Adsorption from a Bidisperse Polymer Mixture

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ABSTRACT: The adsorption of long, linear polymer chains made of N monomers dissolved in a solvent made of shorter chains of P units of similar chemical species is discussed. Various regimes that may be found and the crossovers when either the bulk concentration increases or the length of the smaller chains is increased are also discussed.

Introduction

The configuration of linear polymers at interfaces[1-12] has attracted strong attention the last few years because new experimental methods such as neutron scattering[13] or reflection[14] have become available and also because a scaling approach gives results that are somewhat different from that obtained by more conventional methods. Among this class of problems, chain adsorption has been under continuous study for some time. So far, adsorption at the free surface of a dilute or a semidilute solution in a good solvent was carefully studied in order to show the eventual existence of a self-similar regime that was predicted by the scaling approach.[15] In what follows, I look at a situation that covers, in principle, the whole range of concentrations by changing the length of the adsorbed chains. More precisely, the adsorption of long chains made of N monomers that are dissolved in a melt made of shorter chains with P units is considered. It is assumed that both species are slightly different, but coexist, and that no phase separation occurs. Because of the difference in the species, there may be a difference of affinity for the surface, and it is assumed that the latter attracts the large species. (The opposite case, when the large polymers are repelled by the surface, is also of interest but will not be considered here.) This may be realized for instance with hydrogenated and deuterated species, where very high molecular weights are needed for such demixing. In what follows, I assume, for simplicity, that both species are identical. What is interesting with such systems is that by increasing the molecular weight of the solvent from $P = 1$ to $P = N$, one goes continuously from the situation of a dilute solution to a melt. Thus, by increasing P, one expects to have a different aspect of polymer desorption.

In what follows, results for the bulk behavior of such mixture is recalled. Later, the adsorption of a single long chain and then the case of the plateau will be considered.

Long Chains in a Shorter Matrix

The behavior of a long chain made of N units dissolved in a shorter matrix, made of identical polymers, with P monomers is considered first. When P is on the order of unity, a dilute solution of N in a simple solvent is considered. It is assumed that the latter is a good solvent of the former. On the other hand, for large enough values of P, one expects to recover the behavior of a chain in a melt. This problem was considered some years ago by de Gennes,[16] who wrote the following free energy in the Flory approximation[17]

$$F = \frac{R^2}{R_0^{\,2}} + \frac{v}{P}\frac{N^2}{R^3} \tag{1}$$

where the first term is the elastic contribution and the second one the interaction energy. R_0 is the ideal radius and v the excluded volume parameter, and the presence of P in the interaction term is related to the Edwards screening. Minimizing with respect to R leads to

$$R \sim N^{3/5}P^{-1/5} \tag{2}$$

Relation 2 is valid for small values of P. For larger values, as discussed in the Introduction, one expects ideal behavior, as in a melt. I.e., $R \approx R_0$ with

$$R_0 \sim N^{1/2} \tag{3}$$

When relations 2 and 3 are compared, the crossover from dilute to meltlike behaviors occurs for

$$P^* \sim N^{1/2} \tag{4}$$

Thus, if the matrix is made of chains with mass larger than P^*, one expects ideal behavior for the probe, whereas for shorter chains swelling is expected. It is possible to go one step further in the conformation of the probe chain in the swollen case by estimating the interaction term in the free energy. Assuming ideal behavior, it is

$$F_{\text{int}} \sim \frac{v}{P}N^{1/2} \tag{5}$$

This is smaller than unity for $P \gg P^*$, and this term may be neglected in the free energy. Thus, the structure is ideal. On the contrary, for $P \ll P^*$, the interaction term has to be taken into account, leading to a swollen configuration. Locally, however, the structure remains ideal because the interaction is weak, and it is possible to define ideal blobs made of g_{id} monomers such that $vg_{\text{id}}^{1/2}/P \sim 1$, leading to

$$g_{\text{id}} \sim P^2 \tag{6}$$

and to a size

$$\chi \sim P \tag{7}$$

The structure of the probe chain is then a swollen succession of blobs:

$$R_N \sim \left\{\frac{N}{g_{\text{id}}}\right\}^{3/5}\chi \tag{8}$$

Using relations 6 and 7, one recovers eq 2. If we now consider a mixture of such long chains, with fraction C, in the same matrix of shorter chains, one is led to define

