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Abstract. – A statistical mechanical model is presented to explain recent atomic force microscope (AFM) measurements on the equilibrium forces on a polymer chain adsorbed on a surface with one end attached to the AFM tip. We explore the dependence of this adsorption force on the depth and range of the surface potential and the characteristics of the polymer chain. We show that the force distribution is likely due to energetic surface inhomogeneities. The effect of thermodynamic force fluctuations is also discussed.

In a series of novel experiments the force has been measured on a single polymer molecule, such as polyvinylamine and polyacrylic acid (PAA), attached at one end to an atomic force microscope (AFM) tip and allowed to make contact with the surface of a solid, such as mica or a self-assembled monolayer (SAM), as a function of the distance of the AFM tip from the surface [1–4]. It is found for certain systems that when the AFM tip is retracted slowly, equilibrium is maintained all the way to the point where the polymer molecule loses contact with the surface. In such systems the force is essentially constant for a given sweep and shows a Gaussian-like distribution for different sweeps. In this paper we will give a theoretical explanation —first by analyzing the simple thermodynamics involved and then, using statistical mechanics, by a detailed calculation within a general model. We will concentrate on the adsorption itself and refrain from an analysis of the complex electrochemistry involved when the aqueous solvation medium is altered in its pH and composition; this is already discussed in the experimental papers and elsewhere [5,6]. Very general scaling arguments on this problem were put forward some time ago [7]. Châtellier, Joanny and coworkers treated the long-range electrostatic interactions for polyelectrolytes in contact with a charged surface [8, 9]. Our current calculation is for a short-range surface-polymer interaction and it is valid for all force regimes identified earlier by Châtellier and Joanny.

The assertion that the system is maintaining equilibrium in this experiment needs further elaboration. First of all, the rate of withdrawal of the AFM tip is slow on the scale of the internal relaxation times in which the polymer chain relaxes to its internal free-energy minimum. The resulting equilibrium state is constrained and defined by the "walls" of the

surface and the AFM tip. Moving the tip is thus analogous to moving a piston in a cylinder of gas. The resulting force is therefore an internal adsorption force and not a desorption force which, inherently, is a nonequilibrium phenomenon where the rate of energy transfer rather than attainment of a free-energy minimum is the dominant factor and effects such as friction along the surface play a crucial role.

The fact that the force f is essentially constant implies that the free energy of the polymer is increasing linearly with the distance of the AFM tip from the surface. The change in free energy per removal of a chain segment (not necessarily a monomer in the case of complex polymers) of length b from the surface is due to the loss in its binding energy, V_0, to the surface and the loss of free energy by reducing the part of the molecule more or less freely coiled in its two-dimensional surface potential well by one further monomer. The latter part is dominated by the loss in entropy, $\Delta S < 0$, so that we have

$$\Delta F \simeq fb \simeq V_0 - T\Delta S. \tag{1}$$

For typical forces of 50 to 100 pN and monomer lengths of 1.5 to 2.5 Å for n-alkane and polyacrylic acid, respectively, fb is about 2 to 6 $k_B T$ at 300 K. This is the typical range of the binding energy of H atoms and radical groups attached to the backbone of a polymer with metals or methyl, carboxy or other end groups on a SAM. These values are somewhat larger when charges are present on the polyelectrolyte or on the surface. On the other hand, the change of entropy by reducing the length of a polymer by one unit is maximally $-k_B \ln 3$ for a 3-state model.

In the next section we outline a model for the adsorption of a single polymer chain on a surface under the special condition that one end of it is fixed at some distance above the surface. Estimates of the depth, width and corrugation of the surface potentials that hold the polymers in the surface region can be obtained from quantum-chemical calculations. We then examine the influence of well depth, well width, surface corrugation, and, to a limited extent, the structure of the polymer on the adsorption force. In the final section we address the distribution of the forces which, to the extent that they are not a reflection of the measurements themselves, may be due to energetic surface inhomogeneities. On the other hand, the distribution may be inherent, *i.e.* the result of thermodynamic fluctuations. Both scenarios are explored.

