Tethered polymer chains: surface chemistry and their impact on colloidal and surface properties

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Abstract

In this review the grafting of polymer chains to solid supports or interfaces and the subsequent impact on colloidal properties is examined. We start by examining theoretical models for densely grafted polymers (brushes), experimental techniques for their preparation and the properties of the ensuing structures. Our aim is to present a broad overview of the state of the art in this field, rather than an in-depth study. In the second section the interactions of surfaces with tethered polymers with the surrounding environment and the impact on colloidal properties are considered. Various theoretical models for such interactions are discussed. We then review the properties of colloids with tethered polymer chains, interactions between planar brushes and nanocolloids, interactions between brushes and biocolloids and the impact of grafted polymers on wetting properties of surfaces, using the ideas presented in the first section. The review closes with an outlook to possible new directions of research.

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1. Introduction

The DLVO theory for the stability of lyophobic colloids [1,2] is a milestone along the road of colloid science, marking the beginning of a systematic and quantitative investigation of the forces between charged particles. Ever since, it has been the framework for a large body of experimental and theoretical research up to the present day, and when the precise measurement of surface forces became possible, both long range electrostatic repulsion and van der Waals attraction were very directly confirmed. Of course, refinements and amendments, such as ion correlation [3] and surface roughness [4] effects are continuously finding their way into the theory, and experimental work is extending the knowledge on the properties of many kinds of interfaces and ions, as well as improving the techniques to measure forces, but the understanding of colloidal stability in terms of electrostatic repulsion and electrodynamic (dispersive) attraction has come a long way.

Electrical double layers are not the only method, however, to impart stability to lyophobic colloids against aggregation. The use of polymers for that purpose is older than colloid science itself. For example, the Egyptians and Chinese knew how to disperse lamp black and other pigment to obtain ink [5]. Michael Faraday, who may perhaps be considered as the first colloid chemist, used gelatine to prepare and stabilise gold sols. His samples, dating back to approximately 1850 and on display in the Royal Institute in London, are still stable after some 150 years. In these
classical examples, the stabilising action can be attributed to the fact that the polymers adsorb on the surface of the colloidal particles, thereby creating a sheath of swollen polymer around them. Compression of this layer meets with an increased osmotic pressure, and this is the origin of the repulsive force which keeps the particles at distances large enough to counter the van der Waals attraction. One might now think that physisorption of a polymer from a good solvent is a sufficient condition for providing stability. However, this is not true, because adsorbing polymers may stick to both surfaces. If they do so, they straddle the gap between the surfaces by means of so-called bridges and this leads to an effective attraction. A careful examination of the thermodynamics of physisorbing homopolymer between two surfaces has led to the conclusion that whenever the chemical potential of the polymer is kept constant (i.e. when the adsorbed amount can adjust itself by exchange of polymer with a reservoir) attraction prevails: the osmotic pressure remains low because a large portion of the chains leaves the gap between the particles and the remaining chains form more and more bridges. That adsorbed polymer may nevertheless often be effective is probably because during the short times characteristic for particle encounters in dilute colloidal dispersions, such desorption does not occur, unless the polymer is very flexible and very weakly adsorbed. However, in surface force measurements with colloid probe AFM it has been found that repulsion prevails upon approach, but after a sufficiently long contact time there is a pronounced adhesive force, proving that bridges form. Also, dispersions that are compressed in, e.g. a centrifuge or an osmotic cell tend to become irreversible aggregated whenever the applied pressure exceeds a certain threshold value. The longer the chains, the more bridges they make, and the stronger the adhesive interaction between the particles. Therefore, short chains often make better dispersants, even though they do not form thick layers around the particles.

End-attached chains are far better stabilisers because they cannot leave the surface so that the osmotic repulsion grows rapidly upon compression. Moreover, bridge formation is much less likely to occur. Therefore, chemists have been exploring the use of end-attached (‘tethered’) polymers to prepare lyophobic colloids, particularly for situations where electrical double layers are not an option: aqueous systems with a high salt concentration, or non-aqueous media. End-attached polymers began to draw the attention of (polymer) physicists, who pointed out that densely grafted chains stretch normal to the interface which endows them with unusual properties; the term ‘brush’ was coined for such structures. Theoretical work on brushes flourished from the mid seventies on, and this was followed up by many experimental attempts to prepare brushes and test the theoretical predictions. Meanwhile, the value of brushes in other applications than dispersion stability began to be recognised; in particular their use in controlling deposition of (bio)colloids such as proteins on surfaces, and their role in changing wetting and adhesion in polymer systems received attention. It is the purpose of the present review to discuss such applications and related experiments in the context of recent insights in the structure and thermodynamics of brushes. We limit ourselves to the discussion of
brushes of neutral polymers; work on polyelectrolyte brushes is beginning to emerge and highly interesting but we prefer to await further experimental developments.

The set-up of this review is as follows. First, we examine the preparation and properties of surfaces with grafted polymers. After a brief introduction we start with a general overview of some simple theoretical models for tethered polymers and the most important predictions of these models. The aim of this discussion is to provide tools for the reader to understand the ensuing sections. For more detailed theoretical studies of grafted polymers we refer the reader to the reviews of Szleifer and Carignano, Grest, Halperin et al. and references therein [17–19]. In Section 2.3 the experimental preparation of brushes is considered. The various possible techniques of forming polymer brushes are discussed generically, together with their (dis)advantages. This section is meant to present the reader with the multitude of preparation techniques, rather than to exhaust him with an encyclopaedic array of data. In Section 2.4 we focus on experimental characterisation of the properties of such surfaces, subdivided into the dependence of general parameters such as the thickness and surface pressure on grafting density and chain length, and a more detailed look at the density profile within a brush. The various techniques are briefly discussed and the experimental results are compared with the predictions. We stress, however, that the amount of literature on polymer brushes is vast, so that the choice of presented material inevitably reflects the personal preferences of the authors.

In Section 3 we consider the interactions between tethered polymers and the environment, in particular with particles capable of adsorption (proteins, bacteria, anorganic colloids). In Section 3.2 several analytical models for interactions between grafted chains and colloidal particles are briefly discussed. The different assumptions and approaches in the models are pointed out, as these strongly determine the outcome of the models. In Section 3.3 we then discuss the following cases: interaction between two surfaces with grafted polymers (Section 3.3.1), grafted polymers and small particles (Section 3.3.2), grafted polymers and biocolloids (Section 3.3.3), and grafted polymers and their impact on the wetting properties of surfaces (Section 3.3.4). In these sections the focus is on experimental studies that can be understood in the framework of models introduced in Sections 2.2 and 3.2.

In Section 4 this review closes with a summary of the most important results and an outlook on possible developments in the field of polymer brushes in the future.

2. Tethered polymers

2.1. Introduction

Ever since the first seminal papers of de Gennes and Alexander (AdG) on polymers end-grafted to surfaces, the preparation, properties and application of tethered polymers has excited both academic and industrial researchers [9,10]. In Section 1 we specifically mentioned colloidal stabilisation, but there are other important applications. In the field of lubrication polymers are chemically tethered to surfaces in certain high-end applications, to prevent their migration and thus sustain their lubricating action. Examples are the grafting of fluoro-polyethers to the
surface of computers hard-disks and the grafting of PDMS in UV-curable acrylate coatings [20,21]. As the medical industry increasingly employs surgery techniques based on catheters and microbores, the lubrication of biomedical instruments in body fluids is increasingly important. Here, good results may again be achieved using tethered hydrophilic polymers [22]. In Sections 3.3.2 and 3.3.3 the modification of adsorption properties of surfaces via grafting is discussed, and in Section 3.3.4 wetting is examined, both highly relevant for industrial applications.

From an academic point of view, the grafting of neutral polymers with well-defined length distributions is extremely interesting as well. Early on, the regime in which the polymer grafting density is high enough to induce stretching of the chains normal to the surface has been coined the *brush* regime [9,10]. In the past decade several theoretical brush models of varying complexity have been presented in the literature. The approaches include scaling theories, analytical models, numerical statistical models, Monte Carlo and molecular dynamics models. Variation of parameters as the grafting density, solvent quality and adsorption strength to the grafting plane results in a large variety of predicted behaviour of polymer brushes [17–19].

The experimental preparation of surfaces with end-grafted polymers of controlled length at a controlled grafting density, however, has proven to be rather complex. In general, one can say that the experiments in the field of polymer brushes with well characterised systems lag behind the theoretical developments by several years. There are a number of experimental methods to prepare a polymer brush, each with its own (dis)advantages. The thickness of a brush layer, depending on its manner of preparation, may vary from a few to more than a hundred nanometers. The manner of preparation of surfaces with tethered polymers needs to be selected with the requirements of the system in mind (i.e. a small amount of a carefully prepared and characterised brushed surfaces, or a large amount of less well-defined coated surfaces).

Besides preparation of a brush, the determination of physical properties of the tethered polymer layer, such as the thickness and density distribution, is challenging as well. The experimental techniques generally used including neutron scattering and reflectivity, surface force apparatus, ellipsometry and atomic force microscopy. Recent advances in imaging techniques have proven fruitful for the determination of various brush properties. For instance, the repulsive force exerted by a brush upon compression can be measured quantitatively by AFM, the monomer density distributions can be determined in detail with neutron scattering techniques. For this reason, investigations in polymer brushes take up a prominent position in the forefront of experimental polymer physics in the past decade.

2.2. *Theoretical models*

In this subsection we examine some simple theoretical models for neutral, end-grafted polymer chains. We make a clear distinction between chains end-grafted at low densities and chains end-grafted at high densities. The former have either a globule, a coil or pancake conformation, the latter a brush conformation. These
conformations are discussed in the following, together with the parameters that determine the polymer conformation.

To introduce a number of important parameters, we start with a single homopolymer consisting of \( N \) monomers in a bulk solution. We use a simple mean-field Flory-like approach, in which the free energy of a polymer chain is assumed to consist of the sum of two contributions, namely osmotic interactions in the coil and the conformational entropy (elasticity) of the polymer chain.

\[ F = F_{\text{os}} + F_{\text{el}} \]

The equilibrium conformation is found by minimising this free energy [23]. The osmotic interactions can be written as a Taylor series

\[ \frac{F_{\text{os}}}{kT} = \int d\mathbf{r} \left( \frac{v_0 \rho(\mathbf{r})^2}{2} + \frac{\sigma \rho(\mathbf{r})^3}{6} + \cdots \right) \]

where \( V \) denotes the volume of the coil, \( \rho(\mathbf{r}) \) is the monomer density at position \( \mathbf{r} \) and \( v_0 \) and \( \sigma \) are the second and third monomeric virial coefficient, respectively.

In the most simple approach, \( \rho(\mathbf{r}) \) is assumed uniform throughout the volume \( V \), i.e. equals \( 3N/4\pi R_G^3 \) where the radius of gyration \( R_G \) denotes the average dimension of the polymer coil. The quality of the solvent is characterised by the monomer–monomer interaction coefficient \( v_0 \): if the solvent quality is good, i.e. the temperature is above the \( \Theta \)-temperature, \( v_0 > 0 \) and the binary interactions between monomers are repulsive. If the solvent quality is bad, i.e. the temperature is below the \( \Theta \)-temperature, \( v_0 < 0 \) and the binary interactions between monomers are attractive [24]. The \( \Theta \)-temperature is defined as the temperature at which the attractive and repulsive interactions effectively cancel each other, \( v_0 = 0 \). The binary excluded-volume parameter is sometimes written as \( v_0 = 1 - 2\chi \), where \( \chi \) is the monomer–solvent Flory-Huggins parameter [25]. Following Birshtein and Pryamitsyn [26], the conformational entropy of a Gaussian coil is given as

\[ F_{\text{el}} = \begin{cases} \frac{R_G^2}{R_0^2} - \ln \left( \frac{R_G^2}{R_0^2} \right) & \text{for } v_0 > 0 \\ \frac{R_0^2}{R_G^2} + \ln \left( \frac{R_0^2}{R_G^2} \right) & \text{for } v_0 \leq 0 \end{cases} \]

where \( R_0 \) is the Gaussian radius of a coil, given as \( R_0 \sim N^{1/2}l \) with \( l \) the monomer length [23]. This is the average size of a polymer chain, when its conformation follows the trajectories of a random-walk, and it corresponds with maximal conformational entropy [25]. The equilibrium size of the coil is found by minimising \( F_{\text{os}} + F_{\text{el}} \) with respect to \( R_G \). In a good solvent the asymptotic result for long chains is the well-known Flory scaling law \( R_G \sim N^{3/5}v_0^{1/5} \). The corresponding (uniform) density in the swollen coil scales as \( \rho \sim N^{-4/5} \), i.e. in a good solvent the monomer density of a long polymer chain is very low. Under bad solvent conditions the resultant scaling expression is \( R_G \sim N^{1/3} \left| -\sigma/v_0 \right|^{1/3} \), i.e. the conformation of the
polymer is that of a collapsed globule, with a high density. Thus, the chain size depends strongly on the solvent conditions. Experimentally, the volume of a solvated polystyrene chain of order $10^4$ monomers, for instance, may decrease by a factor 10 with decreasing solvent quality [27,28].

If a polymer chain is end-grafted to a surface, a second interaction must be considered besides monomer–solvent interactions, namely monomer–surface interactions. If the Flory–Huggins parameter of monomer–surface interactions $\chi$ is 0 or positive, the surface is inert to the polymer and the conformation of the latter is roughly that in the bulk. In this case the grafted polymer conformation is a swollen coil in a good solvent and a collapsed globule in a bad solvent.

However, if $\chi < 0$ the polymer is effectively attracted to the surface. The ensuing conformation is a balance between the loss in conformational entropy of the coil as it flattens on the grafting surface, and the energetic gain due to surface–monomer contacts. If $\chi$ is below a certain critical value, then the polymer chain adapts a so-called pancake conformation under good solvent conditions [29]. This critical value of the adsorption energy is of order of 0.2–0.3 $kT$ per monomer. The size of a polymer chain in a pancake conformation, i.e. a 2D self-avoiding walk, is predicted to scale as $R_G \sim N^{3/4}$ [30]. Thus, depending on the solvent conditions and monomer–surface interactions a single grafted polymer may have a globule, a coil or a pancake conformation, as illustrated schematically in Fig. 1.

