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ARTICLE

End-Tethered Polymer Chains under a Membrane with Stickers: Blister and Surface Micelle Formation

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ABSTRACT: A system of end-grafted polymer chains in a good solvent is compressed under a membrane with freely moving stickers which favor the membrane sticking to the surface. For large enough degree of polymerization the membrane is predicted to form blisters, each confining multiple chains extending to form a surface micelle. Multiple chains compressed under a single bump or a blister reduce the free energies due to volume exclusion of the chains and the curvature of the membrane, at the expense of chain stretching energy.

Introduction

Polymers and surfactant membranes are two classic examples of soft matter systems. Individually, these systems are reasonably well understood, and there have been significant advances in systems where both are present and where there may be strong interactions between them. Their interaction is interesting not just from a practical point of view, but because both are easily deformed and can thus strongly deform each other. Despite numerous studies there remain many open and interesting problems, and we partially address one of these in this paper.

Our system consists of a number of polymers with N monomers of size a end-grafted to a hard flat surface with a density of σ chains per unit area. We assume that in the absence of the membrane we are always in the mushroom regime where the chains do not overlap. The persistence length of the chain is l_p, so that for a fully flexible chain $l_p = a$, while for a chain like DNA l_p could be many a. We assume that the chains are in a good solvent. We now bring a membrane close to the surface. The membrane is covered with mobile stickers which decrease their energy by sticking to the surface. Mobile stickers in membranes have been studied by many others,[1,2] and those that are in this system are of similar nature. The purpose of the stickers is to provide the attractive membrane−surface interaction. We ask how the system will behave in equilibrium. In particular, how do the polymers and the membrane deform. Here we argue that despite the fact that the polymers are in a good solvent, they will often stretch and form small clusters "surface micelles" which minimize the free energy of the system. This work is motivated by two previous papers. In the first,[3] it was shown that grafted polymers in *poor* solvents will form octopus micelles at a surface. In the second,[4] the authors argued that a polymer in a *good* solvent trapped in a narrow soft tube should partially collapse and form a bulge in the tube. Both these ideas have been confirmed by computer simulations and/or experiments.[5−10] It is natural to try and combine these two threads. The work[4] suggests that a polymer in a good solvent will partially collapse inside a soft tube, so that it behaves at least in part, as if it were in a poor solvent. Combining these ideas should lead to the formation of surface micelles when polymers are confined by a membrane in a good solvent.

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The study is divided into three parts. First we examine how a single chain interacts with a sticky membrane. We then find the regime where two chains will merge. Finally, we look at the many-chain problem.

Single Chain under a Membrane with Stickers

We first consider a single chain under an membrane of effectively large, but fixed, area. There are three components in this system: chain, membrane, and stickers. It follows that the total free energy of the system has three components.

$$F_{\text{total}} = F_{\text{chain}} + F_{\text{membrane}} + F_{\text{stickers}} \tag{1}$$

We assume the membrane does not stretch and thus only its curvature energy is relevant. Therefore

$$F_{\text{membrane}} = \frac{K}{2}\int C^2 \, \mathrm{d}A \tag{2}$$

where K is the rigidity constant and C is the mean curvature. The membrane will stick to the surface via its mobile stickers away from the polymer, and over the polymer it will form a blister (Figure 1). The shape of the blister in reality may be complex. For our purposes, the only important features of the blister are its height and radius which the curvature energy of the membrane and the compression energy of the chain that is confined in it depend upon. We model the blister as a simple Gaussian with height H and width λ so that the height of the membrane above the surface $g(r)$ as a function of the radius r in the plane of the surface is $g(r) = H \exp(-r^2/\lambda^2)$. The scaling relation of the energies with respect to the height and width of the blister will be the same should any other shape be used as a model. Defining $\eta = H^2/\lambda^2$, we can show that

$$F_{\text{membrane}} = \begin{cases} K\eta & \text{for } \eta < 1 \\ K\eta^{1/2} & \text{for } \eta > 1 \end{cases} \tag{3}$$

where here and throughout the paper unimportant numerical prefactors are dropped unless otherwise stated.

