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Large loops in adsorbed polymer layers

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Abstract. — We discuss the formation of large loops in adsorbed polymer layers when the bulk concentration \( C \) is large. This allows us to introduce a new characteristic length \( \Lambda \) that corresponds to the extension of the loops in the bulk. We find that \( \Lambda \sim NC^{5/4} \) and increases from the screening length \( \xi \) to the radius of the chains when concentration increases. This may be observed for instance by dilution of the solution subsequent to adsorption.

1. Introduction.

Adsorption of linear polymers is interesting both from an applied and a fundamental points of view, and has been of constant interest for a long time [1-19]. A scaling approach was recently proposed by de Gennes [1], Pincus [2], Binder [3], and Eisenriegler et al. [4]. A characteristic result that was obtained is that, in the so-called plateau regime [5], the concentration profile decreases when one gets away from the surface as a power law, in contrast with the exponential decay that a mean field argument would give. This surface regime is obtained for low bulk monomer concentrations, usually well in the dilute regime. For higher concentrations, however, the extent of the polymer was not as clear. This is related to the fact that in a semi-dilute regime, the concentration profile extends to distances of the order of the screening length \( \xi \) so that it becomes harder to examine larger distances. From a conceptual point of view however, it is interesting to know whether the chains make loops larger than \( \xi \) or are constrained within this distance to the adsorbing surface. This may also be relevant to force measurements [20, 21] between polymers adsorbed on plates that are gradually brought towards each other. Finally, this is also related to the existence of trains and loops that was discussed recently by Marques and Joanny [22, 23]. In what follows, we are going to consider the problem from the latter point of view. It is then possible to follow the conformation of the adsorbed chains as bulk concentration is increased. As already discussed by Bouchaud [6], and mentioned above, the plateau regime, where the surface is saturated with monomers is reached for rather low values of \( C \), well below the overlap concentration \( C^* \). It was shown that the concentration profile decays as a power law [1] of the distance \( z \) to the surface, and extends to distances of the order of the radius of gyration of a free chain, as long as the bulk

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concentration is lower than $C^*$. In the semi-dilute regime, however, the gradient is limited to distances of the order of the screening length $\xi$. For larger distances, the average bulk concentration is reached, and the surface properties are apparently lost. So far, the adsorption problem in this concentration range was only addressed in terms of adsorption of blobs [5]. It is of course possible to consider the question from the point of view of chains. The question that arises then is to know their conformations, and the distance $\lambda$ from the surface that they reach by forming loops. One has also to have in mind that whereas in the plateau regime, each polymer has a number of monomers on the surface proportional to $N$, this number is of the order of $N^{1/2}$ in a concentrated solution. One question then is to know when the cross-over from one regime to the other occurs. In connection with this cross-over, the polymer, which is localized in the surface layer for lower concentrations, reaches distances which become larger and larger as concentration is increased until it reaches its free radius of gyration. This is done by developing large loops, with size larger than $\xi$. Therefore the polymer is, in some sense, localized in the adsorbed layer at low concentrations and gradually delocalizes as concentration increases. In what follows, we wish to study this delocalization, and discuss the configuration of the chains in the various regimes. We remind the results on the plateau regime in section 2. Next, we discuss the existence of trains and loops in the adsorbed polymers and their evolution as concentration changes. Finally, we suggest in section 4 a possible way to show the existence of intermediate loops by diluting an irreversibly adsorbed layer.