We remark that $\chi$ is an effective interaction energy, i.e. it is the difference between the solvent–surface and polymer–surface interactions. This is of importance when hydrophilic polymers are grafted to a hydrophobic surface, such as polystyrene or polyethylene, in contact with water. As the water–surface interactions are highly unfavourable, the polymer may adapt a pancake conformation to decrease the interfacial energy, even if the interaction with the surface itself is unfavourable. An example of this is the adsorption of polyethylene-oxide (PEO) at the air/water or membrane–water interface. Although water is a good solvent for PEO [33], it

Fig. 1. Possible conformations of a single grafted chain, depicted schematically: globule (bad solvent, non-adsorbing polymer), coil (good solvent, non-adsorbing polymer) and pancake (good solvent, adsorbing polymer).
adsorbs strongly to the air/water interface [31,32]. This adsorption is not due to favourable air–PEO interactions (PEO has a collapsed globule conformation in air), but results from the high excess energy of the air/water interface, characterised by a high surface tension. The same holds for PEO adsorption on apolar surfaces in contact with water.

If the grafting density increases, the grafted polymers overlap at a certain critical grafting density $\sigma_{cr}$, which approximately equals $\sigma_{cr} \approx (4\pi R_i^2)^{-1}$ where $\sigma$ is defined as the number of chains per unit area [34]. In this expression $R_i$ is either the 2D radius of gyration of a pancake, or the 3D radius of gyration of a chain in a globule or coil conformation. At grafting densities above $\sigma_{cr}$ the intermolecular osmotic interactions result in stretching of the grafted polymers normal to the grafting plane, and at high densities a brush is formed [35,36]. Such brush structures have been investigated with several theoretical models. Generally speaking, these brush models can be divided into three classes of increasing complexity, namely scaling theories, analytical self-consistent-field (aSCF) models and numerical models.

The concept of brushes (strongly stretched polymer chains, densely grafted onto an interface) was first introduced by Alexander in 1977 using a scaling approach, although the phrase brush was introduced later [9]. In this seminal paper non-adsorbing polymer chains with a strongly adsorbing end-group at high densities in a good solvent were described as cigar-like conformations. In 1980 de Gennes modelled such end-adsorbed polymers using a blob or scaling model [10]. In the scaling models of AdG the monomer density is assumed to be constant throughout the brush, the so-called box-model. This implies that the polymers are uniformly stretched and that all chain ends are located at the edge of the brush. The confinement of chains due to the proximity of neighbouring chains results in the formation of a number of blobs per chain, as illustrated in Fig. 2. The definition of a blob is a string of monomers, the conformation of which is unperturbed by intermolecular interactions [37]. The increase in free energy upon formation of a blob is of order $kT$. In the case of a single grafted chain without neighbouring chains the coil forms a single blob of size $R_i$. In the case of closely packed chains the size $\xi$ of blobs in a brush is equal to the spacing between two adjacent grafted chains $\sigma^{-1/2}$. In a good solvent the number of monomers per blob is $g \sim (\xi/h)^{5/3}$ where, in the spirit of scaling theory, numerical prefactors are neglected. Note that the scaling exponent $5/3$ implies good solvent conditions, see the discussion following Eq. (3). The thickness or height of the brush $H$ is simply the total number of blobs per grafted chain $(N/g)$ multiplied by their size $\xi$. This yields the simple scaling law for the brush thickness.

$$H \sim N^{1/3} \sigma^{1/3} \quad (4)$$

The surface pressure $\pi$ of the brush is proportional to the number of blobs per unit area $(N\sigma/g)$ and, as the formation of each blob requires an energy of order $kT$, $\pi$ is proportional to

$$\pi \sim N^{11/6} \sigma^{1/3} \quad (5)$$

The main assumption in the AdG box-model, namely all polymers in a brush are
Fig. 2. A polymer brush according to the box-model of AdG [9,10]. The blobs in the brush are indicated by dashed curves. The average distance between the grafted chains is denoted by $\sigma^{-1/2}$.

equally stretched with their chain ends positioned at a distance $H$ from the grafting surface, is a serious oversimplification which underestimates the conformational entropy of the grafted chains. At the end of the 1980s aSCF models were introduced in which the chain ends are allowed to distribute themselves throughout the brush [11,13,14,38,39]. In the following the aSCF model is discussed briefly in general terms, a more detailed treatment is given in Appendix A.

In the aSCF model the assumption is made that the grafting density is high enough for the brush to be laterally homogeneous. This implies that the monomer density and chain end density are solely functions of the distance to the grafting surface. If a chain end is positioned at a certain distance, then only the most probable chain conformation is considered in the aSCF models. It turns out that this implies that no back-folding of chains is taken into account. With increasing monomer number $s$ ($s$ is 0 for the grafted monomer and $N$ for the free end) the polymer monotonously ‘moves’ away from the grafting surface. The resulting density profile is parabolic (Appendix A).

$$\rho(z) = \rho_0 \left( A - \frac{\pi^2 z^2}{8N^2 l^4} \right)$$

and it follows that the aSCF model predicts a parabolic density profile in the brush.
The constant $A$ is determined by the normalisation condition.

$$N\sigma = \int_0^H dz \rho(z)$$

We may characterise the brush height $H$ in the aSCF model by $r(H)$. Inserting this in Eq. (6) and using the conservation of mass it follows that the aSCF model yields the same scaling expression for the brush height as the AdG scaling model, $H \sim N\sigma^{1/3}$. The surface pressure in the aSCF model is found by integrating the local osmotic pressure in the brush, $1/2v_0\rho(z)^2$, over the total height and scales as $\pi \sim N\sigma^{5/3}$. The power law exponent of $\pi$ as a function of $\sigma$ differs slightly from that of the AdG model (10/6 vs. 11/6, respectively).

As is the case with all elegant physical models, the aSCF model for brushes has its flaws. The most serious simplification is that the grafted chain in the aSCF model assumes its most probable conformation: fluctuations around this conformation are not taken into account. Such fluctuations, however, may be of importance for the brush structure, especially at small grafting densities or in the case of short chains. To include such conformational fluctuations, one can revert to for instance numerical self-consistent-field (nSCF) models or simulations [16,40–46]. It would lead too far to discuss such numerical models in detail in this review. We refer the readers to Refs. [16,40–46] for details. In short, in nSCF models the monomer density in the brush at a given distance $z$ from the grafting plane is the combined sum of the density at $z$ of all possible conformations, weighted by the probability of each conformation. In this respect nSCF models differ from aSCF models, as in the latter only the most probable conformation is considered. In turn, the probability of a given conformation depends on the same density distribution $\rho(z)$ through the osmotic penalty. The equilibrium density distribution $\rho(z)$, that is self-consistent with the distribution of polymer conformations it generates, is determined numerically for a given grafting density, chain length, adsorption properties and solvent conditions (Fig. 3).

In several papers the nSCF results for non-adsorbing neutral polymer brushes are compared to the parabolic density profile, predicted by the aSCF model [16,40,41,44]. In general, it is found that the conformational fluctuations may result in an extended tail region, in which the monomer density smoothly decreases to zero. The contribution of this tail region to the density profile is predicted to decrease with increasing chain length and grafting density [16,44]. Thus, nSCF models predict the parabolic density distribution in a brush to be a good representation for long chains at relatively high grafting densities under good solvent conditions. Also, a depletion region close to the surface is predicted, as the impermeability of the grafting plane is entropically unfavourable. In Fig. 3 the predicted density distributions of the box model, aSCF and nSCF models are shown schematically. The nSCF density distribution is calculated with the Scheutjens–Fleer self-consistent field lattice model (SF-SCF), details of which are found in Ref. [29]. It is clear that the uniform density distribution in the box-model differs significantly from the aSCF and nSCF density distributions. Overall, we may
conclude that for long chains at high grafting densities the nSCF and aSCF density distribution are quite similar, save for the smooth tail region at the end of the brush and the depletion region at the grafting plane. In the same vein, adsorption of the chains to the grafting surface was numerically shown to have a large impact on the density distributions at low and intermediate grafting densities, whereas a high densities the parabolic profile prevails [32].

In the previous paragraphs we have discussed the extreme cases of long chains grafted at either a low grafting density (mushrooms, pancakes) or at a high grafting density (brushes). However, a large number of experimental systems will not meet one of these extreme cases, either due to short chains or an insufficient grafting density to obtain a polymer brush. In the literature this regime has been coined the quasi-brush or pseudo-brush regime [35,47,48]. The density distribution within the quasi-brush layers decreases faster than the parabolic profile in a brush. Overall, a quasi-brush is characterised by a relatively high density near the grafting surface, a regime in which the density drops quickly and a distal regime with a low density that contains a large fraction of the chain ends.

Up to this point, the discussion has focused on polymer brushes in good solvent conditions. As mentioned, however, in a bad solvent a single polymer coil decreases strongly in size. Evidently, bad solvent conditions are expected to have an equally large effect on the brush thickness. This is supported by theoretical models. As the solvent quality decreases, the polymers are predicted to collapse continuously towards the grafting plane [42,49]. The density profiles of a brush for several solvent qualities, calculated with the SF-SCF model, are shown in Fig. 4 [16]. Clearly, the profiles in poor solvent deviate from the parabola, displaying a more ‘box-like’ shape.
Fig. 4. Scheutjens–Fleer nSCF density distribution of a non-adsorbing brush for four decreasing solvent qualities (a–d), as indicated in the figure, for various chain lengths $N=600$, $100$, $50$ and $25$, and $\sigma l^{-2}=0.1$ [16]. The density is given in units of volume fraction $\phi$ and the distance $z$ from the substrate is scaled by the brush height, i.e. $t=z/H$. The dashed line indicates the profile as obtained from the analytical theory which is valid for very long chains. The numerical results deviate from the analytical to an extent increasing with decreasing chain length.

The exact conformation of the grafted layer depends on the grafting density and solvent conditions. For instance, under certain conditions microphase separation into globules and collapsed brushes is predicted to occur [42,50]. We will not consider bad solvency conditions further, as practical usage of polymer brushes is generally limited to good or $\Theta$-solvents.

A different situation arises when the polymer chains are not grafted to a planar surface but to a curved surface. This is the case for colloids with grafted or adsorbed polymers, the radius of which is comparable to the thickness of the grafted layer. A relevant case is that of block copolymer micelles with a relatively small core of insoluble polymer. Ball et al. considered such systems using an aSCF-model, Wijmans and Zhulina did the same using a nSCF-model [51,52]. Two extremes can be identified: that in which the colloidal radius is considerably larger than the layer thickness, in which case a parabolic density distribution similar to the planar case is observed, and that of considerably smaller radius, in which case a star-like polymer is obtained. In the latter case the density distribution drops with a power
law, i.e. decreases much stronger with increasing distance from the grafting plane than in a parabolic distribution. Also, the curvature is predicted to result in the expulsion of chain ends to the outer parts of the grafted layer.

2.3. Preparation of brushes

When one aims at preparing surfaces with end-grafted chains, the method of choice ideally allows for full control over the structure of the grafted layer. One would thus like to control not only the chemical nature and the length (distribution) of the grafted chains within a large range, but also where they are ‘planted’, and up to what density. In addition, it would be very advantageous if one could check and/or modify the result, e.g. by being able to add or remove grafted chains in a controlled manner. Over the years many different approaches to prepare polymer brushes have been developed, each with specific advantages and disadvantages. There is not a single technique that stands out as the best: some techniques are well-suited to prepare small amounts of brushed surfaces typically for use in academic studies, others are better suited to rapidly prepare large amounts of coated surfaces with less precise control of the grafting density and chain length but more suitable for industrial applications. Finally, the chemical structure of the grafted polymer is an important factor, not only because it determines potential applications, but also because it has to be compatible with the method of brush preparation.

In this section we discuss brush preparation methods reported in the literature. The methods can generally be categorized into two kinds: (i) those that rely on in situ polymerisation from the substrate, and (ii) those that use preformed polymer chains.

2.3.1. In situ polymerisation methods

The first class of methods requires that one first prepares a surface with (usually covalently) attached monomers, from which the desired polymerisation can be initiated. During the ensuing polymerisation reaction polymers ‘grow’ from the surface and, provided the density of polymerisation sites is high enough, a brush is formed. Various kinds of polymerisations have been applied within this method. Conventional radical polymerisation [53], but also various kinds of living polymerisations: anionic [54], cationic [55], RAFT [56], controlled radical [57–59], and ring-opening reaction schemes [60]. Obviously, the reactions that can be employed depend on the kind of polymer one wants to obtain.

Because the chains grow from the surface, one avoids the problem of having to accumulate chains at a surface, which can be quite difficult when one deals with a polymer in a good solvent because of the strong osmotic repulsion. As a result, very dense brushes can be prepared with in situ polymerisation methods. In addition, termination reactions (in particular radical recombination) may be much less effective than propagation reactions, as the radicals cannot diffuse away, so that remarkably long chains can sometimes be made. So far, the current known record in (dry) brush thickness stands at 134 nm for polystyrene brushes on gold, prepared via living radical polymerisation by Habicht et al. [62].
The major disadvantage of the surface-initiation approach is that it is difficult to control the grafting density. In order to prepare a surface with grafted initiators one usually reacts the substrate with a large excess of the appropriate precursor so that one ends up with the maximum achievable coverage; varying the grafting density in a controlled manner is thus excluded by this procedure. Even if this problem can be overcome, it cannot be always assumed beforehand that on all grafting sites a chain successfully polymerises [62]. Another problem is that the initiator-carrying surface is vulnerable to reactive contaminants that terminate the polymerisation reaction. Almost always, some ungrafted polymer is also formed during the reaction. This need not be a problem, but sometimes the non-grafted polymer sticks to the grafted layer and inhibits further growth, so that it has to be removed by washing [60].

The result of a surface-initiated polymerisation can be simply assessed by determining the total mass per unit area $\Gamma$ of the dry (solvent free) film, e.g. by means of optical reflection techniques such as ellipsometry. One thus obtains the product of the chain length $N$ and the grafting density $\sigma$. In order to determine $N$ and $\sigma$ separately, an additional measurement is needed. By and large, most grafting studies have been done with silica or glass as substrate. Silica offers a versatile reactive surface because it can form Si–O–C bonds with organic molecules by means of a condensation reaction. This bond is susceptible to hydrolysis, so that grafted chains can be removed and analysed in order to determine their length [53].

With conventional radical polymerisations the chains will be very polydisperse, typically $M_w/M_n$ is between 1.5 and 3 as shown by Prucker and Rühe [53]. A recent improvement is the usage of controlled ('living') radical polymerisation [53,57–59,61]. The advantages of living radical polymerisation are: (a) linear increase of the chain length in time, (b) polymerisation can be re-initiated with a different monomer species, thus enabling the formation of grafted multiblock copolymers, and (c) compatibility of the polymerisation process with a large number of monomeric species, offering the possibility of grafted random copolymers. Husseman et al., for instance, reported a linear relationship between the brush thickness and the degree of conversion for polystyrene [58]. However, the grafting density was not controlled beforehand. In a study of Prucker and Rühe a monosilyl functionalised azo-initiator was convalently attached to silica particles and subsequently polymerised to a polystyrene brush [53]. The surface density was controlled via the concentration of initiator in solution, the chain length via the time of polymerisation. Using this technique, densities up to 85 mg m$^{-2}$ were obtained (in comparison, adsorption techniques result in densities of the order 1 mg m$^{-2}$, see the following section).