Theoretical model. – We model the adsorbing surface by an external potential that accounts for the interactions of each monomer or bond of the polymer molecule with the atoms of the surface. For a metal or insulator these are the atoms fixed at the crystalline positions of the top few layers. For a self-assembled monolayer on a metal we include the interactions with its head groups, *i.e.* methyl, methoxy, hydroxy and carboxy groups. The result is a corrugated external potential that reflects the periodicity of the surface. The potential exhibits a repulsive wall that stops the monomers from penetrating into the surface and an attractive well that confines them into a quasi–two-dimensional adsorption layer. One end of the polymer —grafted to the AFM tip— is fixed at a distance z above the surface. Without the attachment to the tip the polymer is confined to the surface potential well, minimizing its free energy (provided the well is deep enough compared to $k_B T$). Attached to the AFM tip, the molecule will be stretched over the distance z accounting —roughly— for a fraction z/L of its monomers, where L is the contour length of the polymer. The remainder is confined to the surface potential.

The statistical mechanics is done in the Helmholtz ensemble using the transfer matrix (or transfer operator or Green function) method introduced previously for the confinement of a polymer in an external potential [10], except for the fact that we now work in a planar rather

than a cylindrical geometry. As a result, we have the Helmholtz free energy $F(T, z, N)$ for a polymer with N monomers from which we get the average force acting on the AFM tip, $f(T, z, N) = \partial F / \partial z|_{T,N}$.

Surface potentials. – The surface potentials accounting for the interaction of a monomer with the adsorbing surface are calculated using density functional theory (DFT), following established procedures [11]. The calculations proceed as follows: we take a short chain of the adsorbing polymer and a surface area large enough to accommodate this chain when stretched parallel to the surface. In a first step, we optimize the geometry of the chain thus obtaining the minimum of the surface potential. Next, we move the center of mass of the chain toward and away from the surface optimizing the geometry as we go. This will result in the z-dependence of the adsorption potential for that particular point on the surface. Finally, we move the chain's center of mass parallel to the surface and again, for each such new position in the (x, y)-plane, obtain a small number of z-dependent energy curves. To obtain the interaction energy of a single monomer, we repeat these calculations for a few chains with the number of monomers changing and write the energy of a chain with n monomers as a sum of n monomer interaction energies plus a contribution from its terminal groups. Doing this for $n = 2$ and 3 and subtracting the respective energies, we eliminate the interaction of the end groups with the surface and obtain the interaction per monomer. The assumption of linearity can be checked with a further calculation with $n = 4$ monomers and turns out to be roughly correct. The complete corrugated potential energy surface is then obtained by interpolation. For numerical convenience we parametrize the z-dependence by a Morse potential and the x-y dependence by powers of trigonometric functions, *e.g.*, for a surface with rectangular symmetry,

$$V_{\rm s}(x, y, z) = V_0 \big\{ \exp[2\gamma(z_0 - z)] - 2\exp[2\gamma(z_0 - z)] \big\} \times \big\{ 1 - A\cos^2(2\pi x / a_x)\cos^2(2\pi y / a_y) \big\}, \quad (2)$$

neglecting some small x-y dependence in z_0. Corrugation amplitudes are typically less than 10%, particularly for long monomers like acrylic acid which interact via several of their constituent molecular groups along the backbone, thus flattening the corrugation.

For the adsorption of polyacrylic acid on a CH_3-terminated SAM, we find $V_0/k_{\rm B}T$ to be about 4 from our DFT calculations. Allowing for the presence of water in the system via the mean-field PICM approximation, this value is reduced to about 3. For the adsorption of PAA on an OH- or COOH-terminated SAM in the presence of water, we get for $V_0/k_{\rm B}T$ about 7 and 15, respectively.

In a recent paper, it has been shown that even in pure water the auto-ionization of water is enough to deposit negative hydroxide ions on a SAM [12] with typical charge densities of $0.1\,\mu C/cm^2$. It is therefore mandatory, particularly for poly-electrolytes in ionic solutions, to allow for the adsorption of hydronium, hydroxide and other ions on the SAM and for ionization along the polymer when calculating the surface potentials. We found that the presence of negative charges on the SAM or on PAA typically doubles the binding energy as compared to the neutral species. Of particular interest is the fact that the interaction of neutral methyl head groups of the SAM with PAA is very weak but that inclusion of negative charges, on the PAA or embedded as OH^- ions in the SAM, leads to the right order of magnitude.

