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On the Structure and Pressure of Tethered Polymer Layers in Good Solvent

M. A. Carignano and I. Szleifer*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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ABSTRACT: The structural and thermodynamic properties of tethered polymer chains in the good solvent regime are studied using the single-chain mean-field theory. The mushroom to brush transition is found to be broad. For surface coverages below the brush regime, i.e., mushroom regime and crossover region, the relevant length scale of the layers is found to be the bulk radius of gyration of the chains, R_g, while in the brush regime the relevant length scale is the distance between tethering points as assumed in the analytical approaches. The onset of the brush regime corresponds to the beginning of the overlap between the chains as measured by the distance-dependent lateral radius of gyration of the chains. The predictions of the theory for the height of the polymer layer and the lateral pressures as a function of the surface coverage are compared with recent experimental observations of Kent and co-workers. Excellent agreement is found for the height of the brush for all surface coverages. The experimental lateral pressures multiplied by the square of the bulk radius of gyration are found to be a universal function of the reduced surface coverage, $\sigma^* = \sigma\pi R_g^2$. The predictions of the theory are in good agreement with the experimental measurements up to values of the reduced surface coverages $\sigma^* \sim 8$. For higher reduced surface coverages the theoretical results deviate from the scaling found experimentally. This deviation is consistent with the fact that these surface coverages correspond to the brush regime. The theoretical lateral pressure is found to be better described as a universal function of $\sigma n^{0.5}$ from low to relatively high surface coverages. From the analysis of the average conformational properties of the chains, it is argued that the behavior of the measured lateral pressures at high reduced surface coverages may be due to nonequilibrium effects. From the comparisons between the theory and the experiments it is found that most of the measurements correspond to the crossover region between the mushroom and the brush regimes. This explains the scaling found for most experimental properties.

I. Introduction

The understanding of the behavior of tethered polymer chains has received much attention during recent years due to the wide range of practical applications of these systems.[1-3] These include stabilization of colloidal particles, adhesion, and biocompatibility among many others. Moreover, these systems are also very interesting from the fundamental point of view. They combine the usual coupling between flexibility and thermodynamic behavior found in all polymeric systems with the additional constraint of having an interface or a wall to which one of the ends of the chains is attached. Many experimental and theoretical studies have been used to describe tethered layers.[4-25] It was found that the analytical SCF theory and the scaling approach can be used to explain several experimental observations. Recent experimental studies by Kent and co-workers[11-14] were aimed to study directly the interaction within the tethered layers by measuring the surface tension reduction induced by tethered layers in the good solvent regime. These studies were combined with neutron reflectivity measurements that provide information on the structure of the same layers. The analytical and scaling approaches do not seem to predict the behavior observed in these experiments.

In this paper we apply the single-chain mean-field (SCMF) theory[26-28] to study the behavior of the lateral pressures (reduction of surface tension) and the structure of the tethered layers. The SCMF theory is based on looking at a central chain "exactly", and the interactions with the surrounding polymer and solvent molecules are taken within a mean-field approximation. This approach, originally developed to treat short-chain surfactants in amphiphilic aggregates[29] and later generalized for tethered polymer layers, has been shown to provide very accurate information on the average conformational and thermodynamic properties of chain molecules as compared to computer simulations.[30-32] Here we make direct comparison with the experimental observations of Kent and co-workers[11-14] and analyze in detail the molecular organization of the layers. We find that for all the chain lengths treated in our calculations there is a very broad transition region between the mushroom regime, where the chains are isolated from each other, i.e., very low surface coverages, and the brush regime, which corresponds to chains highly stretched perpendicular to the surface, i.e., relatively high surface coverages. We observe that the chains start to interact with each other at much longer distances than those that would be expected from the lateral dimensions of the chains. Moreover, we have found that in the low- and intermediate-density regimes, from mushroom to relatively stretched chains, all the dimensions of the chains can be scaled by the bulk radius of gyration of the chains. The lateral pressures in the same regime are found to be universal in a scaling variable different than previously proposed.

The next section shortly reviews the theoretical approach. Section III presents the results of our calculations for a variety of chain lengths, followed by simple arguments that explain the particular scaling vaiables obtained. Finally, in section IV, we present some concluding remarks.

II. Theory

The central quantity in the SCMF theory is the probability distribution function (pdf) of chain conformations. From the knowledge of the pdf any desired average conformational and thermodynamic quantity

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can be calculated. We present here a brief derivation of the theory based on minimization of the Helmholtz free energy of the system. A more detailed derivation based on expansion of the system's partition function can be found in ref 26. Consider a system composed of N_p tethered polymer molecules and N_s solvent molecules. The polymer chains have a degree of polymerization n, and the solvent molecules are assumed to be of the same volume, v_0, as a monomer of the polymer. We concentrate our attention in the good solvent, athermal, limit. Then, the (mean-field) Helmholtz free energy per unit area, F/A, may be written as

$$\beta\frac{F}{A} = \sigma\sum_{\{\alpha\}}P(\alpha)\ln P(\alpha) + \int_0^\infty \varrho_s(z)\ln[\varrho_s(z)v_0]\,dz \qquad (1)$$

where $\sigma = N_p/A$ is the polymer surface coverage, $P(\alpha)$ is the probability of finding a chain in conformation α, and the sum runs over all the possible single-chain configurations. $\varrho_s = N_s(z)/A$ is the solvent density at distance z from the tethering surface. The first term on the right-hand side of eq 1 is the configurational entropy of chains, and the second term is the translational entropy of the solvent molecules. This last term is z dependent due to the inhomogeneous density as a function of the (normal) distance from the surface, z.

