ACS Macro Letters
Letter
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Scaling Theory for Compressed Polymer-Brush Bilayers

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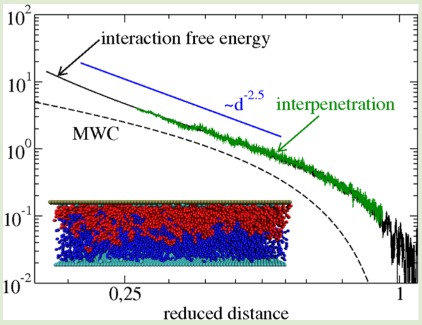
ABSTRACT: We present a novel scaling theory to describe the interaction free energy within a compressed polymer-brush bilayer. For semidilute brushes at intermediate and strong compressions, we predict that the interaction free energy scales with distance, D, between the grafting surfaces as $A(D) \sim D^{-2.5}$; i.e., the repulsive force, $f(D) \sim D^{-3.5}$, measured at the surfaces increases more strongly upon compression than predicted by the classical theory of Milner, Witten, and Cates. We find good agreement with experimental data and excellent agreement with numerical results, which follow our analytical predictions over a wide range of surface separations. The theory is based on the assumption of a strong correlation of the repulsive force and the interpenetration between the brushes. Using our numerical data, we can demonstrate this correlation with great precision.



Grafting linear macromolecules densely onto a surface with one chain end, such that the steric repulsion between the monomers forces the chains to stretch away from the surface and form a polymer brush,[1] is the best way known to us to minimize frictional losses between surfaces during shear motion.[2] Therefore, polymer brushes seem to play an important role in biolubrication.[3] Controlling the repulsive forces between polymer-brush-covered surfaces is essential for many technical applications, such as the stabilization of colloidal dispersions in ink and paint[4] or the construction of artificial joints.[5]

The repulsive forces between two polymer brushes placed on top of each other (polymer-brush bilayer) have been studied theoretically,[6,7] experimentally,[3,8−12] and via computer simulations[13−15] rather extensively over the past two decades. To date, the most popular analytical approach is the mean-field theory of Milner, Witten, and Cates (MWC),[6] which is expected to hold in the asymptotic limit of very long chains. Expressed by the molecular parameters of a compressed brush, i.e., chain length, N, and grafting density, σ, the MWC theory predicts a free energy per chain which reads[6]

$$A(d_h) = k_B TN(\pi^2\sigma^2 v_{ex}^2/12)^{1/3}(1/2d_h + d_h^2/2 - d_h^5/10) \tag{1}$$

where $d_h = h/h_0$ is the reduced distance between the surfaces, h the height of the compressed brush, and h_0 the height of the free, unperturbed brush. k_B, T, and v_{ex}, respectively, denote the Boltzmann constant, temperature, and the excluded volume parameter, characterizing the excluded volume per monomer. The repulsive force per unit area follows from $f(d_h) = -\partial A/\partial d_h$. In the limit of large compression, where $h = D/2$ (D being the distance between the grafting surfaces) and $d_h = d \equiv D/2h_0 \to 0$, one obtains from eq 1

$$A(d \to 0) \sim d^{-1} \tag{2}$$

Equations 1 and 2 are put to a test in Figure 1, where we plot the interaction free energy per unit area[16] as a function of the reduced distance d for a selection of previous experimental and new numerical data.[17] The experimental systems consist of both diblock copolymers, anchored by either a PEG or PI block,[10,12] and a single zwitterionic anchoring group.[8] On a double-logarithmic scale, clear deviations from the MWC theory are found. This is also the case for alternative approaches, such as the theory of Alexander and de Gennes,[18]