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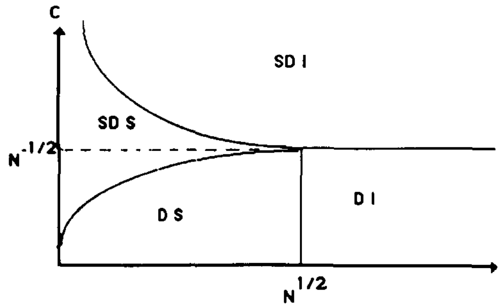

Figure 1. Phase diagram in the C–P plane. The regions are as follows: D S is the swollen and dilute regime for the probe chains; M I is the melt regime where they are ideal; SD S is the semidilute, locally swollen range; SD I is the semidilute regime with ideal blobs for the long chains.

an overlap concentration C^* above which the long chains have large-scale screened behavior. Using relation 2

$$C^* \sim \frac{N}{R^3} \sim N^{-4/5}P^{3/5} \tag{9}$$

Note that, for $N \sim P^2$, relation 9 gives $C^*_{\mathrm{id}} \sim N^{-1/2}$. This corresponds to the fact that although they are ideal in these conditions, the long chains still start overlapping for this concentration. Therefore, for concentrations higher than C^*_{id}, one may still define for instance a screening length ξ, corresponding to the overlap of long chains, which does not take into account the shorter polymers. This may be observed experimentally if the long chains are labeled by deuteration. The corresponding phase diagram is shown in Figure 1. For concentrations in the long chains higher than C^*, one expects a screening of the excluded volume interaction and a screening length

$$\xi \sim C^{-3/4}P^{1/4} \tag{10}$$

Thus, the long chains are swollen as in the dilute case for small scales, in a blob made of g_c units with

$$g_c \sim C^{-5/4}P^{3/4} \tag{11}$$

and screened for larger scales. The overall size of a long polymer is

$$R_N \sim \left\{\frac{N}{g_c}\right\}^{1/2}\xi \sim N^{1/2}C^{-1/8}P^{-1/8} \tag{12}$$

Because the concentration dependences of ξ and χ are different, as C is increased, a crossover occurs when both are of the same order. This corresponds to

$$\tilde{C} \sim P^{-1} \tag{13}$$

For concentrations in long chains larger than $\tilde{C}$, the probe chains are ideal at every scale. The corresponding phase diagram is shown in Figure 1.

Adsorption of a Long Chain

Adsorption of one long polymer dissolved in shorter ones is now considered. It is assumed that to every monomer from the long chain on the surface corresponds an energy gain δ. From previous work[18] it is known that, in the case of a simple solvent, the number N_s of monomers of a chain on a surface is[18,19]

$$N_s \sim N^{\phi} \tag{14}$$

where the crossover exponent ϕ is $^1/_2$ for a Gaussian chain and approximately $^3/_5$ for a self-avoiding walk.[2,20] It is then possible to estimate the number of monomers on the surface in the case when the solvent is made of short chains. As discussed above, one deals with a self-avoiding succession of Gaussian blobs. Every blob contributes

$$N_1 \sim g_{\mathrm{id}}^{1/2} \sim (P^2)^{1/2} \tag{15a}$$

The number of adsorbed blobs is

$$N_2 \sim \left\{\frac{N}{g_{\mathrm{id}}}\right\}^{3/5} \tag{15b}$$

Thus, the number of adsorbed monomers is

$$N_s \sim N^{3/5}P^{-1/5} \tag{15c}$$

The corresponding energy gain is therefore

$$F_a \sim \delta N^{3/5}P^{-1/5} \tag{16}$$

This is to be compared with an energy P per solvent chain. Thus, the relevant parameter is

$$x = \delta N^{3/5}P^{-6/5} \tag{17}$$

When x is small, the energy gain is not sufficient to balance the thermal energy of the solvent molecules. When it is large, the long chains are adsorbed. The adsorption crossover occurs for a value δ^* such that x is on the order of unity.

