Theory and Simulation of Polymers at Surfaces and Interfaces

Verschiedene Polymersysteme an Oberflächen und Grenzflächen sind mit Hilfe von Computersimulationen und Scaling-Methoden untersucht worden. In Simulationen unter Benutzung molekular-dynamischer Methoden wurden Polymer-Bürsten analysiert. Insbesondere wurde die Kräfteverteilung entlang der Bindungen von Polymerketten untersucht. Hier zeigte sich, dass die Bindungskräfte für die Monomere, welche direkt mit der Oberfläche verbunden sind, ein singuläres Verhalten aufweisen: Die Bindungskräfte nehmen mit zunehmender Dichte der Bürste ab, während die gesamte Kraftverteilung entlang der Ketten anwächst. In unseren Simulationen der Langzeit-Dynamik der freien Kettenenden in der Polymer-Bürste konnten dynamische Prozesse identifiziert werden, bei denen die Endmonomere in das Dichteprofil der Bürste für lange Zeit eintauchen. Irreversible Adsorptionsprozesse von Polymerketten auf festen Substraten sind typisch für verschiedene Präparationsmethoden von dünnen Polymerfilmen wie Spin-Casting oder Dip-Casting, bei denen Adsorptionsprozesse weit entfernt vom thermodynamischen Gleichgewicht dominieren. Auf Basis der detaillierten Daten aus unseren Monte-Carlo Simulationen konnten wir ein dynamisches Modell für den irreversiblen Absorptionsmechanismus entwickeln, welches in einfacher Weise die wesentlichen dynamischen Eigenschaften dieser Systeme beschreibt. Weiterhin haben wir zufällige Copolymere an Grenzflächen von stark entmischten Polymerphasen mit Hilfe von Monte-Carlo-Simulationen und Scaling-Methoden betrachtet. Insbesondere wurden hierbei die Details der Reorganisationsprozesse der an der Grenzfläche adsorbierten Copolymere als Funktion der Dichte der Copolymere untersucht.

Keywords
adsorption
copolymer
computer simulation
polymer brushes
scaling theory

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Introduction

There is growing interest in the preparation and design of thin polymer films and surface structures. Understanding the behavior of polymers at surfaces and interfaces is a necessary condition to control the properties of polymer films and polymer-surface-systems and to develop new techniques for their preparation. When long chain molecules interact with surfaces or interfaces there is a complex interplay between the conformational degrees of freedom of the chains, the interactions between monomers and surfaces sites, and geometrical constraints imposed by the the surface or by the layer thickness. This results frequently in a dramatic change of the properties of individual chains. For instance, during adsorption, polymers switch from a three dimensional random coil structure into flat "*pancake-like*" (two-dimensional) conformations. Moreover, if more than one species of monomers is present at the surface, segregation effects take place. These can lead to macroscopic or layer-like demixing patterns for polymer blends on surfaces, but also to micro-phase segregation in copolymers or if chains are chemically grafted to the surfaces. An example for a micro-phase segregated pattern obtained in a symmetric copolymer film is given in Fig.1. Such effects can be used for the preparation of patterned surfaces owing particular features and functionalities [1].

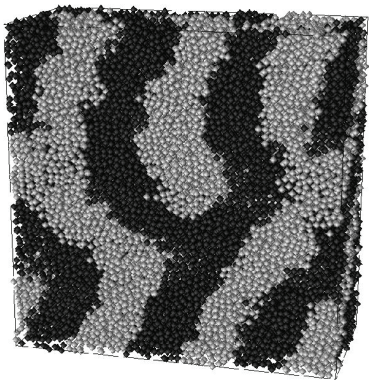

Fig. 1:
Microphase segregated structure of a thin copolymer film as obtained in computer simulations. The copolymers are composed of two blocks of the same length indicated in gray scales

In view of such a variety of features, approaches to understand polymers at surfaces and interfaces have to be considered on different levels.

