Macromolecules **2000,** *33,* 5721−5729

Tensioactive Properties of Semidilute Polymer Solutions

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Received January 20, 2000; Revised Manuscript Received May 8, 2000

ABSTRACT: We present a scaling description of adsorbed polymer layers in the presence of a semidilute solution. Within a very simple model where the layer is treated as a thermodynamic ensemble of loops with a large polydispersity in size, we are able to (a) describe the influence of the semidilute solution on the structure of the layer of adsorbed chains, and (b) estimate the variation of the surface tension γ of the solution as a function of the polymerization index of the chains (N) and the monomer volume fraction in the bulk (Φ_b). Concerning point a, this work provides a continuous picture for the variations of the static properties of the interfacial layer from the dilute case ($\Phi_b \to 0$), to the melt case ($\Phi_b \to 1$). Concerning point b, we find a law $\gamma(\Phi_b, N)$ of the form (good solvent conditions) $\gamma_{VdW} - A\Phi_b^{5/4} + B(\Phi_b^{7/8}/N^{1/2}) \ln(N/\Phi_b^{7/12}N^*)$, where γ_{VdW} accounts for van der Waals interactions and N^* is a characteristic index of polymerization of the polymer under consideration (A and B are calculated within numerical coefficients of order unity). This law is in good quantitative agreement with experimental measurements and generalizes our recent findings on the case of molten polymer liquid. (Aubouy; Manghi; Raphaël. *Phys. Rev. Lett.* **2000**, *84*, 4858.)

1. Introduction

The physics of adsorbed polymers at interfaces is of central interest to such diverse fields as surface treatments, adhesion, and colloidal stabilization. Bulk properties of polymers are quite well understood now, both from a theoretical point of view and from an experimental point of view.[1] This is in contrast to interfacial properties of polymer solutions where a complete picture has not yet emerged, and a certain number of important questions are still under debate.[2] Essentially, this is because polymer solutions form layers at an interface which are inhomogeneous systems. Experimentally, many evidences have been found that the surface tension γ of polymer solutions should be both a function of the molecular weight (MW) and monomer volume fraction (Φ_b) of the sample. That γ should depend on Φ_b is not quite surprising. The dependence on MW is a more subtle effect which leads to preferential adsorption when a polydisperse sample is exposed to an attractive interface. Experimentally, γ is an increasing function of MW for concentrated solutions. Under melt conditions (no solvent whatever), a recent work melt suggests that the dependence of γ on MW results from a competition between the entropy associated with the large distribution of loops formed at the interface (cf. Figure 1) (which favors the longest chains at the interface) and the specific attraction of the chain ends toward the surface (which favors the largest number of chains per unit area). Much less is known about the case where the solution is semidilute.

To be more precise, we consider the following situation: a set of simple polymer chains (linear, neutral, homogeneous, flexible, monodisperse: N monomers per chain of size a) are in solution (good solvent conditions, semidilute regime). This solution is exposed to a flat surface, attractive for the monomers. We assume that the adsorption is reversible and the equilibrium of the layer is reached. This problem has been studied essentially according two directions.

Figure 1. Sketch of the interface of a polymer solution. The polymers in direct contact with the surface form a layer of loops and tails characterized by a large polydispersity in size. In our model, each loop is divided in two “pseudo-tails” and the interface is treated as a thermodynamical ensemble of these “pseudo-tails”.

A major step forward was made by de Gennes in 1981 when he applied the Cahn−Hilliard approach to this problem.[4] In this model, the free energy of the interface is written as a functional of the monomer volume fraction, $\Phi(z)$, where z is the perpendicular distance from the surface. This functional has two contributions: k_BT (where $k_BT\Phi^{9/4}$ is the thermal energy), which accounts for excluded volume interactions, and $^1/_2 k_BTL(\Phi)(\nabla\Phi)^2$ (where $L(\Phi)$ is a Φ-dependent coefficient), which penalizes gradients of concentration. The free energy is then minimized subjected to the boundary condition that the surface is attractive for the monomers. The underlying assumption is that the surface introduces a small perturbation for the bulk. What we get from this approach is an universal and self-similar profile $\Phi(z) \sim z^{-4/3}$ on a distance $\xi_b \cong a\Phi_b^{-3/4}$, the correlation length in the bulk solution.[5] This is satisfactory since the self-similar profile is what we expect in the dilute limit, and a continuous picture emerges from the calculation. On the other hand, the overall treatment raises three questions. (a) On general grounds, we expect that an adsorbed chain has a extension comparable to the natural size of a coil in a semidilute solution: $R_F \cong a\Phi_b^{-1/8}N^{1/2}$. Then the influence of the surface should be felt on distances R_F much larger than ξ_b, and the “small

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10.1021/ma000099u CCC: $19.00

perturbation" hypothesis is questionable. (b) When the surface tension is estimated, no MW dependence is found. This can be traced back to the implicit assumption (in the Cahn–Hilliard approach) that the surface tension is related to bulk properties of the solution. Since these are independent of the MW of the polymer, γ is also independent of MW. However, this conclusion differs from the experimental observations.[6,7] (c) The determination of the coefficient $L(\Phi)$, which depends on solvent conditions, is not quite obvious.

More recently, Semenov and Joanny have tried a different point of view. Essentially, they describe the polymer layer perturbed by the solution.[8,9] Their approach combines a self-consistent field type of theory which goes beyond the standard ground state dominance, and previous results obtained by de Gennes on the dilute regime (the self-similar profile $\Phi(z) \sim z^{-4/3}$ is taken as an input). Two different coupled order parameters are derived for the loops and the tails.[10,11] This theory allows a more detailed description of the interface in terms of regions where the tails dominate the volume fraction (the outer part of the layer of adsorbed chains), and regions where the loops account for the concentration (in the vicinity of the interface). This work represents a considerable improvement in comparison to the Widom–Cahn–de Gennes approach; however, it is desirable to have a theory where the self-similar profile is not taken as an input. To our knowledge, the surface tension of the semidilute solutions has not been calculated from this approach.

In addition to these systematic studies, there are a few scaling results that have been suggested.[12,13] These are limited to the description of the structure of the layer. As they are quite similar in spirit to our approach, we will discuss these results in the core of the article.