$$\delta^* \sim N^{-3/5}P^{6/5} \tag{18a}$$

Note that this value is larger than the corresponding one for a chain in a simple solvent, $P = 1$, and becomes on the order of unity when $N \sim P^2$. This is expected because, as above, it corresponds to the crossover to a bulk behavior. It is expected then that the chains can adsorb only if the monomers do so. Conversely, for a fixed value of δ, the large chains desorb when P becomes larger than P_s^* such that

$$P_s^* \sim \delta^{5/6}N^{1/2} \tag{18b}$$

For values of x (relation 17) larger than unity, the probe is adsorbed and its structure includes three different lengths: The local structure is ideal for distances smaller than the radius $\chi \sim P$ of the ideal blob introduced above (relation 7). For intermediate distances one has an isotropic conformation in a surface blob made of g_{iso} units such that $\delta g_{\mathrm{iso}}^{3/5}P^{-6/5} \sim 1$:

$$g_{\mathrm{iso}} \sim \delta^{-5/3}P^2 \tag{19}$$

The radius of such an isotropic blob is

$$D \sim \left\{\frac{g_{\mathrm{iso}}}{P^2}\right\}^{3/5}P \sim \delta^{-1}P \tag{20}$$

Note that as P increases, so does D. The crossover to the desorbed case occurs when the latter becomes on the order of the free radius of the probe chain. Equating relations 20 and 2, relations 18 are recovered.

For still larger distances, the large chain adopts a pancake shape: Using the isotropic blob as unit, its structure is two-dimensional. Thus, its radius parallel to the adsorbing plane is

$$R_{\parallel} \sim \left\{\frac{N}{g_{\mathrm{iso}}}\right\}^{3/4}D \sim N^{3/4}\delta^{1/4}P^{-1/2} \tag{21}$$

Note that relations 20 and 21 are valid only for $\delta \gg \delta^*$, or for $P \ll P_s^*$, so that it is not expected that they hold for $N \sim P^2$ when δ^* becomes on the order of unity. Under these conditions, ideal behavior of the probe is recovered. Note also that, for $P \sim P_s^*$, both 20 and 21 cross over to isotropic behavior (relations 2 and 3).

Finally, it is possible to estimate the local surface "concentration" inside the pancake. This is not a constant but depends on the scale at which one is probing. For the ideal blob of size χ, the number of monomers on the surface is $(P^2)^{1/2}$. Therefore, the contribution of each blob to the surface concentration is

$$\phi_s \sim \frac{P}{P^2} \sim P^{-1} \tag{22}$$

In the isotropic blob, the number of ideal blobs is, as discussed above, $g_{iso}/g_{id} \sim \delta^{-5/3}$. Thus, the surface concentration is

$$\Phi_s \sim \phi_s\left\{\frac{g_{iso}}{g_{id}}\right\}^{3/5}\left\{\frac{D}{\chi}\right\}^{-2}$$

$$\Phi_s \sim \delta P^{-1} \tag{23}$$

Plateau Regime

The regime where the long chains are saturating the surface is now considered. In a simple solvent, it was shown that this is achieved even when the bulk concentration is small and that such a regime exists already for dilute bulk solutions. In the following, attention is focused on the concentration profile that such adsorption implies. For simplification purposes, it is assumed that the bulk is a melt made of long chains in a "semidilute" solution in shorter polymers. Therefore, the long probe chains are swollen at short distances, below the screening length ξ (relation 10) and ideal for larger distances. The concentration profile is expected to extend from the surface to a distance on the order of ξ. The difference between the present case and a semidilute solution in a simple solvent is the existence at short distances of an ideal blob with size χ. Its mere existence implies that such a blob is not adsorbed. By analogy with dilute solutions, adsorption is expected to take place at distances larger than the isotropic blob with size D discussed above. For distances larger than the concentration blob radius ξ, the concentration is constant and equal to the bulk concentration C_b.