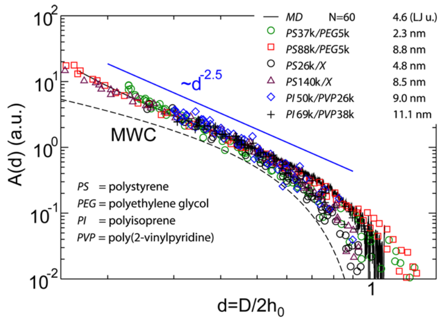


Figure 1. Interaction free energy per unit area (arbitrary units) as a function of reduced distance for data from MD simulations and SFA experiments in toluene of the following diblock copolymers/polymers, where the second block indicated is the anchor block/group: PS37k/PEG5k and PS88k/PEG5k;[12] PS26k/X and PS140k/X, where X is the zwitterionic group $(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3^-$ as indicated in ref 8; and PI50k/PVP26k and PI69k/PVP38k.[10] The last column in the legend is the mean distance between grafting points. We compare to the theory of Milner, Witten, and Cates [MWC, see eq 1] and to our new approach, which states $A(d) \sim d^{-2.5}$ [see eq 12].

Received: August 21, 2013
Accepted: October 2, 2013
Published: October 4, 2013

who predict $A(d \to 0) \sim d^{-1.25}$ for asymptotically large chains. In particular, a different behavior, $A(d) \sim d^{-2.5}$, is found for large compressions. Note that this exponent also seems to describe the data at intermediate distances.

At small compressions, the deviations from eq 1 can be explained and accounted for by including polydispersity effects.[12] At very large compressions, one expects the MWC theory to fail as higher-order terms of the equation-of-state (EOS) become relevant, while the MWC theory assumes a quadratic pressure dependence on the monomer density over the entire range of surface separations. However, also there is not a good agreement with the data in the regime of intermediate densities.

One may try to rewrite $A(d_h)$ based on an EOS including higher-order terms,[12] but this approach only leads to a universal description for systems with similar structures of the EOS. Furthermore, the MWC theory does not allow the two brushes to interdigitate.[19] Hence, the repulsive force solely is a result of the change in configurational entropy when the individual brushes are compressed. This can only be correct in the regime of strong stretching, i.e., in the asymptotic limit of the self-consistent mean-field theory (SCMFT), where fluctuations of the chain conformation around the path that minimizes the (classical) action can be neglected.[20] However, experiments and simulations do not reproduce this limit. Instead, a clear interpenetration between the brushes can be demonstrated either by neutron scattering,[11] computer simulations,[13−15,21] or numerical self-consistent field modeling.[22,23]

In this Letter, we present an alternative approach, which allows the brushes to interpenetrate (see Figure 2). Assuming semidilute brushes under intermediate and large compressions leads to a scaling behavior of the interaction free energy as indicated in Figure 1, i.e., $A(d) \sim d^{-2.5}$. Furthermore, by means of molecular dynamics (MD) simulations, we demonstrate a strong correlation between the interaction free energy and the amount of interpenetration between the brushes.

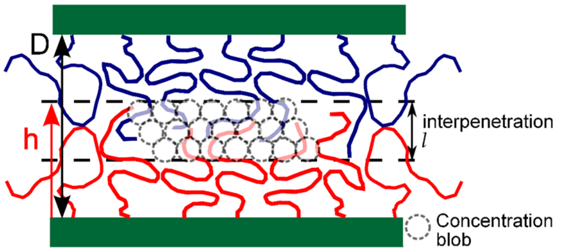


Figure 2. Schematic of a compressed polymer-brush bilayer. In the interpenetration zone, interbrush interactions lead to a repulsion between the brushes. The width of the interpenetration zone, l, is determined by the balance between inter- and intrabrush interactions. The latter predominantly occur outside the interpenetration zone, where the grafted chains are compressed.