Adsorption forces. – To do the statistical mechanics we need a model for the polymer itself. The entropic contributions to the force are secondary as we saw in our introductory discussion, so that a simple polymer model such as the freely rotating chain (FRC) or the rotationally isomeric state (RIS) model suffices; all our numerical examples are for the FRC model. The latter is described by its monomer length, b, its bond angle, ϕ, and the number of monomers, N. Adsorption in a surface potential is therefore characterized by the dimensionless
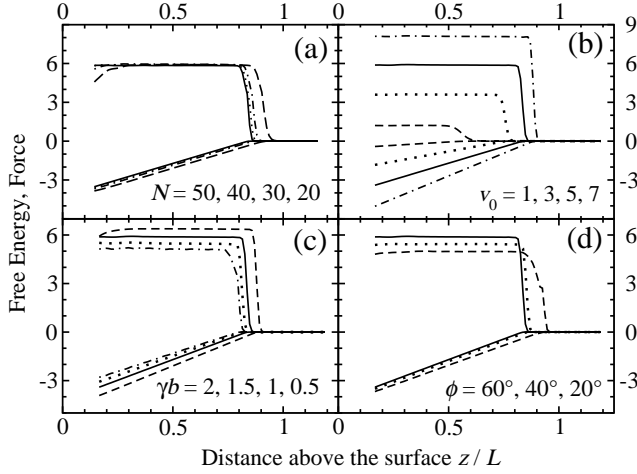
Fig. 1 – In each panel the lower set of (straight) lines are free energies, $F/k_\mathrm{B}T$, and the upper (constant) lines are forces, $fb/k_\mathrm{B}T$. The curves are labeled from left to right, according to the free energies. Except for the variations indicated in each panel, the common parameters (solid curves) are $v_0 = V_0/k_\mathrm{B}T = 5$, $\gamma b = 1$, $N = 50$, $\phi = 60°$.

surface potential depth, $V_0/Nk_\mathrm{B}T$, its normalized width, γb, the dimensionless force, $fb/k_\mathrm{B}T$, and the distance of the anchoring point to the surface, z/L, normalized with the contour length of the polymer, $L = Nb\cos(\phi/2)$.

To explore the dependence of the adsorption force on the physical parameters of the surface potential and of the polymer, we present results from a series of calculations in which we vary these parameters over reasonable ranges. The calculations are based on the transfer matrix or Green function method explained in detail elsewhere [10].

Because the experiments are done with very long polymer chains that are computationally intractable, we must first examine the dependence of our calculations on the number of monomers to establish the minimum length beyond which no further changes occur. In panel (a) of fig. 1 we show the normalized free energy and its derivative, the (dimensionless) force, as a function of the (dimensionless) distance of the anchoring point from the surface for a typical surface potential with $V_0/k_\mathrm{B}T = 5$, $\gamma b = 1$, $\phi = 60°$. As expected, the free energy for all N's beyond 20 is essentially linear and the force is constant over most of the extension range, except at the initial distances of pulling the polymer out of the surface potential, where the anchoring point at the AFM tip is still within the range of the potential so that less force is required to hold it there. At the point of maximum stretching the last monomer leaves the surface potential and this end of the polymer becomes free. According to the force-extension curves for a polymer with both ends fixed in space, its extension at a force $fb/k_\mathrm{B}T = 6$ is 0.93, see fig. 2. Because a chain partially confined in a soft surface potential is not rigidly anchored there, the breaking point where it is pulled completely out of the surface potential is less than that, about 0.8 for $N \approx 50$ but larger for short chains where entropic contributions are less important. Overall, these results show that $N \approx 50$, is sufficiently large to mimic very long chains in this geometry. This is not too surprising considering that for a free freely rotating chain the Kuhn length, $L_\mathrm{K} = bC_N$, is only a few monomer lengths with the characteristic ratio C_N being 2.92 for $N = 50$, within a few percent of its asymptotic limit [13].
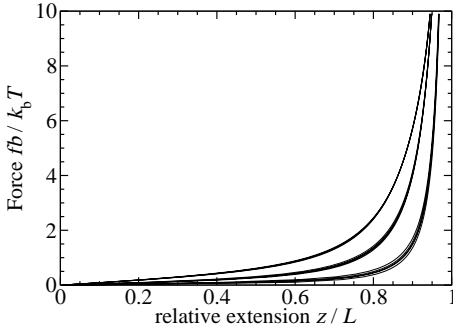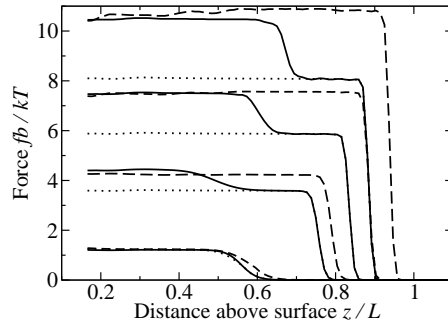
Fig. 2