In this paper, we investigate the problem by making use of an approach that has been initially proposed by Aubouy, Guiselin, and Raphaël (AGR)[14] to describe the structure of polymer layers adsorbed from dilute solutions. In this work, the layer is described as a thermodynamic set of loops and tails in interaction. Within a simple scaling model for the behavior of the loops and the tails, the free energy may be written, which has two contributions: a term of the form $\int_{\text{layer}} \Pi_{\text{os}}(z)\,\mathrm{d}z$ (where Π_{os} is the osmotic pressure) which accounts for both the elasticity and the monomer–monomer interactions and an entropy of the form $-k_{\text{B}}\int_0^N P(n)\ln[P(n)]\,\mathrm{d}n$ (where $P(n)$ is the loop size distribution) which accounts for how many different arrangements of loops are possible. This free energy is able to explain many features of adsorbed polymer interfaces. In particular, this work emphasizes the role of the entropy associated with the polydispersity of the set of loops, a contribution which has not been fully recognized so far, and, we think, is significant whenever we have homogeneous adsorption of long flexible macromolecules. That this entropy contributes to the surface tension of polymer solutions was demonstrated in a recent letter where the case of molten polymer liquid is considered.[3]

Our goals in this work are 2-fold. (a) The first is to identify the influence of a semidilute solution on the layer formed by the polymers in direct contact with the interface. In particular, to understand how do quantities such as the extension of the layer and the amount of material carried by the surface vary with the concentration of the bulk solution. (b) The second is to compute the interfacial tension $\gamma(\Phi_{\text{b}},N)$ of the solution and, notably, to determine the physical processes which drive the dependence of γ on MW.

To carry on this project, we have to generalize the AGR theory in several respects. First we have to compute separately the elasticity and the monomer–monomer interactions for the loops (section 2.1). The reason is that although these two contributions are comparable (within a numerical coefficient) when the loop is isolated (a good enough approximation for adsorption from a dilute solution), this is no longer the case when the coil is in a semidilute solution. The monomer–monomer interactions are screened, whereas the elasticity is renormalized. Second, we have to introduce a new physical feature, namely: the tensioactive role of chain ends. In the weak adsorption regime, to be defined below, this effect is not relevant for the structure of the layer. However, it is an important contribution to the surface tension. Finally, we have to work in the grand canonical ensemble at constant pressure, rather than in the canonical ensemble, to allow for chemical and mechanical equilibriums. The structure of the layer is found by minimizing the thermodynamical potential (section 2.2).

The tensioactive properties of the semidilute solution are considered in section 3. The interfacial tension of the solution is calculated from our estimation of the potential (section 3.1). In section 3.2, we perform a quantitative comparison of our theory with the experimental data. Our concluding remarks are given in section 4.

In all that follows, we use scaling laws to concentrate on the functional dependences of the various quantities.

2. Thermodynamics of the Polymer Layer

In our approach, the surface which supports the polymer chains can be either solid, liquid, or free (provided that the interface is sharp). We assume that the surface is attractive enough so that the loops which form the layer overlap. For definiteness, we consider a saturated surface, which is the most common case in practice. For sake of simplicity, we carry on the calculations for an athermal solvent, i.e., the excluded volume is $v \cong a^3$. The general case of a good solvent ($v < a^3$) and the case of a Θ-solvent are considered in the Appendix.

To describe the ensemble of loops and tails in interaction, we make the following simplifying assumptions. (1) Each loop of $2n$ monomers is considered as two independent "pseudo-tails" of n monomers so that we describe the interface as a thermodynamic set of tails, polydisperse in size, end-attached to the surface. (2) This pseudo-brush is described according to Alexander and de Gennes: the tails behave identically; their conformation is described by a single function $n(z)$ where n is the curvilinear index along the tail. (3) The "free chains" in the bulk do not penetrate the layer formed by the "adsorbed chains". Our main tool is the function S defined as

$$S(n) = a^{-2}\int_n^N P(m)\,\mathrm{d}m \tag{1}$$

where P is the statistical distribution of tail sizes in monomer units.[14] In simple words, $S(n)$ is the *local grafting density*: the number per unit surface of pseudo-tails having more than n monomers. Later on we will call S the "loop profile". The local conservation of monomers inside the layer implies

$$\Phi(z) = a^3\frac{S(n(z))}{\dot{z}(n(z))} \tag{2}$$

where $\dot{z} = (\partial z/\partial n)$.

As the loops overlap, by analogy with a semidilute solution,[1] the layer can be visualized as a closely packed system of blobs and a local correlation length may be defined:

$$\xi(z) \sim a\Phi(z)^{-3/4} \tag{3}$$

2.1. Energetics. In this section, we estimate the free energy of the layer $F\{S,\dot{z}\}$ suitable to describe the layer. The free energy has five contributions: the van der Waals *interactions* between the surface and the solution, the *tensio-activity of the chain ends*, the *excluded volume* interactions, the "*pseudo-tails*" elasticity, and the "*pseudo-tails*" entropy which accounts for the polydispersity in size of the system.

1. We assume that the interactions between the surface and the polymer solution are of van der Waals type. As shown by de Gennes,[4] these long-range interactions have no special effect on the structure of the layer and play a role only at the immediate vicinity of the surface. Therefore, the attraction to the surface can be accounted for by writing

$$F_{\mathrm{s}} \cong \gamma_0 - \kappa\gamma_1 \tag{4}$$

where γ_0 is the solvent/surface interfacial tension and γ_1 the energy gain per adsorbed monomer. The coefficient κ is the two-dimensional concentration of adsorbed monomers, which we set to be $1/a^2$.

2. We have to consider an additional term which accounts for chain ends attraction. From a physical point of view, this attraction arises because the last monomers have a polarizability slightly different from that of a monomer in the middle of the backbone (they only form one covalent bond with an other monomer).[15] This contribution lowers the interfacial tension proportionally to the number of terminal monomer in direct contact with the surface. The number (per cm^2) of adsorbed chains is $\Gamma/N = \int S(n)\,\mathrm{d}n/N$ (Γ is the surface coverage). Assuming an attractive energy $\Delta k_{\mathrm{B}}T$ per chain ends in direct contact with the surface, and two adsorbed ends per polymer, this gives a contribution

$$F_{\mathrm{e}} = -2\Delta k_{\mathrm{B}}T\frac{\Gamma}{N} \tag{5}$$

to the free energy. Because of our hypothesis (1), there is no penalty for forming a loop rather than a tail, and both ends of a given adsorbed chain are situated at the interface as soon as Δ is positive, hence the factor of 2. We expect that Δ should be of order unity in the absence of any chemical modification of chain ends.