A rather unique approach was taken by Wieringa et al. [60]. These authors prepared brushes of polypeptides (polyglutamates) by means of ring-opening polymerisation of N-carboxyanhydrides. Initiation was achieved by means of surface-grafted amines, deposited by means of various methods in order to obtain the maximum possible surface density. The brush thus obtained consists of densely packed oriented helices, slightly tilted with respect to the surface normal, and has
piezo-electrical properties. Deliberate variation of the grafting density was not attempted.

In order to improve control over the grafting density, Devaux et al. used a ‘reactive’ Langmuir–Blodgett method to deposit the initiator on silica; this method allowed them to go from typically ‘dilute’ brushes to very dense ones while keeping the chain length fixed [57]. Clearly, living radical polymerisation has a lot of possibilities for controlled brush preparation.

2.3.2. Brushes from preformed polymers

The second class of methods employs preformed polymers. The obvious advantage here is that one can beforehand determine the properties (length, length distribution) of the polymer and accordingly select chains to be used for making the grafted layer. Also, it is possible to mix chains that differ, e.g. in length or in chemical constitution. The problem one is faced with, however, is that one needs chains which carry the proper functionality on one end. Often, one can obtain such polymers by some kind of living polymerisation, leading either to a di-block copolymer with a block capable of adsorbing on the given substrate, or to an end-functionalised polymer.

Early attempts to prepare grafted layers involved the use of di-block copolymers [63–67]. The idea was that one of the blocks (the anchor block) would bind to the substrate by means of weak, non-covalent bonds (physisorption) so that a layer could be prepared by simple exposure of the substrate to a dilute solution of the appropriate copolymer. Evidently, the brush structure so obtained depends on the lengths of the lyophobic and lyophilic block, and on the ratio of these two quantities. This technique is suitable for the preparation of large areas of coated surfaces. However, for the fabrication of dense and homogeneous brushes the approach turned out to have many limitations. First, it appears necessary to use a non-selective solvent, i.e. a solvent in which both blocks are soluble. If only one block is soluble, the polymer tends to form micelles. If these attach to the surface as such, the resulting layer is very inhomogeneous and it may stay so if the surface-bound chains lack the mobility to allow for changes in structure. Secondly, the average density of chains per unit area tends to remain low. The reason for this is that the adsorption process slows down dramatically as soon as the surface is covered with chains to the point where they begin to touch; incoming chains have to overcome a repulsive barrier that is high enough for the chains to be effectively excluded from making contact with the surface.

Hence, the structure one obtains using di-block copolymer adsorption is far from equilibrium and the amount adsorbed is relatively low. For instance, Marra and Hair adsorbed PEO–polystyrene block copolymers from an heptane/toluene mixture on mica [64]. In this study PEO acted as the anchoring block, as it is nonsoluble in heptane. Depending on the ratio of the PEO and PS block lengths, the adsorbed amount varied between 0.6 and 2.2 mg m$^{-2}$. In a similar study the adsorbed amount of poly(vinylpyridine) (PVP)–PS and PVP–polyisoprene block copolymers of various lengths on mica was of order 2 mg m$^{-2}$ [65]. In the study of Ansarifar and
Luckham the surface density of PVP–poly(t-butylstyrene), adsorbed from toluene on mica, did not exceed 1 mg m\(^{-2}\) as well [63].

Layers prepared by adsorption from a non-selective instead of a selective solvent are more homogeneous but they are no better as regards the grafting densities and introduce a new problem, namely that whereas one chooses the solvent to be non-selective, one wants the surface to be selective in the sense that only one of the blocks tends to adsorb. These two requirements are often conflicting, so that the block which one wants to stand off the surface and into the solution is in reality adsorbed as well [68]. For short chains anchored by means of one or a few functional groups at the chain end it may be possible to obtain equilibrated layers of end-adsorbed chains. One example is oligomeric polystyrene with zwitterionic end groups adsorbing from an apolar solvent onto mica [66]. However, the total adsorbed mass in these cases again tends again to be limited to 1–2 mg m\(^{-2}\). The limited grafting density in equilibrium (i.e. when the chemical potential of the adsorbed polymers is equal to that in the bulk) is the result of a balance between the entropic cost and energetic gain of grafting polymers to a surface. At a certain grafting density the free energy gain upon adsorption of a lyophobic block on the surface is effectively zero. This situation is examined in a crude approximation with the box-model of AdG in Appendix B. The overall conclusion of this most simple analysis is that the final grafting density decreases strongly with increasing chain length and solvent quality (via the second virial coefficient \(v_0\), \(\sigma \sim N^{-3/2}v_0^{-1}\), which virtually excludes spontaneous formation of dense brushes of long chains when the end group anchoring energy is no more than a few \(kT\) per chain.

A slightly better approach is to bring the substrate in contact with a melt of block copolymers, and to anneal this thermally to allow the anchor block to attain a high density on the substrate. After cooling, one can often employ a selective solvent to wash away non-adsorbed polymer without affecting the anchor layer [69]. As silica has proton donating properties, proton accepting polymers such as amines and pyridines have good anchoring abilities. Variation of \(\sigma\) is possible: the shorter the anchor block, the higher the grafting density. The length of the soluble (‘buoy’) block can also be varied. However, it is not possible to set the grafting density at a predetermined value and very dense brushes with the concomitant strong stretching are not obtained in this way. Despite such limitations, block copolymer adsorption may be appropriate for several practical applications, provided the grafting density is sufficient for the desired properties of the coated surfaces.

To obtain a true parabolic density profile in a brush, together with the predicted scaling behaviour for the brush thickness, a minimum adsorbed density of order of 10 mg m\(^{-2}\) is required (we return to this in the following section), i.e. much higher than with the above-mentioned adsorption techniques [70]. This may well be achieved using polymers with reactive end groups; for these, the final grafting density may be of order 10–40 mg m\(^{-2}\). This method has been employed by Auroy et al. to prepare brushes by reacting PDMS chains with terminal OH groups in heptane with the silanol groups of a silica surface and by Tran et al. who used a trichlorosilane end group to graft polystyrene onto silica [55,71–74]. Maas prepared
brushes by means of vinyl-terminated polystyrene; the terminal vinyl group reacts with a hydrogenated silicon surface, giving a Si–C bond between the chain end and the surface, which is more stable than the Si–O linkage [75]. Interestingly, the vinyl group turned out to react also with oxidised silicon, forming an Si–O–C linkage. This may be a relatively simple and efficient way to prepare dense chemisorbed brushes from preformed chains.

The rate of grafting via reactive end groups can be controlled by means of the polymer concentration of the solution in contact with the substrate, and typically takes many hours. The chemisorption approach produces dense and stable brushes, particularly when no solvent is used. The exact grafting density, however, cannot be controlled beforehand, but has to be determined after preparation via optical techniques. Accurate measurement of the amount of grafted chains is difficult, especially at low grafting densities [70]. In general, the grafting density increases with increasing polymer concentration and chain length, but it also depends on the time of annealing and on washing procedures etc. [55,72,73]. Not surprisingly, it is possible to prepare mixed brushes, consisting of a single kind of polymer but with a predetermined mixture of chain lengths [75]. It has also been attempted to construct brushes composed of two (or more) chemically different attached chains. These latter brushes are expected to allow for very unusual ‘chameleon’ properties of the surface, e.g. with respect to wetting [76]. The problem (as yet unsolved) is that the chemically different chains are usually not compatible, i.e. they may well segregate before any reaction has taken place. One then gets a ‘patchy’, chemically inhomogeneous brush.

If one could graft a fixed number of chains to an expandable interface, one would be able to vary σ in a simple way, keeping the chain length fixed. To some extent this can be done with block copolymers on a liquid/liquid interface; this approach has been used by various investigators in order to obtain a straightforward test of the scaling relations for brushes proposed by AdG. The easiest liquid surface to handle is the water–air interface; expansion and compression can be achieved using the familiar Langmuir trough equipped with movable barriers [32,70,77–80]. A schematic illustration of this method is shown in Fig. 5. The block copolymers are dissolved in a spreading solvent, which has to be immiscible with the bulk solvent. After spreading the solution on the interface with a micropipet the spreading solvent evaporates and the block copolymer is anchored to the interface by an insoluble anchoring block. The desired grafting density can then be obtained by compressing the polymeric monolayer in a Langmuir trough, see Fig. 5 [81]. During this compression the surface pressure of the polymeric monolayer can be measured continuously as a function of the grafting density. It is evident that upon spreading and compression no loss of polymers into the bulk phase may occur in order for the grafting density to be known accurately. This can be checked by examining the reproducibility of the surface pressure isotherms upon repeated compression and expansion. Many papers report a loss of polymer, either during spreading or during compression [77–80]. In such cases the surface density must again be determined indirectly via optical measurements.
The choice of polymers that can be used with water as the subphase is limited; only di-block copolymers with one water soluble block and one very hydrophobic block can be used. An ‘inverted’ case of a solvent-free brush, formed from liquid-like hydrophobic polyisobutylene chains with a short hydrophilic anchor block has been studied by Goedel et al. [82]. A non-aqueous subphase (ethyl benzoate) was used by Kent et al. [79]. Water–oil interfaces can probably be used as well but the technical difficulties are greater and this possibility has therefore not had any attention. The case best studied is PEO–PS on water [32,70]. Using highly hydrophobic PS anchoring blocks consisting of 35 monomers, Bijsterbosch et al. were able to obtain PEO brushes with a density of order 10 mg m$^{-2}$ [32]. In contrast, using less hydrophobic alkane groups as an anchoring block $(\text{CH}_2-(\text{CH}_2)_{11,15})$ for PEO blocks of varying length, Barentin et al. were not able to obtain densities above 1 mg m$^{-2}$ [80].

A different kind of expandable surface is a sheet of elastomeric material. Recently, the assembly of closely packed monolayers and brushes was reported on PDMS substrates that were mechanically stretched [83,84]. These substrates either reacted with end-reactive molecules or chains were grown from the surface using ATRP. After completion of the grafting steps the elastic surfaces were relaxed and the grafting density of the chains increases. This method was coined mechanically assisted polymer (monolayer) assembly and may lead to, for instance, highly hydrophobic surfaces using fluor-containing molecules [83].

End-attached polymers on a liquid interface are an interesting option if one wants to study brush structures without disturbing the subphase. However, such brushes are delicate and can be easily destroyed, e.g. by stirring. As mentioned, desorption
of the polymers is possible under certain conditions. Such conditions may be high densities upon compression of the monolayer in a Langmuir trough [80], but also desorption of adsorbed block copolymers on a solid substrate due to strong shearing of the solvent [85].

One therefore wonders whether it is possible to combine the robustness of brushes on a solid substrate with the ease and flexibility of preparation offered by a liquid surface. Such an approach has indeed been used successfully in a three-step method [86,87]. In the first step, a brush is prepared by spreading a di-block copolymer on a water surface and adjusting the surface area so as to obtain the desired chain density. In the second step the classical Langmuir–Blodgett method is used to transfer the brush to a solid substrate precovered with a homopolymer film that is compatible with the anchor block. In order to improve the adhesion of this film to oxidised silicon substrate, the substrate was first rendered hydrophobic by adsorbing PVP–PS block copolymers from a toluene solution [88,89]; the PVP adsorbs on the polar Si wafer, and the apolar PS group is placed on the top. An alternative for this hydrophobisation is chemical binding of styrene monomers to the wafer [90,91]. During the LB transfer, the polymeric density at the interface (or, equivalently, the surface pressure) is kept constant, to ensure LB-films with a homogeneous density.

In the third step, the so obtained film is thermally annealed, during which the anchor block diffuses into the homopolymer film. Upon cooling, the film vitrifies and one has a very stable grafted layer with complete control over the key variables grafting density and chain length. In principle, Langmuir methods allow the preparation of well-defined mixtures such as brushes with a bimodal chain length distribution, but only very few examples of this have been reported [70]. A drawback of the LB-technique is the fact that implementation on a large scale is cumbersome. The LB-technique is suitable for preparation of small quantities of well-defined coated surfaces. As it is very sensitive to contaminants and the preparation of an LB-film is mechanically complicated, the technique is ill-suited to prepare large quantities of coated surfaces on a reasonable time-scale.

To summarise the above, the five methods discussed for the preparation of polymer brushes are listed in Table 1, together with their main (dis)advantages.

2.4. Characterisation of surfaces with grafted polymers

In Section 2.1 we briefly discussed three classes of theoretical models for neutral polymer brushes, namely scaling, analytical and nSCF models. Interesting features of these models are the predicted scaling behaviour for the brush thickness and surface pressure as a function of the chain length and grafting density, Eqs. (4) and (5), and the density distribution as a function of the solvent quality (Fig. 4). In this section we briefly review some experimental results for the various quantities of interest and compare these results to the theoretical predictions. We start with the scaling properties of the thickness and surface pressure of neutral polymer brushes, thereafter the monomer density profiles of polymer brushes are considered.

As mentioned in the introduction, the experimental determination of properties of grafted polymers is not straightforward, and polymer brushes have been used as
Table 1
The five generic methods of making polymer brushes, with their (dis)advantages

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic polymerisation</td>
<td>Long chains may be grafted at high grafting densities</td>
<td>Grafting density not controlled, polydisperse grafted sample, need reactive surface</td>
</tr>
<tr>
<td>Living radical polymerisation</td>
<td>High densities and long chains, chain structure may be varied</td>
<td>Grafting density not controlled, time-consuming, need reactive substrate</td>
</tr>
<tr>
<td>Polymer chains with functionalised end-groups</td>
<td>High densities, monodisperse, easy to prepare large quantities</td>
<td>Reactive substrate necessary, grafting densities not controlled</td>
</tr>
<tr>
<td>Adsorption block copolymers</td>
<td>Monodisperse samples, high quantities easily and quickly</td>
<td>Grafting density low and uncontrolled</td>
</tr>
<tr>
<td>Langmuir–Blodgett technique using block copolymers</td>
<td>Chain length and grafting density controlled, high grafting densities attainable</td>
<td>Difficult to prepare large quantities, substrate needs special treatments</td>
</tr>
</tbody>
</table>

model systems for numerous new experimental techniques. Generally, one can distinguish between optical techniques, techniques that probe the grafted layer mechanically and techniques that focus on the internal chemical composition of the layer. The first include neutron scattering or reflectometry, ellipsometry and reflectometry, the second include AFM, surface force apparatus, surface pressure and contact angle measurements and the third XPS, ESCA and solid state NMR.