First, the adsorption of single chains at surfaces and interfaces can be understood using well developed methods from statistical mechanics. The interplay between conformational degrees of freedom of the polymers and the adsorption energy results in a collapse of the chain in the direction perpendicular to the surface. As a consequence, the chain extension in the direction perpendicular to the surface no more depends on the chain length but is controlled by the surface interactions only. One can imagine the chain as an effective two-dimensional chain composed of "*adsorption blobs*", see Fig.2. When many chains are present the surface is occupied by monomers (saturation) already at very low bulk concentrations [2]. In this state, excluded volume effects lead to the formation of long loops and tails far above the proximal layer. Theoretical understanding can be achieved using approximation schemes such as a mean-field-approach (disregarding some fluctuation effects of the many chain system), or scaling. The same is true for the understanding of grafted polymer chains where excluded volume effects lead to strong stretching of the individual chains in the direction perpendicular to the surface.

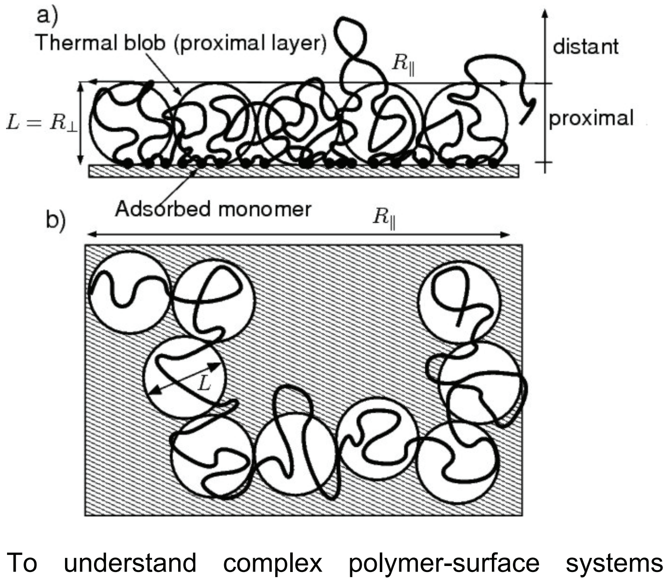

Fig. 2:
Sketch of a chain adsorbed onto a flat surface. The upper part displays the chain viewed from the side, which has collapsed into a (proximal) layer of a thickness independent of the chain length. This thickness defines the "blob" size. The lower part indicates the conformation of the chain viewed from above. Here, the blobs form the effective self-avoiding units (segments) of the chain.

To understand complex polymer-surface systems computer simulations play an important role. Here, it is possible study all microscopic properties in order to find out their impact on the macroscopic, observable features of the system.

However, the idea here is not to just simulate systems but to extract the most essential features and to find clues for a deeper theoretical understanding. In general, simulation models use certain universal properties of polymer systems. In most cases it is not necessary (and even impossible) to take into account all microscopic details of the system. For polymer systems there are two simulation methods which dominate most of the literature.

Lattice based Monte Carlo (MC) models are most useful to simulate universal properties of polymer systems on comparatively long time and length scales (up to some millions of monomers). One of the most important models for lattice polymer simulations is the bond fluctuation model (BFM), which is illustrated in Fig.3. Here, it is assumed that properties of polymer systems do not depend on atomistic details in an "*essential way*", but that the interplay of chain flexibility and monomer interactions lead to the observed behavior. The atomistic (and thus the chemical details) manifest themselves in the values of the parameters applied in the simulations such as the (statistical) segment length or the interaction parameters between the monomers and the between the monomers and the environment (surfaces, solvent quality, impurities, etc.).

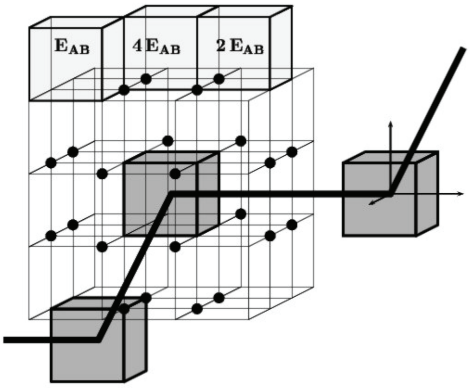

Fig. 3:
The bond fluctuation model. Here monomers occupy a unit cube on a three dimensional lattice and are connected by bonds of fluctuating length along the chain.