3. The monomer−monomer interactions are accounted for by integration of the osmotic pressure on the layer width. In a good solvent, the osmotic pressure is given by the des Cloiseaux law: $\Pi_{\mathrm{os}} \sim \Phi^{9/4}$. Using eq 2, we find

$$F_{\mathrm{vol}} \cong \int_{\mathrm{layer}}\Pi_{\mathrm{os}}(z)\,\mathrm{d}z \cong \frac{k_{\mathrm{B}}T}{a^2}\int_0^N (a^2S(n))^{9/4}\left(\frac{\dot{z}(n)}{a}\right)^{-5/4}\mathrm{d}n \tag{6}$$

4. The elastic part of the free energy is the sum of the elastic energy of each pseudo-tail

$$F_{\mathrm{el}} \cong \int_0^N -S'(n)E(n)\,\mathrm{d}n \tag{7}$$

where $E(n) \cong k_{\mathrm{B}}T\int_0^n ((\mathrm{d}z/\xi)/(\mathrm{d}m/g))^2\,\mathrm{d}m/g$ is the elastic energy of one pseudo-tail of n monomers. Each blob of size ξ is an elementary spring with a characteristic constant $\sim k_{\mathrm{B}}T$. Then each monomer has a "spring constant" equal to $k_{\mathrm{B}}Ta^2g/\xi^2 \cong k_{\mathrm{B}}T\Phi^{1/4}$. Integrating eq 7 by parts and using eq 2 yields

$$F_{\mathrm{el}} \cong \frac{k_{\mathrm{B}}T}{a^2}\int_0^N (a^2S(n))^{5/4}\left(\frac{\dot{z}(n)}{a}\right)^{7/4}\mathrm{d}n \tag{8}$$

5. The last contribution accounts for the polydispersity in size of the pseudo-tails. The estimate is[14]

$$F_{\mathrm{ent}} \cong \frac{k_{\mathrm{B}}T}{a^2}\int_0^N (-a^2S'(n))\ln(-a^2S'(n))\,\mathrm{d}n \tag{9}$$

Gathering all these results, the free energy (per cm^2) of the layer $F\{S,\dot{z}\}$ is given by

$$F\{S,\dot{z}\} \cong \gamma_0 - \kappa\gamma_1 + \frac{k_{\mathrm{B}}T}{a^2}\int_0^N \left\{(a^2S(n))^{9/4}\left(\frac{\dot{z}(n)}{a}\right)^{-5/4} + (a^2S(n))^{5/4}\left(\frac{\dot{z}(n)}{a}\right)^{7/4} + (-a^2S'(n))\ln(-a^2S'(n)) - \frac{2\Delta}{N}a^2S(n)\right\}\mathrm{d}n \tag{10}$$

It is simple to show that the estimate of F for the dilute case[14] is obtained by setting $\Delta = 0$ in eq 10 and minimizing the functional with respect to $\dot{z}$.

When the bulk solution is semidilute, it exerts a pressure Π_{b} on the layer. Moreover, the system can exchange polymeric chains with the bulk. Thus, the suitable thermodynamic potential is not the free energy but the grand potential at constant osmotic pressure in the bulk (per unit surface), $\Omega = F + \Pi_{\mathrm{b}}H - \mu_{\mathrm{b}}N_{\mathrm{mon}}$ where H is the thickness of the layer, N_{mon} the number of monomers (per unit surface) in the layer and μ_{b} the monomer chemical potential in the bulk. Hence

$$\Omega\{S,\dot{z}\} = F\{S,\dot{z}\} + \Pi_{\mathrm{b}}\int_0^N \dot{z}(n)\,\mathrm{d}n - \mu_{\mathrm{b}}\int_0^N S(n)\,\mathrm{d}n \tag{11}$$

where $\Pi_{\mathrm{b}} \cong k_{\mathrm{B}}T/a^2\Phi_{\mathrm{b}}^{9/4}$ and $\mu_{\mathrm{b}} \cong (^9/_5)k_{\mathrm{B}}T\Phi_{\mathrm{b}}^{5/4}$.[16]

2.2. Determination of the "Loop Profile" at Equilibrium. Minimization of Ω with respect to changes in $\dot{z}$ and S results in two standard Euler−Lagrange equations (numerical factors are omitted)

$$(a^2S(n))^{5/4}\left(\frac{\dot{z}(n)}{a}\right)^{3/4} + \Phi_{\mathrm{b}}^{9/4} = (a^2S(n))^{9/4}\left(\frac{\dot{z}(n)}{a}\right)^{-9/4} \tag{12}$$

$$(a^2S(n))^{5/4}\left(\frac{\dot{z}(n)}{a}\right)^{-5/4} + (a^2S(n))^{1/4}\left(\frac{\dot{z}(n)}{a}\right)^{7/4} + \frac{S''(n)}{S'(n)} - \frac{2\Delta}{N} = \Phi_{\mathrm{b}}^{5/4} \tag{13}$$

Equations 12 and 13 have a simple physical interpretation. The first one expresses the local mechanical equilibrium of the layer. At equilibrium, a slice of size

δz balances (a) two compressive forces (lhs of eq 12)—the elastic restoring force exerted by the assembly of tails (spring constant: $k \sim \Phi^{1/4}$) in parallel (hence the additive rule for the equivalent spring constant: $kS\,\dot z$) and the bulk osmotic pressure—and (b) the osmotic pressure within the layer directed toward the bulk (rhs of eq 12). Equation 13 is equivalent to the local balance of chemical potential (written per monomer). The rhs of this equation is the monomer chemical potential in the bulk.

We solve this system of differential equations by considering the asymptotic regimes. We find two regions in the layer.

Near the surface ($a \le z \le \xi_b$ or $1 \le n \le n_c$), bulk contributions and chain ends effects may be neglected. This is because this region of the layer does not “feel” the presence of the bulk solution. Equations 12 and 13 simplify into

$$(a^2S(n))^{5/4}\left(\frac{\dot z(n)}{a}\right)^{3/4} = (a^2S(n))^{9/4}\left(\frac{\dot z(n)}{a}\right)^{-9/4} \qquad (14)$$

$$(a^2S(n))^{5/4}\left(\frac{\dot z(n)}{a}\right)^{-5/4} + (a^2S(n))^{1/4}\left(\frac{\dot z(n)}{a}\right)^{7/4} + \frac{S''(n)}{S'(n)} = 0 \qquad (15)$$

which solutions are power laws:[17]

$$S_{\mathrm{eq}}(n) \cong \frac{1}{a^2 n^{6/5}} \qquad (16)$$

$$z_{\mathrm{eq}}(n) \cong a n^{3/5} \qquad (17)$$

Equation 17 is the Flory relation for the extension of an isolated coil of n monomers in good solvent conditions. This indicates that the loops are only marginally stretched by the presence of the others. Making use of eq 2 gives the variations of the volume fraction

$$\Phi(z) \cong \left(\frac{a}{z}\right)^{4/3} \qquad (18)$$

which is precisely the self-similar profile characteristic of a layer of adsorbed chains exposed to a dilute solution.[14] At larger distances, our neglect of the bulk contributions is no longer valid. This happens when $S_{\mathrm{eq}}(n_c)^{9/4}\,\dot z_{\mathrm{eq}}\,(n_c)^{-9/4} \sim \Phi_b^{9/4}$ which defines a characteristic index $n_c \cong \Phi_b^{-5/4}$. Translated in terms of extension, we find a distance $a n_c^{3/5} \cong a\Phi_b^{-3/4} \cong \xi_b$, the correlation length of the bulk solution.