2. The plateau regime.

Let us assume that we have a dilute polymer solution in a good solvent. Every chain is made of $N$ units of length $\ell$ each. The bulk monomer concentration $C$ is in the dilute range. We also assume that the surface is attractive to the polymers. This is the case for instance when the surface tension of the solvent is smaller than that of the pure polymer. Let $\delta$ be the energy gain of a monomer when it is located at the surface. We assume it to be smaller than unity. For long enough polymers, such as $\delta N^{1/3} \gg 1$, or for high enough surface interactions, $\delta \gg \delta^* \sim N^{-3/5}$, the polymers adsorb onto the surface. The number $N_s$ of monomers on the surface which, for a self avoiding walk, is of the order of $N^{3/5}$ for a non adsorbed chain, becomes, when it is adsorbed

$$N_s \sim N \delta^{2/3}$$

(1)

There is a partition of the polymers between the bulk of the solution and the surface states. Because of the exponential involved in the Boltzmann distribution, the surface concentration rises very rapidly and reaches a plateau where it roughly saturates [6]. One is then left with a dilute solution and a concentrated surface. Calling $z$ the distance normal to the surface, it is easy to realize that there is a concentration profile $\Phi(z)$ that is continuous and decreases as $z$ increases. This was calculated recently in a scaling approach, and it was shown that such decrease is a power law function of the distance. In the case when $\delta$ is small which we will consider, three distance ranges were found [2]:

In the proximal range, $\ell \ll z \ll D$, there is a slight variation

$$\Phi(z) \sim \Phi_s(z/\ell)^{-1/3}$$

(2)

where $\ell$ is the size of the monomer, $D$ is the so-called extrapolation distance, and depends only on the monomer-surface interaction $\delta$:

$$D \sim \delta^{-1} \ell$$

(3)
and $\Phi_s$ is the surface concentration:

$$\Phi_s \sim \delta.$$  \hfill (4)

In the central range, $D \ll z \ll R$, with $R$ the radius of non adsorbed chains, the profile was shown to be self-similar, and we have locally a semi-dilute regime:

$$\Phi(z) \sim (z/\ell)^{-4/3}$$  \hfill (5)

Finally, in the distal range $z \gg R$, the profile goes exponentially to the bulk concentration value.

Therefore, in the plateau regime, as long as the bulk of the solution is dilute, the surface layer where the concentration profile is present extends to distances of the order of the radius of gyration of a chain in the solution

$$R \sim N^{3/5} \ell$$  \hfill (6)

where we used the Flory approximation to the excluded volume exponent.

When concentration is increased and the bulk becomes semi-dilute, the profile remains unchanged, but extends only to a distance of the order of the screening length $\xi$

$$\xi \sim C^{-3/4}.$$  \hfill (7)

We note that the blobs are adsorbed: the number $g_s$ of monomers per blob directly on the surface is [6] proportional to the number $g$ of units in a blob

$$g_s \sim g \delta^{2/3} \sim C^{-5/4} \delta^{2/3}.$$  \hfill (8)

Desorption of the blob occurs when its size becomes comparable to $D$. This happens for a concentration $\tilde{C}$ such that

$$\tilde{C} \sim \delta^{4/3}.$$  \hfill (9)

For higher concentrations, the blobs are no longer adsorbed.

So far, in the semi-dilute regime, we considered only the local adsorption of blobs, and we did not look at the large scale properties of the chains. The way we used to think about is was to assume that the chains are no longer adsorbed in this regime, and that only blobs could be. This is recalled in next section. Another approach however was initiated very recently by Marques and Joanny [22, 23], and we would like to analyze here its consequences. In this approach, it is assumed that as concentration becomes larger than $C^*$, there is a localization effect of the adsorbed chains by the free ones. Then, just above $C^*$, the polymers on the surface do not extend to their radius of gyration anymore, but only to $\xi$. We will call trains those chains, or part of chains made of $t$ monomers that are localized within the screening length. With this definition, a chain is made of one train in the semi-dilute range just above $C^*$. Clearly, this will not hold at very large concentrations: for larger $C$, trains are going to become shorter, and loops with size larger than $\xi$ will be included in the conformation of the adsorbed polymers. Therefore, other cross-overs are present, as found by Marques and Joanny. We evaluate them in section 4.