We consider a quasi-stationary compression of the bilayer, such that at all distances thermal equilibrium demands a uniform normal pressure profile throughout the bilayer. Upon compression, an interpenetration zone is established in the interface of the bilayer (see Figure 2). Within this zone, interbrush interactions lead to a repulsion between the brushes. As the brushes try to avoid interpenetration, the grafted chains have to compress, and intrabrush interactions increase. Mechanical equilibrium demands a balance between inter- and intrabrush interactions; otherwise, the interpenetration zone would either shrink or increase. In other words, inter- and intrabrush interactions must provide the same contribution to the interaction free energy.

It appears rather challenging to account for interpenetration and chain deformation due to compression simultaneously. However, the above argument shows that it is sufficient to calculate the interaction free energy only in the interpenetration zone, where the interbrush repulsion takes place, and that the repulsive forces of a polymer-brush bilayer are determined completely by the mutual brush interpenetration.

For semidilute bilayers under intermediate compressions, the monomer density profile is uniform, and thus the size of concentration blobs, ξ, is the same everywhere in the bilayer. To first order, the interaction free energy per unit area then is given as

$$A(d) \sim n_i k_B T \tag{3}$$

where n_i denotes the number of concentration blobs within the interpenetration zone.

This approach is very different from the original blob picture by Alexander and de Gennes,[18] who calculate the interaction free energy from all the concentration blobs of two non-interpenetrating brushes. Such a procedure does not account for the interpenetration between the brushes.

We next derive an expression for the number of concentration blobs per unit area, which are located inside the interpenetration zone of width l. To this extent, we write

$$n_i = cl/g \tag{4}$$

where $c = 2N\sigma/D$ is the monomer concentration of a semidilute bilayer with uniform density profile. The number of monomers in the concentration blob can be derived via[21,26]

$$g \sim (\xi/a)^{1/\nu} \sim (ca^3)^{1/(1-3\nu)} \sim (N\sigma a^3/D)^{1/(1-3\nu)} \tag{5}$$

where a is the monomer size and $\nu \approx 0.588$ is the Flory exponent.

The interpenetration width, l, has been calculated in an earlier study.[21] The starting point is the interpenetration width under melt conditions for a bilayer at compressions with $h = D/2$[7,24]

$$l^{\text{melt}} \sim (N^2 a^4/D)^{1/3} \tag{6}$$

This relation follows from assuming a parabolic molecular field for the single brush and allowing for fluctuations of the brush height beyond the mean brush height h.[25] With the transformation[26]

$$N \to N/g \text{ and } a \to \xi \tag{7}$$

one finds for a semidilute bilayer under intermediate and strong compressions[21]

$$l \sim a[N^{2\nu}(\sigma a^2)^{2(1-2\nu)}(a/D)^{1-\nu}]^{1/3(3\nu-1)} \tag{8}$$

This relation has been tested using MD simulations.[27] Using eqs 4 and 5 yields

$$n_i \sim a^{-2}[N^{11\nu}(\sigma a^2)^{2+5\nu}(a/D)^{8\nu+1}]^{1/3(3\nu-1)} \tag{9}$$

as the number of concentration blobs per unit area in the interpenetration zone. Thus, from eq 3, we finally obtain

$$A(d) \sim k_B T a^{-2}[N^{11\nu}(\sigma a^2)^{2+5\nu}(a/D)^{8\nu+1}]^{1/3(3\nu-1)} \tag{10}$$

which states that the interaction free energy per unit area scales with $d = D/2h_0$ as

$$A(d) \sim d^{(8\nu+1)/3(1-3\nu)} \tag{11}$$

With $\nu \approx 0.588$, this yields approximately

$$A(d) \sim d^{-2.5} \tag{12}$$

which motivates the exponent introduced in Figure 1.

Regarding this result, one may criticize that the compression cannot be sustained solely by the interpenetration since the zone of overlap between the brushes is rather small compared to the entire width of the bilayer. Even though this is true for intermediate (and small) compressions, the above argument shows that this contribution to the free energy change upon compression must be of the same functional form as for the total bilayer.