At larger distances ($\xi_b \le z \le R_F$ or $n_c \le n \le N$), we reach a second regime where the elastic contribution in eq 12 is not relevant. In this region, the bulk osmotic pressure directly balances the osmotic pressure within the layer. Equations 12 and 13 are simplified into

$$a^3\frac{S(n)}{\dot z(n)} \cong \Phi_b \qquad (19)$$

$$\frac{(a^2S(n))^2}{\Phi_b^{7/4}} + \frac{S''(n)}{S'(n)} - \frac{2\Delta}{N} = 0 \qquad (20)$$

We expect that Δ should be of order unity, and the chain end effects should not affect the structure of the layer. This argument will be made more quantitative a posteriori. For the moment, let us assume $\Delta = 0$. Equations 19 and 20 yield

$$S_{\mathrm{eq}}(n) \sim \frac{\Phi_b^{7/8}}{a^2 n^{1/2}} \qquad (21)$$

$$z_{\mathrm{eq}}(n) \sim a\frac{n^{1/2}}{\Phi_b^{1/8}} \qquad (22)$$

Note that $\Phi = \Phi_b$. Both $S_{\mathrm{eq}}(n)$ and $z_{\mathrm{eq}}(n)$ depend on Φ_b, which is a signature of the influence of the bulk solution. In this outer region, the dependence of z_{eq} on n follows the Daoud law for the extension of a polymeric coil in a semidilute solution, again indicating that the loops are only marginally stretched away from the surface.[18] An alternative way to find the “loop profile” eq 21, is to renormalize the “loop profile” for the melt case $S(n) \sim a^{-2}n^{-1/2}$: the monomer size $a \rightarrow \xi_b$ and the monomers index $n \rightarrow n/n_c$ (n_c is also the number of monomers within a correlation volume ξ_b^3).[13]

Inserting the solution of eq 21 into eq 20, we find that our neglect of the chain ends effects is valid whenever $n \ll N/2\Delta$ for any $1 \le n \le N$. If Δ is large, $N/2\Delta \ll N$, and the solution of eq 21 is not suitable. In this strong adsorption regime, the adsorbed chains do not keep their Gaussian shape: they stretch away from the interface to increase the number of adsorbed ends.[14] However, for small values of Δ (*weak adsorption regime*), $N/2\Delta \gg N$, the structure of the layer is not affected by this contribution to the free energy. In physical terms, this means that there is a range of values $0 \le \Delta \lesssim 1/2$ where all the chains ends are captured by the surface without disturbing the overall Gaussian shape of the chains. In practice, there is a further restriction to our model because there are two regimes in the weak adsorption limit: at very low Δ, only a fraction of ends of the adsorbed chain are captured.[19] This means that eq 10 is valid only for values of Δ larger than $1/2$. In what follows, we will assume that both conditions are fulfilled ($\Delta \sim 1/2$), and we will use eq 10 together with the solution of eq 21.

Note that this is a crude resolution of the system, and rigorously, the crossover between these two regions is smooth.

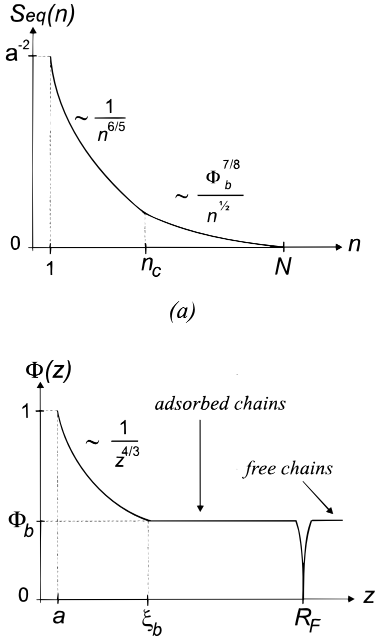
2.3. Discussion. At our scaling level, the “loop profile” at equilibrium in the weak adsorption regime is (Figure 2)

$$S_{\mathrm{eq}}(n) \sim \begin{cases} \dfrac{1}{a^2 n^{6/5}} & \text{for } n < n_c \sim \Phi_b^{-5/4} \\ \dfrac{\Phi_b^{7/8}}{a^2 n^{1/2}} & \text{for } n_c < n < N \end{cases} \qquad (23)$$

Then we can estimate the thickness of the layer made of adsorbed chains

$$H = \int_0^N \dot z_{\mathrm{eq}}(n)\,\mathrm{d}n \cong a\Phi_b^{-1/8}N^{1/2} \qquad (24)$$

We see that $H \cong R_F$, the natural size of one chain in the semidilute solution. Note that H is also $\xi_b(N/n_c)^{1/2}$, which means that, from the point of view of the extension, the interfacial layer is equivalent to a closely packed system of blobs of size ξ_b (this picture is not quite correct as explained below). The surface coverage (num-



(a)

(b)

Figure 2. (a) Qualitative plot of the loop profile S_{eq} vs n in the adsorbed layer from a semidilute solution (volume fraction Φ_b in the bulk). Two regions appear: self-similar for $1 < n < n_c$ and Φ_b -dependent for $n_c < n < N$ (see text). (b) Monomer volume fraction vs the distance from the adsorbing wall z.

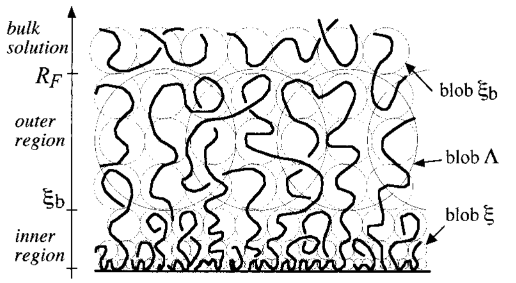


Figure 3. Scaling representation of the adsorbed layer.

ber (per cm^2) of monomers from adsorbed chain) is

$$\Gamma = \int_0^N S(n)\,\mathrm{d}n \cong a^{-2}(1 + \Phi_b{}^{7/8}N^{1/2}) \qquad (25)$$

This law for the surface coverage was first proposed by Marques and Joanny using a linear interpolation.[20] As mentioned by Daoud and Jannink,[12] eq 25 suggests that we distinguish two limits: when $\Phi_b \ll N^{-4/7}$, $\Gamma \cong a^{-2}$, and the average number of adsorbed monomer per chain scales as N; whereas when $\Phi_b \gg N^{-4/7}$, $\Gamma \cong a^{-2}\Phi_b{}^{7/8}N^{1/2}$ and the average number of adsorbed monomer per chain scales as $N^{1/2}$.

There is a simple geometrical picture associated with our results although the inner and outer regions have quite different structures (Figure 3).

The inner region (extension ξ_b) is formed of several self-similar blobs of size $\xi(z) \sim z$. At a scale smaller than the blob size, chain segments are self-avoiding. At a larger scale, the tails form linear strings of nonoverlapping blobs elongated in the z direction.