2.4.1. Scaling laws

In various studies grafted polymers layers have been probed mechanically to determine the structure of the layers. One of the earliest studies to investigate the power law for the brush thickness $H \sim N \sigma^{1/3}$ is that of Patel and Tirrell [92]. We focus on this study as it gives a good picture of several features of polymer brushes. In this study the repulsive force between two mica cylinders, on which PVP–polystyrene di-block copolymers in toluene were adsorbed, was measured with the surface-force apparatus (for details on this method see Ref. [93]). Toluene is a nonsolvent for PVP and it therefore adsorbs strongly in a compact conformation to the mica cylinders whereas the PS forms swollen, grafted layers on the mica cylinders. Patel and Tirrell investigated PS brushes with $N$ ranging from 600 to 1500. Upon compression of the coated mica cylinders, a large repulsive force was measured, as shown in Fig. 6. As is clear from Fig. 6, a large repulsive force between the cylinders occurs at separation distances of order 100 nm. This repulsive force stems from the mutual compression of the swollen PS layers as $D \leq 2H$. Effectively, upon compression the monomer density in the grafted layers is increased above the equilibrium value. The additional osmotic interactions in the compressed layers result in an effective repulsive force normal to the interfaces. Using the box-model of AdG to interpret the force–distance profiles, the results favourably compared with the predicted power law $H \sim N \sigma^{1/3}$. However, the assumption had
Fig. 6. The force–distance profiles as a function of the separation distance $D$ for adsorbed PVP–PS diblock copolymers in toluene, taken from Patel and Tirrell [92]. The numbers indicate the molecular weights in thousands for the PVP and PS blocks, respectively. The insert shows the force-distance curve plotted double-logarithmically.

to be made that the mica surface was completely covered with collapsed PVP-globules, i.e. $\sigma \sim R_G^{-2}$. Thus, the surface density cannot be determined independently from the force curve.

In subsequent surface force studies various scaling results were obtained, ranging from a much weaker dependence $H \sim N^{0.6}$ to a stronger dependence $H \sim N^{1.2}$ [63,66,94]. However, in all these studies, it was implicitly assumed that irreversible adsorption of block copolymers leads to a brush, and the experimental results were compared with the AdG box-model. As discussed in Section 2.2, in such systems the grafting density is expected to be too low to ensure strong stretching of the lyophilic chains. In other studies using small angle neutron scattering and neutron
Fig. 7. Experimental scaling of the surface pressure of the brush $\pi_b$ vs. the area per chain $\sigma^{-1}$ of PEO chains consisting of 90, 148, 250 and 700 monomers. A line corresponding with a scaling exponent $5/3$ is drawn as an illustration.

reflectivity (NR) Auroy et al. concluded the above scaling law to be valid whereas Kent et al. concluded the exponent $v$ in the power law $H \sim N\sigma^v$ to be less than $1/3$ [71,79].

Because of the higher dependence on the grafting density, see Eq. (5), the surface pressure was chosen to investigate the scaling laws by Bijsterbosch et al. and Currie et al. [32,46]. To do this, PS–PEO block copolymers were deposited as in Fig. 5; the surface pressure of the PEO brush, corrected for adsorption contributions, $\pi_b$, is plotted double-logarithmically against the area per chain for several PEO block lengths and for the nSCF data, see Fig. 7. A line corresponding with a predicted mean-field power law exponent $5/3$ is drawn for comparison (Eqs. (5) and (7)). The power law exponent of $\pi_b$ obtained at high densities for the block lengths 700 and 445 (not shown) approximately equals the value predicted by scaling relationships of aSCF models. The surface pressure of PEO brushes consisting of long chains thus agreed with the scaling law predicted by the aSCF model. This scaling behaviour, however, is not reproduced by PEO chains below 250 monomers. NR data for the PEO brush height of the same layers yielded an exponent 0.33 for $N$ 700 and 0.35 for 445. This result demonstrated that scaling relationships for polymer brushes should be verified experimentally with sufficiently long chains at sufficiently high densities.

2.4.2. Density profiles

In this subsection we consider experimental studies concerned with monomer density profiles in polymer brushes. Such density profiles may be of importance for
the interactions with colloidal particles, which are discussed in the following part of the review. As mentioned in Section 2.2, these profiles are expected to depend strongly on the solvent quality (see, for instance, Fig. 4) and on the grafting density.

In a study of Zhao et al. [55] the surface of a silicon wafer with chemically end-grafted PS chains at several grafting densities exposed to air was scanned with AFM. Air can be considered a rather bad solvent of PS. They observed that the structure of the surface depends on the grafting density. At high grafting densities a homogeneous layer of collapsed PS chains was observed. As the grafting density decreases, the surface becomes inhomogeneous as PS chains ‘clump’ together, as shown schematically in Fig. 8. The experimental results of Zhao et al. corroborate theoretical predictions on lateral density inhomogeneities in brushes in a bad solvent [42,50].

The solvent dependence of the density profiles of PS brushes was shown by Karim et al. [73]. The resulting density profiles obtained from NR are shown in Fig. 9. The density profile in toluene corresponds qualitatively with the nSCF profile for a good solvent (Fig. 4, $\nu_0 = 1$), i.e. the brush extends far into the bulk phase ($H \approx 85$ nm) and the rather low monomer density decreases roughly parabolically. As the solvent quality decreases (d-cyclohexane with decreasing temperature) the PS brush collapses towards the grafting surface and the density distribution becomes increasingly block-like. This agrees with the nSCF profiles in Fig. 4 with increasing value of the $\chi$ parameter.

Recently, Currie et al. presented a NR study of hydrogenated PS–PEO di-block copolymers at the air/D$_2$O interface [70]. It was concluded that the best fit for the lower grafting densities is obtained using block-like profile with a significant degree of roughness, that of the highest is obtained using parabolic model and at intermediate densities a combination of both. A parabolic profile with a tail at the brush edge was also observed by Marzolin et al. using NR [95]. As mentioned in Section 2.2, the distal tail region originates from fluctuations in the conformation of weakly stretched chain ends. The experimental NR results indicate that fluctuations of the chain ends of the grafted chains contribute strongly to the structure of
the grafted layer up to high grafting densities. This outcome agrees with the nSCF calculations of Wijmans et al. [16].

3. Effect of tethered chains on colloidal interactions

3.1. Introduction

When a layer of grafted polymers on a particle or substrate is compressed or otherwise deformed from its equilibrium structure, it responds with a restoring force. If that force is large enough, it may successfully counteract any attractive interactions and the unfavourable effects thereof, such as particle aggregation or deposition of foreign species onto a substrate. The attractive force may be a van der Waals force (e.g. in the case that there is no electrostatic repulsion), an electrostatic force (for particles of unlike charge), a magnetic force, an osmotic force or even an external force, e.g. due to centrifugation or gravity. In all these cases the restoring force is the same: upon compression the increase in osmotic interactions in the grafted layer promotes separation to the equilibrium thickness of the layer. Given all the possible attractive interactions, keeping surfaces or colloidal particles apart over nanometric distances is a major technological challenge which still necessitates a lot of research.

For instance, making a pristine surface is in general relatively easy, but the preservation of a pristine surface is an art. In time, ‘dirt’ from the surrounding...
environment will generally adsorb on the surface. In a large number of systems involving surfaces or interfaces of man-made materials, adsorption of various entities from a bulk phase constitutes a problem. Biofouling, for instance, is the (undesired) accumulation of biological, organic materials at surfaces. It occurs widely wherever biological fluids are in contact with surfaces. Surfaces of synthetic materials are especially vulnerable to biofouling, whereas natural surfaces, such as biological membranes and cell walls, are in the rule non-fouling.

In materials science, one of the challenges is to disperse and stabilise pigments or inorganic particles in non-aqueous media such as polymer melts, without compromising the properties of the final product. This requires good (complete) wetting and adhesion between the particle and polymer melt; if the polymer tends to wet the particle surface partially, the particles tend to stick together in order to minimise unfavourable particle/melt contact. This is especially important in the case of dispersing nanoparticles (e.g. clay particles) in a polymer melt to improve the final mechanical or gas barrier properties. Generally, dispersion agents such as surfactants, reactive prepolymers and so on are necessary to allow dispersion.

Clearly, in order to understand the relevant interactions in such systems we can use the models and properties of grafted polymers in equilibrium, as presented in the previous chapter. We therefore start by reviewing theoretical work in this area of polymer-colloid interaction, which closely follows the reasoning as applied in Section 2.2. In subsequent sections we confront the theoretical points of view with experimental studies on surface forces (Section 3.3.1), adsorption and deposition of various entities on grafted surfaces (Sections 3.3.2 and 3.3.3), and wetting of surface with tethered chains (Section 3.3.4).

3.2. Theoretical models

The modelling of the impact of grafted polymers on the colloidal interactions has been a main focus point of various theoretical studies, as the ideas have direct relevance for practical applications. Most of the early studies focused on the stabilisation of colloidal dispersions by tethered polymers [11,97]. A mean-field analysis was performed for planar and spherical particles coated with polymer brushes by Zhulina et al. [11]. It was concluded that in the case of weak particle–particle van der Waals interactions and good solvency conditions, the interaction potential only has a shallow secondary minimum, thus the dispersions are thermodynamically stable. In the case of strong particle–particle interactions, the primary and secondary minima are separated by a maximum in the interaction potential, resulting from the osmotic pressure necessary for compressing the brush. The stabilisation in these systems is thus essentially kinetic in nature, and resembles that of electrostatic stabilisation of colloids. Whether or not the primary minimum is actually reached in specific cases is open to controversy, though.

In this section we concentrate more on the interactions between particles and brushes, although the mechanisms are similar to those of colloids stabilised by grafted polymers. Various theoretical analyses of particle–brush interactions have been presented, and three generic modes of interaction may be distinguished: (i)
Fig. 10. Three generic modes of adsorption of a particle on a polymeric layer grafted to a substrate: (i) primary; (ii) secondary and (iii) ternary.

diffusion of the particle through the brush and adsorption at the grafting surface (coined primary adsorption), (ii) adsorption of the particle at the brush–solvent interface (coined secondary adsorption), and (iii) adsorption of the particles either within the grafted layer or on the grafted chains (coined ternary adsorption). These three adsorption mechanisms are illustrated schematically in Fig. 10. Evidently, the size of the adsorbing particles is an important factor in determining the adsorption mechanism, but also the distance between the grafted chains, chain length, chain–particle interactions, particle–surface interactions and so on. In the following a few theoretical models that employ such parameters to evaluate the adsorption mechanism are discussed. In this discussion we intend to focus on the general ideas employed and when possible to point out the similarity between brush–particle interactions and electrostatic stabilisation.

One of the earliest models for the interactions of a polymer brush with adsorbing particles was that of Jeon et al. [98,99]. The model stems from the box-model of AdG, in which the monomer density is assumed constant throughout the brush (Fig. 3). The size of the adsorbing particle is an order larger than the distance between the grafted chains, so in order to approach the surface it must compress a part of the brush. This is secondary adsorption, as illustrated in Fig. 10. In the model of Jeon et al. the particle is attracted to the surface by hydrophobic and van der Waals interactions; between the polymer segments and the particle there is no specific attractive interaction besides a short-range repulsion, so that the particle can be considered as ‘inert’ with respect to the brush. The grafted chains thus act as a barrier towards adsorption. (In other words, the particle acts like a piston compressing the brush with a certain force. This situation is very similar to the situation of two brushes compressing each other, and thus leads to the same equations). As discussed in Section 2.2, the ‘bare’ brush thickness in the box-model is determined by the minimum in the sum of the osmotic interactions (which promote stretching in a good solvent) and the entropic or elastic contribution (which opposes stretching). Therefore, compression of a brush by an adsorbing particle, as illustrated in Fig. 10, is unfavourable. However, as the particle approaches the surface the attractive
van der Waals interactions increase in strength, which may result in an effective lowering of the free energy.

It is instructive to examine this model using the parameters introduced in Section 2.2. As shown, the free energy of a chain stretched to a distance $H$ using a mean-field approach within the box-model is:

$$
\frac{F(H)}{kT} = N v_0 \rho + \frac{H^2}{2 N l^2}
$$

where $\rho$ is the uniform density in the brush, given by $N \sigma / H$ and provided $H > R_G$.

We recall that the equilibrium thickness $H_0$ is given by $N (\sigma v_0 l^2)^{1/3}$, see Eq. (4).

The increase in free energy per unit area $\Delta f_b$, upon compression of a brush to a thickness $H$ has two terms, a positive one due to the increase of excluded volume interactions, and a negative one coming from the reduction in stretching, i.e. increase in conformational entropy:

$$
\frac{\Delta f_b}{kT} = N^2 v_0 \sigma^2 \left( \frac{1}{H} - \frac{1}{H_0} \right) + \frac{\sigma}{2 N l^2} (H^2 - H_0^2)
$$

In Fig. 11 these both contributions are plotted together with the total free energy per unit area, and it is clear that as the thickness of the brush deviates from its equilibrium thickness by either compression or stretching the free energy increases. From this we can deduce the force $R_b$ per unit area exerted by a brush compressed (or extended) to a thickness $H$ by taking the derivative of $\Delta f_b$ with respect to $H$. 

![Fig. 11. The osmotic and conformation entropy contributions to the free energy of a brush (dashed lines) together with the total free energy per unit area (solid line) in the mean field box approach.](image-url)
This yields
\[
\frac{R_{\text{H}}(H)}{kT} = -\frac{N^2\sigma^2\nu_0}{H^2} + \frac{H\sigma}{N^2} \tag{9}
\]

Note that for \( H = H_0 \) the force equals 0, i.e. the brush is in mechanical equilibrium. As said above, this analysis is valid for the compression of a brush by either an inert bare particle, (e.g. a bacteria) or by a colloidal particle coated with a polymer brush. This model predicts the strongest repulsive force to be exerted by brushes consisting of long chains at a high grafting density in a good solvent (the latter resulting in a large value of \( \nu_0 \)). Note that the interactions are purely steric, stemming from a reduction in polymer/solvent mixing of the grafted chains. These interactions are calculated here up to second order in the density; higher order terms are neglected. From the analysis of the scaling of the surface pressure of polymer brushes, as discussed in Section 2.4.1, it is known that this assumption is strictly valid only for long chains [46]. For shorter chains or brushes at very high densities higher order osmotic interactions are important as well.

