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Short Communication

**Grafted polymers in bad solvents: octopus surface micelles**

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**Abstract.** — Polymer chains are irreversibly grafted to a surface in a good solvent and the solvent quality is then reduced dramatically. The chains then collapse. If the grafting density is very high then the collapsed layer should be fairly uniform. However, at lower grafting densities the chains are predicted to form surface "micelles". These micelles minimize the exposed surface area of the collapsed globules at the expense of chain stretching energy. We also discuss grafting to a line and to a three dimensional network.

The grafting of polymer chains to surfaces has been much studied in recent years, both theoretically, experimentally, and by simulation [1, 2]. Grafting provides a method of studying polymer deformation, and has applications in colloidal stabilization and the prediction of block copolymer microphases. Experimentally the conformations of grafted chains can be studied using neutron scattering and by the surface force apparatus.

Densely grafted polymers in *good* solvents swell and stretch away from the surface. These systems have been much studied theoretically as have grafted polymers in the melt regime. Here we are interested in grafted chains in *bad* solvents [3-10]. In a bad solvent an individual chain collapses to form a globule [11]. Under some circumstances this collapse will produce a uniform layer of polymer, completely covering the surface. Here we examine a more unusual situation - that of surface micelle formation. We first discuss ungrafted chains in bad solvents. An isolated chain, with degree of polymerization $N$, in a bad solvent is acted upon by two effects. Firstly, it wishes to *minimize* its contact with the solvent by *minimizing* its surface area. This is best done by forming a collapsed spherical globule of radius $R \sim aN^{1/3}$, with $a$ a monomer size (here we neglect all numerical coefficients). An entropic free energy penalty is paid for this collapse [11], of order $kTR_g^2/R^2$, where $R_g = aN^{1/2}$ is the unperturbed radius of a chain in a melt or theta solvent. In general the surface term totally dominates the entropic penalty, and a spherical globule results. $n$ chains can further lower their energy by forming one large sphere of radius $R \sim a(nN)^{1/3}$ Bulk phase separation of the solvent and polymer is the result. For irreversibly grafted chains this bulk phase separation is impossible. Depending on

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the grafting density $\rho$ (the number of chains per unit area), we believe three different scenarios are possible:

i) at very high grafting density a fairly uniform collapsed layer will form;

ii) at very low grafting density each chain will form its own individual "tadpole" globule;

iii) in the intermediate regime surface "micelles" will form.

Case i) is the situation assumed in [5, 4] and was studied in detail in [3,7-9]. Case ii) is in many ways trivial. Our interest here is in iii), which seems not to have been studied before. There has previously been some work on surface micelles in diblock copolymer systems [12, 13]. In those works the chains were not irreversibly grafted and were free to move from the bulk to the surface and to move anywhere on the surface. These surface micelles are thus generalizations of bulk micelles to two dimensions. The surface micelles discussed here are very different. The chains are homopolymers which are grafted irreversibly and the micelles occur because of a balance between chain elasticity and surface tension. We concentrate mainly on the case where the polymer does not wet the surface, so that $\gamma_{\text{polymer-solvent}} < \gamma_{\text{polymer-surface}} + \gamma_{\text{surface-solvent}}$, where $\gamma$ is a surface tension.

![Fig. 1. — A collapsed grafted polymer in a bad solvent. In a) two isolated chains form tethered tadpole globules. In b) these chains have lowered their surface energy by forming a single globule. This costs each some stretching and surface energy to form the tethers. In c) many chains have fused to form an "octopus" surface micelle. We have drawn the tethers approaching the nucleus individually. If there are a large number of tethers they may wish to join each other at points far away from the nucleus and thus lower their surface energy [3, 10]. The effective tethers would then get thicker and less numerous near the nucleus, much like a suburban road network. Such an arrangement would not affect the scaling laws described here.](image)

