A “Jumping Micelle” Phase Transition

Chandralekha Singh, Ekaterina B. Zhulina, Dilip Gersappe, Galen T. Pickett, and Anna C. Balazs*

Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Received May 28, 1996
Revised Manuscript Received August 21, 1996

An effective means of binding two surfaces is to coat each with a polymer solution and bring the coated surfaces into contact. The polymer chains form bridges that extend from one surface to the other and, thus, provide the necessary adhesion.[1] If the chains contain end groups that have a strong, attractive interaction with the surfaces, this binding can be irreversible. Previous studies focused on the behavior of these bridging polymers in the presence of a good solvent,[2] and a few researchers characterized the properties of these connecting chains in a poor solvent.[3,4] The poor solvent case is unique in that the tethered chains aggregate into “pinned micelles,” which consist of a dense, inner core and outer segments that connect the core to both surfaces.[4] In this study, we concentrate on the poor solvent case and determine the behavior of the bridging chains as the surfaces are pulled apart. As detailed below, we observe a novel phase transition: as the distance between the surfaces increases, the pinned micelles “jump” from one surface to the middle of the gap between the two. The findings illustrate the dramatic effect that confining polymer solutions between surfaces can have on the phase behavior of the system. Furthermore, the results reveal a new means of tailoring the microstructure of polymer films confined between two surfaces and provide insight into possible failure mechanisms of thin adhesives layers.

To capture this behavior, we first use a self-consistent field (SCF) theory.[5] The advantage of the SCF theory is that we can readily calculate the lowest free energy or equilibrium structure of the tethered chains. Since the chains form distinct micelles, the structure of the bridging layer is not laterally uniform. Thus, we must implement a two-dimensional SCF model,[6] which allows us to determine the polymer densities in both the vertical and lateral directions. Through these density profiles, we can visualize the shape of the pinned micelles at various surface separations. We then use scaling arguments to further characterize the size of the micelles and the nature of the “jumping” transition.

Our SCF method is derived from the theory developed by Scheutjens and Fleer.[5] In this treatment, the phase behavior of polymer systems is modeled by combining Markov chain statistics with a mean field approximation for the free energy. The distribution of all the components in the system are calculated by defining Green’s functions of the type $G(r_1,N'|r_2,N'')$, which represent the combined statistical weight of all conformations of a subchain starting with segment N' at r_1 and ending with segment N'' at r_2. Given the probability of finding a single monomer in a particular layer and the fact that all the monomers in a chain are connected, the Green’s functions for chains of arbitrary length can be obtained through a series of recursion relations. These recursion relations also involve the potential of mean-force acting at a point $\mathbf{r}$. This potential, in turn, is determined from the local distribution of all the components at the point $\mathbf{r}$, as well as the Flory−Huggins interaction parameters, or χ’s, between the different components. Solving this series of equations numerically and self-consistently yields the equilibrium distribution of polymer and solvent segments in the system.[5] In the two-dimensional SCF theory, the equations are written explicitly in terms of both the vertical (Z) and lateral (Y) directions.[6] The X direction is assumed to be translationally invariant. As a consequence, the pinned micelles assume a cylindrical geometry. Though the micelles are roughly spherical in three dimensions, it is anticipated that the SCF theory will nonetheless capture the qualitative features of the 3D system, which is analyzed via the scaling theory.

Our system involves two parallel surfaces that are bridged by homopolymers. In particular, one end of each polymer is grafted to surface 1 and the other end of the chain is grafted to surface 2.[7] In the SCF calculations, we fix the length of the polymers at $N = 80$ and the grafting density is given by $\rho = 0.025$. (In a poor solvent, pinned micelles only occur at relatively low grafting densities; at high grafting, the layer remains laterally uniform.[4,8]) To model the poor solvent, the polymer−solvent energy, χ_{ps}, is set at 2. The polymer−surface energy, χ_{pw}, is zero. Figure 1 shows the density profiles for the system as H, the vertical separation between the plates, is increased. When H is small ($\leq$the height of the unperturbed micellar core[4]), the system forms continuous bridging “bundles” (Figure 1a).[9] As the distance between the surfaces is increased, the bundles break up into pinned micelles that preferentially adsorb onto one of the surfaces (Figure 1b). While the tethering segments are relatively stretched, this conformation is energetically favorable because the polymers on the surface avoid contact with the solvent. As H is increased further, the cost of stretching the chains increases and finally exceeds the gain in energy associated with having the micelles adsorbed on the wall. At this point, there is a discontinuous “jump” of the micelles to the center of the gap. Figure 1c shows the conformation of this “centered” or “desorbed” micelle.