On the other hand, off-lattice models of polymers can be treated by standard molecular dynamics (MD) methods. Here, Newton's equation of motion is solved iteratively using a finite time step for the integration. MD methods can be considered as the most universal simulation scheme which is used in many areas of physics, chemistry and molecular biology. There exist ready to use software packages and program libraries providing the full source code and support for parallelization. For the implementation of MD schemes there exists various approaches ranging from most realistic all-atom simulations to course grained bead-spring models with the implementation of Langevin-type (dissipative) forces. For polymers, MD methods can be of advantage if strong interactions (such as crystallization) should be modeled where lattice MC methods provide some pitfalls by trapping the system in meta-stable artificial states. Moreover, the time series obtained from MD methods corresponds to the realistic motion of simulated particles provided that all interesting effects (such as hydrodynamic effects due to the solvent) are included. Furthermore, it is easier to simulated polymer systems with different properties such as different sizes of monomers (for instance to model functional groups or nanoparticles). The crucial point in more realistic MD simulations is the design of the "*force fields*", which means the interaction potentials included for the integration of the equations of motion.

Here, the interface to quantum mechanics must be established, since molecular forces such as Van der Waals forces or hydrogen bonds are of quantum mechanical origin.
In the following we will demonstrate how the various mathematical and simulation methods can be used to investigate polymers at interfaces by choosing some examples.

Polymer Brushes

When monomers of a polymer chain are chemically grafted to a surface brush-like structures emerge. Here, chains are stretching out in the direction perpendicular to the surface because of excluded volume constraints. This is sketched in Fig. 4.

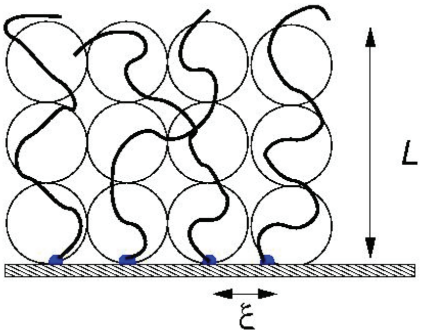

Fig. 4:
Sketch of a polymer brush

In a simplified view one can consider the chains as being composed of blobs which size is given by the averaged distance between two grafting points $\xi = 1/\sqrt{\sigma}$, where σ denotes the grafting density of chains. Under excluded volume conditions (good solvent) the number of monomers per blob scales as $g \sim \xi^{1/\nu}$, where ν denotes the Flory exponent $(\nu \cong 3/5)$. For chains having N monomers the height of the brush is given by $L \sim (N/g)\xi \sim N\xi^{-1/\nu+1} \sim \sigma^{(1-\nu)/2\nu}$. Using the approximate value for the Flory exponent, we obtain $L \sim N\sigma^{1/3}$. Thus, the height of a brush scales linearly with the degree of polymerization which is in marked contrast to the behavior of free chains where the extension scales like N^{ν} only. This feature is very important for the application of polymer brushes for lubrication and colloid stabilization. The obtained brush heights can be much larger than the characteristic range of van-der-Waals forces of the bare surfaces.
In oder to study the properties of polymer brushes we have applied MD simulations. A snapshot of a typical system is shown in Fig. 5.

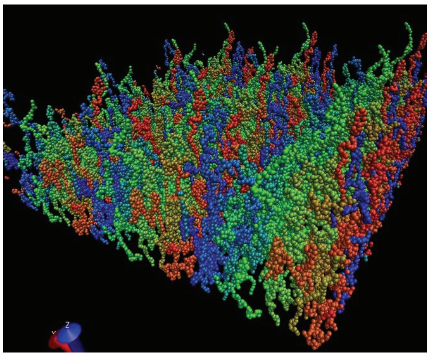

Fig. 5:
Snapshot of a simulates polymer brush. The colors indicate different chains.

Using different chain lengths and grafting densities ranging from isolated chains (non-overlapping "*mushroom*" state) up to very high densities we are able to test theoretical prediction and to investigate various static and dynamic quantities.