In the outer region, there are two different length scales: ξ_b and Λ. The basic unit is the blob of size ξ_b. For sake of clarity, we will call these blobs "Daoud blobs".[18] Again, at a scale smaller than ξ_b, the segments are self-avoiding. At a scale larger than ξ_b, the layer is equivalent to a melt of chains exposed to an interface provided that both the monomer size ($a \to \xi_b$), and the index of polymerization ($n \to n/n_c$) are renormalized. By analogy to the melt case, there is a second type of "blob" in the outer region. These are made of Gaussian strings of Daoud blobs, the important point being that these "super" blobs overlap laterally and their size is not given by the average local distance between tails, D.[21,22] Rather, their size scales as $\Lambda(n) \cong \xi_b(D(n)/\xi_b)^2$, and thus $\Lambda(z) \cong (\xi_b S_{eq}(n(z)))^{-1} \cong z$. At a scale larger than Λ, we have linear strings of the "super" blobs elongated in the z direction.

That our theory allows a continuous picture for the structure of the layer between dilute solutions and melt is easy to understand. In the case of dilute solutions ($\Phi_b \to 0$), we may neglect Π_b and μ_b, and what we minimize is F rather than Ω. Mathematically this is equivalent to set $\Phi_b = \Phi^* \cong N^{-4/5}$ in eqs 12 and 13. Then we have $n_c \sim N$ and the outer region vanishes. The autosimilar "loop profile" $S_{eq}(n) \cong 1/a^2n^{6/5}$, $z_{eq}(n) \cong an^{3/5}$ and the thickness $H \cong aN^{3/5}$ are recovered.[14] The case of molten polymer liquids can be found by setting $\Phi_b = 1$. Then the inner layer vanishes. In particular, the loop profile is $S(n) \sim a^{-2}n^{-1/2}$ and the extension of the layer is of the order of the Gaussian extension of a polymer chain.

Our results concerning the structure of the layer should be compared with the works of Semenov and Joanny[8,9] and Daoud and Jannink.[12] Essentially, our theory is in agreement with their results, and we will concentrate on the differences that we find. Daoud and Jannink have found that the size of large loops scales as $N\Phi_b^{3/4}$ for $\Phi_b < N^{-4/7}$ and as R_F for $\Phi_b > N^{-4/7}$. We find that all sizes between ξ_b and R_F are allowed for the loops, whatever Φ_b is in the semidilute regime. This is due to the entropy associated with the polydispersity in size of the loops.

Semenov and Joanny have found a (small) depletion hole at a distance H from the surface, whatever the regime: dilute, semidilute, or concentrated. Although we expect a depletion hole for the dilute case, that it may also be present in the semidilute case is rather counterintuitive. In our theory, Φ varies monotonically with z, and we do not find any depletion. Not withdrawing that this may be due to the absence of "smoothing functions" in our approach, we do not expect any depletion hole: the cost per unit surface to create a depletion hole of size l is $l\delta\Pi_{os}$ and may be huge.

Also Semenov and Joanny find an "anomalous" variation of Γ: the surface coverage decreases with N in the limit of very large N. Here again, we disagree. Consider the surface coverage Γ: $\Gamma \simeq \Gamma_1 + a^{-2}\Phi_b H$, an expression that is also found in the work of Semenov and Joanny. The quantity Γ_1 corresponds to the amount of monomers within the first sublayer. Significantly, Γ_1 is independent of N (and varies very slowly with Φ_b). Suppose we increase N at constant volume fraction. As H increases with N, we see that Γ always increases with N. In particular, we do not expect a nonmonotonic variation of Γ with N. It may well be that these results are artifacts of the self-consistent field theory.

3. Interfacial Tension

3.1. Case of Semidilute Solution. The surface tension γ is defined as the energy difference between the phase-separated system and the coexisting homogeneous system at the boundary

$$\gamma = \Omega\{S_{\mathrm{eq}},\dot{z}_{\mathrm{eq}}\} - \Omega\{\mathrm{bulk}\} \tag{26}$$

The thermodynamic potential $\Omega\{\mathrm{bulk}\}$ is solely the elastic energy in a slice of the bulk of thickness H. Thus, we have $\Omega\{\mathrm{bulk}\} \cong (k_{\mathrm{B}}T/N)\Phi_{\mathrm{b}}H \cong k_{\mathrm{B}}T(\Phi_{\mathrm{b}}{}^{7/8}/N^{1/2})$.

In what follows, we work in the limiting case $\Phi_{\mathrm{b}} \gg N^{-4/7}$, and we approximate $\Gamma \cong a^{-2}\Phi_{\mathrm{b}}{}^{7/8}N^{1/2}$. Keeping the complete expression in eq 25 would lead to unnecessary complications. Note that the range $N^{-4/5} \ll \Phi_{\mathrm{b}} \ll N^{-4/7}$ is very small in practice. Substituting eqs 17, 22, and 23 into eq 11 enables the interfacial tension for semidilute solutions to be calculated. For this calculation we should notice that for the interval $n_{\mathrm{c}} \leq n \leq N$, F_{vol} is compensated for by $(\mu_{\mathrm{b}}\Phi_{\mathrm{b}} - \Pi_{\mathrm{b}})H$ so that only elastic and entropic terms remain. The result is

$$\gamma(\Phi_{\mathrm{b}},N) \cong \gamma_0 - \kappa\gamma_1 + \frac{k_{\mathrm{B}}T}{a^2}\left\{-\alpha\Phi_{\mathrm{b}}{}^{5/4} + \beta\frac{\Phi_{\mathrm{b}}{}^{7/8}}{N^{1/2}}\ln\left(\frac{N}{\Phi_{\mathrm{b}}{}^{7/12}N^*}\right) + \delta\Phi_{\mathrm{b}}{}^{3/2}\right\} \tag{27}$$

where α, β, and δ are positive numerical factors of order unity. The sign of the coefficient δ is not easy to determinate: this coefficient results from the sum of different terms of the same order of magnitude. However, a mean field calculation of γ in series of Φ_{b} shows that the corresponding term ($\Phi_{\mathrm{b}}{}^{3/2}$) has a positive coefficient. Thus, we will assume that this term is positive. The quantity $N^* \cong e^{8/3\Delta}$, which appears in eq 27, is a characteristic polymerization degree of the polymer under consideration.