To find the pdf, $P(\alpha)$, and the solvent density, $\varrho_s(z)$, we minimize the free energy of the system, eq 1, subject to the packing constraints imposed by the assumption that the system is incompressible. Namely, we assume that for all distances z from the tethering surface the total volume available is occupied by solvent molecules or polymer chains. These constraints can be expressed as

$$\sigma\langle n(z)\rangle v_0 + \varrho_s(z)v_0 = 1, \qquad 0 \le z < \infty \qquad (2)$$

with $\langle n(z)\rangle\,\mathrm{d}z = \sum_{\{\alpha\}}P(\alpha)n(z;\alpha)\,\mathrm{d}z$ being the average number of segments per chain at distance z from the surface.

The minimization can be carried out by defining $\{\pi(z)\}$ as the set of Lagrange multipliers conjugated to the packing constraints to give

$$P(\alpha) = \frac{1}{q}e^{-\int_0^\infty \beta\pi(z)v_0 n(z;\alpha)\,\mathrm{d}z} \qquad (3)$$

for the pdf with q the normalization constant, and

$$\varrho_s(z)v_0 = e^{-\beta\pi(z)v_0} \qquad (4)$$

for the solvent density profile. The Lagrange multipliers, $\pi(z)$, represent the lateral pressures at each distance z from the surface necessary in order to have a constant solvent chemical potential throughout the layer.[26] These quantities are found by replacing the pdf, eq 3, and the solvent density profile, eq 4, in the constraint equations, eqs 2. The result is a set of equations in which the only unknowns are the lateral pressures and the input necessary to solve them is the set of single-chain conformations and the surface coverage, σ.

The main difference between the single-chain mean-field approach and the numerical self-consistent field approaches is in the way that the chain molecules are introduced in the solution of the problem. We have shown[26] that the single-chain mean-field theory becomes identical to the SCF approach in the case that the chains are generated by Green's function, or the equivalent lattice matrix multiplication. However, in our approach the chains are not generated in the presence of the external field, namely, the interactions with other molecules, but in the absence of any intermolecular interactions. In other words, the single chains are generated with all their intramolecular interactions and the boundary conditions imposed by the geometry of the tethering surface. This has three advantages: One is that the chains are generated only once and then the same set is used to solve the nonlinear equations, eqs 2, for all different conditions. The second is that we can see how the weights of the exact same set of configurations change due to the intermolecular interactions. The third is that the theory is independent of the chain model and therefore can be applied for any chain architecture.[27]

The calculations presented in section III were carried out using the rotational isomeric state (RIS) chain model[33] to generate the single-chain conformations. In this model each bond can have three possible configurations (trans, gauche$^+$, and gauche$^-$) in which the bond between sements i and $i+1$ is at angle of 0° (t), 120° (g$^+$), and $-120°$ (g$^-$) with respect to the plane spanned by the bonds between segments i, $i-1$, and $i-2$. We take the three configurations to be of equal energy; i.e., the chains are fully flexible. The conformation is generated by randomly assigning a state to each of the bonds; if the distance between any two (nonbonded) segments is less than the bond length, the conformation is discarded and a new set of bond states is generated. Once the chain conformation is found to be self-avoiding, a random direction for the chain conformation with respect to the surface is chosen. We generate a set of 10^6–10^7 independent chain conformations for each chain length that is used to solve the set of equations (2).

The results obtained from our calculations are in excellent quantitative agreement with MD and MC simulations of tethered chains on surfaces of planar, spherical, and cylindrical geometries at all the surface coverages that simulations are available.[28,30-32] This is a very good test of the approximations of the theory due to the fact that the simulations are the "exact" solution for the model system chosen.

From the expressions of the pdf and solvent density profile, we can write the free energy as a function of the pressure profiles to give

$$\beta\frac{F}{A} = -\sigma\ln q - \int_0^\infty \beta\pi(z)\,\mathrm{d}z \qquad (5)$$

with

$$q = \sum_{\{\alpha\}}\exp[-\int_0^\infty \beta\pi(z')v_0 n(z';\alpha)\,\mathrm{d}z'] \qquad (6)$$

being the single-chain partition function that is coupled to the "mean field" of the interactions through the lateral pressure profile, $\{\pi(z')\}$. The total lateral pressure is obtained by taking the derivative of the Helmholtz free energy with respect to the area. This yields

$$\beta\Pi_a = \int_0^\infty \beta\pi(z)\,\mathrm{d}z - \sigma n \qquad (7)$$

which can be readily obtained once the local pressures are calculated. The lateral pressure Π_a has to be understood as the excess pressure, excess over the pure solvent bulk isotropic pressure, arising from the inhomogeneous mixture of solvent molecules and polymer