Similar to the DLVO theory, this repulsive force is complemented by a force directed towards the surface, that stems from attractive van der Waals interactions. If we neglect the contribution of the grafted chains to the van der Waals interactions and if the particle radius \( R_p \) is much larger than the thickness of the grafted layer, this potential \( U_{v\text{dW}} \) may be expressed as [100,101].

\[
\frac{U_{v\text{dW}}(H)}{kT} = -\frac{A_H R_p}{6H} \left( 1 + \frac{H}{2R_p + H} + \cdots \right) \tag{10}
\]

In the above equation the constant \( A_H \) is the Hamaker constant, which characterises the strength of the van der Waals interactions between the particle and grafting surface. For protein–silica interactions in a water environment the value of \( A_H \) is typically of order \( kT \) [101]. Jeon et al. explicitly took the van der Waals interactions between the brush and adsorbing particle into account [98,99]. This modifies the above expressions, but gives qualitatively the same result. As it does not contribute to a deeper insight in the problem we neglect this contribution for simplicity. In the case of rodlike particles of radius \( R_p \) and length \( L \) Halperin used a similar expression, namely [102].

\[
\frac{U_{v\text{dW}}}{kT} = -\frac{A_H R_p^{1/2} L}{12\sqrt{2} H^{3/2}} \tag{11}
\]

According to several authors, hydrophobic interactions between uncharged hydrophobic surfaces are generally 10–100 times stronger than the van der Waals interactions at separation distances below 20 nm [103–106]. Following Jeon et al. we can use the expression of Pashley et al. for the free energy of two hydrophobic surfaces [104]. This gives an additional ‘solvation’ force \( R_{\text{H}} \) towards the surface,

\[
\frac{U_{\text{H}}(H)}{kT} = -10e^{-H/d} \tag{12}
\]
However, one could argue that this term is superfluous, as the grafting of hydrophilic particles at a total mass of $\Gamma = N\sigma$ renders the surface hydrophilic, so that this contribution is negligible. We therefore neglect this in the following discussion. Finally, at very close distances the steric interactions between the surface and the adsorbing particle are dominant. Thus, for $H \sim 0$ the steric surface–particle force is highly repulsive.

In this simple model the total force acting on a particle is the sum of these three contributions (electrostatic attraction is not considered). Evidently, if no brush is present the particle is attracted towards the surface until, at close distances of separation, the steric and van der Waals interactions are balanced. We now plot the total force per unit area acting on a particle in the case of a polymer brush. In Fig. 12 this potential curve is plotted for a given parameter set (solid curve), together with the separate contributions (dashed curves). A negative value denotes an attractive potential acting on the particle, a positive value denotes a repulsive potential. Evidently, the potential initially is repulsive as the particle compresses the brush. Only when the brush is compressed to a relatively high extent does the interaction turn from repulsive to attractive. In this respect the kinetic stabilisation resulting from a brush is similar to the kinetic stabilisation resulting from surface charge in the DLVO theory. One obvious outcome of the model of Jeon is that the osmotic barrier for adsorption increases as the chain length and/or the grafting density of the grafted chains increase.

In the model corresponding with Fig. 12 adsorption takes place by significant compression of the brush by the particle. Another scenario is also possible. In the case of a dense brush of limited thickness the particle can adsorb on the edge of the brush. The reason for this is clear: for a brush with small value of $N$ and a high
value of $\sigma$ and $v_0$, $U$ may be negative for $H \sim H_0$. This entails that hydrophobic and van der Waals interactions are not strong enough to compress the brush, but are strong enough to keep the particle positioned in a potential well at the edge of the brush. Evidently, for such secondary adsorption to occur, the depth of the potential well must significantly exceed $kT$, otherwise Brownian motion will prevent adsorption. From Eq. (9) it follows that $H_0 \leq 1/6A_0 R_p$ for secondary adsorption to be able to occur. Thus, increasing $H_0$, i.e. $N$, is an effective way of suppressing secondary adsorption.

In the above the particle is much larger than the average distance between the grafted chains. However, when the size of the particle is of the order of the distance between two grafted chains, primary adsorption may occur, the ‘tunneling’ of the particle through the brush. The primary adsorption process is illustrated in Fig. 10. In this case the brush forms a potential barrier which must be surmounted for adsorption to occur. Halperin modelled this adsorption process using the same box-model and the Kramers rate theory [102,103,107]. We consider the insertion of a small spherical particle in a brush of uniform density. The size of the particle is of the order of the distance between the grafted chains and much smaller than the total brush height, i.e. $\sigma^{-1/2} \ll R_p \ll H_0$. If the particle reaches the surface, then it acquires an attractive energy $U_0$ (resulting from hydrophobic interactions) to which the osmotic penalty due to the high monomer density must be added. The osmotic penalty in our mean field model amounts to $U_0 \approx R_p^2 v_0 p^2$ and increases strongly with increasing particle size, grafting density or solvent quality. If $U_0 + U_b > kT$, primary adsorption is thermodynamically unfavourable and unlikely to occur. A critical grafting density can be defined, given as

$$\sigma_{cr} = \left( \frac{U_b^{4/3}}{R_p^{1/3} v_0} \right)^{3/4}$$

above which primary adsorption is thermodynamically unfavourable. Note that the relationship between the particle size and the grafting density is the most pronounced, i.e. the most efficient way to suppress primary adsorption of particles of a given size is to increase the grafting density.

However, if $U_0 + U_b < 0$, the height and length of the barrier, formed by the brush, determine whether primary adsorption occurs on a realistic time-scale or not. Within a simple modelling of adsorption through a brush using the Kramers theory, the rate of adsorption is a function of three parameters, i.e.

$$k_{ads} \sim e^{-U_*/kT} D/\alpha H_0$$

where $U^*$ is the maximum potential encountered by the particle, $D$ the diffusion constant, $\alpha$ the width of the potential barrier and $H_0$ the brush thickness in equilibrium. The final expression obtained by Halperin, using the blob approach of de Gennes, is [102].

$$k_{ads} \sim e^{-(R_p/\sqrt{\sigma})^3} \frac{kT}{\eta RH_0^3 \left( \frac{\sqrt{\sigma}}{R_p} \right)^3}$$
where $\eta$ is the viscosity of the solvent. Evidently, the rate of diffusion decreases strongly with increasing $R_y/\sqrt{\sigma}$ ratio, both due to the increase in osmotic repulsion (exponential term) and the decrease in diffusivity of the particle through the brush (linear term). The overall conclusion of this analysis is that increasing the grafting density hinders primary adsorption both thermodynamically and kinetically. Obviously, secondary adsorption does not involve an activation energy, and is therefore thermodynamically determined.

As discussed in Section 2.2, the box-model is a rather crude description of the grafted layer and nSCF methods are more realistic. Szleifer et al. [108] proposed a nSCF model for grafted chains interacting with nanocolloids, in which the particle is modelled as a volume from which the polymer chains are excluded, thus resulting in an effective osmotic repulsion. The numerical conclusions from the results are similar to those obtained with the above simple model.

All the afore-mentioned models have in common that the polymer–particle interactions are purely repulsive. This, however, is an incomplete description of a more complex reality. For instance, the surface of protein molecules and that of most biological cells is heterogeneous. Furthermore, in an aqueous environment the a-symmetry of the water molecules leads to orientation-dependent interactions between the surface and the polymer chains. A prime example of attractive polymer–particle interactions are those between hydrophilic polymers and surfactant micelles, the last containing a partially hydrophilic, partially hydrophobic surface.

In a recent series of papers Currie et al. examined grafted polymers which may form complexes with grafted chains [87,109–111]. The ternary adsorption in this approach is induced by an effective adsorption energy per complex, but at the same time adsorption enhances the osmotic pressure in the grafted layer. In this case the outcome is contrary to that of the above models. In general, long chains offer more adsorption sites, so that grafting longer chains does not reduce the adsorption but enhances it. Furthermore, there is a maximum in the adsorption as a function of the grafting density: the effect of enhancing the number of adsorption sites is outweighed by the increase in osmotic pressure in the grafted layer. This mechanism is shown schematically in Fig. 13, for details we refer the reader to the afore-mentioned papers.

3.3. Experimental results

3.3.1. Interaction between colloids with tethered chains

The stability of colloidal particles with grafted chains has been amply investigated; a careful review of the work up to 1983 is to be found in Napper’s monograph [112]. The general qualitative finding is that colloidal particles irreversibly covered with a sufficiently thick layer of polymer in good solvent remain stable under conditions where the bare particles would certainly not. For example, Vincent and Young investigated the deposition of small positive polystyrene latex particles on much larger negative latex particles [113]. Both types of particles were covered with a layer of polyvinylalcohol (PVA), resulting in a kind of ‘pseudobrush’ [114]. The thickness of the PVA layer could be varied by means of the PVA molar mass.
The electrostatic attraction between the particles of opposite charge lead to a secondary minimum in the interaction potential, which became shallower as the steric layer became thicker. In another study, end-attached PEO was found to be most effective in stabilising PBMA latex particles, which served to establish a method to prepare core-shell latex particles of PS and PBMA. In this method, PEO-stabilised cationic PBMA particles were first homogeneously deposited on much larger anionic PS latex particles. The PEO was crucial to obtain a dense and homogeneous PBMA particle coverage. During an annealing treatment at approximately 50 °C, the deposited particles were fused into a homogeneous shell around the PS particle. During this step, the PEO served to keep the dispersion fully stable.

For stabilising lyophobic particles in apolar media, there are virtually no good methods other than using polymer brushes. Many examples of this kind have been investigated by the group of Vincent, e.g. silica with grafted polystyrene in CCl₄. One particularly striking success is the dispersion of silica particles in liquid xenon by means of end-attached polydimethylsiloxane chains. Similar systems were prepared and studied by Philipse et al.

Tethered chains can also be used to weaken the effects of depletion interactions. Non-adsorbing polymer chains in a good solvent are known to induce an attractive force between two surfaces because such chains behave as non-deforming spheres.
and their centers of gravity are excluded from the vicinity of the surfaces. Once the zones devoid of polymer (the ‘depletion’ zones) of any two surfaces overlap, attraction sets in. The range of these forces is set by the size of the polymer coils, and their strength by the osmotic pressure due to the free polymer in solution. If the depletion zone is filled with a number of grafted polymers similar to the ones in solution, an additional repulsive effect is introduced which, to some extent, compensates the depletion attraction. This process is illustrated schematically in Fig. 14. There is an optimum grafting density: if the grafted layer is too dilute, it fails to provide sufficient repulsion, but if it is too dense to allow (partial) penetration of free polymer chains, the depletion zone is simply shifted to the edge of the

![Diagram](image)

**Fig. 14.** A schematic illustration of depletion interaction and the effect of grafted chains on the colloidal stability.

![Graphs](image)

**Fig. 15.** Strength of depletion attraction, in terms of free energy of interaction per unit area, between two surfaces with tethered polymer, as function of the grafting density [119].
Fig. 16. Phase behaviour of colloidal particles with end-attached chains of varying length on their surface in the presence of free polymer; the variables are particle volume fraction and free polymer concentration [116].

grafted layer and the full depletion attraction is restored. This is similar to the balance of van der Waals vs. osmotic interactions between a polymer brush and a colloidal particle, as discussed in Section 3.2. Numerical calculations on such systems supporting these conclusions have been reported by Van Lent, see Fig. 15 [119].

In successfully stabilised dispersions the weak, long range attraction caused by the free polymer together with the strong shorter range steric repulsion by the grafted polymer create a shallow secondary minimum, the depth of which can be tuned by means of the concentration of the added free polymer, the solvent quality, and the length and grafting density of the brush. The weak attraction causes the particles to phase separate (‘floculate’) whenever their volume fraction in the dispersion exceeds a critical value. However, this phase separation is reversible in contrast to phase separation in electrostatically stabilised colloidal dispersions. We give one example of phase diagrams obtained for such systems (Fig. 16). Such ‘soft depletion’ has been detected in experiments with polymer stabilised colloidal particles [120].

Quantitative measurements of the repulsive force between surfaces with attached polymer were pioneered by Ottewill et al. [121]. A cell was constructed in which
Fig. 17. Disjoining pressure between particles with tethered polymer (poly-12-hydroxy stearic acid) on their surface, as measured by the osmotic method of Cairns and Ottewill (adapted from Ref. [112]).

the dispersion could be compressed in a controlled way, and the particle volume fraction monitored. An example for poly methylmethacrylate particles, stabilised by grafted poly(12-hydroxystearic acid) in dodecane is presented in Fig. 17.

Somewhat similar data were reported on polystyrene particles stabilised by short PEO chains [122]. These early data, however, cannot easily be compared with theories for polymer brushes, as the chains were relatively short, probably somewhat polydisperse, and also because the grafting density was not known, nor variable. Some 10 years later, much better data were obtained with the surface force apparatus, as discussed in Section 2.4.1. Patel et al. prepared brushes of polystyrene by adsorbing polystyrene–PVP di-block copolymers on mica, and studied the normal pressure between these in toluene at 32 °C [92,123]. In these experiments, the grafting density was not an independent variable, as the layer was formed by physisorption from dilute solution. As a rule, this does not produce large grafting densities, $\Gamma = \sigma N$ being of order unity, see Section 2.3. They found that the experimental results could well be described by an equation similar to Eq. (10). The authors themselves used a slightly different expression which takes into account density fluctuations as proposed by de Gennes for semi-dilute polymer systems in good solvents, but the mean field expression worked equally well. As Eq. (10) shows, the free energy of interaction as a function of distance $H$ between the surfaces has two contributions, a small (and decreasing) negative contribution from the reduction of stretching (increase in conformational entropy of the grafted
chains), and a larger and increasing positive contribution due to the increase in segmental osmotic interactions. Since the entropic contribution is relatively small, its effect on the compression curve is experimentally not easily assessed. The expected dependency on $G_s$ could therefore not be checked (Fig. 18).

Another careful study was that of Taunton et al. [66]. These measurements were carried out with polystyrene chains carrying a polar (PEO or zwitterionic) group at one end; the solvent was toluene. An example is shown in Fig. 19. It was checked that the forces between one covered and one bare surface were always repulsive and similar to those between two covered surface, thus proving that polystyrene does not adsorb on mica from toluene and excluding the occurrence of bridging. As the brushes studied by Patel et al., the grafting density was set by the adsorption process from dilute solution; grafting densities were typically of order $N^{-1}$ so that extensive stretching did probably not occur. The thickness of the brushes, defined as half the distance of onset of the repulsive force, turned out to scale as $N^{3/5}$ and the authors argued that this result is to be expected because of the constant anchoring energy per chain. Again, fitting to either a mean field expression like Eq. (10), or to a scaling expression did not make much difference. As Eq. (10) brings out, one
expects the repulsive energy (as a function of the scaled distance $H/H_0$) to vary linearly with $N$ and as the $5/3$ power of the grafting density. This is quite a strong effect which has not yet been verified directly by experimental data.