The stickers can only stick to the surface if the membrane is within a small distance s (of order a) above the surface. The part of the membrane that is further than s from the surface we call the

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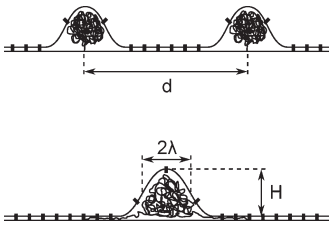

Figure 1. Two end-grafted polymer chains confined under a membrane in a good solvent. The top picture shows the two chains each forming a separate blister. In the lower picture the chains have merged under a single blister. It can be favorable for the chains to merge even in a good solvent because this reduces the bending energy of the membrane.

"blister". This blister has area

$$A_b = \begin{cases} \lambda H & \text{for } \eta > 1 \\ \lambda^2 \ln\left(\frac{H}{s}\right) & \text{for } \eta < 1 \end{cases} \quad (4)$$

Each sticker in contact with the surface has a binding energy $-\varepsilon kT$ ($\varepsilon > 0$). Those that are part of the membrane in the blister thus pay an eneregtic penalty of $A_b\rho_b\varepsilon kT$, where ρ_b is the number of stickers per unit area of the membrane within the blister. The sticker contribution to the free energy also has an entropic part which arises from redistributing the stickers away from the blister to a region where they can stick to the surface.

If ρ is the initial area density of stickers on the membrane in the absence of the blister, then the entropic penalty of having a blister is

$$F = kTA_b\left(\rho - \rho_b + \rho_b \ln\left(\frac{\rho_b}{\rho}\right)\right) \quad (5)$$

Combining the two sticker energies and minimizing over ρ_b yields the expected Boltzmann distribution $\rho_b = \rho e^{-\varepsilon}$ and a free energy for the stickers of

$$F_{\text{sticker}} = kTA_b\rho(1 - e^{-\varepsilon}) = kTA_b a^{-2}\theta \quad (6)$$

where we have introduced the reduced sticker density $\theta \equiv \rho a^2(1 - e^{-\varepsilon})$. Assuming ε is of order 1 or larger, it is clear that $\rho(1 - e^{-\varepsilon}) = \rho$. The size of each sticker must be at least a, so that $\theta < 1$ and in many cases $\theta \ll 1$. We now turn to the free energy of the polymer chain. As in ref 4, we use a Flory approximation for this, which is a reasonable approach for the first attempt at the problem. In this approximation the size R_F of an isolated chain is given by a balance between the stretching free energy and the excluded volume term.

$$F_{\text{Flory}} = kT\frac{{R_F}^2}{Nal_p} + kT\left(\frac{N}{g}\right)^2\frac{v}{{R_F}^3} \quad (7)$$

Here $v = {l_p}^2 a$ is the excluded volume associated with a section of chain equal to one persistence length, and $g = l_p/a$ is the number of monomers in such a length of chain. This yields a chain size $R_F = N^{3/5}(a^4 l_p)^{1/5}$. This result is valid provided R_F is larger than the unswollen chain (ideal) value of $R_0 = (Nal_p)^{1/2}$. When a single isolated chain is compressed under a membrane in the interesting regime where it is strongly confined, the free energy of the chain can be written as the sum of a *compression* term and an excluded volume term. In this case the blister will be more-or-less hemispherical so that $H = \lambda = R$ for the Gaussain blister. The chain free energy is then

$$F_{\text{chain}} = kT\frac{Nal_p}{R^2} + kT\left(\frac{N}{g}\right)^2\frac{v}{R^3} \quad (8)$$

The first term is the compression of the chain and the second term arises from excluded volume. Here R^3 is the volume under a blister when $H = \lambda = R$.