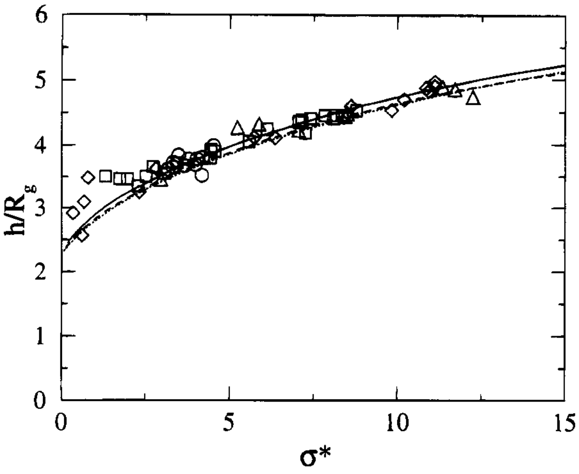

Figure 1. Height of the polymer layer scaled by the bulk radius of gyration, h/R_g, as a function of the reduced surface coverage, $\sigma^* = \sigma\pi R_g^2$. The symbols belong to the experimental observation of Kent et al. for four different molecular weights: 4–30 (circles), 4.5–60 (squares), 21–169 (diamonds), and 28–330 (triangles). The first number is the molecular weight of the PDMS block while the second is that of the tethering PS block; both numbers should be multiplied by 10^3 *g/mol*. The lines belong to the predictions of the theory for systems composed by chains of 50 (dotted line), 70 (dashed line), and 100 (solid line) segments.

chains due to the tethering of the polymers. Thus, it is also the reduction of the surface tension due to the presence of the polymer chains at the surface or interface.

III. Results

In this section we show comparisons of the theory with recent experimental observations by Kent and coworkers.[11–14] They have studied the properties of polystyrene–poly(dimethylsiloxane) (PS–PDMS) at the ethyl benzoate–air interface. The solvent is good for the PS chain; however, it is a nonsolvent for PDMS. Therefore, the PDMS blocks are located at the interface while the PS blocks are tethered toward the solvent. These experimental studies are the first ones in which the lateral interactions within the layer are studied together with the structural properties of the film. These studies were done for a variety of molecular weights of the polymer chains.

Figure 1 shows the comparisons of the theory and the experimental observations for the height of the polymer layer, scaled by the radius of gyration of the chain in dilute bulk solution, as a function of the scaled surface coverage. In the theoretical approach, the height of the layer is not a well-defined quantity since the profile does not have a simple form. Therefore, the results shown are for twice the first moment of the profile, i.e.

$$h \rightarrow 2\langle z\rangle = 2\frac{\int z\langle\phi_p(z)\rangle\,dz}{\int\langle\phi_p(z)\rangle\,dz} \qquad (8)$$

The agreement between the experimental results and the theory is excellent. Since the quantities are plotted in a scaled form, there is no adjustable parameter in the comparison. A close look at the results shows that in reality the three different chain lengths calculated from the theory do not perfectly scale. However, the closeness of the three curves suggests that the bulk radius of gyration of the chains may be a relevant length scale in the problem, as suggested by Kent et al.[13] This is not in line with scaling theory[16] and analytical SCF approaches[21,24] which suggest that the only relevant length scale of the tethered layer is given by the distance between the grafting points. However, this assumption is true only in the brush regime, and as will be discussed below, the experimental observations are mostly in the transition region between the mushroom and layer structures. Therefore, the radius of gyration being the relevant length scale is not in contradiction with the analytical approaches.

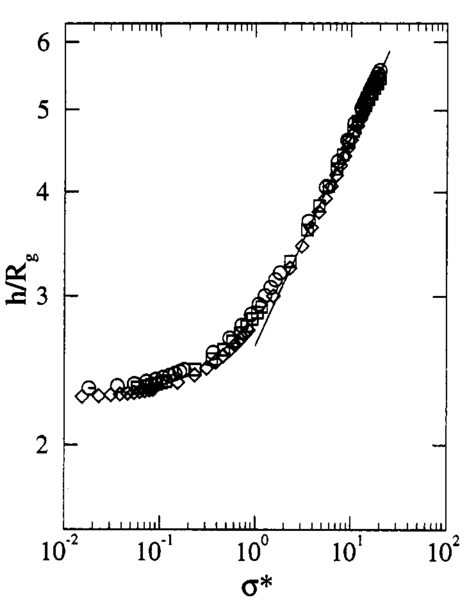

Figure 2. Mushroom to brush transition represented by the scaled height of the layer as a function of the reduced surface coverage, σ^*, in a log–log representation. The transition occurs in a wide range of reduced surface coverages around $\sigma^* \sim 1$. The systems considered here are for chains of 50 (circles), 70 (squares), and 100 (diamonds) segments. The solid line with a slope of 0.25 defines the brush regime.

Figure 2 shows the predictions of the theory for the same quantity as in Figure 1, but in a log–log form so that one can observe the mushroom to brush transition. The transition is not sharp, as is expected from the fact that our calculations are for relatively short chain lengths. However, from the comparison of Figure 1, it is clear that the experimental observations are also not in the brush regime but cover the region from the dilute polymer layer well into the stretched regime. Therefore, it is not appropriate to attempt to compare the experimental observations with the scaling predictions since these are valid only in the proper brush regime.

In the mushroom regime the relevant length scale is the radius of gyration of the chains, since the chains are “isolated” from each other. The fact that the radius of gyration seems to be the scaling variable for a wide range of surface coverages suggests that in the crossover region between the mushroom and the layer this is still the relevant length scale, while the distance between grafting points becomes the only length scale in the brush regime. This will be further confirmed by the results shown in Figure 7.