Whenever $\Phi_{\mathrm{b}} \ll 1$ it is sufficient to keep the leading terms of eq 27

$$\gamma(\Phi_{\mathrm{b}},\mathrm{N}) \cong \gamma_{\mathrm{ext}} - \alpha\frac{k_{\mathrm{B}}T}{a^2}\Phi_{\mathrm{b}}{}^{5/4} + \beta\frac{k_{\mathrm{B}}T}{a^2}\frac{\Phi_{\mathrm{b}}{}^{7/8}}{N^{1/2}}\ln\left(\frac{N}{\Phi_{\mathrm{b}}{}^{7/12}N^*}\right) \tag{28}$$

where $\gamma_{\mathrm{ext}} \cong \gamma_0 - \kappa\gamma_1$ is the value of γ extrapolated to zero dilution. Equation 28 is our central result. Two limiting cases are interesting.

In the limit of *infinite MW*, we find

$$\gamma(\Phi_{\mathrm{b}},N \to \infty) \cong \gamma_{\mathrm{ext}} - \alpha\,\frac{k_{\mathrm{B}}T}{a^2}\Phi_{\mathrm{b}}{}^{5/4} \tag{29}$$

This expression is precisely the result of the Widom–Cahn–de Gennes approach.[4] The result in eq 29 may be recovered directly by integration on the autosimilar domain of the Gibbs equation $\mathrm{d}\gamma/\mathrm{d}\mu = -\Gamma$ using the scaling law $\mu \cong k_{\mathrm{B}}T\Phi^{5/4}$. We can easily understand why its sign is negative: when the monomer chemical potential in the bulk increases, the formation of the interface costs less energy. The last term of eq 28 is the correction to the approximation of infinite MW. It arises from the competition between end chain effects and entropy of loops.

If we extrapolate eq 27 to the *concentrated regime*, we find

$$\gamma(\Phi_{\mathrm{b}} \to 1,N) \cong \gamma_\infty + \beta\frac{k_{\mathrm{B}}T}{a^2}\frac{\ln{(N/N^*)}}{N^{1/2}} \tag{30}$$

where

$$\gamma_\infty = \gamma_{\mathrm{air/melt}} - C\frac{k_{\mathrm{B}}T}{a^2} \tag{31}$$

where C is of order unity. This is what we find for the interfacial tension of molten polymer liquids.[3]

3.2. Comparison with Experiments. Although our approach has omitted several numerical coefficients of order unity, a quantitative comparison with experimental data is possible. Experimental measurements of the surface tension of semidilute solutions of polymers are scarce. To the best of our knowledge, we only know about old data concerning poly(dimethylsiloxane) (PDMS) in toluene (at, respectively, 24 and 19.5 °C).[6,7] However, these allow a good test of our approach for three reasons. First, because they provide data for the same polymer at rather different molecular weight and volume fraction. Second, because they are originated from different groups and type of experiments. Third, because we have already fitted experimental data of the same polymer in the concentrated regime (melt) with our theory.[3] These fits show that the variations of the interfacial tension with the MW follow eq 30. This work provides values for parameters such as N^* and β.

The interfacial tension is now identified with the surface tension of the system air/polymer solution. Written in terms of MW, eq 28 becomes

$$\gamma(\Phi_{\mathrm{b}},M_{\mathrm{n}}) \cong \gamma_{\mathrm{ext}} - \alpha\frac{k_{\mathrm{B}}T}{a^2}\Phi_{\mathrm{b}}{}^{5/4} + \beta M_{\mathrm{n0}}{}^{1/2}\frac{k_{\mathrm{B}}T}{a^2}\frac{\Phi_{\mathrm{b}}{}^{7/8}}{M_{\mathrm{n}}{}^{1/2}}\ln\left(\frac{M_{\mathrm{n}}}{\Phi_{\mathrm{b}}{}^{7/12}\,M_{\mathrm{n}}{}^*}\right) \tag{32}$$

where M_{n0} is the molecular weight of a monomer and $M_{\mathrm{n}}{}^* = N^*M_{\mathrm{n0}}$.

The comparison of eq 32 with the experimental data raises different problems. (a) We have to take into account the finite flexibility of the polymer backbone. The “theoretical” monomer (size a and MW M_{n0}) should be identified with an effective monomer of size $C_\infty l$ (Kuhn persistence length) and MW $C_\infty m$, where l and m are, respectively, the size and the MW of the chemical monomer. We find in the literature[23] $C_\infty = 5$ for PDMS and so we take $a = 0.73$ nm and $M_{\mathrm{n0}} = 185$ g·mol^{-1}. (b) Toluene is considered as a good solvent for PDMS, but we are far from the athermal situation (the Flory parameter χ defined by $v = a^3(1 - 2\chi)$ is 0.45).[24] In the Appendix, the loop profile and the interfacial tension are computed for the case of good solvents with $v < a^3$. Factors such as $v^{1/8}$ and $v^{1/12}$ appear in the expression of γ. However, their numerical values are very close to 1, and the law given in eq 28 that we have found is not essentially modified. Thus, we have fitted the data with the law in eq 32, which is valid for an athermal solvent.

It is important to realize that we only have two free parameters. In principle, the unknown parameters in eq 32 are: γ_{ext}, α, β, and $M_{\mathrm{n}}{}^*$. However, in the melt case,[3] we have fitted the law eq 30 for PDMS, and we have determined the empirical values of $M_{\mathrm{n}}{}^*$ and the coefficient β for PDMS: $M_{\mathrm{n}}{}^* = 17.6 \pm 0.1$ kg/mol; $\beta = 0.14 \pm 0.04$. They should be independent of both MW and concentration. In what follows, we have made use of these results, and we are thus left with two free parameters: γ_{ext} and α. Table 1 displays the empirical values of the different parameters that we have used

Table 1

α	0.46
β	0.17
M_n* (kg/mol)	17.58
γ_{ext} (M_n = 1 kg/mol) (mN/m)	24.86
γ_{ext} (M_n = 1.6 kg/mol) (mN/m)	24.90
γ_{ext} (M_n = 3.7 kg/mol) (mN/m)	25.00
γ_{ext} (M_n = 500 kg/mol) (mN/m)	25.37

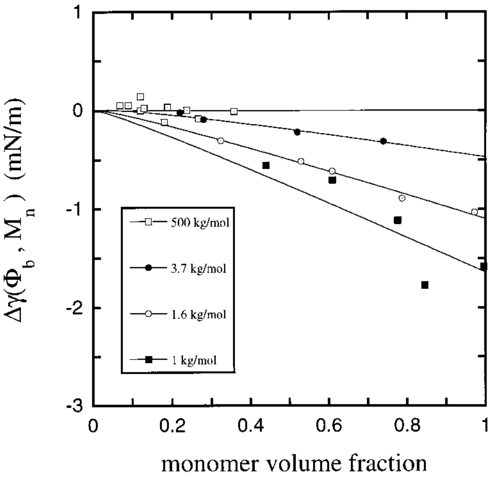


Figure 4. Variations of $\Delta\gamma(\Phi_b,M_n)$ (eq 33) for semidilute solutions of PDMS in toluene vs the monomer volume fraction Φ_b for several MW. The different symbols correspond to experimental data: T = 24 °C, M_n = 500 kg/mol,[6] and T = 19.5 °C, M_n = 1, 1.6, and 3.7 kg/mol.[7] Full lines are from eq 34 (see text for details).

in the fitting procedure. Note that α is indeed a numerical coefficient of order unity.