In the theory of polymer brushes, chains are considered in the semi-dilute state (see the blob-model above). Thus the lateral fluctuations of the monomers should follow a scaling behavior as

$$\rho / \rho_0 = f_\rho(\sigma / \sigma^*) ,$$

where ρ denotes the average size of the monomer fluctuation in the lateral direction and σ^* denotes the grafting density at which the chains start to overlap $(\sigma^* \sim 1/\rho_0^2)$. Here, ρ_0 gives the lateral extension of fluctuations for non-overlapping chains, i.e. $\rho_0 \sim N^\nu$. In the brush regime $(\sigma >> \sigma^*)$ semi-dilute scaling predicts $\rho \sim N^{1/2}\sigma^{-1/12}$. The result of our simulations for two different chain lengths and various grafting densities is displayed in Fig.6. The general scaling holds only for low grafting densities (and even in this region it is not perfect). The expected slope of about –1/6 turns over in a much stronger negative slope of about –0.64 for higher grafting densities.

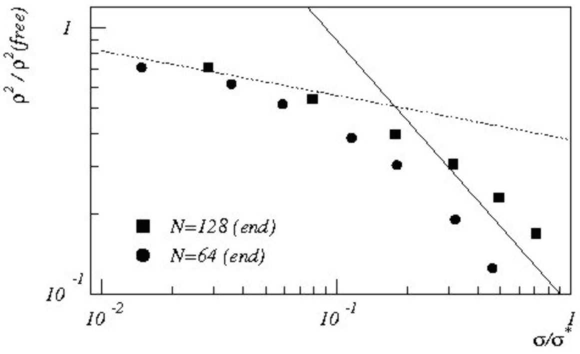

Fig. 6:
Scaling plot of the lateral fluctuations of monomers in a polymer brush. The rescaled averaged mean squared fluctuations are plotted versus the scaled grafting density.

In order to explain this behavior we have applied a model involving finite extensibility of chains. Unlike the Gaussian chain model (which is applied in the prediction for the semi-dilute scaling) stretching of the chain in the direction perpendicular to the surface reduces the fluctuation in the lateral direction.

Another interesting observation has been obtained by considering the forces acting on the bonds between the monomers. Since the grafting sites are made by chemical bonds, there is a limiting force which can be supported to form densely grafted brushes. To measure the forces acting on the bonds we calculate the gradient of the bond potential (which holds the monomers together within the chain). The result of this calculations is displayed in Fig. 7. The forces decrease towards the free ends (note the negative sign). By increasing the grafting density the average force is increased as it is expected intuitively. However, the first bond directly connected to the surface shows a singular behavior: The force acting on this bond is about two times stronger and *decreases* with grafting density. This effect could be explained by the geometrical constraint of the surface. The first bond can only orient in a half space, thus experiences a additional entropic force which tends to stretch the bond.

When the grafting density is increased, the lateral fluctuations of the all bonds are decreased and the gain of entropy by stretching the first bond is reduced. Thus, the effective force acting on this bond can be reduced as well. These results illustrate that the bond forces are presumably not a limiting factor by increasing the grafting density in a polymer brush.

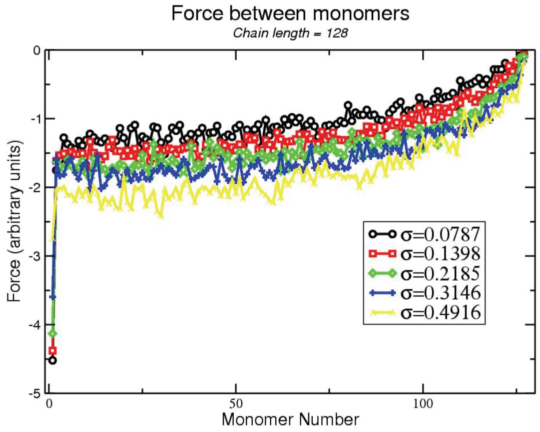

Fig. 7:
Forces acting on the bonds between monomers as a function of the monomer number along the chain, starting from the grafting bond.

Further investigations concern the dynamic properties of polymer brushes. By considering the dynamics of fluctuations of the free ends of the brush we have observed an interesting long-time behavior related to "*diving*" events of chains. This is illustrated in Fig.8. In a dense brush the chain ends are normally extended out of the main profile (white conformations in Fig. 8). However, on long time scales events take place where chains are diving into the brush profile (red conformation in Fig. 8). If such happens the chain can remain in the dived state for longer time. This is because the expelling force is small – the brush profile is rather flat (Note that the gradient of the profile provides the expelling force). This observation and a more detailed understanding of this effect can be of importance for experiments with functionalized end-groups or nanoparticle decorated ends of brush chains.