For distances $\xi \gg z \gg D$, the profile is self-similar. It may be obtained by arguing, as in simple solvent,[21] that because the local concentration is in the semidilute range, one may define a screening length $\xi(z)$, related to the local concentration $\phi(z)$, by

$$\xi(z) \sim \phi(z)^{-3/4}P^{1/4}$$

Because only one length is present in the problem, the latter has to be on the same order as the distance z. Thus, in the central range

$$\phi(z) \sim z^{-4/3}P^{1/3} \qquad D \ll z \ll \xi \tag{24}$$

For smaller distances, in the proximal region, the decay is much slower than above:

$$\phi(z) \sim \Phi_s\left\{\frac{z}{\chi}\right\}^{-1/3} \sim \delta P^{-1}\left\{\frac{z}{P}\right\}^{-1/3} \qquad \chi \ll z \ll D \tag{25}$$

Finally, the concentration is constant inside the ideal blob:

$$\phi(z) \sim \Phi_s \sim \delta P^{-1} \qquad z \ll \chi \tag{26}$$

The corresponding profile is shown in Figure 2. Different limits may be obtained by changing the various parameters. When the concentration is increased, the isotropic blob becomes on the order of the concentration blob for $C \sim \tilde{C}$ and the probe chains adopt locally an isotropic configuration. When relations 10 and 20 are compared, eq 27 is obtained. Note that at $\tilde{C}$ the bulk concentration is on

$$\tilde{C} \sim P^{-1}\delta^{4/3} \tag{27}$$

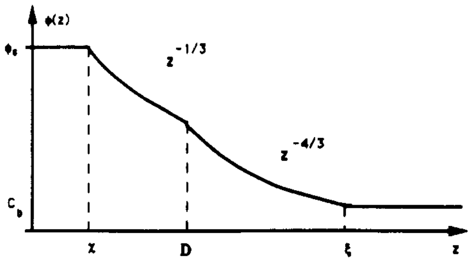

Figure 2. Concentration profile in the semidilute regime. Key: SD S, see Figure 1; χ is the ideal blob; D is the isotropic blob; ξ is the screening length.

the same order as $\phi(D)$, so that for higher concentrations the central zone does not exist anymore. Note also that there is still a slight decrease of the concentration within a distance D as long as the bulk concentration is smaller than the surface concentration Φ_s. When the latter is compared with the former, a concentration $\tilde{C}_1$ above which no decrease is present is found. Using relation 26, the following is found:

$$\tilde{C}_1 \sim \delta P^{-1} \tag{28}$$

Note also that, for values of δ on the order of unity, the difference between the latter two concentrations vanishes. Increasing the length P of the solvent polymers or decreasing δ leads to the same effect.

Localization of the Probe Chains

So far, adsorption of the concentration blobs with size ξ in a semidilute solution was considered. The configuration of the chains was left apart. It is reasonable to assume that the chains are still adsorbed above C^*, so that the number of their monomers directly in contact with the surface is proportional to N. As concentration (or P) increases, this number has to become proportional to $N^{1/2}$, that is, to its bulk value. A related question is to know whether these probes are actually located within the region where the concentration is higher or if they extend deeper into the bulk, to distances on the order of their radius of gyration. The latter is also the situation that is valid in a melt of identical polymers. This question was addressed by Joanny and Marques[22] in the case of a simple solvent, and their analysis is used for the mixtures considered here. It is then possible to consider the adsorption problem in the bulk dilute regime and to follow the conformation of the chain as bulk concentration is increased. If the plateau regime is considered, the surface is saturated with monomers, while the bulk is dilute. There is a concentration profile that extends to distances on the order of the radius of a chain and ensures the continuity between the surface and the bulk. Above the bulk overlap concentration $C_b{}^*$, the concentration profile extends only to distances on the order of the screening length ξ. For larger distances, the concentration is constant and equal to its bulk value. The de Gennes–Pincus theory is valid at short distances and implies a loop structure of the adsorbed layer that was already discussed. However, one might wish to know the structure of the chains for distances larger than ξ. Among others, in a semidilute solution in a simple solvent, $P = 1$, one might argue that the number L of large loops is