**Two-chain micelles.** — We first discuss the case of two grafted chains separated by a distance $d$. Such chains have two choices. They can either form two separate tadpole globules (Fig.1), or they can fuse together to form a single globule with two tethers connecting it to the surface. Fusion is best accomplished by forming a spherical globule midway between the grafting sites with two tethers connecting the globule to the surface. As shown in [14] the most favourable tether, when the end-to-end distance is fixed, is one monomer thick. The free energy of each
single globule consists of a surface term \(\sim (kT/a^2)a^2N^{2/3}\) plus a confinement term, which in this case is negligible. The polymer-solvent surface tension is roughly \(kT\) per monomer area, \(\sim kT/a^2\). For the fused globule the surface term is \((kT/a^2)a^2(2N)^{2/3}\). Each tether must stretch to the surface of the fused globule. This involves \(N_t = d/a\) monomers stretching through a distance \(d\) and so the stretching penalty per tether is \(\sim kTd^2/(N_t a^2) = kTd/a\). Here we have neglected non-linear corrections to the Gaussian stretching energy. Each tether also has a surface of \(da\) and hence a surface energy of \((kT/a^2)da = kTd/a\). The free energy difference between the fused globule and the two separate globules is then

\[
F/kT = (2N)^{2/3} + 4(d/a) - 2N^{2/3}
\]

This is negative for grafting distances \(d < d_c \sim aN^{2/3}\). The critical grafting distance \(d_c\) is quite large. It is a factor of \(N^{1/3}\) larger than the overlap threshold between two isolated globules \(\sim aN^{1/3}\), and is slightly larger than the Flory radius of a swollen coil in a good solvent \(R_F \sim aN^{3/5}\). Thus, the grafting density can be very low (i.e. in the "mushroom" regime in a good solvent) and yet paired globules will form in a bad solvent. The physics of the fusion is very simple. By joining together the two globules lower their total surface energy. However, to fuse they must stretch and hence pay a deformation and surface penalty for the tethers. If this tether penalty is small fusion will result. Note that this requires polymers which are irreversibly anchored. Polymers which are not anchored pay no tether penalty and will undergo bulk phase separation.

Octopus micelles. — We now look at the possibility of \(n > 2\) chains fusing and forming a single "octopus micelle" (Fig.1). We refer to this structure as a "micelle" because its shape is reminiscent of micelles seen in surfactant and diblock copolymer systems. It must be born in mind however that in our system neither the core nor the corona of the micelle are in a good solvent. Such micelles (or something very like them) have been seen in computer simulations [8, 7] and possibly also in experiments [15]. Suppose all the chains in a circle of radius \(R_c\) collapse to form a globule of radius \(R_n\), with \(R_n/R_c \ll 1\). The surface and stretch energy for the tethers is then \(\sim (kT/a)\rho \int_0^{R_c} dr r^2 \approx (kT/a)\rho R_n^3\). The surface energy of the globule is \((nN)^{2/3}kT\), with \(n \sim R^2\rho\). Thus the free energy per unit area of the grafting surface is

\[
F/kT \sim (\rho/a)R_c + (R_n^2\rho N^{2/3}R_c^{-2}
\]

which has a minimum at \(R_c = aN^{2/5}(\rho a^2)^{-1/5}\) and hence \(n = N^{4/5}(\rho a^2)^{3/5}\) chains per micelle. The ratio of the globule size to the corona size is \(R_n/R_c = N^{1/5}(\rho a^2)^{2/5}\). Now let the grafting distance be \(d \sim aN^\alpha\). We can examine a number of cases here:

a) for barely overlapping mushrooms in a good solvent \(\alpha = 3/5\);
b) for barely overlapping mushrooms in a \(\theta\) solvent \(\alpha = 1/2\);
c) for barely overlapping tadpoles in a bad solvent \(\alpha = 1/3\);
d) for strongly stretched chains in a melt brush we require \(\alpha = 1/4\).