The line shown in Figure 2 corresponds to $h/R_g \propto \sigma^{*1/4}$, which we define as the brush regime. It is important to note that this is not the scaling predicted by the analytical SCF theory[21,24] or the scaling approach of Alexander.[16] However, as was shown already by Grest, the 1/3 exponent (instead of the 1/4) will be expected for higher molecular weights.[31] The figure shows that there is a well-defined range of reduced surface cover-

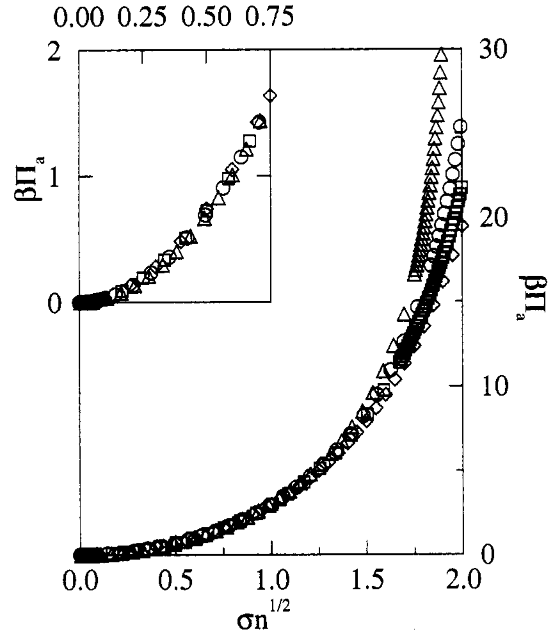

Figure 3. Calculated lateral pressure as a function of the surface coverage scaled by the square root of the chain length. The results correspond to chains of 30 (triangles), 50 (circles), 70 (squares), and 100 (diamonds) segments. Note that in this representation the calculated pressures are universal up to $\sigma n^{0.5} \leq 1.4$. The inset shows the low surface coverage region in a larger scale to show that the scaling variable describes the system even in the mushroom regime.

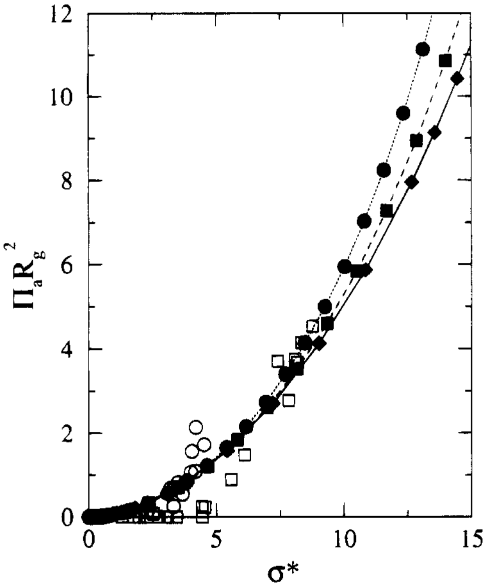

Figure 4. Lateral pressures scaled by the square of the bulk radius of gyration, shown in units 10^{12} *erg*, as a function of the reduced surface coverage. The open symbols correspond to the experimental observations of Kent et al. for two molecular weights: 4–30 (circles) and 4.5–60 (squares). The filled symbols are the results from the theoretical calculations for chains of 50 (circles), 70 (squares), and 100 (diamonds) segments. The arbitrary energy scale of the theory was assumed to have the value $\beta = 10.32 \times 10^{12}$ erg^{-1} to fit the experimental observations.

ages where the 1/4 exponent seems to properly predict the behavior of the layers. For the dependency of the height of the layer with molecular weight, as observed from the data in Figure 2, we have that $h/R_g \propto \sigma^{*1/4}$; i.e., $h \propto \sigma^{1/4}R_g^{3/2} = \sigma^{1/4}n^{9/10}$, where we have used $R_g \propto n^{3/5}$, a result that we obtain for our chain model in bulk solutions. This result shows almost the same chain length dependency as the one predicted by the analytical approaches. Two points are important to mention. First, as mentioned above, the experimental observation of Kent and co-workers should not be compared with the analytical predictions since only some of the experimental observations correspond to the brush regime. Second, our calculations are for relatively short chain length. However, due to the good comparisons with experimental observations without any adjustable parameters, the behavior of the polystyrene blocks up to molecular weights of the order of 300 000 g/mol seem properly predicted by these chain lengths and the asymptotic regime is not reached for these molecular weights, e.g., the dependence of the height of the layer with the surface coverage in the brush regime.

MD simulations[31] as well as predictions from our theory[28] have shown that the lateral pressure does not follow the scaling predictions for intermediate chain length. In order to see if one can identify the proper scaling variable, even though a single exponent is not expected, we have chosen to look at what one should expect in the limit of very low surface coverages. In this limit, the chemical potential must be linear in the degree of polymerization (up to logarithmic corrections) due to the fact that the number of self-avoiding walks of end-grafted chains scales[34] as $z_{\mathrm{eff}}^{\,n}n^{\gamma-1}$, where z_{eff} is an effective coordination number and γ is the enhancement exponent. Therefore, the pressure must also be linear in the degree of polymerization. We have also shown, as it is expected from first principles, that for very low surface coverages that lateral pressure of the grafted system scales as σ^2. Then, in the low-density regime $\Pi \propto n\sigma^2$. Therefore, we think that a natural scaling variable, at least in the low-density regime, should be $\sigma n^{0.5}$. As shown next, this variable seems to be appropriate up to relatively high surface densities, suggesting that a virial-like expansion in $\sigma n^{0.5}$ represents a very good description of these systems.