$$L \sim \left(\frac{N}{g}\right)^{1/2} \tag{29}$$

This is related to the fact that in a melt the chains are ideal and cross any surface $N^{1/2}$ times and that a semidilute solution may be considered as a melt if one takes a blob as a statistical unit. A difference between a solution and the melt resides then in the length of the sequences that are adsorbed: Whereas in a melt the chain has merely one (or a finite number of) contact each time it encounters the surface, it may remain on the wall and form trains in a solution. This is one possible way of crossing over from the adsorbed situation, with N monomers on the surface to the nonadsorbed state, with only $N^{1/2}$ units on the plane. In a semidilute solution then, it is possible to define such trains where the polymer remains within a distance ξ from the surface. It is then important for the state of the macromolecules to know whether the total number of monomers in these trains is on the order of N or smaller. This will be used below to determine the desorption of the chains. It is possible to estimate, in the limit $\delta \approx 1$, the crossover concentration above which loops develop and the chains start desorbing. This is done by estimating the size of the trains. Trains are portions of the chain made of g_t monomers, for which the number of monomers close to the surface, within a distance ξ, is proportional to g_t. Thus, at low concentrations, around C^*, the probe chains consists of one single large train with size its radius R_N. For larger concentrations, the trains are both shorter and smaller in size but their number increases. For large enough concentrations, the part of the chain on the surface eventually becomes on the order of $N^{1/2}$ and the chain adopts its melt configuration. Two crossover concentrations were introduced by Marques and Joanny. C_1 is the crossover concentration between the dilute regime, where a train may be identified to the chain, and a regime where a chain has several trains of smaller size. Above C_1, the total number of monomers in the trains is still proportional to N. The latter proportionality does not hold anymore above the second crossover concentration C_2. In the concentrated range $C \gg C_2$, the number of monomers in the trains becomes of the order of $N^{1/2}$, as it is in a melt where the polymers are no longer adsorbed. Discussion begins with the case of concentrated solutions and then to crossover as the concentration is decreased.

From relation 11 it was seen that every blob has $g_c \sim C^{-5/4}P^{3/4}$ monomers. For $\delta \approx 1$, the proximal regime does not exist but the local structure is still made of Gaussian blobs, made of g_{id} monomers, with size χ. Thus, the number of monomers per concentration blob directly on the surface is

$$g_s \sim \frac{g_c}{g_{id}} {g_{id}}^{1/2} \sim C^{-5/4}P^{-1/4} \tag{30}$$

If a surface ξ^2 is considered with surface concentration $\Phi_s \sim P^{-1}$ (relation 23), there are n_s chains in contact, with

$$\Phi_s \sim n_s \frac{g_s}{\xi^2} \tag{31a}$$

and

$$n_s \sim C^{-1/4}P^{-1/4} \tag{31b}$$

Because of the self-similarity of the profile, only one of these chains may escape from the surface layer of width ξ. Therefore, a chain has a probability ${n_s}^{-1}$ of escaping, and thus the average length t of a train is

$$t \sim n_s g_s \sim C^{-3/2}P^{-1/2} \tag{32}$$

Relation 29 gives the number of loops, which is also the number of trains. Therefore, the total number of monomers T in the trains is

$$T = tL \sim N^{1/2}C^{-7/8}P^{-7/8} \tag{33}$$

This is to be compared with the total number N/P of possible monomers of the probe chain on the surface. The latter estimate takes into account the fact that only P of the P^2 monomers of the ideal blob are on the surface. When these variables are equated, a crossover concentration

$$C_2 \sim N^{-4/7}P^{1/7} \tag{34}$$

is found. Therefore, for concentrations lower than C_2, the total number of monomers in the trains is independent of the concentration C of the bulk and is on the order of the number N of monomers in the probe chain. For higher concentrations, this number becomes dependent on C. Note that as discussed above, in this regime the length of a single train is independent of N but that the number of trains makes the compensation. Note also that the number of loops (or trains) at C_2 is, using (29), (32), and (34)

$$L(C_2) \sim N/t \tag{35}$$

So far, only the concentration profile in long chains close to the surface has been considered. In order to do this, the adsorbance Γ is considered. This is the total number per unit surface of monomers linked to the surface. For a dilute solution, this is identical to the surface excess Γ_s

$$\Gamma_s = \int_a^\infty \{\phi(z) - \phi(\infty)\}\,dz \tag{36}$$

where a is the step length and $\phi(\infty)$ is the bulk concentration C. This identity is related to the fact that in a dilute solution the concentration profile extends to distances on the order of the radius of the adsorbed chains. In a semidilute solution, however, the profile extends only to distances on the order of the screening length, whereas the adsorbed chains may still go to distances on the order of their radius, and the two quantities may be different. For such solutions, the Marques–Joanny[22,23] conjecture is assumed.