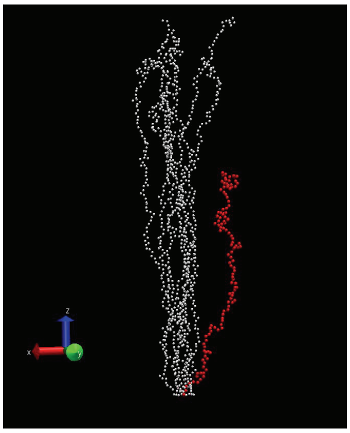

Fig. 8:
Several snapshots of an individual chain in the brush. White conformations indicate the normal, extended state. The red conformation shows the chain as diving into the brush

If two species of chains are present (mixed brush) repulsion forces between monomers lead to demixing. However, because of the anchoring of the chains onto the surface such segregation effects can only take place on a nanometer scale which is characteristic for the size of the chains. Such kind of microphase separation processes can be used to obtained patterned functional surfaces in the nanometer range and, therefore, experiments with such systems have attracted much attention [5]. Our simulation model allows the study mixed brushes and their dynamic behavior.

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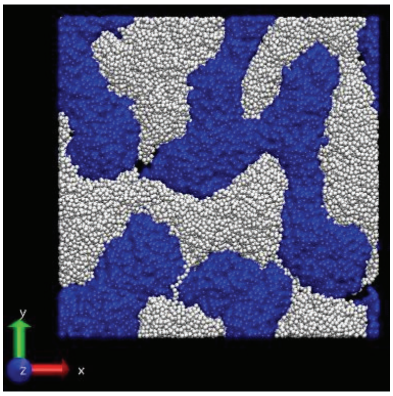

Fig. 9:
View from the top into an partially ordered mixed brush

Irreversible Adsorption of Polymers at Surfaces

If polymer chains are strongly attracted by the substrate equilibrium concepts fail to describe their behavior. The dynamical processes in the adsorbed state are two slow to allow for relaxations within experimentally accessible (and technologically interesting) time scales. On the other hand, such interactions are encountered in many real systems where functional groups form hydrogen bonds with the surface (such as most biological molecules do) or strong van der Waals interactions occur. In standard experimental techniques for the preparation of thin polymer films such as spin coating or dip coating, polymers in dilute solution are strongly adsorbed on a substrate. Thus, the behavior of polymer chains under the influence of quasi-irreversible adsorption processes (adsorption energies per statistical segment of more then $10kT$, where k denotes Boltzmann's constant and T is the absolute temperature) is of great interest.

In this case questions emerge which are related to dynamic, non-equilibrium phenomena in the first place: What happens to a polymer chain if it collapses onto a strongly attracting surface? What governs the kinetic processes under such non-equilibrium situations?

We have addressed such problems using Monte Carlo simulations (BFM) and dynamical scaling models. As a model system, we have considered an end-grafted chain which experiences a sudden strong (irreversible) attraction from the surface. Based on our simulation results that the process of collapsing is non-linear and can be described a power-law behavior as a function of time, we have introduced a two-phase model for the chain. Here the chain is described by an adsorbate portion and a corona portion formed by non-adsorbed monomers, and both parts are connected by an extended part (stem), see Fig. 10.

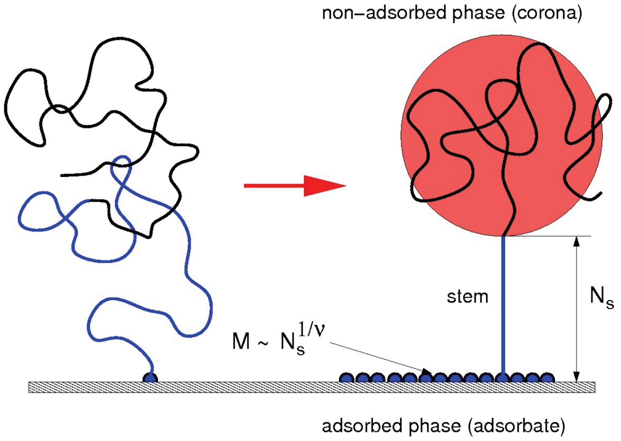

Fig. 10:
Two phase model of the polymer during irreversible adsorption. The monomers which are close to the surface are rapidly adsorbed which leads to the formation of a stretched part (stem) just above the last adsorbed monomer. The rest of the chain is not perturbed and forms a corona-phase. In oder to adsorb the next monomers, the stem must move cooperatively towards the surfaces. As more monomers belong the adsorbate as longer will be the stem. This leads to a sub-linear behavior of the number of adsorbed monomers as a function of time. When the stem reaches the size of the chain the rest of the chain (corona) will eventually collapse onto the substrate.