Further increases in H cause the micelles to grow in size (see below) and the distance between them to increase. The aggregation of chains into larger micelles further reduces the unfavorable polymer−solvent contact and is thus energetically favored. When the separation is increased so that $H \sim N$, the stretching energy dominates over the polymer−solvent interaction and the monomer density and size of the micelles decreases. Finally, the micelles disappear and we obtain single, stretched chains with a uniform polymer density between the surfaces. We find that this transition from desorbed micelles to stretched chains is smooth and continuous.

Similar results were obtained when the grafting density was increased to $\rho = 0.050$, and when χ_{ps} was decreased to 1 (still a poor solvent). However, when we introduced a polymer−surface repulsion that is comparable to χ_{ps}, the pinned micelles no longer adsorb on one of the walls, but are always located in the center of the gap.

To explore the features of this system, we adopt a scaling model where the pinned micelle is composed of a spherical core, which contains the majority of the monomers, and strongly stretched tethers, or “legs”.[10] In this model, the core is viewed as a densely packed system of thermal blobs, each of size $\xi \approx a/\tau$. Here, a is the monomer size, and given that T is temperature, $\tau = ((\Theta - T)/\Theta) > 0$ is the relative deviation from the

S0024-9297(96)00759-0 CCC: $12.00

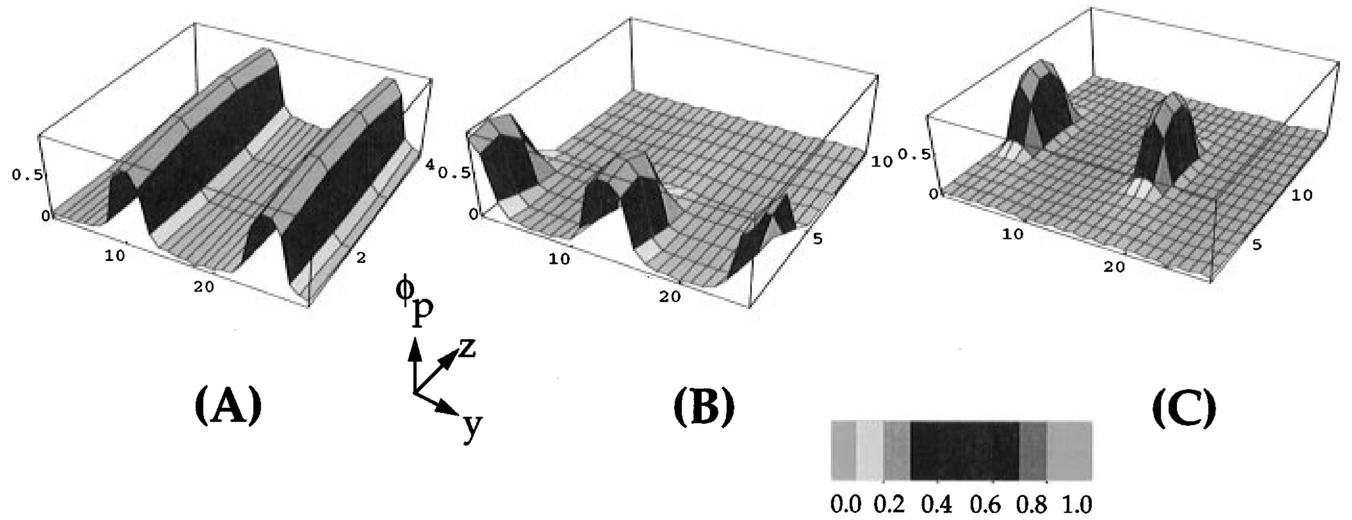

Figure 1. Plots from the SCF calculations showing the effect of increasing the surface separation, H. Here, $N = 80$, $\rho = 0.025$, and $\chi = 2$. The chains are grafted in the XY plane and the two surfaces are being separated along Z. The parameter ϕ_p is the polymer density. The magnitudes of ϕ_p are also indicated in the color bar. (A) The surfaces are highly compressed, and thus, the micelles associate into "bundles" that extend from one surface to another. (B) Increasing H causes the micelles to absorb onto one of the surfaces. (C) Further increases in H drive the micelles to desorb and localize in the center of the gap, since the cost of stretching is greater than the gain in the free energy of interaction.