$$\Gamma \approx \Gamma_s + CR_N \tag{37}$$

This is readily evaluated. For $P \ll N^{1/2}$, $P \ll C^{-1}$, and $\delta \approx 1$

$$\Gamma \sim a^{-2}(1 + N^{1/2}P^{-1/8}C^{7/8}) \tag{38a}$$

and for $P \gg C^{-1}$

$$\Gamma \sim a^{-2}N^{1/2}C \tag{38b}$$

where the first term comes from the constant part of the profile and the second one from the large distance contribution for $z \gg \xi$. This implies two different regimes, corresponding to each of these contributions. This allows introduction of a crossover concentration C_2 separating two regimes: For low concentrations, the first term in eq 38a is dominant and the adsorbance is on the same order as the surface excess. On the contrary, for concentrations higher than C_2, the main contribution to Γ comes from the second term in (38a) and the adsorbance is larger than the surface excess. Using (38a)

$$C_2 \sim N^{-4/7}P^{1/7} \qquad P \ll C^{-1} \tag{39}$$

Equation 38a implies also that the number $N_0 \sim N\Phi_s/\Gamma$ of monomers directly in contact with the surface is, for concentrations smaller than C_2,

$$N_0 \sim N/P \qquad (40)$$

and, in the opposite limit,

$$N_0 \sim N^{1/2}P^{-7/8}C^{-7/8} \qquad C_2 \ll C \ll P^{-1} \qquad (41)$$

Note that, for $C \sim P^{-1}$, relation 41 crosses over to the classical melt limit, namely $N_0 \sim N^{1/2}$ and $C_2 \sim \tilde{C}$ for $N \sim P^2$. For concentrations smaller than C_2, most of the above analysis remains valid. The only exception concerns the number of loops, or trains L, which are assumed to crossover from the proportionality to $N^{1/2}$ (relation 29) to a proportionality to N as in relation 35. Namely, it is assumed that the number of loops is proportional to the length of the probe chain divided by the length of a train. One may also check at the end of the present section that if one assumes a general relation such as $L \sim N^aC^b$ and looks for a and b such that the number of loops is of order unity for C_1, to be determined below, and $L \sim N^{1/2}$ for C_2, one recovers relation 35, namely

$$L \sim N/t \qquad C_1 \ll C \ll C_2 \qquad (35a)$$

Therefore, for concentrations smaller than C_2, the number of trains decreases faster than above C_2, while their length increases. There is a concentration C_1 where there is only one train left, with a length of the order of the probe chain. Using relation 32 and equating this number to the maximum number N/P of monomers on the surface (see discussion below eq 33)

$$C_1 \sim N^{-2/3}P^{1/3} \qquad (42)$$

One may check that, at this concentration, the number L of trains indeed becomes on the order of unity, so that the chain is confined within a distance ξ from the surface and hence makes only one train, as for more dilute solution.

For concentrations below C_2, the probe chains are made of one train, and very few loops get out of the adsorbed layer with size ξ. One should then define another characteristic length Λ, corresponding to this gradual increase of loops between C_1 and C_2. Assuming a homogeneous variation, this may be written in the following form:

$$\Lambda \sim \xi f(C/C_1) \qquad (43)$$

Assuming that $f(x)$ has power law behavior and insisting that Λ becomes on the order of the radius of gyration of the probe chain, $R_N \sim N^{1/2}C^{-1/8}P^{-1/8}$ for concentrations on the order of C_2, one gets

$$\Lambda \sim NC^{3/4}P^{-1/4} \qquad C_1 \ll C \ll C_2 \qquad (44)$$

Note that, in the regime $C_1 \ll C \ll C_2$, relations 37 and 38 have to be changed because the adsorbed polymers extend to Λ and not to the radius R_N of the chains. Instead of (37), one has

$$\Gamma \approx \Gamma_s + C\Lambda \qquad (45)$$

Using (44), this becomes

$$\Gamma \approx \Gamma_s + NC^{7/4}P^{-1/4} \qquad (46)$$

The latter relation crosses over smoothly to relation 38 for $C \sim C_2$.