The factor $v_0$ in the first (osmotic) term of Eq. (10) represents the excluded volume which in general is temperature dependent. The effect of temperature on the repulsion between a bare tip and brushes of PS in cyclohexane (grafted from silicon, polydisperse) and PEO in water (adsorbed as PMAA–PEO di-block copolymer) was considered in one study [124]. Given the lack of information on grafting density and the polydispersity, a quantitative comparison with the theoretical results is not possible. However, the increase of repulsive force with temperature for PS in cyclohexane is as expected. For PEO in water, a temperature effect could not be established; perhaps it is too small for these measurements to be picked up.

3.3.2. Brushes and small bare particles

Most studies concerning brush/bare particle interaction deal with biocolloids, and we discuss these in the next section. Yet, there is no reason why the modes of adsorption discussed in Section 3.2 would not generally apply to small colloidal particles. One such case, which has been largely overlooked so far, is that of (weak) attractive interaction between polymer segments and particle surface, leading to binding of small particles to tethered chains. However, because the polymer chains are densely end-grafted they cannot assume the adsorbed configuration of lowest free energy that they would have when free, so that the binding is somehow...
constrained and remains low. Hence, uptake of the particles within the brush would on the one hand optimize their binding energy, but as argued in Section 3.2, it would on the other hand lead to an osmotic penalty. As a result, the number of bound particles is expected to vary with grafting density in a non-monotonic way.

As far as we know, there is one study that shows the effect very clearly for binding of small silica particles to grafted long PEO chains \((N = 700)\) [125]. PEO tends to adsorb on silica by means of hydrogen bonding between surface silanols and ether oxygen in the chain; the adsorption is pH dependent because the silanol groups dissociate at high pH. In Fig. 20 we reproduce the adsorbed amounts of particles as a function of grafting density for various pH values. As can be clearly seen, the adsorbed amount has a pronounced maximum which is high for low pH and decreases when the pH increases. Although the particles in this study were much larger than the average distance between chains, one sees that the grafting density effect is still there, indicating that the more the grafted chains are constrained to attach to the silica, the weaker the binding.

### 3.3.3. Brushes and biocolloids

Most of the applications of surfaces carrying tethered polymer chains are in the biotechnological and biomedical fields. They are more often than not based on the fact that attachment of water-soluble polymers at a surface makes that surface more difficult to approach by particles or molecules. PEO or, otherwise called, polyethylene glycol (PEG) are often used for such applications. This is, in the first place,
because PEO molecules in aqueous environment are highly mobile [126] and attain extremely large exclusion volumes [127]. Second, PEO is non-toxic [128] and only weakly immunogenic [129]. Hence, PEO has been approved by the FDA for internal consumption. Moreover, PEO is compatible with living cells [130] so that it can be used in tissue engineering and artificial organs.

PEO is applied for various medical purposes. Deleterious responses to transplanted organs often begin with biological recognition at extracellular surfaces (e.g. glycocalyx) within the body. Such interactions may be suppressed by using drugs that competitively bind to the appropriate ligands or receptors. Alternatively, the recognition process, which is governed by short-range interactions, may be prevented by attaching soluble polymer molecules to (one of) the surfaces thereby sterically avoiding close contact between ligand and receptor [131]. Such a generic, physical approach is in particular useful when multiple receptor–ligand interactions are involved in the overall biological response.

Another application is the attachment of PEO to medical proteins administered for different treatments [129]. Enveloping a protein molecule by PEO greatly reduces its immunogenecity and antigenecity therewith increasing its lifetime in the body. Because of its swollen, highly hydrated conformation the attached PEO causes only a small loss of the biological activity of the protein (e.g. enzyme). For similar reasons small drug molecules (antibiotics, sedatives, etc.) may be associated with PEO. Moreover, the PEO may enhance the water-solubility of the pharmaceutical [132].

A further application is to stabilise liposomes that are used to encapsulate, carry and deliver therapeutic agents [133,134]. Normally, liposomes are rapidly, say, within half an hour, removed from the blood stream by phagocytes residing in the liver and the spleen. Inclusion of PEO in the lipid bilayers of the liposomes retards interaction with the phagocytes which extends the circulation time up to hours or days.

The applications mentioned so far are important and deserve attention. However, by far most of the practical interest in tethering PEO molecules to surfaces is to prevent or, at least, to retard biofouling, i.e. the formation of a layer of organic material at surfaces [135]. Biofouling is initiated by the adsorption of proteins and this triggers the deposition of biological cells, bacteria and other microorganisms in a so-called biofilm. Biofilms may be desired, for instance in bioreactors where enzymes and even complete biological cells are immobilized, or in soils and wastewater where immobilized microorganisms are used to degrade toxic compounds. However, in many cases biofouling causes serious problems, e.g. in food and pharmaceutical industries and also in potable water production. Biofilms on various processing units may hamper transport of matter and heat. Moreover, they may be a source of microbial contamination. Biofilms on ship hulls promote the deposition of algae and even shells leading to more energy consumption due to perturbation of the streamlining of the vessel. Similarly, biofouling occurs on synthetic materials used for artificial organs and for extracorporeal assist devices as contact lenses, hemodialysis membranes and medical utensils as catheter tubings, blood bags, etc. Fouling of such medical systems is always detrimental.
In this context it is noted that unlike synthetic materials natural surfaces are usually non-fouling. Hence, in modifying a synthetic surface with the aim to resist fouling, it could be wise to be guided by nature. Surfaces of biological materials, such as biomembranes and bacterial cell surfaces, are usually dominated by highly swollen hydrophilic polysaccharides. These layers contain receptor molecules which enable specific biological interaction with other cells or ligands, but non-specific adsorption and adhesion are sterically impeded by the dense polymer layer. Thus mimicking the structure of the extracellular polymer layer at bacterial surfaces or the glycocalyx at the external region of a cell membrane may provide a clue to produce non-fouling surfaces.

We will review and comment on some experimental results concerning the influence of tethered polymer chains on the adsorption or adhesion of ‘particles’ on surfaces. In most cases the particles are globular protein molecules and in a few examples they are bacteria or other biological cells such as blood platelets. The experimental data will be presented against the background of the theoretical models discussed in Section 3.2. In particular, the influence of the thickness of the tethered polymer layer and the grafting density at the supporting surface are emphasized.

It must be realized that each model is an incomplete description of a more complex reality. For instance, the surface of the particles is often heterogeneous, as is the case for protein molecules and most biological cells. Similarly, the conformation of the polymer chains in the tethered layer and, consequently, their interaction with the solvent and the incoming particle may depend on the location in the layer and may respond to the particle. Furthermore, in an aqueous environment the asymmetry of the water molecules leads to orientation-dependent interactions with the surface, the polymer chains and the particles. All these complications are not accounted for in the examined theories.

Experimental data on protein adsorption and cell adhesion to surfaces coated with PEO (＝PEG) molecules, often called PEGylated surfaces, are not always unambiguous, if not controversial. A main reason for this is the various ways the PEO layers are applied: physical adsorption of di-block, tri-block or comblike polymers and covalent grafting being the most popular ones. In most studies the grafting density and, consequently, the thickness of the tethered layers are only poorly controlled, to say the least. Hence, it is not always clear whether we deal with grafted polymer chains that are in a non-overlapping mushroom, an overlapping
mushroom or a brush conformation (Fig. 21 and the discussions in Section 2.3).
Because of this uncertainty the effects of variables as grafting density and layer thickness can only be qualitatively traced. In some publications, however, the density and thickness are well defined which allows a more quantitative interpretation.

On essentially all PEGylated surfaces particle deposition is reduced by the presence of the polymer, irrespective of the way the polymer is attached to the surface. Among the first reports on interaction between blood constituents and PEO, those of the group of Nagaoka [138,139] may be the most classical. Using PEO hydrogels and PEO molecules grafted on polyvinyl chloride they observed that adsorption of plasma proteins and adhesion of platelets decrease with increasing degree of polymerisation of PEO (Fig. 22).

We now proceed to discuss some trends in the influence of various variables on PEO–particle interaction. In doing so we refer to a representative selection of publications.

For various proteins Gölander et al. [140] report that adsorption decreases with increasing molar mass or, for that matter, increasing degree of polymerisation of the PEO molecules. The influence of molar mass on protein adsorption is strong up to 1500 Da (corresponding to 34 ethylene oxide (EO) units). Further increase of the degree of polymerisation results in only a marginal extra reduction of protein adsorption. Gombotz et al. [141] observed a qualitatively similar behaviour for serum albumin and fibrinogen. They report that the optimum molar mass to suppress adsorption is at approximately 3500 Da. The deviation from the molar mass optimum mentioned by Gölander may be due to different grafting densities. Gombotz et al. analysed the grafted layers gravimetrically and found much higher EO contents in the layers formed by the lower molecular mass PEOs. The PEO-covered surfaces were furthermore probed for water wettability by determining the water contact
angle. The contact angle decreases sharply from 55° to 35° when the PEO molar mass increases to approximately 1000 Da and at higher molar mass the wettability only slightly increases. The combined trends in the EO density in the PEO layer and in the wettability, both as a function of the molar mass of the PEO, suggests that the phenomenon of a minimum length of the PEO chains to successfully resist proteins is caused by hydration of EO units which becomes stronger as the number of EO units in the chains increases up to a certain value.

Kim et al. [142] applied PEO of molar masses 400, 1000 and 4000 Da, respectively, to reduce blood platelet adhesion to agarose beads. Remarkably enough, they found the lowest adhesion using PEO-1000.

The influence of the molar mass of tethered PEO chains on bacterial adhesion was studied by Park et al. [143]. They applied layers of PEO of molar mass 1000 and 3500 Da to polyurethane surfaces. Adhesion of Staphylococcus epidermis was not much influenced by PEO-1000, but PEO-3500 renders the surface resistant. Adhesion of E. coli was strongly reduced by both PEO lengths. These results suggest secondary adsorption of S. epidermis at the outer edge of the PEO-1000 layer.

Vacheethasanee and Marchant [144] used PEO-containing copolymers to reduce adhesion of S. epidermis. They concluded that effective blocking of adhesion requires full coverage of the surface by PEO which implies a PEO chain density beyond the onset of brush formation. According to Kwon et al. [145] relative short chains, i.e. containing 4–5 EO units, suffice to effectively suppress adsorption of plasma proteins and adhesion of blood platelets, provided that the oligoEO is densely packed. This result is controversial with the theories of Jeon et al. [98,99] and Halperin [102,135], which would predict secondary adhesion of the platelets at the relatively thin oligoEO layers.

Lee et al. [146] were among the first determining the extension of the tethered PEO chains. They adsorbed tri-block copolymers of the type \((\text{EO})_a-(\text{PO})_b-(\text{EO})_a\), with varying values for \(a\) and \(b\), at polystyrene surfaces. The polypropylene parts, \((\text{PO})_b\), anchor at the hydrophobic surface leaving the polyethylene, \((\text{EO})_a\), buoys to dangle in the surrounding aqueous medium [147]. The (hydrodynamic) extension of the PEO chains, as derived from the diffusion coefficient, scales with \(a^{0.84}\). It suggests that the PEO buoys assume an intermediate conformation between coils (exponent \(~0.6\)) and extended chains (exponent \(~1\)). The adsorbed layer effectively resists protein adsorption beyond a minimum value for the thickness of the PEO layer. With human serum albumin this thickness is a few nm, but for the much larger fibrinogen molecules a minimum thickness of approximately 10 nm is required. These results point to steric repulsion as the predominant mechanism for preventing protein adsorption.

The results of Lee et al. are qualitatively confirmed by Huang et al. [148] who found that a rather dense \((\text{EO})_{45}\) brush largely reduces the adsorption of proteins from human blood serum. However, significant adsorption of the relatively large fibrinogen molecules still remains, suggesting that fibrinogen is accommodated at the outer edge of the brush. The assumption of secondary adsorption is corroborated by the relatively easy displacement of fibrinogen from PEO-brushed surfaces [131].
Winblade et al. [159] PEGylated surfaces of living cells to block biological recognition interactions. With polymer chains comprising 113 EO moieties (radius of gyration approximately 4.7 nm) they needed an adsorbed amount of 5 mg m\(^{-2}\), implying a distance of 1.5 nm between PEO chains, to prevent biological recognition. Hence, a rather dense brush is required to keep specific ligands away from the receptors at the cell surface.

Adsorbed layers of tri-block copolymers of the type \((\text{EO})_a-(\text{PO})_b-(\text{EO})_a\) were characterised by Schroën et al. [147] in terms of mass per unit area of sorbent surface and hydrodynamic layer thickness. They selected two copolymers with \(a/b\) combinations of 24/34 and 127/48, respectively. At hydrophilic surfaces both copolymers adsorb in a flat ‘pancake’ conformation with a maximum adsorbed amount of 0.4–0.5 mg m\(^{-2}\) and a thickness of approximately 1 nm. It is inferred that the PEO parts are adsorbed in a flat conformation at the hydrophilic surface. In such a conformation the pre-adsorbed copolymer only partly prevents subsequent protein adsorption. On a hydrophobic surface adsorption is much larger for the copolymers with the longer PEO parts (i.e. 1.8 and 1.0 mg m\(^{-2}\) for 127/48 and 24/34, respectively) and the corresponding layer thicknesses are 1.0 and 1.5 nm. It is concluded that the copolymer is adsorbed with its PPO part anchored at the hydrophobic surface and PEO parts extending in the solution thus determining the layer thickness. Protein adsorption is completely blocked by an (almost) saturated adsorbed layer of copolymer. Unsaturated layers retard subsequent protein adsorption considerably. For instance, 10% saturation of the hydrophobic surface by \((\text{EO})_{127}-(\text{PO})_{48}-(\text{EO})_{127}\) retards the adsorption of a lipase molecule (radius approximately 3 nm) down to 5% of the adsorption rate at the bare surface. According to Jeon’s theory the separation distance between PEO chains (containing 120 EO monomers) to maximally resist adsorption of particles having a radius of 2 nm is approximately 1 nm. At conditions of adsorption saturation (1.8 mg m\(^{-2}\)), where lipase adsorption is completely blocked, and the average distance between the PEO buoys is more than twice as large as the optimum value predicted by Jeon.