Fig. 3

Fig. 2 – Force-extension curves for FRC with bond angle $\phi = 60°$, $40°$ and $20°$ (groups of curves from left to right). Within each set of curves $N = 20, 30, 40, 50, 200$ (left to right).

Fig. 3 – The force-extension curves for the defects described in the text. There are four sets of curves for $v_0 = 1, 3, 5$, and 7. The four dotted curves are those of fig. 1(b), the solid curves have the defect at a distance $R = 20b$ and the dashed curves have the defect at $R = 0$.

Next we explore in panel (b) of fig. 1 the dependence of the free energy and force on the well depth, V_0/k_BT. The normalized force, fb/k_BT, is somewhat larger than V_0/k_BT, with the breaking point occurring at distances less than the corresponding extensions for the polymer with both ends fixed, for forces 8, 5.7, 3.5, and 1.1 these are 0.93, 0.90, 0.85, and 0.6, see fig. 2. The deviations are less so for shallower potentials for which the entropy loss in (1) tends to compensate the energy loss. This point is clearer when we vary the range of the potential, panel (c) of fig. 1. The narrower the potential the more the polymer is restricted to truly two dimensions. Consequently, entropic loss in going from 2D to 1D confinement is minimal and the first term in (1) dominates the force completely. As the potential well is widened, at the same depth, the entropy increases because the confinement is now quasi-3D and its loss by stretching adds to the force.

Finally, we explore the effect of different bond angles in panel (d) of fig. 1. A smaller bond angle makes the polymer stiffer so that the entropy loss is decreased upon stretching. When the bond angle becomes very small the polymer is essentially a stiff rod (with an asymptotic characteristic ratio $C_\infty = 32.2$) that cannot be bent from being parallel to the surface to being perpendicular to it. Rather, one tilts the whole rod slowly out of the potential well at some angle so that many monomers are gradually and simultaneously lifted out, rather than one monomer at a time. The force needed is actually less than the first term in (1) and slowly drops as the anchoring point moves further away, because fewer monomers remain in contact with the surface. This continues until the last monomer is in the well but now oriented perpendicular to the surface. To remove it then requires a force of the order of the first term in (1), at maximum extension, giving the shoulder at $z/L = 1$. Indeed, for a short chain with $N = 10$, this shoulder becomes a narrow spike.

So far we have given examples for flat surfaces. We have examined the effect of surface corrugation (as expected on a SAM) in a series of calculations in which we varied the parameters A, a_x, and a_y in eq. (2). One finds that as long as a_x and a_y are of the order of b, the adsorbed molecule sees an average surface potential: although the monomers prefer to be in the bottom of the potential corrugation, the connection between adjacent monomers prevents this from happening, hence the average potential.

Distribution of forces. – The experimental data show not one value of the adsorption force, but a Gaussian-like distribution with a width of about 20% of the average force for many sweeps [1–4]. Apart from the possibility that the distribution of the forces is due to experimental difficulties such as reproducibility or drift, two explanations for this distribution come to mind: i) It may reflect inhomogeneities (in addition to surface corrugation) of the substrate surface, *i.e.* a distribution of well depths that has, via (1), the same width as the distribution of the adsorption force itself. ii) It originates in thermodynamic fluctuations.