The basic idea is to consider the main stage of the adsorption process as "*zipping*" of monomers (along their order in the chain), where the friction coefficient is determined by pulling an extended chain part (stem) down to the surface. The stem is created as a non-equilibrium response to the fast zipping process which takes in rapidly all monomers close to the surface. This idea is sketched on the right hand side of Fig.10. Based on our model we can derive a scaling relation for the time of adsorption $t(M)$ as a function of the number M of adsorbed monomers. We obtain

$$t(M) \sim M^{\alpha} \text{ with } \alpha = 1 + \nu$$

where ν again denotes the Flory exponent. In Fig. 11, we show the result of Monte Carlo simulations, which is in good agreement with the predictions of the model. The analysis of the various density profiles as well as of the dynamics of loop formation during adsorption supports our theoretical model.

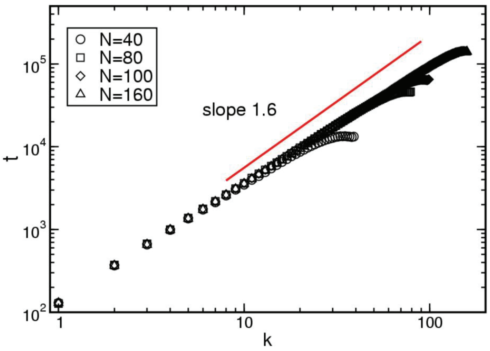

Fig. 11:
Time of adsorption as a function of the monomer index of adsorbed monomers counted from the grafting point. Good agreement with the scaling prediction is obtained.

The process of irreversible adsorption is illustrated by the time evolution of the density profile of a chain in Fig. 12. Here, one can clearly recognize that monomers are removed from the center of the profile while the shape is stable until the whole profile collapses with the adsorption of the last monomers.

This work give an example for a successful scaling approach to a problem on polymer dynamics far from equilibrium [3]. Further investigations should address the irreversible adsorption behavior of many chains. Here, blocking of adsorbed sites on the surface gives rise to different conformations of chains which adsorb later on the surface (for instance during a spin casting process).

Thus the history of the adsorption process manifests itself in the structure of the layer.

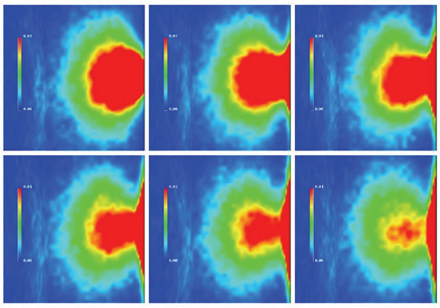

Fig. 12:
Density profiles of a polymer chain during irreversible adsorption. The colors indicate the density (red-high density). The density profiles are obtained by averaging over 20,000 independent realization of the adsorption process. The first profile (upper left) corresponds to the start of the adsorption process, the subsequent profiles are calculated after 2,000 Monte Carlo units of time in succession.

Adsorption of Random Copolymers at Selective Surfaces

Polymers are usually only poorly miscible which inhibits many interesting applications of polymer "*metallurgy*", where mixing of different polymer species are used to improve the properties of polymeric materials. The origin of this effect is the fact that the mixing entropy (the thermodynamical driving force for mixing) is of the order of kT per chain (translational degree of motion), while the interaction energy in a perfectly mixed system is proportional to the number of monomers. Thus, very small repulsive interaction energies per monomer (of the order of $1/N$ where N denotes the number of monomers) is sufficient to drive the system in the phase separated state. As a consequence, demixing morphologies (for instance droplets) are formed on the size of micro-meters with consequences for optical, mechanical and thermodynamic properties of the material. Similar effects concern the adhesion of two layers made of different polymers. Here, phase separation effects at the boundary between the layers greatly reduce the adhesive strength of the material. The common question in both cases is: Can we reduce the interface tension between two polymer phases by adding a small amount of polymers which compatibilize the phases? Candidates are diblock copolymers and random copolymers. The mechanism for diblock copolymers is quite obvious: Each bock prefers one of the phases and thus localizes at the interface. On the other hand it is by far not obvious why random copolymers should adsorb at interfaces.