Figure 3 shows the calculated lateral pressures for four different chain lengths as a function of $\sigma n^{0.5}$. The results show that up to quite large values of the surface coverage, the lateral pressures are a universal function of the product $\sigma n^{0.5}$. The scaling is very good, as expected, also for low surface coverages as indicated by the inset in Figure 3.

The observations of Kent et al. for the reduction of the surface tension do not follow this scaling relationship. However, as explained next, there is an alternative way to represent the data in which a direct comparison of the experimental observations with the theoretical results can be made.

In order to compare the predictions of the theory for the pressure isotherms with those of the experimental observations, it is best if one can find a scaled form so that no parameters have to be used. We do not expect to have a simple scaling relationship between the pressures and the surface coverage. However, one can find a simple form in the limit of very low surface coverages. In this limit we follow Flory's argument[35] that the second virial coefficient should scale approximately as that of hard spheres of a size given by the radius of gyration of the chains. We generalize this argument to our quasi-two-dimensional system. In this case the cross-sectional area of a single chain is proportional to the square of the bulk radius of gyration. Then we can write that $\Pi_a \propto R_g^2\sigma^2$. However, from dimensional arguments it will be best to multiply both

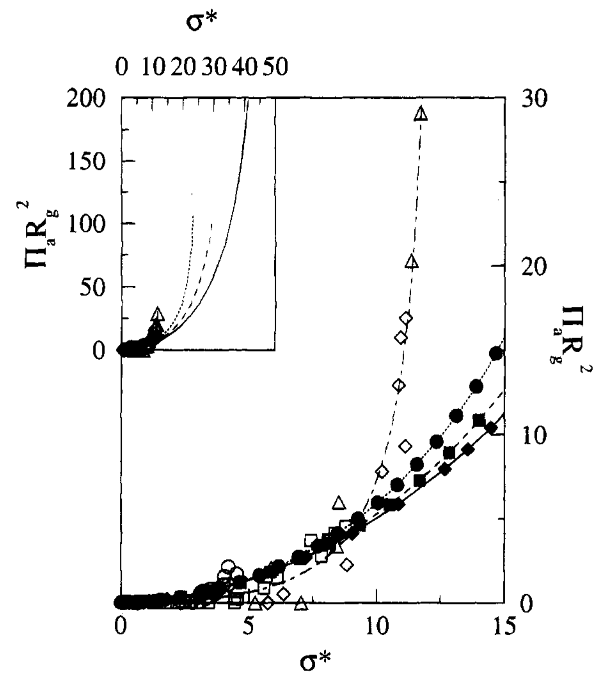

Figure 5. Same as Figure 4 but with the four experimental molecular weights with symbols as in Figure 1. The dash-dotted line is the best fit obtained from the van der Waals equation, eq 9. The filled symbols correspond to the calculated pressures as in Figure 4. The inset shows a larger range of reduced surface coverages where it can be seen that the calculated pressures also show a very sharp increase with surface coverage. However, this is observed at much larger σ^* than the experimental measurements; see text. The lines in the inset correspond to $n = 50$ (dotted), 70 (dashed), and 100 (solid).

sides by R_g^2, giving in the dilute tethered solution limit $\Pi R_g^2 \propto \sigma^{*2}$. This result suggests that, at least up to σ^* of order unity, the pressure multiplied by the square of the radius of gyration should be a universal function of the scaled surface coverage. Following this argument, Figure 4 shows the predictions of our theory and the experimental observations for two different lengths of the diblocks in scaled form. The agreement between the measured pressures and the calculated ones is rather good.

The results of the calculations suggest that following the Flory idea the pressures scale up to $\sigma^* \simeq 7$, even though one would expect this type of argument to hold up to $\sigma^* \simeq 1$. This, again, suggests that the bulk radius of gyration of the chains is a relevant length scale up to relatively large values of the surface coverage, slightly beyond the onset of the brush regime; see Figure 2. It is important to emphasize that this scaling is not as good as the one suggested by Figure 3. However, it is the only scaling form in which the experimental observations and the theory can be compared, and it sheds light, as will become clear below, on the behavior of the systems.

It turns out that the experimental observations suggest that R_g is an important length scale for all the range of surface coverages covered by the measurements. In order to see that, we show in Figure 5 the scaled pressure as a function of the reduced surface coverage for four different molecular weights measured by Kent et al. The results suggest that this scaling is appropriate for all the range of surface coverages that can be measured at the air–solvent interface.