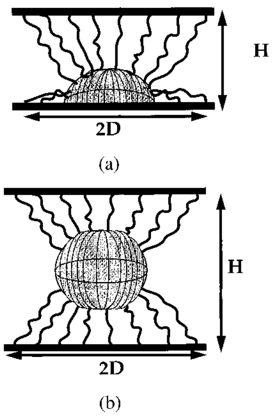

Figure 2. Schematic drawing of (a) an adsorbed pinned micelle and (b) a desorbed micelle.

Θ-point. In addition, the micellar legs are considered to be strings of thermal blobs. The lateral size of the micelle is given by $D = (fs)^{1/2}$, where s is the area per grafted chain and f is the number of chains within this aggregate. We assume that the polymer–surface interaction is energetically more favorable than the polymer–solvent interaction; thus, the pinned micelles can partially wet and adsorb on the surface. In order to analyze the transition from the "adsorbed" to the "desorbed" state (centered in the middle of the gap), we calculate the equilibrium size and free energies for the micelles in each of these states (see Figure 2 for a schematic representation of the two states).

In the adsorbed state (Figure 2a), the core is deformed and partially spread on the grafting surface. This spreading is driven by the energetic gain experienced by polymer units in contact with the surface. We let δ be the adsorption energy per unit monomer (measured in thermal units). We consider the case where $|\delta| \ll \tau$, which allows us to assume that the average concentration of units within the core remains $\approx\tau$. Then the shape of the core can be approximated by a spherical cap with a contact angle θ, which is determined by Young's law:

$$\gamma_{\mathrm{sw}} - \gamma_{\mathrm{cw}} = \gamma \cos \theta \tag{1}$$

Here γ_{sw}, γ_{cw}, and $\gamma \approx \xi^{-2} \approx t^2/a^2$ are the surface tensions at the solvent–wall, core–wall, and core–solvent interfaces, respectively. The parameter $\Delta \equiv \cos \theta$ is related to the adsorption energy δ by[11]

$$\Delta = (\gamma_{\mathrm{sw}} - \gamma_{\mathrm{cw}})/\gamma \approx (\delta/\tau) \tag{2}$$

where $\delta > 0$ (<0) corresponds to an attractive (repulsive) interaction.

The equilibrium value for f, the number of chains in the spread or deformed micelle, can be obtained by minimizing ΔF, the free energy per chain in this micelle,

$$\Delta F = \Delta F_{\mathrm{s}} + \Delta F_{\mathrm{el}} \tag{3}$$

where ΔF_{s} is the surface free energy per chain of the partially spread core and ΔF_{el} is the free energy of stretching each leg (string of thermal blobs).

To determine the expression for ΔF_{s}, note that the core of an adsorbed micelle consists of densely packed blobs; hence, the volume of the core is given by

$$V \approx (Nfa^3/\tau) \tag{4}$$

Given the height of the core, h, and Δ, simple geometric considerations show that the volume of the core is $V = (\pi h^3/3)((2 + \Delta)/(1 - \Delta))$, and the area in contact with the wall is $A = \pi h^2((1 + \Delta)/(1 - \Delta))$. The surface area of the spherical cap is $S = 2\pi h^2/(1 - \Delta)$. Therefore, $\Delta F_{\mathrm{s}} = (S\gamma - \gamma\Delta A)/f$. Using eq 4 and the latter definition of V, we can eliminate h from ΔF_{s}, and we find that for a partially spread globule, the equilibrium surface free energy per chain is

$$\Delta F_{\mathrm{s}}/kT \approx (\tau^{4/3}N^{2/3}/f^{1/3})g(\Delta) \tag{5}$$

The term $g(\Delta) = (1 - \Delta)^{2/3}((2 + \Delta)/4))^{1/3} \leq 1$ accounts for the deformation of the core.