The total free energy of a single chain under a sticky membrane can thus be written as

$$\frac{F_1}{kT} = Nal_p R^{-2} + N^2 a^3 R^{-3} + R^2 a^{-2}\theta + \kappa \quad (9)$$

where $\kappa \equiv K/kT$ and where the four terms are chain compression, chain excluded volume, stickers, and membrane bending. The first and second terms favor large H, the third small H, and the final term is a constant. In the limit of large N the blister size H is determined by a balance between excluded volume and sticker effects yielding

$$R_1 = aN^{2/5}\theta^{-1/5} \quad (10)$$

We can check self-consistently that neglecting the compression term implies $g < N^{3/5}\theta^{1/5}$ so that for large enough N our result should be valid. It is of interest to compare the ratio of our chain size to the chain size before the membrane is present. This ratio is $R_1/R_F = (Ng\theta)^{-1/5}$. The chain thus shrinks under the membrane although the shrinkage will not be great, even for large N.

Two-Chain Micelles

Here we condsider two chains compressed under a membrane. There are two possible cases: the two chains could form two separate blisters, or they could stretch to meet each other and form a single blister. This is the scenario introduced in ref 3 for octopus micelles in poor solvents. Forming separate blisters would have double the energy of a single trapped chain. In this section we include some numerical factors to indicate that there are two chains involved in the system, and we shall see that depending on whether the two chains are separate or combined, these factors affect different terms in the equation, thereby making them important. Later, in the many chain case, these numerical factors will be substituted with the grafting density.

$$F_{\text{separate}} = 2kT(2N^{4/5}\theta^{3/5} + \kappa) \quad (11)$$

In order to form a single blister, the chains must stretch, which costs a free energy. There are two possible ways of doing this. In the first, the two chains form tunnels under the membrane to get to the blister. These tunnels will be approximately in the form of half a circular cylinder, of length $d/2$ and unknown radius r. Each tunnel will have n monomers in it, with the remaining $2(N - n)$ monomers in the blister iteself. The free energy of the system in this configuration is given by

$$\frac{F}{kT} = 2(2N - 2n)^{4/5}\theta^{3/5} + \kappa + 2\left(gna^2 r^{-2} + \frac{1}{4}d^2(nga^2)^{-1} + 2n^2 a^3(dr^2)^{-1} + \frac{1}{2}\kappa dr^{-1} + \theta rda^{-2}\right) \quad (12)$$

The first two terms here are the free energy of the central blister. There follows the free energy of the two tunnels consisting of chain compression, chain stretching, excluded volume, membrane bending, and the sticker term. The parameters r and n may be chosen by the chains in order to minimize the free energy. One can minimize over r analytically and then minimize over n numerically to find F_{tunnels}. The second method of getting to the blister is to form two fully stretched tethers, each of length $d/2$ and with $n = d/2a$ monomers in each, as was done in ref 3. In this case

the free energy is

$$\frac{F_{\text{tethers}}}{kT} = 2(2N - 2da^{-1})^{4/5}\theta^{3/5} + \kappa + d(ga)^{-1} \quad (13)$$

As before, the first two terms are the blister free energy, and the last, simple term is merely the stretching free energy of the tethers. Note that in this model it is assumed that the chain lies flat on the surface and that the membrane is effectively undeformed by the tethers. One can numerically compare F_{tunnels} and F_{tethers} and show that for most reasonable values of the parameters (κ, θ, N, d/a) the tether model has less free energy. We thus adopt this model here.

Comparing the energies for the two separate blisters and the single blister micelle, we find a micelle is preferred for $d < d_c$, where $d_c = ag(^1/_2N^{4/5}\theta^{3/5} + \kappa)$. Here was have neglected the monomers used up in getting to the blister in finding the energy of the blister; i.e., we have neglected d/a in comparison to N. A better approximation for d_c is $d_c = ag(^1/_2N^{4/5}\theta^{3/5} + \kappa + 1.4gN^{3/5}\theta^{6/5})$.