To demonstrate this, one could measure the interpenetration width and try to see how it relates to $A(d)$.[28] While this is a difficult task for experimental systems,[11] it can be performed rather easily in numerical studies. However, the interpenetration width has to be extracted from the monomer density profiles, and this is not very precise and also a rather large effort. Instead, we characterize the amount of interpenetration via the number of binary monomer contacts between the brushes, $I(d)$. Previous investigations[15,21,27−30] have shown a strong correlation between $I(d)$ and the response of the bilayer to shear motion, indicating that $I(d)$ should be strongly related to the amount of interpenetration.

Figure 3 shows our numerical data for $I(d)$ and $A(d)$ as a function of the reduced distance. The correlation between the two functions is remarkable; it is even possible to shift $I(d)$ with an (arbitrary) factor such that the two functions coincide with great precision. This clearly demonstrates a strong correlation between the amount of interpenetration and the repulsive force measured at the surfaces.

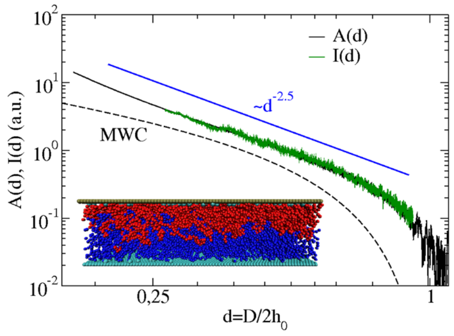


Figure 3. Data from MD simulations for the interaction free energy per unit area, $A(d)$, and the number of binary monomer contacts between the brushes, $I(d)$, in arbitrary units. We obtain a strong correlation between the two functions. Below, we show a snapshot of our MD simulation. Note the clear interpenetration between the upper (red) and lower (blue) brush.

Finally, we emphasize that the validity of eq 10 is limited to moderate compressions. At small compressions, where the brushes just come into contact, the size of concentration blobs is nonuniformly distributed over the bilayer. In the middle, where the monomer density is small, ξ is larger than close to one of the surfaces. Moreover, polydispersity effects can become important for small compressions. In the opposite limit of very large compressions, the bilayer attains melt density, and the explicit EOS comes into play. This can be seen in Figures 1 and 3 for the numerical data, which reveal a slight increase toward a somewhat larger exponent for very large compressions ($d \leq 0.1$). Since experimental chains are much larger than those in the simulation, the deviations appear at even smaller values of d, in a regime beyond the accessibility of current experiments.[31]

So far, we focused on the dependence of A on the distance between the surfaces. Future studies may test eq 10 with respect to the molecular parameters (N and σ) of the brushes. Because of their relevance in biological systems, approaches similar to the one presented here may be developed for polyelectrolyte brushes, if possible.

In conclusion, we present a novel, rather simple, and straightforward way to calculate the interaction free energy (or the repulsive forces) for intermediately and strongly compressed polymer-brush bilayers. Our approach is based on the assumption that $A(d)$ is closely related to the amount of interpenetration between the brushes. We have shown this correlation by means of MD simulations.

The essential idea underlying our scaling theory has already been applied to sheared bilayers. Together with these results, our approach provides a consistent picture describing compressed bilayers not only in equilibrium but also in stationary[21] and nonstationary[29] shear motion.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge interesting discussions with A. Johner, T.L. Kuhl, and C.M. Marques. Also, we are indebted to J.-U. Sommer for carefully reading the manuscript. In addition, we thank the Chateaubriand Fellowship (Paris, France) and the German Science Foundation (DFG-KR 2854/3-1) for financial support.

■ REFERENCES

(1) *Polymer Brushes*; Advincula, R. C., Brittain, W. J., Caster, K. C., Rühe, J., Eds.; Wiley: Weinheim, 2004.

(2) Binder, K.; Kreer, T.; Milchev, A. *Soft Matter* **2011**, *7*, 7159.

(3) Klein, J. *Proc. IMechE J.* **2006**, *220*, 691. Klein, J. *Science* **2009**, *323*, 47.