The elastic stretching of the legs is

$$\Delta F_{\mathrm{el}}/kT \approx (\tau/2a)[(H^2 + fs)^{1/2} + (fs)^{1/2}] \tag{6}$$

where the two terms in eq 6 correspond to the legs attached to the upper and lower surfaces, respectively. Minimizing eq 3 with respect to f, with eqs 5 and 6 taken into account, one obtains the scaling dependence for the equilibrium number of chains, f_1, in the adsorbed pinned micelles,

$$f_1 \approx (\tau^{2/5}N^{4/5}/s^{3/5})g(\Delta)^{6/5} \tag{7}$$

It follows from eq 7 that for higher values of δ, f_1 becomes smaller, i.e., the adsorbed, spread ($g < 1$) pinned micelles are smaller than the nonadsorbed ($g = 1$) micelles. While neglected from the above equation, minimizing eq 3 also shows that f_1 displays a weak dependence on H, increasing with an increase in H.

The second state of a pinned micelle is that in the middle of the gap between the two surfaces (see Figure 2b). Here, the core is undeformed; i.e., it is a sphere of radius R_0 and the legs emanating from both surfaces are stretched to the same extent.[4] For a centered micelle containing f chains, the volume of the core satisfies $4\pi R_0^3/3 \approx (Nfa^3/\tau)$. The surface and the elastic components of the free energy are given by

$$\Delta F_{\mathrm{s}}/kT = (4\pi\gamma R_0^{\ 2}/f) \approx (\tau^{4/3}N^{2/3}/f^{1/3}) \tag{8}$$

$$\Delta F_{\mathrm{el}}/kT \approx (\tau/a)(H^2/4 + fs)^{1/2} \tag{9}$$

Minimizing the total free energy, $\Delta F_{\mathrm{s}} + \Delta F_{\mathrm{el}}$, one obtains the equilibrium number of chains, f_2, in a "desorbed" micelle;[4] asymptotically,

$$f_2 \approx \begin{cases} (\tau^{2/5}N^{4/5}/s^{3/5}) & H \ll \tau^{1/5}N^{2/5}s^{1/5} \quad (10\mathrm{a}) \\ (\tau^{1/4}N^{1/2}H^{3/4}/s^{3/4}) & H \gg \tau^{1/5}N^{2/5}s^{1/5} \quad (10\mathrm{b}) \end{cases}$$

Thus, in the second or "desorbed" state, the number of chains in the micelle increases noticeably with increasing H. These predictions agree with observations from the SCF calculations noted above.

By substituting the exact values of f_1 into eqs 5 and 6 and the complete expression for f_2 into eqs 8 and 9, we can readily compare the equilibrium free energies (for a given value of δ). This is shown graphically in Figure 3. At small values of H, the pinned micelles will be in the adsorbed state. Here, the partial wetting of the surface by the core wins over the losses associated with the nonuniform stretching of the legs. Thus, each micelle has its core localized and partially spread on one of the surfaces. An increase in H leads first to the rearrangement (an increase in size) of the adsorbed cores, but they still remain localized at the surfaces. However, at a critical value $H = H^*(\Delta)$, the free energy curves cross (see Figure 3) and any increase in H causes the cores of the micelles to jump abruptly into the middle of the gap. This transition is accompanied by a noticeable increase in the size of the micelles (now given by $f_2(a)$ and then $f_2(b)$ at larger values of H), especially for higher adsorption energies, $\delta > 0$. In the limit of long chains, $N \rightarrow \infty$, the "adsorbed–desorbed" transition of the pinned micelles is a first-order phase transition, leading to a discontinuous change in both the position and size of the cores.

With increasing δ, the value of H necessary to "desorb" the micelles also increases. However, increasing $\delta > \tau$ destroys the globular structure of the core. In this case, the grafted chains absorb on the surfaces as Gaussian chains, covering both surfaces.