3. Desorption at $C^*$.

In this section, we remind briefly the results that we used to accept. It was implicitly assumed that above the overlap concentration $C^*$, in the semi-dilute regime, the chains are no longer adsorbed, as is the case in a melt. The number $B_s$ of blobs on the surface is therefore

$$B_s \sim (N/g)^{1/2}$$  \hfill (10)
Thus the number of monomers per chain directly on the surface is, using relation (8),
\[ N_s \sim N^{1/2} g^{1/2} \delta^{2/3} \] (11)
and crosses over to \( N^{1/2} \) for \( C \sim \tilde{C} \), relation (9). Thus, in the semi-dilute regime, the normal extent of the adsorbed chain is of the order of its radius of gyration
\[ R \sim N^{1/2} C^{-1/8} \ell \] (12)

Recently however, Marques and Joanny introduced the concept of trains that was not taken into account so far: in the previous approach, the chains are made of loops only. In what follows, we are going to consider the possible formation of trains as described in reference [22], and this brings a very different phase diagram, as we will see.

4. Shorter trains and larger loops: desorption at \( C_1 \).

In the semi-dilute regime, it is possible to evaluate the size of the trains, following reference [22]. As shown by de Gennes [1], the concentration profile is self similar for distances smaller than \( \xi \). Because of this, only one chain at most may leave the adsorption layer within a surface \( \xi^2 \). Therefore, the probability that a polymer leaves the surface, and makes a loop larger than \( \xi \) is \( n \xi^{-2} \), where \( n \) is the number of chains that are needed in order to ensure the surface concentration. Indeed, the contribution \( \Phi_{s1} \) of one blob to the surface concentration is, using relation (8)
\[ \Phi_{s1} \sim g_s / \xi^2 \sim g \delta^{2/3} / \xi^2 \]
Therefore, the number of chains that are needed in order to have the surface concentration \( \Phi_s \) is
\[ n \sim \Phi_s / \Phi_{s1} \sim \delta^{1/3} g^{1/5} \] (13a)
and the probability of escape for a polymer is
\[ p \sim \delta^{-1/3} g^{-1/5} \] (13b)
Thus, the average length \( t \) of a train, that is the average number of monomers within a distance \( \xi \) from the surface is
\[ t \sim g^{6/5} \delta^{1/3} \sim C^{-3/2} \delta^{1/3} \] (14)
When the concentration is small, a train is essentially the chain itself. Because \( t \) has to be smaller than \( N \), we find a first cross-over concentration \( C_1 \),
\[ C_1 \sim N^{-2/3} \delta^{2/9} \] (15)
Note that \( C_1 \) is larger than \( C^* \sim N^{-4/5} \) and that both merge when \( \delta N^{3/5} \sim 1 \).

An important consequence of the existence of the above cross-over is that for lower values of \( C \), the adsorbed chain consists in a single train. The reason for the breakdown of the above derivation of \( t \) at \( C_1 \) is in the evaluation of the number of loops, or equivalently in the estimate of the probability of escape for a chain. Therefore, below \( C_1 \), one might consider the chains as being confined to the surface. Note however that this does not exclude the possibility for the polymers of having tails, that is dangling ends with size larger than \( \xi \), and possibly some loops.
Above this cross-over value on the other hand, the above derivation for the length of the trains holds, and larger loops start forming at distances greater than $\xi$. It is possible to get their number $L$. Assuming that the distribution of train lengths is not singular, $L$ is merely the length of the chain divided by the average length of the trains. We get

$$L \sim NC^{3/2}\delta^{-1/3}$$

(16)

Thus, we get that whereas below $C_1$, the length of the trains is proportional to $N$, and independent of concentration, both their length and their number are dependent on concentration above the cross-over.