McPherson et al. [108] did a similar study with \((\text{EO})_a-(\text{PO})_b-(\text{EO})_a\) adsorbed on a hydrophobic surface. In this study \(a\) varied between 75 and 128 and \(b\) between 30 and 67. Unlike the systems studied by Schroën et al., the adsorbed layers are in the ‘mushroom’-regime. Consequently, adsorption of a small protein as lysozyme is somewhat lowered, mainly by PPO parts blocking adsorption sites rather than by strong steric hindrance of the PEO parts. Adsorption of the larger fibrinogen is hardly affected by the size of the PPO parts. Apparently, even the largest PPO block is too small to accommodate fibrinogen. Unlike lysozyme, fibrinogen adsorption sharply decreases when the PEO chain grows from 98 to 128 monomers. It points to adsorption reduction primarily caused by a steric barrier for deposition. Halperin’s model predicts that the activation energy of sterically hampered particle deposition at a brush-coated surface scales with \(N^3/\sigma^3\). The conclusion made by Gombotz et al. [141] that a low surface density of high molecular weight PEO is more effective in reducing protein adsorption than a high surface density of low molecular weight PEO is clearly at odds with Halperin’s predictions.
A detailed and accurate study has been undertaken by Sofia et al. [149]. PEO molecules of different degree of polymerisation (227 and 454) were chemically grafted on hydrophobic surfaces. The density of the PEO chains at the surface was calculated from the grafted mass obtained by XPS and ellipsometry. The PEO-coated surfaces were tested for the adsorption of cytochrome c, human serum albumin and fibronectin. Among proteins, those three are considered to be small, medium and large, respectively. Remarkably enough all three proteins, irrespective of their size, reached zero adsorption at a PEO content of approximately 1 mg m\(^{-2}\). The conclusion is that there is no specific molar mass nor universal grafting density for protein adsorption prevention. Shorter PEO chains require higher grafting densities. Apparently, as suggested by Szleifer [108], there is a trade-off between penetration resistance and attraction to the sorbent surface which both increase with increasing size of the interacting particle, or protein molecule.

An interesting phenomenon reported by Currie et al. [110] is shown in Fig. 23 where it is observed that at low grafting densities long PEO chains in a brush stimulates the adsorption of bovine serum albumin. At higher grafting densities the adsorption gradually decreases. This result can only be explained by accepting an attractive interaction between the PEO chains and the protein molecules which, in one way or another, depends both on the length and the density of PEO in the brush. Such chain length-dependent attraction would also explain the interaction of blood platelets with a PEO-coated surface, as reported by Kim et al. [142].

Most of the controversy in the results reviewed above concerns the question whether the length of the PEO chains or the grafting density dominate particle adhesion resistance. In this respect the study of Prime and Whitesides [150] is important. These authors prepared self-assembled monolayers of short oligoEO on gold surfaces. The number of EO moieties in the oligomers varied between 1 and
The minimum number of oligoEO chains to eliminate protein adsorption is the same for four different proteins having molar masses varying between 14 000 and 340 000 Da. The protein resistance increases with increasing number of EO units in the oligomer. Nevertheless, very short chains, even as short as one EO unit, can effectively resist protein adsorption, provided sufficiently dense packing which can be achieved by preparing self assembled monolayers via thiol–gold coupling. At first sight there seems to be a conflict between this observation and those of others that report the requirement of long PEO chains to render surfaces protein repelling. However, the controversy may be solved by assuming that protein resistance is determined by complete coverage of the surface by an EO-layer of any thickness and thereby realizing that longer chains can cover the surface underneath more effectively than shorter chains. Clearly, in densely packed monolayers osmotic interaction does not play a significant role and, therefore, Prime and Whitesides’ conclusions may not be fully applicable to compressible, less dense layers of longer PEO chains.

Later reports (e.g. [151,152]) on self assembled monolayers of oligoEOs revealed that protein resistance is determined by the molecular conformation of the EO moieties in the layer. When the oligoEOs assume a helical or amorphous conformation they were found to be protein repelling, whereas in an all-trans conformation they attract protein molecules. It has been reasoned that this conformation-dependent protein resistance is related to the hydration of EO. Helical and amorphous conformations are strongly hydrated, whereas water interacts only weakly with EO in an all-trans conformation [153].

It could well be that the conformation of the EO moieties in the tethered oligoEO or PEO molecules changes as a result of altering (environmental) conditions thereby inducing a concomitant change from particle (e.g. protein) repulsive to particle attractive interaction or vice versa. The loss of protein resistance of PEO layers on raising the temperature [140,154] may be explained along these lines. Indeed, the solubility of (P)EO in water is lower at elevated temperatures [151]. When long PEO molecules are densely packed in a self-assembled monolayer they do not turn into a protein-attractive mode upon heating [151]. The dense packing possibly prevents conformational transitions in the PEO chains.

The particle attractive PEO brushes, observed by Currie et al. [110] and Kim et al. [142] might imply that the conformation of the EO moieties in a brush is influenced by a combined effect of the length of the PEO chain and the grafting density. Such an influence (at relatively low grafting density) of brush dimensions on the conformation of the EO units is, as yet, difficult to conceive.

In recent years direct force measurements have been performed to quantify the interaction between tethered PEO chains and approaching particles. For instance, Razatos et al. [156] used atomic force microscopy to measure the effect of \((\text{EO})_{102}-(\text{PO})_{62}-(\text{EO})_{102}\) (adsorbed with its PPO block on a hydrophobic silanized glass surface) on the adhesion of \(E.\) coli cells. Fig. 24 shows attraction to the silanized surface over a distance as large as 100 nm. This long-range interaction might be caused by cell surface appendages adsorbing at the hydrophobic sorbent
surface. The PEO brush causes complete blocking of the long-range attractive interaction. The PEO chains extending in the solution over a distance of approximately 12 nm introduces repulsion of the bacteria of which the onset is observed at approximately 30 nm separation. A loosely structured coating of polysaccharide at the E. coli cell surface may explain that the distance over which repulsion is measured exceeds the thickness of the PEO brush.

The most informative and clarifying data are reported by Leckband’s group. Here we reflect on their data reported in e.g. [157] at some length. They applied PEO on mica surfaces and the grafting density was controlled by the Langmuir–Blodgett technique. A monolayer of the protein streptavidin was tightly bound to another biotinylated mica surface (via streptavidin–biotin conjugation). Forces between the two modified mica sheets were monitored as a function of their separation distance using a surface force apparatus. The experiments were performed with PEOs of different degrees of polymerisation, i.e. (EO)$_{114}$, (EO)$_{45}$, (EO)$_{18}$ and (EO)$_{3}$ and for each polymer at 25 and 37 °C. (EO)$_{114}$ molecules were grafted at different densities to yield mushroom- and brush-structured layers. The other polymers were all in the brush regime.

Both in the mushroom and brush conformation and at both temperatures the (EO)$_{114}$ attracts the protein at the outer edge of the layer with an adsorption energy slightly more than one $kT$ per protein molecule. This is hardly sufficient to keep the molecule adsorbed. Force–distance curves for the (EO)$_{114}$ brush at 25 °C are presented in Fig. 25. Upon repeated force–distance runs, the interaction with the (EO)$_{114}$ brush remains essentially unaltered, but for the mushroom the adsorption energy reaches a value as large as $-8.5\ kT$ per streptavidin molecule. It could be reasoned that the protein penetrates relatively easily between the sparsely grafted PEO chains and therefore successive measurements lead to more contact with EO
Fig. 25. Force distance curves measured by means of AFM between protein and a PEO brush with 114 monomer units per chain (adapted from Ref. [157]).

moieties. Another possibility is that closer to the mica surface the EO segments adopt a different, more protein-attractive, conformation.

The behaviour of shorter brushes, made of (EO)$_{45}$ chains, is quite different. At 25 °C the approaching streptavidin and PEO layers do not spontaneously jump into adhesive contact. A compressive load has to be applied to overcome an activation energy for adsorption. The activation energy increases with increasing brush density from a few to almost 50 $kT$ per protein molecule. When this energy barrier is surpassed PEO-streptavidin contacts are stabilised by 1–2 $kT$ units. Hence, adsorption of streptavidin at the PEO-coated surface is an activated process and it is therefore expected to be accelerated by raising the temperature. Indeed, at 37 °C the activation energy is essentially zero.

With the oligomer (EO)$_{17}$ and (EO)$_{3}$ much denser brushes were prepared. The activation energy for adsorption on the (EO)$_{17}$ brush is in the range of a few tens of $kT$ before reaching an attractive interaction of approximately 2 $kT$ per protein molecule. The lifetime of the protein-attractive state of the brush is relatively short; it relaxes back to the protein-repellent state within 30 min. The magnitude of the compressive load and the time of contact between the protein and the brush required to induce attraction decreases when the temperature is raised from 25 to 37 °C.

Interaction between streptavidin and the very short and densely packed (EO)$_{3}$ moieties can be well fitted to electrical double layer repulsion as described by the DLVO theory for colloid stability. At a separation of approximately 1 nm the repulsion increases steeply, probably due to steric repulsion by the (EO)$_{3}$ groups. Here too, upon imposing a compressive force the streptavidin adsorbs to the (EO)$_{3}$
with an adhesive interaction of $0.5 - 3 \, kT$, the value depending on the magnitude of the force. The activation energies are $2.6 \, kT$ (at 25 °C) and $1.7 \, kT$ (at 37 °C). It is therefore remarkable that the energy barrier for protein–PEO contact reaches a maximum at intermediate length of the polymers, i.e. 17–45 monomers in the study of Efremova et al.

Under conditions where the adsorption energy is $< |1 - 2| \, kT/\text{protein molecule}$ and the activation energy is considerably higher, the adsorption process is so slow that the PEO layer virtually manifests itself as protein resistant. Then, the interaction may be described by the before-mentioned theoretical models. At some conditions the adsorption energy is $> |2 \, kT|$ and when the activation energy is not too high the PEO layer promotes protein adsorption. The results of Efremova et al. reveal that the PEO molecules in the brush can attain (at least) two different states: a protein-repulsive and a protein-attractive state. Surface force measurements are, at least qualitatively, in line with the before-mentioned trends in protein adsorption and cell adhesion on PEO-coated surfaces. In particular, the influence of temperature [140,154], chain length [142,110] and grafting density [110] are corroborated by the surface force data. In view of Prime and Whitesides’ [150] observation of zero protein adsorption at dense layers of oligoEOs, the low activation energies for such systems is unexpected. However, the small adhesive forces may be responsible for the absence of significant protein adsorption. (Prior to measuring the protein mass, they pass the oligoEO-coated surface through an air–water interface. Protein molecules that are weakly attached to the oligoEO monolayer may be transferred to the air–water interface during passage.)

Thus, the results of Efremova et al. [157] combined with those of Prime and Whitesides [150], indicate that the interaction between protein molecules, as well as, probably other particles and PEO or oligoEO brushes is an activated process in which segments of the PEO chains are re-arranged from protein-repulsive, polar, helical or random structures into a protein-attractive, apolar, all-trans structure. Halperin [158] predicted segregation of such different states within a brush with the protein-repelling segments at the outer periphery and the protein-attractive segments close to the supporting face. Moreover, the structural transition is shifted by changing environmental conditions. As for PEO molecules in solution the PEO brush loses hydration water upon compression and temperature rise [155] and, consequently, the protein-attractive state is favoured. The reason why the degree of polymerisation influences the conversion, especially its effect on the activation energy of transfer from the protein-repulsive to the protein-attractive state, is more difficult to understand.

In conclusion, the conventional theories describing protein resistance of grafted PEO layers based on (a) steric or osmotic repulsion between the protein and the polymer chains and (b) repulsion between EO moieties and protein explain only a part of the observations. They do not account for the conformational transitions in the polymers which, in turn, largely determine whether or not the PEO layer is protein-resistant. Similar features may, mutatis mutandis, control protein adsorption and cell adhesion on grafted polymers other than PEO. Currently, there is no
theoretical model available that adequately takes into account the subtleties involved in the mutual interactions between tethered polymer, protein (or other particles) and water.

### 3.3.4. Effects of tethered chains on wetting

In addition to the effects on particle–particle interaction, brushes can also have a major effect on the interaction between a particle and the liquid it is dispersed in. In other words, tethered chains can modify the wettability of a given substrate. One obvious example to decrease the wettability of a surface, i.e. to make it more hydrophobic in the case of water. This was shown for instance by Genzer et al., who prepared highly hydrophobic surfaces by close grafting of fluor-modified chains \[84\].

The opposite case is that when the liquid is a good solvent for the attached polymer. It is obvious that the uptake of solvent by a brush lowers the free energy of the system, and this may readily drive an initially finite contact angle (referred to as ‘partial wetting’) in a vapour/liquid/substrate three-phase system to zero (a case referred to as ‘complete wetting’). One might expect that the effect becomes stronger as the osmotic pressure in the brush is larger, i.e. as the brush density increases. Yet, there are cases where this rule of thumb is not obeyed. We discuss here the special case of a brush in contact with a polymer melt made up by the same chains. The case is special because the system is athermal; mixing of free chains with end-attached chains occurs without any change of enthalpy. Therefore, entropy dictates the behaviour of such a system.

For polymer chains in contact with a solid substrate the number of allowed conformations is reduced, roughly in proportion to the number of atomic bonds lying in the surface plane. If the polymer segments are neither attracted nor repelled by the substrate (one might call such a substrate indifferent), one expects that the polymer wets such a substrate partially (i.e. there is a finite contact angle) rather than completely, on account of the unfavourable entropy. Making a thermodynamically stable thin film of polymer on such a substrate is then impossible; the film will tend to break up into droplets. This is observed in many instances.

It has been shown that one can use grafted polymers in order to improve the wettability [89,160]. However, the wettability is not a monotonic function of the grafting density. At low grafting density, the free chains are able to mix readily with the grafted ones because the grafted chains can swell and there is a concomitant increase in mixing entropy. As the grafting density increases, though, the swelling must lead to more and more stretching of the grafted chains, and this entropic penalty eventually outweighs the favourable mixing entropy. As a result, uptake of free chains in the brush becomes less and less, particularly for long free chains because these contribute relatively little to the mixing entropy. Eventually the system becomes more and more comparable to a polymer melt in contact with an indifferent substrate, which we expect to wet partially. Hence, qualitatively the contact angle is expected to go through a minimum when one varies \(\sigma\), and to increase monotonically when one increases the length of the free chains \(P\) [161–165]. The
Fig. 26. A polymer melt in contact with (a) a dilute brush and (b) a dense brush.

effect is pictorially shown in Fig. 26 and in Fig. 27 we present calculations showing that this is indeed theoretically predicted.