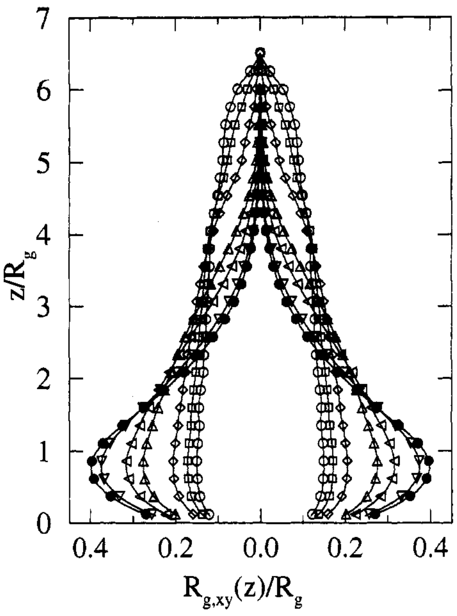

Figure 6. Average shape of the polymer molecules represented by the z-dependent lateral component of the radius of gyration as a function of the distance from the tethering wall. All the distances are scaled by the bulk radius of gyration. All the results are for chains with 100 segments. The filled circles correspond to the free chain and the others are for $\sigma^* = 0.181$ (triangles down), 0.905 (triangles left), 1.81 (triangles up), 5.42 (diamonds), 9.05 (squares), and 12.67 (circles). Note the variation of the shape of the molecules due to the repulsions even for the lowest value of the reduced surface coverage.

We have fitted all the experimental data by a scaled van der Waals-like equation of state of the form

$$\Pi R_g^2 = \frac{CR_g^2}{a - a_0} - \frac{CR_g^2}{a} = C'\sigma^*\left(\frac{\sigma_0^*}{\sigma_0^* - \sigma^*} - 1\right) \quad (9)$$

where $C' = C/\pi$ is a constant, a is the area per molecule, and a_0 is the "hard-core" cross-section area of the molecules. Note that this form of the van der Waals equation automatically has the scaling form proposed above. This equation of state corresponds to the excess lateral pressure, excess over the translational contribution to the pressure, as it is the experimentally reported value. Therefore, if expression 9 is expanded in a virial-like expansion, the first term will be quadratic in σ^*. It is important to emphasize that we do not take $C = kT$ as it is in the usual van der Waals equation. The reason is that in reality the systems that we are dealing with have a contribution to the pressure that arises from the deformation of the chains. This contribution is not taken into account in the equation, but we let the parameter C correspond to the best fit of the equation and thus we obtain a good agreement with the experimental observations for all values of the surface coverage. If we take $C = kT$ the shape of the isotherm is an inverted L-like shape that can fit the data only for the highest surface coverages; see, e.g., ref 12.

The "hard core" scaled surface coverage that best fits all the data is $\sigma_0^* = 12.65$. These results suggest that it is not possible to form a layer with reduced surface coverage larger than this value. The value of the energy constant is $C = 0.194\pi \times 10^{-12}$ erg, which is much larger than kT, reflecting the additional free energy cost of deforming the polymer chains at low to intermediate surface coverages.

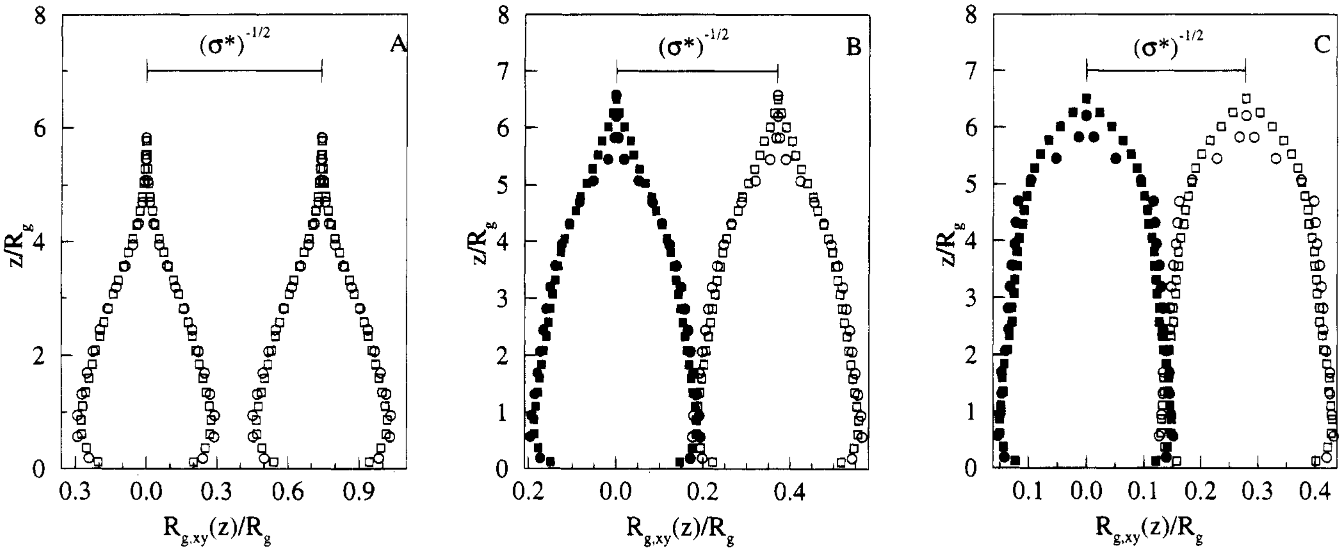

Figure 7. Two neighboring chains represented by their average shapes (as in Figure 6). The distance between the tethering points is $\sigma^{*-0.5}$. The circles (squares) are the results for chains of 50 (100) segments. (A) $\sigma^* = 1.81$. (B) $\sigma^* = 7.21$. The symbols of the left molecules are filled for clarity. Note that the lateral dimensions of the chains are starting to overlap for this reduced surface coverage. (C) $\sigma^* = 12.67$. This value of the surface coverage is slightly higher than the predicted divergency of the experimental observations. There is a large overlap between neighboring chains and the shapes of the molecules do not scale anymore with the bulk radius of gyration since this is well in the brush regime; see text.