The micelle is then described by \(R_c = aN^{(2+2\alpha)/5}, n = N^{(4-6\alpha)/5}, R_n/R_c = N^{(1-4\alpha)/5}\). Note that for cases a) and b) \(n\) is \(\sim N^{2/25}, N^{1/5}\). The exponents here are very small, and since \(N\) is limited to about \(10^6\), \(n\) is of order 2 and 10 respectively. However, for cases c) and d) we find \(n \sim N^{2/5}\) and \(N^{1/2}\) respectively and so the number of chains per micelle can be large \(\sim 250\) and 1000.

For high grafting densities, or short grafting distances which are less than tadpole overlap, \(d \sim aN^{1/3}\), it is important to compare the free energy of surface micelles with that of a uniform layer of polymer. In the latter case the free energy per unit area is of order \(F_{layer} = (kT/a^2)\).
The free energy per unit area for micelles (2) is \( F_{\text{micelle}} = (kT/a^2)N^{(2-8\alpha)/5} \). We thus require \( \alpha > 1/4 \) for micelles to have lower free energy than grafted layers. This is reasonable since at \( \alpha = 1/4 \) we have \( R_n/R_c \sim N^0 \) and the micelle nucleus becomes the same size as the corona. Thus micelles will occur provided the grafting density is below that of a strongly stretched melt brush.

For the sake of simplicity we have studied only spherical micelles. For bulk micelles in diblock copolymers, other geometries, in particular cylindrical micelles, are known to occur. The driving force for these micelles is the fact that the nuclear chains can stretch less in a cylinder than they would be forced to in a sphere. This driving force is absent in our system. However, there may still be some distortions from the spherical shape to an oblate ellipsoid. This kind of distortion increases the surface energy of the nucleus but allows the coronal chains to stretch less. It should be unimportant in the limit we are interested in, where \( R_n/R_c \ll 1 \).

**Micelles on rods and inside networks.** — In the above we have considered the two dimensional case (i.e. polymers grafted to a flat surface), but it is easy to generalize to the other relevant dimensions. Thus we can study polymers grafted to a line, as for instance occurs when isolated rod polymers have flexible polymers grafted along their length. This system is used in the processing of rigid-rod polymers [16]. If the rods are not isolated then bulk aggregation of the rods, via the grafted polymers, can occur. A three dimensional example would be the grafting of flexible polymers inside a rigid-rod network. The results for arbitrary dimensionality, \( d \), are

\[
R_c = a(\rho a^d)^{3/d} N^{3/2}, \quad n = (\rho a^d)^{3/d} N^{3/2}, \quad R_n/R_c = (\rho a^d)^{3/d} N^{5/3}
\]

where in \( d = 1 \), \( \rho \) is the grafting density per unit length, and in \( d = 3 \), \( \rho \) is the grafting density per unit volume. If the grafting distance \( s \) scales like \( s = aN^\alpha \) then the grafting density is \( \rho = a^{-d}N^{-\alpha d} \) and we have

\[
R_c = aN^{2+\alpha d}, \quad n = N^{d(2-3\alpha)/3+\alpha d}, \quad R_n/R_c = N^{d-1+2\alpha d/3+d}
\]

In general we require \( R_n/R_c \ll 1 \) and this occurs provided \( \alpha > \alpha_c = (d-1)/2d \) (we limit our discussion here to \( 1 < d < 3 \)). Thus the critical exponent, \( \alpha_c \) in \( d = 1 \) is 0, and in \( d = 3 \), \( \alpha_c = 1/3 \), (i.e. chain overlap), whilst in \( d = 2 \) it is \( \alpha_c = 1/4 \), as discussed above. To have micelles with a significant number of chains we require \( n \sim N^\mu \) with \( \mu > 0 \). This occurs provided \( \alpha < 2/3 \) in all dimensions. Thus in \( d = 1 \) the condition is globule overlap (\( \alpha = 1/3 \)) whilst in \( d = 2 \), \( \alpha < 2/3 \). In \( d = 3 \) it is sufficient to have \( \alpha < 1 \) i.e. the chains must be separated by no more than their fully stretched length. Thus the higher the dimensionality the easier it is to form micelles.