The possible existence of such length might be checked by dilution and will be discussed elsewhere. Such length might be responsible for a recent observation by Klein,[24] who found in a force experiment that in some cases the distance below which a force appears is much larger than the radius of gyration of chain, and rather proportional to an extended length of the polymer than to its isotropic radius.

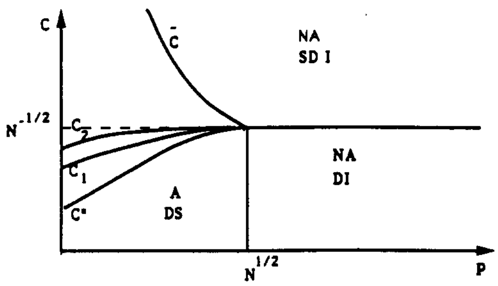

Figure 3. Surface regimes. Key: A refers to adsorbed and NA to nonadsorbed; C^* is the bulk overlap concentration. Above C_1, loops and trains start forming but the total number of monomers in the surface layer is proportional to N. Above C_2, most of the contribution to the adsorbence comes from the outer region $z > \xi$. Between C_1 and C_2, it is possible to introduce a new length Λ corresponding to the extent of the probe chain.

Conclusion

A mixture of long polymers dissolved in shorter chains was considered. The interest of such a system is that it allows the study of adsorption and desorption of large macromolecules simply by varying the length of the short ones. In the single (long) chain limit, there is an ideal, nonadsorbed blob, with size $\chi \sim P$ present locally. The width D of the adsorbed chain is larger than in a simple solvent. $D \sim \delta^{-1}P$. The long chain may then be considered as a two-dimensional array of blobs with size D. Increasing the size P of the solvent polymers thus leads to an increase of both χ and D and to a gradual return of the probe chain to a three-dimensional configuration. Crossover to the isotropic, nonadsorbed state occurs for $\delta N^{3/5}P^{-6/5} \sim 1$. This implies that when P increases, the crossover value for the interaction δ also increases. One gets the upper limit $\delta \sim 1$ for $P \sim N^{1/2}$.

In the case of the plateau regime, where the surface is saturated with long chains, a concentration profile is found that is constant for distances smaller than χ corresponding to the ideal blob. For larger distances, the same behaviors as in a simple solvent are recovered, except for the characteristic distances. This is shown in Figure 2. Desorption is obtained either by increasing the bulk concentration in probe chains or by increasing the molecular weight P of the solvent molecules. Two different concentrations are found, generalizing an argument by Marques and Joanny in simple solvents. For concentrations smaller than the first one, C_1, an adsorbed chain, is basically confined in a layer of width ξ at the surface. It only makes a finite, small number of loops larger than ξ. For concentrations larger than C_1, larger loops start forming and the number of monomers in the trains starts decreasing and depending on concentration. Their number, however, increases in such a way that the total number of monomers in the trains that are confined within a distance ξ from the surface remains proportional to N. Between C_1 and C_2, however, contribution to the adsorbance that comes from the region between the surface and ξ is larger than the one that comes from the outer region, between ξ and the extent Λ of the polymer in the solution. This is reversed above C_2. It is possible to introduce a new characteristic length between C_1 and C_2 that gives the extension of the adsorbed polymers in the solution Using scaling, one finds $\Lambda \sim NC^{3/4}P^{-1/4}$. It crosses over to the screening length ξ for $C \sim C_1$ and to the radius of the chains in the bulk of the solution $R_N \sim N^{1/2}C^{-1/8}P^{-1/8}$ for $C \sim C_2$. Finally, above C_2, the polymer desorbs in the sense that the number of monomers in the trains becomes proportional to $N^{1/2}$ rather to N, as it was below C_2. For still higher concentrations, $C \sim \check{C}$, the blobs are no longer adsorbed. These results are summarized in Figure 3, which shows the various surface regimes.

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