Note that the ratio of the critical distance to the micelle size is of order $d_c/R_1 = gN^{2/5}\theta^{4/5}$, which will be significantly greater than 1 for large enough N. However, there is also clearly a regime where d_c is of order R_1, and in that case tethers would not be necessary to form a two-chain blister—the blister would in fact cover the grafting sites of both chains.

Many-Chain Case

We now consider a system with many chains randomly end-grafted to the surface. There are σ chains per unit area. We divide the surface into circles of radius R_c, the capture radius. Chains within one circle form a single blister with the blister radius being R_b. The number of such chains is $n = \sigma R_c$, and the number of monomers involved is thus $N\sigma R_c^2$. We assume that $R_b \ll R_c$. We also neglect the number of monomers "used up" in stretching to the blister, so that $R_b \ll Na$. Each chain must stretch a distance of order R_c to get to the blister, giving a stretching energy of $nkTR_c/ga = kT\sigma(R_c^3/ga)$. The free energy per unit area is then

$$\frac{F_M}{kT} = R_c^{-2/5}(\sigma N)^{4/5}\theta^{3/5} + \sigma\frac{R_c}{ga} + \kappa R_c^{-2} \quad (14)$$

Balancing the first two terms gives a capture radius of

$$R_c = \left(\frac{N^4\theta^3 g^5 a^5}{\sigma}\right)^{1/7} \quad (15)$$

and an inner blister radius of

$$R_b = (a^{11}g^4N^6\sigma^2\theta)^{1/7} \quad (16)$$

It is convenient to introduce a dimensionless grafting density $s \equiv \sigma R_F^2 = \sigma a^2 g^{2/5} N^{6/5}$, which takes as its length scale the Flory radius. Thus, if $s < 1$, we are in the mushroom regime (little chain overlap), whereas if $s > 1$, we have the brush regime where the chains are crowded and distort each other even with no membrane present. To check that our approximations are self-consistent, we write the ratio of the blister radius and the capture radius as

$$\frac{R_b}{R_c} = s^{3/7}g^{-11/35}N^{-8/35}\theta^{-2/7} \quad (17)$$

the ratio of the capture radius to the chain contour length as

$$\frac{R_c}{Na} = g^{27/35}\theta^{3/7}N^{-9/35}s^{-1/7} \quad (18)$$

the number of chains involved in each blister as

$$n = g^{8/7}N^{2/7}s^{5/7}\theta^{6/7} \quad (19)$$

and the ratio of the blister size to a segment of chain one persistence length long as

$$\frac{R_b}{ga} = g^{-19/35}N^{18/35}s^{2/7}\theta^{1/7} \quad (20)$$

For self-consistency, we require the first two of these quantities be small while the third and fourth should be large. For large enough N this is the case. For example, with $N = 10^4$, $s = 1$, $g = 10$, and $\theta = 10^{-2}$, we find $R_b/R_c = 0.2$, $R_c/Na = 0.08$, $n = 4$, and $R_b/ga = 17$. It should be emphasized that these numbers should not be taken too seriously given the many approximations made, but they show that our model is not unreasonable. In particular, there should be a regime where there are small, well-separated blisters, each with several chains. The only difficulty is that n will generally be fairly small unless N is very large. For example, even with $N = 10^6$ in the above calculation, we find $n = 14$. Thus, if we limit ourselves to the mushroom regime, each blister will contain only a moderate number of chains.