As can be seen from Figures 4 and 5, the results of the theory are in agreement with the measurements up to $\sigma^* \leq 8$. For higher values of surface coverage there is no agreement between the measurements and the predictions of the theory. However, as was seen in Figure 1, the agreement between the theory and experiments for the height of the brush seems to hold for all the surface coverages measured in the experiments. Moreover, experimental observations by Auroy et al.[8,10,36] cover much larger values of surface coverages which, according to the pressure experiments, should not be possible to achieve due to the divergency of the lateral pressure. The inset of Figure 5 shows the calculated pressures up to very high surface coverages. It can be seen that the theoretical pressures also show a very sharp increase for large enough surface coverages. This "divergency" depends very strongly on the molecular weight of the polymer and for long chains it demonstrates that the surface coverage observed by Auroy et al. can be equilibrium structures. The regime where the calculated pressures diverge is *not* the so-called brush regime, but it corresponds to much higher surfaces coverages where the local volume fraction of polymers is very high. We now turn to a possible explanation that will put all these findings in perspective.

In order to gain some understanding of the source of the surface pressures, it is useful to look at the lateral component of the radius of gyration as a function of the distance from the tethering surface for different values of surface coverage, i.e.

$$\langle R_{g,xy}{}^2(z)\rangle = \frac{1}{2}[\langle R_{g,x}{}^2(z)\rangle + \langle R_{g,y}{}^2(z)\rangle] = \frac{1}{2n}\sum_{\{\alpha\}}P(\alpha)[\sum_{i=1}^{n}(x_i(z;\alpha) - x_{\rm cm}(z;\alpha))^2 + (y_i(z;\alpha) - y_{\rm cm}(z;\alpha))^2] \quad (10)$$

where the subscript cm denotes center of mass. The quantity defined in eq 10 defines the average shape of the molecules. Figure 6 shows the lateral radius of gyration as a function of the distance from the tethering surface for chains of $n = 100$ from the limit of an isolated chain on the surface (free chain) to relatively high surface coverages. As expected, as σ increases, the chains are "compressed" in the lateral directions and they stretch perpendicular to the surface. The larger compressions are in the regions in which the free chain is more extended laterally. The figure demonstrates that the lateral dimensions of the chains decrease as the perpendicular dimension increases, due to the chain crowding and the connectivity of the chains. This general behavior is qualitatively similar to that of the density profiles and their shape changes as the surface coverage increases.[26]

It is interesting to note that even at very low surface coverages the chains feel the repulsions of the neighboring polymer molecules, even though the distance between them is much larger than the average lateral dimensions of the chains. This is the reason for the continuous increase in the height of the layer, even at low surface coverage, i.e., in the so-called mushroom regime (see Figures 1 and 2).

In order to relate the shape changes to the lateral pressure, Figures 7A–C show the shape of the chains in scaled form for three different reduced surface coverages. The results are for chains of $n = 50$ and $n = 100$ and the figures show all the lengths scaled by the bulk radius of gyration. Figure 7A corresponds to a low reduced surface coverage. The average (scaled) distance between tethering points is large, even though the chains are compressed as compared to a free chain (see Figure 6). For this σ^* it is seen that the scaled deformation of the chains is identical for both chain lengths. Therefore, one would expect the same scaled free energy cost of deformation as confirmed by the results of Figure 4. Figure 7B shows the shape of chains at a value of σ^* where the calculated pressure starts to deviate from the Flory-like scaling. As it can be seen, the shape of the molecules shows similar deformation but the crowding is large enough that the lateral dimensions of the chains are just starting to overlap. This overlap marks the onset of the brush regime, as can be seen from Figure 2. The reduced surface coverage shown in Figure 7B is also the one where the measured pressures and the calculated ones start to deviate; see Figures 4 and 5. Figure 7C shows the shape of the molecules for a σ^* that according to our fit to the experimental measurements the pressure will diverge. Note that there is an appreciable amount of overlap between the lateral dimensions of neighboring chains. The van der Waals equation, eq 9, describes a system with a "hard core" area. Clearly, polymer molecules can interpenetrate into each other, as shown in Figure 7C, and thus one should expect a soft core rather than a chain–chain excluded volume.

The reduced surface coverage shown in Figure 7C is well in the brush regime. The scaling of the shapes of the chains is not good anymore and that is clear in the height as well as in the lateral extension of the chains. This is a manifestation of being in the brush regime where the relevant length scale is not the radius of gyration but the distance between tethering points.

The agreement between the measured lateral pressures and the calculated ones for $\sigma^* \leq 8$, together with the van der Waals-like divergency at higher surface coverage and the overlap of the lateral radius of gyration of the chains, suggests that the experimental observation at high surface coverage corresponds to a system that is unable to relax to its equilibrium structure. Such high surface coverages have been realized in grafted systems from semidilute solution[10] and therefore the lateral interactions, even though high, cannot be divergent. At high surface coverage there will be some kind of entanglement between the chains. Thus, as explained by Kent and co-workers,[13] probably the grafting from semidilute solution is such that the chains are, already in the solution, in a structure close to that of the final grafted layer, while the time scale of relaxation to that structure in the interfacial experiments seems to be too long. In other words, in the experiments of Kent et al. the polymer layer is prepared by depositing a copolymer grain into the interface. The surface coverage is increased by the addition of more grains. Thus, it seems that there is a reduced surface coverage above which addition of further diblock does not allow full relaxation of the added chains, resulting in a strong repulsion that may be due to localized regions of high density of polymer. However, further experimental work is necessary to see if this nonequilibrium effect is the reason for the measured divergency of the lateral pressure.