Our goal in this section is 2-fold: (a) to show that there is an experimental dependence of $\gamma(\Phi_b,M_n)$ with MW, and (b) to show that this dependence is well captured by our theory with no adjustable parameter. To this aim, we subtract the terms in eq 29, which are independent of MW. Explicitly, we plot $\Delta\gamma(\Phi_b,M_n)$ as a function of Φ_b and M_n where

$$\Delta\gamma(\Phi_b,M_n) = \gamma(\Phi_b,M_n) - \left(\gamma_{ext} - \alpha\frac{k_BT}{a^2}\Phi_b^{5/4}\right) \qquad (33)$$

and the experimental data are fitted with the equation

$$\Delta\gamma(\Phi_b,M_n) \cong \beta M_{n0}^{1/2}\frac{k_BT}{a^2}\frac{\Phi_b^{7/8}}{M_n^{1/2}}\ln\left(\frac{M_n}{\Phi_b^{7/12}M_n*}\right) \qquad (34)$$

Figure 4 displays the dependence of $\Delta\gamma$ on the monomer volume fraction for different MW solutions. To report experimental data, we have used the values of α and γ_{ext} given in Table 1. The significant point is that we observe a splay of experimental data for different MW when Φ_b increases. The splay is a signature of an explicit dependence in MW which is well fitted by eq 34. The relative correction due to this effect is of order 10% and has not be considered so far. At fixed Φ_b, we find an increase of γ with MW. This is explained by the fact that $M_n^* \cong 18$ kg·mol^{-1}, and then, the rhs of eq 32 is an increasing function of MW. For $M_n = 500$ g·mol^{-1}, this corrective term is negligible and the asymptotic law, eq 29, is reached.

It is worth mentioning that we have allowed for a small variation of γ_{ext} with the MW (see Table 1). In fact, rigorously, there is an additional contribution of the form $-(2\Delta M_{n0}/M_n)(k_BT/a^2)$ in γ_{ext} which comes from the first term of the rhs of eq 25. This contribution is expected to be always negligible both in comparison to $\gamma_0 - \kappa\gamma_1$ and to $(k_BT/a^2)\Phi_b^{7/8}/M_{n0}^{1/2}\ln(M_n/\Phi_b^{7/12}M_n^*)/M_n^{1/2}$. From the values displayed in Table 1, we see that this variation is indeed very small for the set of data published in ref 7: $\gamma_{ext} \cong 24.90$ mN/m. For the set of data published in ref 6, we obtain a slightly larger value ($\gamma_{ext} \cong 25.37$ mN/m), which is most probably due to a systematic error in the experimental data.

4. Concluding Remarks

The above analysis provides a framework for studying the behavior of polymers at interfaces which can be generalized to other solvent conditions and other geometries. The use of a "scaling functional theory" enables us to calculate both the structure of the interface, and the interfacial tension of the polymeric solution. This is done "from first principles", without any a priori assumption concerning the structure of the adsorbed chains.

Among the most important results, we find a dependence on MW of the interfacial tension of semidilute solutions. This dependence reflects the competition between the entropy associated with a large distribution of loop sizes at the interface and the specific attraction of the chain ends. That our approach provides such a dependence (unlike the case of the Widom–Cahn–de Gennes approach, e.g.) is due to our use of a different tool to describe the interface. We focus on a quantity called "loop distribution profile", $S(n)$, which is a function related to the distribution of sizes of the various loops and tails that adsorb at the interface. In certain cases, (adsorption from a dilute solution, e.g.), this function is a similar tool as the volume fraction profile $\phi(z)$ (in the sense that both functions carry the same information concerning the structure of the interface). In other cases, however, this is not true and the functions S and ϕ are essentially different objects. The "outer region" of the adsorbed layer provides a good example of this difference. There, $\phi(z)$ is constant ($\phi(z) \sim \phi_b$), whereas $S(n)$ is a power-law type of function $S(n) \sim n^{-1/2}$. Hence, ϕ does not give us any clue about the structure of the layer. From this example, we see that this function S is probably a more fundamental tool to study interfaces of macromolecules.

The functions S and ϕ are not simply related. It is not clear at present whether our functional F (written in terms of S) contains the same physics as the functional used in self-consistent field type of approaches (written in terms of ϕ). For example, we have an explicit entropic contribution in F associated with the wide loop size distribution, whereas it is not obvious that this term exists in SCF theories. At least, it is not explicitly written. That both approaches give essentially the same result in numerous cases (Θ-solvents, e.g.) suggests that both theories carry the same physics at a more fundamental level. Although it would be desirable to explicit this aspect, this is clearly out of the scope of this article. We leave this point for another study.

We have considered only saturated surfaces ($\gamma_1 \gtrsim k_BT/a^2$). It would be simple to generalize our model to cases where the first layer of adsorbed monomers is not dense. This would amount to leaving the quantity $S(0)$ free, subjected to an additional minimization of the functional. We expect that an additional sublayer appears, very close to the surface, where the "loop profile" would depend on the value of γ_1.[25,26] Unless we go to very small values of γ_1, it is reasonable to think that our essential results will not be drastically modified.

In principle, our model in valid for $\Delta \lesssim {}^1/_2$. The upper bound is not a serious limitation in practice, unless the ends have been chemically modified. That Δ should not be too small is a more delicate matter. In the absence of any experimental measurement, we cannot assert that this condition is satisfied for the polymers that we have considered.

In this model, we do not describe the interpenetration of the free chains and the adsorbed chains, which is a crude hypothesis. The question is to know whether this effect would introduce a new characteristic length into the problem. It is plausible that free chains penetrate the adsorbed layer on a length equal to the size of the last "super blob" $\Lambda(N) \sim R_F$. If this is so, no additional characteristic length appears. In other words, this effect should modify the numerical factors in front of eq 23, but not the scaling dependences. A direct confirmation of that point is provided by experiments on irreversibly adsorbed layers, where the loop distribution in the melt limit is measured after the free chains have been removed.[27]

Although scaling laws have been used, a quantitative comparison with experiments is possible. Our conclusions were successfully confronted with the experimental data that are available in the literature. This study, together with that concerning the melt case,[3] brings both a coherent picture for the interfacial properties, and a theoretical explanation of the various experimental features of polymeric liquids in the semidilute regime and concentrated regime.

Appendix

In this Appendix we estimate the "loop profile" and the interfacial tension first for a Θ -solvent and then for a solvent which is good but not athermal.