We have modeled possible surface inhomogeneities by assuming that, at a lateral distance R from the point on the surface below the AFM tip, we have a region where the surface potential is deeper. To preserve some symmetry in the problem (for reasons of computational expediency) we assumed that this region is actually an annulus with radius R and a width of a few monomer lengths. If R is larger than the contour length L of the polymer there is no effect on the adsorption force. At the other extreme, if R is less than a few monomer lengths, all of the polymer is to be pulled from this deeper potential, thereby increasing the force. In fig. 3 this is shown as the dashed lines for a potential inhomogeneity that is 50% deeper. Lastly, if $b < R < L$, then the initial force for small z corresponds to the larger force of the surface inhomogeneity, and a drop to the force corresponding to the surface potential outside the annulus occurs when $N(R/L) \gtrsim N(1 - z/L)$. The drop is closer to the equality of this relation when the potential of the inhomogeneity is deeper. This is seen in fig. 3. The fact that the drop is rather smooth is a reflection of the entropic term in eq. (1). Note that we are not claiming that the drops in the experimental data (due to multiple attachments of polymer strands) are due to such surface inhomogeneities but rather to the force distribution. Whether surface inhomogeneities are the cause of the observed distribution of forces can be checked experimentally by controlling the quality of the surface.

We comment briefly on the role of force fluctuations. Although they do not seem to be observed in the experiments [4] (because the combined molecule-cantilever system was overdamped), their role is worth pursuing and worth some attention in future experiments. The argument goes as follows: at forces of tens to hundreds of pN we are in the regime of conformational conversion from shorter to longer chains and the fluctuations would be a reflection that many conformations are still contributing. Of interest are the fluctuations only of that part of the chain already pulled out of the surface potential and kept under a constant force load. With the force held constant, the conjugate variable, the length, will exhibit fluctuations which are given by

$$\frac{\delta z}{z} = \left[\frac{k_{\mathrm{B}}T}{zK_T}\right]^{1/2}, \qquad (3)$$

where $K_T = z\partial f/\partial z|_T$ is the stretch modulus or chain elasticity. We can easily estimate these fluctuations within the FRC model; for an analytical approach one could use the global force-extension fitting function proposed by Livadaru *et al.* [14] or any of its limiting forms. One finds that, for a typical force $fb/k_{\mathrm{B}}T \approx 5$, the portion of the chain (for a bond angle of $60°$) outside the surface potential is stretched to 89% of its maximal end-to-end length, and $K_T \approx 10^4$ pN for $b = 2$ Å. Thus the length fluctuations for a chain of length 4000 Å are about 4 Å and the corresponding force fluctuations $\delta f = (k_{\mathrm{B}}T/\delta z)\,(c_{\mathrm{f}}/c_{\mathrm{l}})$ are about 10 pN. c_{f} and c_{l} are the molecular specific heats at constant force and at constant length, respectively. This result is in quantitative agreement with available experimental data. We would therefore like to propose that the stretch modulus of the polymer chain at the constant stretching force can

be extracted from fitting a Gaussian with half-width, $2\delta f$, to the force distribution according to

$$K_T = \frac{z(\delta f)^2}{k_\mathrm{B}T} \frac{c_\mathrm{l}}{c_\mathrm{f}}, \tag{4}$$

where c_l and c_f are the specific heats of the chain at constant length and force, respectively.

Note that the square of the force fluctuations is proportional to the inverse length of the molecule so that K_T is, for long chains, independent of their length. Measurements of PAA chains of typical lengths around 4000 Å give average forces around 50–70 pN, depending on the terminal groups of the SAM. Half-widths are around 4–6 pN [4]. Using (4) we then find that PAA has a chain stretch modulus in the range from 2500 to 8100 pN depending on how we extract δf from the measured force distributions. This is in rough agreement with fits of a wormlike chain model of polyvinylamine for which values of 4000 and 13600 pN have been quoted [2]. It should also be remembered that the stretch modulus is a strong function of the extension or, equivalently, the corresponding stretch force, see fig. 2. A more detailed and careful examination of data is required to narrow this range. In particular, these experiments would have to be done with a soft cantilever where the force fluctuations dominate. The current experiment was done with very stiff cantilevers [4]. There is an independent experimental check on these ideas, namely to measure, in the standard experiment, the force-extension curve with one end fixed to the surface and the other to the AFM tip. Differentiation of this curve also gives the stretch modulus, which should be the same as that extracted from the fluctuations (at the given force).

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