IV. Discussion and Conclusions

The predictions of the single-chain mean-field theory for the height of the layer are in very good agreement with the experimental observations of Kent and co-workers for all the ranges of surface coverages. The corresponding lateral pressures are in good agreement up to a value of the reduced surface coverage of $\sigma^* \simeq 8$. This comparison between theory and experiments has been carried out without any adjustable parameters, beyond the arbitrary energy scale of the theory that is needed for the pressures, since the comparisons are for scaled quantities. In both cases the relevant quantity to scale the height, surface coverage, and lateral pressure is the bulk radius of gyration of the chains. Since the single-chain mean-field theory considers chains that are self-avoiding walks, there is not need to add any information on the bulk radius of gyration, but use the bulk radius of gyration of the same model chain in bulk. This is not the case if one is comparing with SCF theories, in which the chains are modeled by random walks in the field of the osmotic pressures. This is due to the fact that the chain molecules in bulk, according to the SCF approach, have Gaussian statistics, which is not a good model for dilute bulk polymers in the good solvent regime.

We have seen that the mushroom to brush transition occurs around $\sigma^* \simeq 1$ as expected; however, the transition is not very sharp for the molecular weights studied here. There is a continuous increase of the height of the brush from the mushroom regime up to values of $\sigma^* \sim 6$ where the brush regime appears. The onset of the brush regime corresponds to the overlap of the z-dependent lateral radius of gyration of the chains. The predictions from the theory show that the brush regime corresponds to a scaling of the form $h \propto n^{9/10}\sigma^{1/4}$, which is consistent with the analytical predictions for the molecular weight dependence but is not for the surface coverage dependence. As already discussed in the literature,[31,37] longer chain length will give the exponent in the brush regime predicted by the analytical approaches. However, the experimental observations of Kent et al. seem to be better described by the predictions of our approach, even though they include molecular weights up to 300 000 g/mol. More importantly, it is clear that the experimental observations should not be analyzed only in terms of the brush regime since most of them correspond to the transition regime between the mushroom and the brush. This regime is not the one that corresponds to the region where the analytical theories are applicable. This also explains the findings that the radius of gyration is a relevant length scale in the problem. Namely, in the mushroom and in the crossover regimes the relevant length scale for thermodynamic and conformational properties is the bulk size of the chains. However, in the brush regime this is not the case and only the distance between tethering points becomes the relevant length scale, in agreement with the analytical predictions.

The predictions of the theory show that from very low to quite large surface coverages the lateral pressure is a universal function of $\sigma n^{0.5}$. However, the experimental observations do not agree with this scaling and therefore the scaling with the radius of gyration enables us to make a quantitative comparison with the experiments, even though the theoretical results do not show perfect scaling.

For large reduced surface coverages the experimental observations suggest a divergency of the lateral pressure that can be represented by a purely repulsive two-dimensional van der Waals equation of state. This implies that there is a "hard core" reduced area per molecule above which it is impossible to pack the chains. The predictions from the theory show that the systems can be packed at much higher reduced surface coverages than those expected on the van der Waals analysis of the experimental data. Moreover, experimental observations of very dense grafted layers demonstrate that they indeed are possible to form, even though it seems that they can be formed only by chemical grafting.

The question that arises is then why the theoretical predictions describe the height of the brush for all surface coverages, while the pressures show a significant difference for large values of the reduced surface coverage. The reason is that the height of the brush for $\sigma^* \geq 10$ does not vary very dramatically because the chains are already quite stretched. As can be seen in

Figure 7 the changes in the whole shape of the molecule are not very large and it is the overlap between the chains that is responsible for the different pressures, while this effect does not affect very much the height.

The "shapes" of the polymer molecules as a function of the surface coverage suggest that the divergency observed in the experimental observations coincides with the overlap in the lateral components of the radius of gyration, namely, when the chains are strongly stretched and they would interpenetrate laterally into the neighboring chains. This happens already in the regime where the relevant length scale of the problem changed from the bulk radius of gyration to the distance between tethering points. This may imply that the experimental observations at large surface coverages are performed in a system that cannot reach full equilibrium, probably due to the long time scales necessary for lateral interpenetration in highly stretched polymer layers. This explanation is in line with the reasoning of Kent and co-workers that the high surface coverages obtained in the experiments of Auroy et al. are realized from semidilute solutions where the chains are already interepenetrating into each other.

The conclusions drawn above suggest that in order to confirm these points more experimental observations are necessary. It will probably be desirable to study the reduction of the surface tension of the interface between two immiscible solvents in the presence of a diblock copolymer that each solvent is good for one of the blocks but a poor solvent for the other. In this way the reduction of the surface tension will be directly related to the lateral pressures of two parallel layers. Therefore, there will be no need to assume that the contribution of the adsorbed block is independent of molecular weight as is the case in the PDMS–PS at the ethyl benzoate–air interface. This type of experiment will enable a direct comparison with the theoretical approaches and thus further clarify the important issues discussed here.

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