Membrane Sticking Condition

If the grafting density is too great, then it would be energetically unfavorable for the membrane to come in contact with the surface for the stickers to stick. In such a situation the blisters will not form. The free energy per area of the state where the membrane does not stick to the surface is

$$\frac{F_{NS}}{kT} = \rho\varepsilon \quad (21)$$

Only when this free energy is greater than that of the state where the membrane does stick to the surface, and hence forming the blisters, is the membrane going to stick to the surface. Therefore, the maximum grafting density in which the blisters will form, ignoring the membrane curvature contribution, can be determined by considering the condition when $F_{NS} = F_M$

$$\sigma_{\max} = (\rho\varepsilon)^{7/6}(ga)^{1/3}N^{-2/3}\theta^{-1/2} \quad (22)$$

This maximum grafting density, $\sigma_{\max}$, must be greater than the critical grafting density, $\sigma_c = 1/d_c^2$, for the surface micelle blisters forming regime to be available.

$$\frac{\sigma_{\max}}{\sigma_c} = [a^2g^2(N^{4/5}\theta^{3/5} + \kappa)^2][(\rho\varepsilon)^{7/6}(ga)^{1/3}N^{-2/3}\theta^{-1/2}]$$
$$= g^{7/3}a^{56/15}(\rho\varepsilon)^{28/15}N^{14/15} \quad (23)$$

This ratio must be greater than unity. We introduce $p = \rho Na^2 g$, which is the number of stickers which cover an area of the size of one chain in an ideal solvent.

$$\frac{\sigma_{\max}}{\sigma_c} = (g\varepsilon^4)^{7/15}\left(\frac{p^2}{N}\right)^{14/15} \quad (24)$$

Roughly, $p > \sqrt{N}$ is the requirement for $\sigma_{\max}/\sigma_c > 1$. This requirement is not hard to meet, unless N becomes very large.

Conclusion

In polymer systems in a poor solvent clustering of the chains is the norm. For grafted chains in a poor solvent this can lead to octopus micelles. In a good solvent, however, no such clustering will usually take place. However, we have been able to show that for a system of grafted chains in a good solvent when compressed

by a membrane a certain amount of clustering can take place, driven by the tendency of the membrane to stick to the surface and the bending penalty of the membrane. Essentially membrane bending can be reduced by having a smaller number of blisters under which several chains are grouped. It should be emphasized that we have assumed the system can reach thermodynamic equilibrium, and it is thus appropriate to minimize the free energy. In practice, the system might sometimes be trapped and clustering might then be more difficult.

For the case of octopus surface micelles in poor solvents there have been numerous experiments and simulations showing their existence.[5−8] There has been at least one experiment on the kind of system we are interested in,[11] but it is not clear to what extent the conditions agree with ours and to what extent nonequilibrium effects are important in the experiment.

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References and Notes

(1) de Gennes, P.-G.; Puech, P. H.; Brochard-Wyart, F. *Langmuir* **2003**, *19*, 7112–7119.
(2) Rozycki, B.; Lipowsky, R.; Weikl, T. R. *Phys. Rev. Lett.* **2006**, *96*, 048101.
(3) Williams, D. R. M. *J. Phys. II* **1993**, *3*, 1313–1318.
(4) Brochard-Wyart, F.; Tanaka, T.; Borghi, N.; de Gennes, P.-G. *Langmuir* **2005**, *21*, 4144–4148.
(5) Pattanayek, S. K.; Pereira, G. G. *Macromol. Theory Simul.* **2005**, *14*, 347–357.
(6) Pattanayek, S. K.; Pham, T. T.; Pereira, G. G. *J. Chem. Phys.* **2005**, *122*, 214908.
(7) Furukawa, K.; Ebata, K.; Fujiki, M. *Adv. Mater.* **2000**, *12*, 1033–1036.
(8) Koutsos, V.; van der Vegte, E. W.; Pelletier, E.; Stamouli, A.; Hadziioannou, G. *Macromolecules* **1997**, *30*, 4719–4726.
(9) Avramova, K.; Milchev, A. *J. Chem. Phys.* **2006**, *124*, 024909.
(10) Chen, J. Z. Y. *Phys. Rev. Lett.* **2007**, *98*, 088302.
(11) Hisette, M.-L.; Haddad, P.; Gisler, T.; Marques, C. M.; Schroeder, A. P. *Soft Matter* **2008**, *4*, 828–832.