through the fixed end. Quantitatively one finds that  $N_1$  is independent of  $N$  while  $\tilde{N}_1 \sim N^{1-\nu}$  increases with  $N$ , for  $N \rightarrow \infty$ . The  $\mathcal{E}=0$  state of the chain can be called 'nonadsorbed' or 'desorbed'. The same behavior persists for  $\mathcal{E}/k_B T$  below a certain threshold,  $\mathcal{E}/k_B T < \alpha$ . However, for  $\mathcal{E}/k_B T > \alpha$  the polymer is in an 'adsorbed' state with  $N_1 \sim N$  for  $N \rightarrow \infty$ . The 'adsorption threshold',  $\mathcal{E}/k_B T = \alpha$ , is a multicritical point<sup>c</sup> where  $N_1 \sim N^\Phi$  increases with an exponent  $\Phi$  which is different from 0 and 1. In line with the desorbed—adsorbed picture, the mean distance  $R_1$  of the free end from the surface increases with  $N$ ,  $R_1 \sim N^\nu$ , in the nonadsorbed (and threshold) state while it becomes independent of  $N$  in the adsorbed state. In the adsorbed state the endgrafted chain is 'bound', as a whole, to the surface and shows features of a chain in  $d-1$  dimensional bulk. For example, the projection  $R_\parallel$  of the end-to-end distance parallel to the surface increases  $\sim N^{\nu^{(d-1)}}$ . Here  $\nu^{(d-1)}$  is an exponent of a bulk universality class in  $d-1$  dimensions which is determined by bulk and surface properties of our semi-infinite system.

<sup>b</sup>For simplicity we disregard here more complicated surface interactions such as an additional monomer pair interaction if the monomer pair is in the surface. These may be relevant in certain cases (compare, e.g., Chapters 6 and 8).

<sup>c</sup>There is a physically appealing qualitative correspondence of this surface-multicritical point with the theta point in bulk where the adsorbed phase for the former corresponds to the collapsed phase for the latter.

It is important to notice that there also exist surface properties which are universal. One example is the exponent in the  $N$ -dependence of  $N_1$  for large  $N$  which is 0,  $\Phi$  and 1 in the nonadsorbed, threshold and adsorbed state, respectively, as mentioned above. These universal surface properties are again independent of most details, e.g. independent of the lattice structure in polymer lattice models. They depend, however, not only on the bulk universality class<sup>d</sup> but in addition on the type (nonadsorbed, threshold, adsorbed) of surface behavior. One may thus say that each bulk universality class splits into several surface universality classes.

We mention other interesting universal surface properties which are found in solutions of polymers. Consider a dilute monodisperse solution bounded by a surface in the nonadsorbed or threshold state and observe the mean densities of monomers or of chain ends as a function of distance  $z$  from the surface. These densities approach the corresponding bulk densities if  $z \gg R$ . Here  $R$  is the end-to-end distance of a chain in bulk which for large  $N$  is much larger than all other microscopic lengths  $l$  in the problem.<sup>e</sup> An interesting  $z$ -region is  $l \ll z \ll R$ , which is sometimes called the 'short distance' region, and where the densities follow power laws  $\sim z^\lambda$ . Here the power law exponents  $\lambda$  are universal surface properties. They depend only upon the bulk universality class (e.g. ideal, excluded volume or theta), the surface class (nonadsorbed or threshold) and the type of density (monomers or chain ends). Moreover, if the densities are properly scaled by dividing through the density in bulk and by measuring  $z$  in units of  $R$  one obtains whole (scaling) functions which are universal surface properties.

The forces which the surface exerts on the monomers are assumed to be 'short range'. The universal surface properties are—to a certain extent— independent of how rapidly these forces decay to zero if one moves away from the surface. This is of practical importance since the surface forces will in general have a van der Waals contribution which decays to zero only with a power law. As it turns out, this van der Waals decay is still in the short range surface universality class.

The big advantage in the evaluation of universal properties is the possibility

<sup>d</sup> The exponents  $\Phi$  for a chain with excluded volume interaction in bulk and a chain which is ideal in bulk are different.

<sup>e</sup> Here we consider the surface either at threshold or *deep* in the nonadsorbed state, i.e. far away from the threshold. For a nonadsorbing surface with  $\varepsilon/k_B T$  close to the threshold value, there appears in addition to  $R$  another macroscopic length (a 'crossover' length) and the  $z$ -dependence becomes more involved; compare Sec. 5.6.4.