**Micelles of blobs.** — It is of interest to discuss one previous study collapse and segregation [3]. These authors calculated the structure factor for a grafted layer in a poor solvent and concluded that the polymer collapses to a *uniform layer*. This seems to contradict the present study. The calculation in [3] is in fact in a very different solvent regime than that considered here. In [3] the quality of the solvent is reflected in a virial expansion in the polymer concentration. This is valid at low concentrations, but becomes untenable in the regime of very bad solvents discussed here where the polymer becomes very concentrated in a small region and solvent-polymer interaction is entirely through a surface term. In the language of diblock copolymers the Ross-Pincus study concentrates on the "weak segregation limit", whereas we study the "strong segregation limit". There is thus no contradiction between the two studies. Note
however, that very recently Yeung et al. [9] have re-examined the collapsed brush problem numerically and found a densely grafted brush can be unstable to "dimpling". This dimpling, although akin to our surface micelles, occurs near the $\theta$ temperature and is driven by bulk, rather than surface effects. As the solvent quality is reduced below the $\theta$ temperature the monomers experience attractive interactions. The polymer thus has two ways of lowering its bulk interaction free energy. It can either segregate laterally or normal to the wall. In [9] it is argued that both effects can occur, resulting in dimpling of the brush surface.

Although we have considered here the limit where all the solvent is expelled from the polymer it is possible to extend the results to the case where the solvent quality is somewhat better. This can be achieved using the blob concept [17]. If $\theta$ is the $\theta$ temperature of the polymer and $\Delta T$ is the degree of cooling below the $\theta$ temperature then the polymer collapses to a series of blobs of radius $\xi = a\theta/\Delta T$ each containing $(\theta/\Delta T)^2$ monomers [18, 19]. Inside each blob the excluded volume interactions are weak and the polymer conformation is ideal. On length scales larger than a blob size the blobs interact as attractive hard spheres with blob-solvent surface tension $kT/\xi^2$. The blobs may be treated as renormalized monomers and all our results carry over with the substitutions $N \rightarrow N(\theta/\Delta T)^{-2}$ and $a \rightarrow a(\theta/\Delta T)$. Obviously if $\Delta T \ll \theta$ there are very few blobs and we do not expect surface micelles to form. However, when $\Delta T \gg \theta N^{-1/2}$ the number of blobs becomes substantial and surface micelles can result.

Conclusions. — The octopus micelles described here are the equilibrium morphology for a collapsed brush at moderate grafting density. However, the actual morphology present depends strongly on the history of the sample. Consider polymers which are grafted so that their mushrooms overlap in a good solvent. We now slowly reduce the solvent quality from good to very bad. Our prediction for the bad solvent collapse would be the formation of octopus micelles with at least two chains per micelle. However, as the solvent quality is reduced slightly below the $\theta$ temperature each chain individually collapses to form its own globule. These globules do not overlap and at this point there is no reason to form a micelle [20]. The globules continue to contract until each globule contains no solvent. By this stage the globules would like to fuse and form micelles, but they no longer are in contact and micelle formation is thus difficult. The system is frustrated in much the same way that two separate drops of a non-wetting liquid on a surface are frustrated, and equilibrium is not achieved. In order to produce micelles it is necessary to suddenly reduce the solvent quality. If the molecular weight is high enough the individual chains have no time to disengage from one another and micelles are the result.

One method of directly observing octopus micelles would be to use the surface forces apparatus. We expect that when one attempts to compress a layer of grafted polymer the force will increase rapidly when the distance between the plates is of the order of a micelle diameter. This diameter is much larger than that of a single collapsed chain or the thickness of a grafted layer, which would normally announce the onset of large forces.

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References

[20] Note however that near the $\theta$ point the surface tension is very low and fluctuations are important.