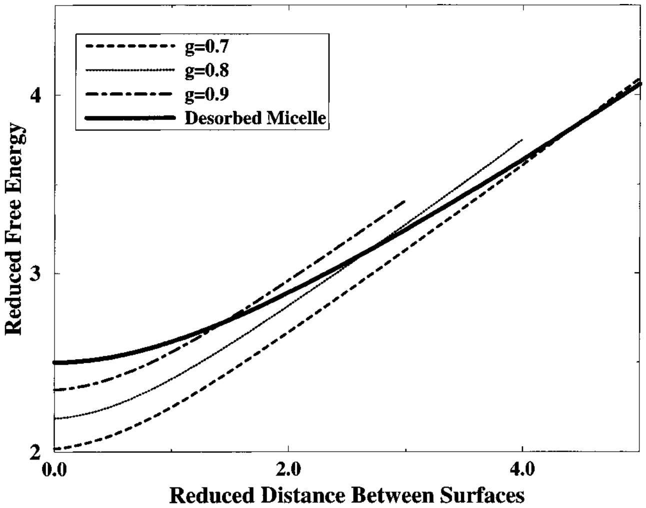

Figure 3. Reduced free energy, $\Delta F/(\tau^{6/5}s^{1/5}N^{2/5})$, versus the reduced distance between the surfaces, $H/(\tau^{1/5}s^{1/5}N^{2/5})$, for the adsorbed (dashed lines) and desorbed (solid line) states of the pinned micelles. For the adsorbed state, the curves are for different values of g.

We note that our two-state scaling model does not constitute an exhaustive analysis of the transition. Nonetheless, we anticipate that the jumping transition is an intrinsic feature of the system.[12]

In summary, we isolated a novel phase transition for polymers restricted between two surfaces and immersed in a poor solvent. The properties of these tethered polymers change dramatically as a function of the separation between the surfaces. The abrupt changes should be experimentally accessible, for example, by the chemical forces apparatus.[13]

The changes in polymer density with surface separation will also lead to changes in the index of refraction or viscosity of the fluid. Thus, the system can be used to modulate the propagation of light in the medium or control the diffusion rate of particles through slits and channels. Though some hysteresis may be inevitable in actual systems, one can cycle back and forth between these states. Due to this distinctive change in morphology, the entire assembly could be used as a force sensor, altering the nature of a signal that passes through the layer when the confining surfaces change their separation.

Acknowledgment. A.C.B. gratefully acknowledges financial support from the Materials Research Center, funded by AFOSR, through grant number F49620-95-1-0167, the DOE for financial support through grant DE-FG02-90ER45438, and ONR, through grant N00014-91-J-1363. C.S. also gratefully acknowledges financial support from NSF grant DMR-92-17935 to D. M. Jasnow.

References and Notes

(1) Avalos, J. B.; Johner, A.; Joanny, J. F. *J. Chem. Phys.* **1994**, *101*, 9181.
(2) (a) Johner, A.; Joanny, J. F. *Europhys. Lett.* **1991**, *15*, 265. (b) Zhulina, E. B.; Halperin, A. *Macromolecules* **1992**, *25*, 5730. (c) Milner, S. T.; Witten, T. A. *Macromolecules* **1992**, *25*, 5495. (d) Misra, S.; Mattice, W. L. *Macromolecules* **1994**, *27*, 2058.
(3) Halperin, A.; Zhulina E. B. *Macromolecules* **1991**, *24*, 5393.
(4) Zhulina, E. B.; Birshtein, T. M.; Priamitsyn, V. A.; Klushin, L. I. *Macromolecules* **1995**, *28*, 8612.

(5) Fleer, G.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T. Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, 1993.

(6) (a) Huang, K; Balazs, A. C. *Phys. Rev. Lett.* **1991**, *66*, 620. (b) Huang, K; Balazs, A. C. *Macromolecules* **1993**, *26*, 4736.

(7) The ends of the chains can be randomly grafted along each surface. The random grafting does not alter the findings described below.

(8) Yeung, C.; Balazs, A. C.; Jasnow, D. *Macromolecules* **1993**, *26*, 1914.

(9) Singh, C.; Balazs, A. C. *J. Chem. Phys.* **1996**, *105*, 706.

(10) (a) Klushin, L. I. Preprint (1992). (b) Williams, D. R. M. *J. Phys. II* **1993**, *3*, 1313.

(11) Johner, A.; Joanny, J. F. *J. Phys. II* **1991**, *1* 181.

(12) Zhulina, E.; Pickett, G.; Singh, C.; Gersappe, D.; Balazs, A. C. Manuscript in preparation.

(13) Hadziioannou, G.; et al. Poster presentation, Tribology Workshop, Bar Harbor, ME, Aug 27−Sept 1, 1995 and private communication.

MA960759O