(4) Fischer, E. K. *Colloidal Dispersions*; Wiley: New York, 1950.

(5) Moro, T.; Takatori, Y.; Ishihara, K.; Konno, T.; Takigawa, Y.; Matsushita, T.; Chung, U.; Nakamura, K.; Kawaguchi, H. *Nat. Mater.* **2004**, *3*, 829.

(6) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610. Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413.

(7) Zhulina, E. B.; Borisov, O. V.; Prymatsyn, V. A. *J. Colloid Interface Sci.* **1990**, *137*, 495.

(8) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.

(9) Klein, J.; Perahia, D.; Warburg, S. *Nature* **1991**, *352*, 143.

(10) Watanabe, H.; Tirrell, M. *Macromolecules* **1993**, *26*, 6455.

(11) Mulder, D. J.; Kuhl, T. L. *Soft Matter* **2010**, *6*, 5401.

(12) Balko, S. M.; Kreer, T.; Costanzo, P. J.; Patten, T. E.; Johner, A.; Kuhl, T. L.; Marques, C. M. *PLoS ONE* **2013**, *8*, e58392.

(13) Murat, M.; Grest, G. *Phys. Rev. Lett.* **1989**, *63*, 1074.

(14) Toral, R.; Chakrabarti, A.; Dickman, R. *Phys. Rev. E* **1994**, *50*, 343.

(15) Kreer, T.; Binder, K.; Müser, M. H. *Langmuir* **2003**, *19*, 7551.

(16) We define the interaction free energy as the free energy difference between a compressed bilayer and two unperturbed brushes.

(17) We performed molecular dynamics simulations using the same stretching factor σR^2 (R^2 is the mean square radius of gyration of an isolated chain in solution) as for the experimental system of ref 12. To this extent, we used chains of average length $N = 60$ with a grafting density of $\sigma \approx 0.047$ (in LJ units). The lengths of the chains are taken from a Flory−Schultz distribution with a polydispersity of 1.23. Details of the numerical model are described elsewhere.[12,21]

(18) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.

(19) This is a direct consequence of the equal-flight-time argument used in ref 6.

(20) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733.

(21) Galuschko, A.; Spirin, L.; Kreer, T.; Johner, A.; Pastorino, C.; Wittmer, J.; Baschnagel, J. *Langmuir* **2010**, *26*, 6418.

(22) Wijmans, C. M.; Zhulina, E. B.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3238.

(23) Amoskov, V. M.; Birshtein, T. M.; Pryamitsyn, V. A. *Macromolecules* **1998**, *31*, 3720.

(24) Witten, T. A.; Leibler, L.; Pincus, P. A. *Macromolecules* **1990**, *23*, 824.

(25) Note that the assumption of a parabolic molecular field does not enforce a parabolic monomer density profile, as predicted by the MWC theory. The MWC profile is a consequence of the mean-field approximation together with a quadratic EOS.

(26) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: New York, 1979.

(27) Spirin, L.; Galuschko, A.; Kreer, T.; Johner, A.; Baschnagel, J.; Binder, K. *Eur. Phys. J. E* **2010**, *33*, 307.

(28) We do not imply $A(D) \sim l(D)$. When l is chosen as a measure for the amount of interpenetration, one has to use the relation $A(D) \sim l(D)^{(8\nu+1)/(1-\nu)}$, as it follows from eqs 8 and 11.

(29) Spirin, L.; Galuschko, A.; Kreer, T.; Binder, K.; Baschnagel, J. *Phys. Rev. Lett.* **2011**, *106*, 168301.

(30) Spirin, L.; Galuschko, A.; Kreer, T. *Macromolecules* **2011**, *44*, 9399.

(31) In simulations, the bilayer can be compressed even down to almost a monolayer. The lowest distance, at which the repulsive forces can be measured in experiments, should be given by the onset of adhesive forces between the surfaces.