A quantitative experimental study of this scenario was recently carried out by Maas et al. [166]. In this study monodisperse polystyrene brushes were prepared on silicon wafers in two different ways, namely by physical adsorption of di-block copolymers of PS and PVP, and by chemical grafting onto (Refs Joost). The PVP block is known to anchor strongly onto silica, and one can vary the grafting density by varying the length of the anchor block: a shorter block produces a denser brush. The chemical grafting employed vinyl-terminated polystyrene chains that can react with a clean, hydrogenated silicon surface to form a covalent Si–C bond. The

Fig. 27. Cosine of the contact angle of a polymer melt on a surface with tethered polymer (chain length 100) as a function of grafting density, for various values of the length of the free chains in the melt (adapted from Ref. [166]).
Fig. 28. Wettability phase diagram for a polystyrene melt of chain length $P$ on a surface with grafted polystyrene chains of constant length, represented in the (grafting density, chain length) plane, as determined in terms of stability of a very thin (6 nm) film of the melt. Three regions are visible: unstable films (‘allophobic’), stable or metastable films, and unstable films (‘autophobic’). Near the transitions, special surface patterns are observed (adapted from Ref. [166]).

Grafting density could be varied by co-reacting vinyl-terminated PS oligomers, which cover a (concentration-dependent) fraction of reactive sites but are too short to make a real brush. The wettability of the surfaces so obtained was investigated by covering them with a very thin film of polystyrene and to anneal the samples for several days at a temperature of 140 °C, at which PS is in a liquid state. The length of the free chains was varied over a wide range. Films that after the thermal treatment were free of holes or that had not broken up into droplets were considered as stable and to represent cases of complete wetting, whereas all others were considered as cases of partial wetting. In this way, a wettability diagram in the $P$, $\sigma$ plane was obtained as presented in Fig. 28.

One sees that this diagram has three regions. At low $\sigma$ there is partial wetting; the brush is simply too dilute. When the grafting density exceeds a certain critical level, complete wetting is observed. Upon a further increase of $\sigma$, complete wetting disappears again at high $P$, but the region of complete wetting widens towards lower $P$, and for low $P$ no second region of partial wetting is observed. The region of complete wetting at high $\sigma$ is often called the autophobic regime, because the partial wetting is due to the unfavourable (entropic) interactions of polymer chains of the same chemical nature. The partial wetting at low $\sigma$ then should then be called the allophobic regime, as it is caused by unfavourable polymer/substrate interactions.
Comparison with theoretical calculations brought out a surprise. That the complete wetting regime narrows as $P$ is increased narrows is in agreement with theory. However, whereas the theory predicts that this narrowing continues with increasing $P$ and eventually leads to a complete disappearance of the complete wetting regime, there was in the experiments always a regime with stable films, even up to very high $P$. At first sight, this seems to falsify the theoretical result. However, inspection of the calculations (Fig. 27) reveals that at high $P$ the true thermodynamic contact angle has a (broad) minimum which indeed remains finite (i.e. partial wetting) but that the thin films are metastable rather than unstable in a certain range of grafting densities. As a result, no dewetting is observed in this range, despite the fact that the thermodynamic contact angle is non-zero. When the films eventually begin to destabilise at higher or lower grafting density one observes peculiar patterns where one sees not only the original film, but also dry patches and droplets, often in a concentric arrangement. We show an AFM image of one such state; one sees a film with circular holes, and in the center of each hole sits a droplet (Figs. 28 and 29).

4. Outlook

In a review as broad as presented, it is our opinion that an outlook on possible future developments is fitting. One could say that the trend in the references in this
review already gives the reader a sense of direction: overall, the theoretical advancements in the modelling of brushes occurred in the 1980s, in the 1990s the controlled preparation and characterisation of tethered surfaces was reported, and at the beginning of 2000 new and interesting studies of exotic wetting phenomena, complexation of brushes with foreign species and chemically heterogeneous brushes were presented. Another way to perceive this is that over 20 years since de Gennes first applied his blob model to grafted polymers, the focus has shifted from the grafted polymers themselves to their interaction with the neighbouring environment.

This leads us to the conclusion that the understanding of generic brush properties via modelling is close to completion. However, there is a lack of understanding of the interactions of brushes with foreign heterogeneous particles, an example in case being proteins. As shown in Section 3.3.3, simple models such as the mean field box are not sufficient to understand the interactions between close packed chains and biological surfaces. As stated by Halperin and Leckband [167] ‘formulation of a realistic model allowing for the interactions between PEO and proteins awaits further developments’. It is in this area that modelling may provide valuable insights in the near future.

Experimentally, it is in the same field that many challenges lie. The interactions between grafted chains and (in)organic particles that display a specific affinity to the grafted chains are not yet understood. Examples that are open for investigation are brush–surfactant interactions, brush–proteins, and brush–bacteria. As discussed in the previous section, most studies focusing on the prevention of biofouling were performed with poorly controlled grafted layers. It is the usage of layers of controlled architecture that may lead to surprising results. Besides preventing sorption altogether, one can also envision various reversible sorption–desorption processes between grafted chains and the environment which are technologically interesting. In the case of grafted polyelectrolytes the charge density on the chains, particle and the ionic strength are additional parameters for controlling such processes. It is our belief that exciting and new properties are to be expected from such systems.

One of the drawbacks of the usage of brushes is the intrinsic weakness of a single layer of grafted polymer chains to highly localised mechanical stresses, i.e. scratching, scouring etc. An interesting approach was taken by Mays et al. [168] who used a polymer matrix filled with amphipolar block copolymers, in contact with water. In equilibrium, such a system would have a brush-like structure at the matrix/water interface. The block copolymers would therefore have the tendency to migrate towards bare matrix/water interface provided the matrix would be in a liquid state, thus ‘repairing’, in a way, patches where the brush had been removed or damaged.

The external region of a cell membrane, the glycocalyx, may be considered as nature’s own brush. It is dominated by a dense layer of poly- or oligo-saccharides that protrude out into the (aqueous) surroundings, giving the cell surface non-adhesive properties. The glycocalyx further accommodates specific receptors allowing for biological recognition processes. Mimicking the glycocalyx by oligo- or poly-saccharide brushes in which receptors are incorporated provides potential
solutions to various kinds of clinical problems associated with implant devices and artificial organs [136].

Appendix A:

In Section 2.1 a simple derivation of the parabolic density profile of a polymer brush in a good solvent using an aSCF model was given. In this appendix a more general approach is given, which follows the analysis of Zhulina et al. [169].

In the case of a brush of chain length $N$ and grafting density $\sigma$, the free energy per unit area can generally be written as a sum of two contributions: the elastic energy $F_{el}$ and the osmotic energy $F_{os}$,

$$ F = F_{el} + F_{os} $$  \hspace{1cm} (A1)

Evidently, the osmotic term may be defined as

$$ F_{os} = \int_{H_0}^{0} dz \ f_{os}(z) $$  \hspace{1cm} (A2)

where the osmotic free energy density $f_{os}(z)$ is assumed homogeneous laterally. In the mean field approximation in Section 2.2 the latter contribution is approximated by second-order virial interactions, $f_{os} = \nu_0 \rho(z)^2/2$ but for the sake of generality it may be left unspecified. The elastic contribution may be written as a function of $E(z, z')$ and $g(z')$: the first gives the average stretching at a distance $z$ of chains with their end-segment at $z'$, the second is the probability distribution for a chain to have its end-segment at a distance $z$.\(^1\)

$$ F_{el} = \frac{\sigma}{2} \int_{H_0}^{0} dz' g(z') \int_{0}^{z'} dz E(z, z') $$  \hspace{1cm} (A3)

Note that the above equation is approximate: the degree of stretching at $z$ of a chain with its end-segment at $z'$ is assumed to be the most probable degree, i.e. that which minimises the overall free energy. Fluctuations in $E(z, z')$ are not considered in this model. This is the so-called classical approach, and it is in this respect that aSCF models differ from numerical models that do take such fluctuations into account.

As mentioned, we have to find the two functions $E(z, z')$ and $g(z')$ that minimise the overall free energy, taking two boundary conditions into account:

$$ \int_{0}^{H_0} \frac{dz}{E(z, z')} = N \text{ for all } 0 < z' \leq H_0 $$  \hspace{1cm} (A4)

and

\(^1\) The reader may remark that a grafted chain may back-fold, and thus that chains with the end-segment at $z' < z$ may also contribute to the overall density. However, in the ‘classical’ approach back-folding of chains is not considered. Equally, in the pendulum analogy the pendulum always swings towards its lowest point. Evidently, back-folding is taken into account in numerical models. For a discussion on this issue, see Ref. [44].
The first condition implies that the total length of each chain must equal the chain length \( N \), regardless of the position of the end-segment, the second that the overall density must equal the total grafted amount. It is clear that only chains with their end-segment at a position \( z' > z \) contribute to the overall density. Moreover, the contribution is inversely proportional to \( E(z, z') \). We can thus express \( r(z) \) as

\[
\rho(z) = \sigma \int_0^{H_0} dz' \frac{g(z')}{E(z, z')}
\]

It is now convenient to define a new function \( \tilde{F} \) to be minimised, which equals

\[
\tilde{F} = F_\alpha + F_{os} + \lambda_1 \int_0^{H_0} dz \rho(z) + \int_0^{H_0} dz' \lambda_2(z') \sigma \int_0^{z} \frac{dz}{E(z, z')}
\]

The parameters \( \lambda_1 \) and \( \lambda_2(z') \) in the third and fourth term are undetermined Lagrange multipliers. As the third and fourth term are proportional to \( N_s \), the function \( \tilde{F} \) merely differs from the free energy \( F \) by a constant. The differential of \( \tilde{F} \) equals

\[
\partial \tilde{F} = 
\left. \int_0^{H_0} dz' \int_0^{z} \frac{dz}{E(z, z')} \right| \partial E \left( \frac{g(z')}{E} \right) - \left( \frac{\partial f_{os}(z)}{\partial \rho(z)} + \lambda_1 \right) g(z')
\]

where we have denoted \( g(z') \) as \( g \) and \( E(z, z') \) as \( E \), for simplicity. As the equilibrium conformation is considered, i.e. a minimum in the free energy, or equivalently, in \( \tilde{F} \), the above expression must equal zero for all \( \partial g \) and \( \partial E \). In the case of the term containing \( \partial E \) this reduces to

\[
\frac{E}{2} = \frac{\partial f_{os}(z)}{\partial \rho(z)} + \lambda_1 + \frac{\lambda_2}{g}
\]

On the other hand, in a good or \( \Theta \) solvent \( E(z, z') \) must equal zero at \( z = z' \), i.e. the elastic force at the end of a grafted chain is zero. Eq. (A9) may therefore be rewritten in terms of an unknown function \( \Psi(z) \) as \( E(z, z')^2 = \Psi(z') - \Psi(z) \). If this is inserted in the first boundary condition, Eq. (A4), the solution for \( \Psi(z) \) is simply

\[
\Psi(z) = \frac{\pi^2}{4N^2z^2}
\]

If we combine this with Eq. (A9) and use \( f_{os}(z) = u_0 \rho(z)^2 / 2 \) the result is

---

\(^2\)In the literature the exact value of the numerical prefactor \( A \) varies. In some papers the prefactor equals \( \pi^2 / 8N^2l^2 \) as the grafted chain is considered a 3D object [49]. Here we follow the convention of Milner et al., in which the chains effectively are 1D objects [13,14].
\[ \rho(z) = \nu_0^{-1} \left( A - \frac{\pi^2 z^2}{8N^2} \right) \]  
(A11)

where \( A \) contains all other terms that depend on the second boundary condition, Eq. (A5). This is the parabolic density profile presented in Section 2.2.

**Appendix B:**

In this appendix the thermodynamic limited grafting density obtained via adsorption of di-block copolymers on an adsorbing surface, as discussed in Section 2.3, is examined theoretically in the most simple manner possible. To proceed, we make use of the mean-field box-model, which, as we have seen, qualitatively gives a reasonable description of brush properties. This entails that the density distribution in the brush \( \rho \) is considered uniform, and all end-groups of the adsorbed block copolymers are found at a distance \( H \) from the surface. The monomeric solvent is considered to be good, i.e. the monomeric virial coefficient \( v_0 \) is positive. We furthermore assume that the only contribution of the lyophobic adsorbing block is an (unspecified) amount of adsorption energy \( u_{ads} \), there are no steric interactions between the adsorbed lyophobic blocks or between the lyophobic and lyophilic blocks are not taken into account. The block copolymers adsorb from a bulk solution of density \( \rho_{bulk} \) with a concomitant chemical potential \( \mu_{bulk} \). The overall density in the brush is assumed low enough that only the monomeric virial coefficient \( v_0 \) for the solvent needs to be considered.

The free energy per unit area of the adsorbed brush-like layer in this simple approach is

\[ \frac{f}{k_B T} = \sigma \frac{H^2}{2N} + \frac{v_0}{2} \rho^2 H + \sigma u_{ads} \]  
(B1)

where we set the monomer length equal to unity for convenience. The first term is the elastic energy involved in stretching the polymer chains, the second the repulsive monomer–monomer interactions, and the third the adsorption energy per unit area. The conditions for equilibrium are

\[ \frac{\partial F}{\partial H} \bigg|_\sigma = 0, \quad \mu_{brush} = \frac{\partial F}{\partial \sigma} = \mu_{bulk} \]  
(B2)

The first condition yields the same scaling law as found in Section 2.2, \( H = N(v_0 \sigma/2)^{1/3} \) as evidently the brush height at a given grafting density \( \sigma \) is independent of the bulk concentration in our approach. Using the expression for \( H \) the second condition yields the equality

\[ \mu_{brush} = Nv_0^{2/3}\sigma^{2/3}C + u_{ads} = \mu_{bulk} \]  
(B3)

where \( C \) is a constant close to unity, in this case it equals \((25/24)^2^{-2/3}\). The grafting density resulting from adsorption is thus
\[
\sigma = \frac{(\mu_{\text{bulk}} - \mu_{\text{ads}})^{3/2}}{N^{3/2}C^{3/2} \nu_0}
\] (B4)

We find that for a given bulk concentration and adsorption energy, the grafting density decreases strongly with increasing chain length and/or increasing solvency. This is due to the increasing entropic cost of grafting a chain to a surface with increasing chain length.

References

[24] We remark that many hydrophilic polymers like PEO and PNIPAM exhibit an upper-point, i.e. the solvency decreases not with decreasing but, on the contrary, with increasing temperature. The generalisation of our discussion for this case, however, is straightforward.
[34] We remark that in many papers in the brush literature $\sigma$ may also denote the area per grafted chain. We employ the definition that $\sigma$ denotes the number of chains per unit area, i.e. the area per chain is defined as $\sigma^{-1}$.
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