As concentration increases, the length of the trains decreases and their number increases to compensate in such a way that the total number of monomers remains of order $N$. We know however that in the case of concentrated solutions, as in the melt, the number of loops is proportional to $N^{1/2}$ rather than to $N$. Therefore, we expect a second cross-over concentration $C_2$ between these two regimes. This may be evaluated in a more precise way by noting that the number of contacts of a chain in a melt with a surface is of the order of $N^{1/2}$. This is related to the fact that an ideal chain has that number of contacts with a plane. For a semi-dilute solution, a polymer has $(N/g)^{1/2}$ blobs on the surface, and therefore the same number of large loops. Equating this with $L$, relation (16), we get

$$C_2 \sim N^{-4/7}\delta^{8/21}$$

(17)

Note that $C_2$ is larger than $C_1$, and that both merge with $C^*$ for $\delta \sim N^{-3/5}$. The corresponding phase diagram is shown in figure 1. What we found so far is that the various adsorbed polymers are made of small loops that are confined within a distance $\xi$ for bulk concentration lower than $C_1$. Between $C_1$ and $C_2$, larger loops develop, and reach the size of the free polymer at the upper limit of the range. Above $C_2$, large loops are present, and the polymers cannot be considered as adsorbed: the number of blobs per chain on the surface is of the order of $N^{1/2}$. Therefore a scale transformation using a blob as unit leads to a melt, where the chains are no longer adsorbed. Note that such result does not hold below $C_2$. The number of units on the surface is then proportional to $N$. Thus the size of the loops increases between $C_1$ and $C_2$ from $\xi$ to the radius $R$ of a chain in the bulk, semi-dilute, solution. We know from previous studies (25) that in these conditions, we have

$$R \sim N^{1/2}C^{-1/8}$$

(18)

Fig. 1. — The phase diagram in a concentration-surface interaction plane. Only the bulk semi-dilute regimes are sketched. Below $C_1$, chains are trains, basically localized within a distance $\xi$ from the surface. Between $C_1$ and $C_2$, loops larger than $\xi$ develop and reach the radius of the free chain at $C_2$. Above $C$, the loops are no longer adsorbed. $\delta^* \sim N^{-3/5}$ corresponds to the adsorption energy limit of a chain.
One may assume a scaled form for the size $A$ of the loops

$$A \sim C^{-3/4} f(C/C_1).$$

Assuming a power law behavior for the function $f(x)$, insisting on the condition that $A$ is of the order of $R$ for $C \sim C_2$, and using relations (15), (17), and (18), we get

$$A \sim \xi \left( \frac{C}{C_1} \right)^{3/2} \sim NC^{3/4} \delta^{-1/3}$$

Note that although $A$ is linear with $N$, it is much smaller than the radius of the free isotropic chain, and that it increases with concentration, as discussed above.

5. Discussion.

Let us first consider only the loops in the structure of the adsorbed polymers, thereby neglecting the eventual presence of tails. What we find then is that below $C_1$ only small loops are present, with size at most $\xi$, corresponding to the concentration profile. This implies that in the bulk semi-dilute regime, the adsorbed chains are confined by the free ones within the surface layer. Larger loops start forming only when the concentration is high enough, above $C_1$. They reach their maximum value at $C_2$. For higher concentrations, this large loop structure is present as in a melt. The only difference lies in the unit distance which is a blob in this semi concentrated regime, whereas it is the monomer in the melt. Therefore the region between those two concentrations is best from the point of view of the interpenetration of the adsorbed layer and the bulk of the solution. For a practical use, the vicinity below concentration $C_2$ is probably the best region because it is the region where the loops are the largest and the polymer still has about $N$ monomers on the surface. Above $C_2$, the loops are large, but the chains start desorbing, so that the number of units on the surface becomes of the order of $N^{1/2}$, and decreases as concentration increases. Below $C_1$, there is limited mixing of the adsorbed chains with the free ones.