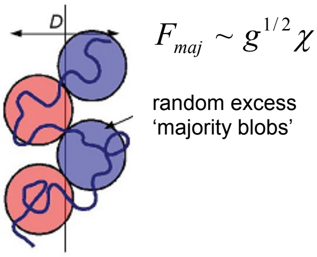

Fig. 13:
Sketch of the principle of adsorption of random copolymers at selective interfaces

In Fig. 13, we display the principle of the adsorption mechanism for random copolymers at selective interfaces [4]. The essential idea is the fact that in any randomly selected set of two species (such as monomers along the chain) one species has a average excess which scales like the square root of the number of items selected (Gaussian law of large numbers). Thus, if we pick out a group of g monomers, we obtain in average an excess of $g^{1/2}$ of one species in average. Now, this group tries to avoid the side of the interfaces which is not preferred by the majority species ("*democratic selection rule*"). If the product of the interface selectivity (difference between the Flory interaction parameter between both side of the interface) times the excess quantity, $x \cdot g^{1/2}$, exceeds the value of kT considerably, the gives group of

monomers (blob) will stay on the preferred side of the interface. Given the chain is long enough, there are many blobs having alternate excess of species.
Thus, the chain will localize at the interface by self-organizing into majority blobs in order to optimize (lower) the free energy.
The above sketched idea yields a universal scaling variable given by $y = N^{1/2}x$ which controls the adsorption behavior of random copolymers at selective interfaces. The consequences have been nicely proved by computer simulations. An interesting feature of the adsorption process is that individual chains can respond to external fields by reorganization of the blob structure. Such is the case when the concentration of chains is increased. In order to accommodate more chains on the interface, blobs can be reformed and the chains can stretch out into the bulk. This leads to over-saturation effects in adsorbed random copolymer layers as we have observed in computer simulations. In Fig. 14, we display the distribution of the number of loops (blobs) per chain. At low concentrations (isolated chains at the interface) the number of loops is narrowly distributed and depends strongly on the interface selectivity. This is in accord to the above given scaling picture. At higher concentrations the results change dramatically. Now, the number of loops has a wide distribution where the biggest loops (small number of loops per chain) are dominating. Furthermore, the distribution depends only weakly on the interface selectivity.

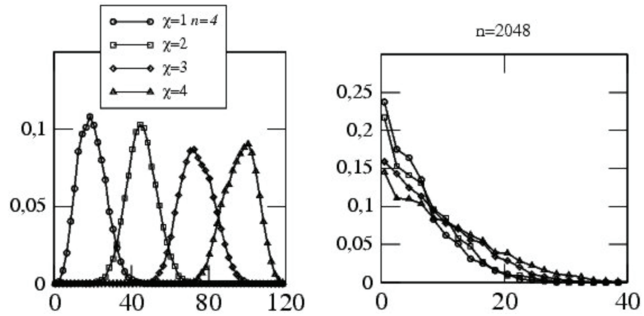

Fig. 14:
Probability to find a loop of a given length in an adsorbed random copolymer chain. Left hand side: Very low concentration of chains in the system (4 chains). Right hand side: higher concentration of chains (2048 chains).

Conclusions

In this work we have demonstrated the combination of scaling methods and computer simulations to explore the behavior of complex polymer systems at surfaces and interfaces. The interplay between polymer entropy (the tendency of polymer chains to explore as many conformations as possible), surface interactions and geometrical constraints gives rise to pattern formation and self-organization effects. Polymer brushes provide unique features due to the strong excluded volume interactions between the monomers and provide strong modifications of surface properties including nanoscale patterning in multi-component systems. Random copolymers can be used to improve interfacial properties. The understanding of irreversible adsorption processes gives us insight into the formation of thin polymer films prepared under non-equilibrium conditions.

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