For a Θ -solvent, the two-body interactions vanish and three-body-interactions dominate. Thus, an isolated coil is nearly ideal. The semidilute regime has the following characteristics:[1] the overlap threshold is $\Phi^* \simeq N^{-1/2}$, the correlation length is $\xi = a\Phi^{-1}$, and the osmotic pressure is $\Pi \simeq k_B T/a^3\Phi^3$. The osmotic contribution eq 6 and the elastic one eq 8 are changed into

$$F_{\rm vol} \cong \frac{k_B T}{a^2}\int \Phi(z)^3\,{\rm d}z \cong \frac{k_B T}{a^2}\int_0^N (a^2 S(n))^3 \left(\frac{\dot z(n)}{a}\right)^{-2} {\rm d}n \qquad (35)$$

and

$$F_{\rm el} \cong \frac{k_B T}{a^2}\int_0^N a^2 S(n) \left(\frac{\dot z(n)}{a}\right)^{2} {\rm d}n \qquad (36)$$

Proceeding in the same manner than in section 2, we get the following equilibrium "loop profile"

$$S_{\rm eq}(n) \sim \begin{cases} \dfrac{1}{n} & \text{for } n < n_c \cong \Phi_b^{-2} \\ \dfrac{\Phi_b}{n^{1/2}} & \text{for } n_c < n < N \end{cases} \qquad (37)$$

Then the interfacial tension, from eq 26, is

$$\gamma_\Theta(\Phi_b,N) \cong \gamma_{\rm ext} + \frac{k_B T}{a^2}\left\{(-\alpha + 2\eta \ln \Phi_b)\Phi_b^{\,2} + \beta\frac{\Phi_b}{N^{1/2}}\ln\left(\frac{N}{\Phi_b^{\,2/3}N^*}\right)\right\} \qquad (38)$$

where η is a constant of order unity.

A solvent that is good but not athermal is defined by $v < a^3$ (in what follows, we will define the excluded volume parameter as $\tilde v \equiv v/a^3$). These semidilute polymer solutions are characterized by two correlation lengths: $\xi \sim a\tilde v^{-1/4}\Phi^{-3/4}$ for two-body interactions and $r_B \sim \tilde v^{-1}$ for three-body interactions (r_B is smaller than ξ).[1] At scales $r < \xi$, a chain behaves as a free chain: for $r < r_B$, the chain is nearly ideal; for $r_B < r < \xi$, the chain is swollen (excluded volume interactions dominate). At scales $r > \xi$, the solution is a melt of semidilute blobs.

There are two technical modifications that we must perform to describe this situation for an adsorbed layer: (a) for $z < r_B$ (or $n < g_B \sim \tilde v^{-2}$), the osmotic and elastic contributions are similar to those in eqs 35 and 36; (b) for $z > \xi$, eqs 6 and 8 are valid provided that the explicit dependence in $\tilde v$ is inserted. Thus, we have for the osmotic energy

$$F_{\rm vol} \cong \frac{k_B T}{a^2}\int_{r_B}^{H} \tilde v^{3/4}\Phi(z)^{9/4}{\rm d}z \cong \frac{k_B T}{a^2}\int_{g_B}^{N} \tilde v^{3/4}(a^2 S(n))^{9/4}\left(\frac{\dot z(n)}{a}\right)^{-5/4}{\rm d}n \qquad (39)$$

The spring constant of each monomer is now $k_B T(a^2 g/\xi^2) \sim k_B T(a^2 g/\xi^2)(\xi^{5/3}/a^{5/3}\tilde v^{1/3}) \sim \tilde v^{-1/4}\,\Phi^{1/4}$, and the elasticity eq 8 is modified into

$$F_{\rm el} \cong \frac{k_B T}{a^2}\int_{g_B}^{N}\left\{\tilde v^{-1/4}(a^2 S(n))^{5/4}\left(\frac{\dot z(n)}{a}\right)^{7/4}\right\}{\rm d}n \qquad (40)$$

This yields for the "loop profile"

$$S_{\rm eq}(n) \sim \begin{cases} \dfrac{1}{n} & \text{for } n < g_B \sim \tilde v^{-2} \\ \dfrac{1}{\tilde v^{2/5} n^{6/5}} & g_B < n < n_c \sim \tilde v^{-3/4}\Phi_b^{-5/4} \\ \dfrac{\Phi_b^{\,7/8}\tilde v^{1/8}}{n^{1/2}} & \text{for } n_c < n < N \end{cases} \qquad (41)$$

and for the interfacial tension, from eq 26

$$\gamma(\Phi_b,N) \cong \gamma_{\rm ext} + \frac{k_B T}{a^2}\left\{(-\alpha + 2\eta \ln \tilde v)\,\tilde v^{3/4}\Phi_b^{\,5/4} + \beta\frac{\tilde v^{1/8}\Phi_b^{\,7/8}}{N^{1/2}}\ln\left(\frac{N}{\tilde v^{1/12}\Phi_b^{\,7/12}N^*}\right)\right\} \qquad (42)$$

As is expected, we recover the athermal case (eq 28) by setting $\tilde v = 1$, and the Θ-solvent case (eq 38) by identifying $\tilde v \cong \Phi_b$.

Acknowledgment. We are grateful to Elie Raphaël and Mohamed Daoud for useful discussions.

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(16) The volume free energy is in fact $F_{\mathrm{vol}} = \int f_{\mathrm{vol}}\,\mathrm{d}z = \int(-\Pi_{\mathrm{os}} + \mu\Phi)\,\mathrm{d}z$ where Π_{os} and μ are respectively the osmotic pressure and the chemical potential in the layer. According to scaling laws $\Pi_{\mathrm{os}} = \Phi^2[\partial(f_{\mathrm{vol}}/\Phi)/\partial\Phi] = (k_BT/a^3)\Phi^{9/4}$ gives $f_{\mathrm{vol}} = {}^4/_5(k_BT/a^3)\Phi^{9/4}$ and $\mu = {}^9/_5(k_BT/a^3)\Phi^{5/4}$. Thus, although f_{vol} and Π_{os} are different from a thermodynamical point of view, they are proportional.

(17) As we use scaling laws, the calculated quantities will be power laws of the form $n^{-\rho}$ with $\rho > 0$. Some of this quantities, when integrated, leave a divergence in 0 which has no physical meaning. This is because we forget the "smoothing functions" which would bring technical complications without much physics. As an example, the mathematical solution of eqs 14 and 15 is $S_{\mathrm{eq}}(n) \sim 1/(n + b)^{6/5}$, where b is a constant of order unity, rather than eq 16. Constants such as b would make all the integrals converge. A simple way to mimic the presence of these constants is to keep the scaling form $n^{-\rho}$ but to perform the integration over a smaller range of values: $\int_1 n^{-\rho}\,\mathrm{d}n$ rather than $\int_0 n^{-\rho}\,\mathrm{d}n$.

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MA000099U