If the conformation was made only of loops, it would be rather straightforward to observe experimentally this structure. This could be realized for instance by first quenching those monomers that are located on the surface, by chemical reaction or by irradiation for instance, and then by dilution of the bulk of the system. The resulting profile would still be independent of the molecular weight of the adsorbed macromolecules, because of the quenching procedure. It is also possible that ellipsometric measurements provide such information. However, the structure of the adsorbed layer includes in principle, in addition to the small loops, both tails and some large loops even below $C_1$, as discussed in the beginning of last section.

Direct observation of the number of monomers in contact with the surface may be done by N.M.R. or infrared spectroscopy. We remind briefly the various results in the different regimes that we discussed above, as summarized in figure 2.

![Figure 2](image_url)

Fig. 2. — Sketch of the various surface regimes in figure 1. The chains are adsorbed below $C_2$ and desorbed above.
Below $C_1$, the number $n_s$ of monomers per chain on the surface is proportional to $N$. Between $C_1$ and $C_2$ this number becomes concentration dependent. We found

$$n_s \sim C^{-3/2} \delta^{1/3}$$

Between $C_2$ and $\tilde{C}$, the blobs are adsorbed, but the chain is not. Therefore $(N/g)^{1/2}$ blobs of a chain are on the surface. This leads to

$$n_s \sim N^{1/2} C^{-5/8} \delta^{2/3}$$

Finally, above $\tilde{C}$ the blobs are no longer adsorbed, so that

$$n_s \sim N^{1/2} C^{-1/8}$$

We now discuss the possible influence of these large loops and tails. This may be seen directly by surface force experiments, such as performed by Israelachvili [21] or Klein [22] for instance. The onset of the force corresponds to the large loops present. In what follows, we will always assume that the structure on the surface is quenched after the adsorption process has come to equilibrium. This may be realized either by chemical reaction with the surface, or by irradiation for instance. Therefore, we will assume that the surface concentration is kept constant. Then the system is washed, so that the bulk is essentially made of a good solvent. The force experiment would be made on such prepared system.

**Diluted Solution.** — In this section, we will consider the extent of the adsorbed layer for various initial conditions. By this, we mean the concentration range where the surface monomers were quenched on the surface before the dilution of the system. For a melt, this was considered very recently by Guiselin [24] and de Gennes for $\delta \approx 1$. Their approach makes the analogy between these large swollen loops and grafted polymers. For a melt, we know that there are $N^{1/2}$ monomers per chain on the surface. Therefore the density $\sigma$ of grafting is of the order of $N^{-1/2}$. After dilution, using the Alexander-de Gennes scaling approach to grafted chains, it is possible to introduce a swollen blob, made of $g_b$ monomers, with size $\lambda$ such that

$$\lambda \sim \sigma^{-1/2} \sim N^{1/4} \ell.$$  \hspace{1cm} (21)

The overall size $H$ of the adsorbed layer is

$$H \sim \lambda N/g_b.$$  \hspace{1cm} (22a)

Assuming that the blob is swollen, i.e. $\lambda \sim g_b^{3/5}$, we get the Guiselin result:

$$H \sim N^{5/6} \ell \quad \text{(melt).}$$  \hspace{1cm} (22b)

This also holds for a semi dilute solution as long as the concentration is larger than $C_2$. One has merely to replace the monomer size $\ell$ by the radius $\xi$ of the blob. We get

$$H \sim N^{5/6} C^{7/24} \quad (C > C_2).$$  \hspace{1cm} (22c)

For concentrations smaller than $C_1$, upon dilution, the adsorbed layer should swell back to the dilute regime, so that we get

$$H \sim N^{3/5} \ell \quad (C < C_1).$$  \hspace{1cm} (22d)
Finally, interpolating between $C_1$ and $C_2$, we get

$$H \sim N^{16/15} C^{7/10} \ell \quad (C_1 < C < C_2).$$  \hspace{1cm} (22e)$$

One may check easily that the latter result is in between the previous two ones in the concentration range where it is valid.

It would certainly be extremely interesting to test these laws and to check which of the approaches is valid.

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