

Organization of polymers at interfaces

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We consider a set of “simple” polymer chains (linear, flexible, neutral, homogeneous) in the presence of a flat solid-liquid interface, where the surface is attractive and the chains adsorb reversibly. We show that the scaling approach recently proposed by Aubouy, Guiselin, and Raphaël (AGR) [*Macromolecules* **29**, 7261 (1996)] to describe polymer layers theoretically is able to explain the major features of these interfaces: (i) The polymer chains build an interfacial layer with a well-defined structure. (ii) There is preferential adsorption of the longest chains in the dilute regime. (iii) There is preferential adsorption of the shortest chains in the concentrated regime. (iv) Ultrathin polymer films dewet surfaces that thick films would wet. We can thus (a) identify a single physical process responsible for all these different behaviors, namely: the competition between the entropy of the set of loops (which favors the “dense states” of the layer) and the repulsive loop-loop interactions (which favors the “dilute states” of the layer), and (b) show that the AGR approach may provide the basis of a powerful and wide-ranging theory of polymers at interfaces. [S1063-651X(97)14309-4]

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I. INTRODUCTION

The subject of polymers at surfaces or interfaces has been the focus of intense experimental and theoretical study in recent years for a variety of reasons. The first is the technical importance of the subject, with applications in adhesives, wetting, lubrication, and colloid stabilization [1], to name but a few (for a general survey of the field see [2] and [3]). The second driving force is that there has been considerable progress made in the understanding of bulk properties of polymers. However, there are deeper problems when one considers surfaces and interfaces, which must be inhomogeneous systems. In spite of this interest, and a vast body of literature, it is reasonable to argue that the physical processes involved are not fully understood [4].

In this paper, our main interest will be in systems where a set of “simple” chains (linear, flexible, neutral, homogeneous) are in the presence of a flat solid-liquid interface, where the surface is attractive and the chains are reversibly adsorbed. This is the “simplest” situation (at least conceptually) and many unambiguous experimental results have been collected so far. Some of the most interesting features are the following: (i) In the dilute regime, the polymer chains build an interfacial layer with a well-defined structure [5–7]. (ii) If a mixture of two sets of chains differing in length only is exposed to the same surface, there is preferential adsorption of the longest chains in the dilute regime [8–13]. (iii) If a melt (i.e., polymer chains without any solvent whatever) comprised of two kinds of chains differing in length only is put in the presence of a surface, there is preferential adsorption of the shortest chains [14–17]. (iv) Dry polymer films, which would normally wet a surface, were observed to dewet the surface when the film thickness fell below a certain threshold [18–20].

On the theoretical side, the situation is complex. Each of these effects has received both a different theoretical explanation and a different theoretical treatment. For example,

Scheutjens and Fleer [21] devised a very detailed self-consistent field theory for preferential adsorption in the dilute regime [point (ii)]. However, their work is a mean-field type of analysis that ignores the effects of chain correlation, and is therefore not appropriate for describing the equilibrium structure of the layer [point (i)], where fluctuations cannot be neglected. This has been shown by de Gennes [7]. In addition, their arguments do not account for what happens in the concentrated regime [point (iii)]. Another example is de Gennes’ description of an adsorbed layer at equilibrium [7] [point (i)]. This model is based on a powerful scaling argument and the result is quite straightforward. This approach has one disadvantage, however: it does not give us any clue concerning the driving force behind the construction of the layer. This means that de Gennes’ arguments cannot be used to discuss related situations, such as those listed above, very easily.

Very recently, however, Aubouy, Guiselin, and Raphaël [22] (AGR) presented a new approach that complements the earlier scaling description of polymer interfacial layers. The basic idea is to describe an arbitrary polymer layer as a population of loops and tails. By a loop, we mean a chain segment between two adsorbed monomers that does not touch the surface. The layer is then treated as a statistical ensemble of these objects. This idea was first postulated in the 1960s and has been used already by Silberberg [23] and Hoeve *et al.* [24]. However, these authors considered a very detailed picture for the loops and tails, and the resulting scheme appeared complicated. The new approach (a) finds a simple description for the loops and tails that retains the essential physics and allows for analytical results, and (b) incorporates scaling laws [25]. Fortunately, this appears to be feasible, and works quite well. In particular, one can write a free energy term that accounts for the structure of the layer whatever the solvent conditions may be. This method provides an entirely new way to recover de Gennes’ results [7] (which were experimentally confirmed [5]), and has far reaching

consequences. In particular, the construction of the layer can be understood as a compromise between entropy (which favors polydispersity of the set of loops), and repulsive interactions (e.g., two-body interactions in “good” solvent conditions), which favor states with the lowest number of loops per unit area.

In this paper, we show that the AGR approach may be applied successfully to describe the situations listed above, which correspond to the most specific features of polymer interfacial layers. The complete modeling of each of these situations is a formidable task, and is beyond the scope of this paper. Rather, our aim is to (a) identify a single physical process responsible for all these different behaviors, namely, the competition between entropy and repulsive interactions, and (b) show that the AGR approach may provide the basis of a powerful and wide-ranging theory of polymers at interfaces. In view of this, we concentrate our attention on the physical processes involved in these layers. Accordingly, we restrict our attention to “simple” situations and mainly qualitative discussions. By “simple” situations, we refer to monodisperse or bidisperse solutions in either the dilute or the melt regime.

Firstly, the AGR approach [22] is introduced (Sec. II) by describing an arbitrary polymer layer in terms of the loop distribution profile S , defined as

$$S(n) \text{ is the number (per unit surface) of loops or tails having more than } n \text{ monomers.} \quad (1)$$

To an approximation, it can be shown that the free energy (per unit surface) of the interfacial layer (\bar{F}) can be simply written as a functional of S . Minimizing \bar{F} with respect to S gives the equilibrium loop distribution profile, S_{eq} . This result allows discussion of the equilibrium structure of the layer [point (i)].

The problem of preferential adsorption in the dilute regime [point (ii)] is then considered (Sec. III). The free energy of the layer, $\bar{F}[\{S_{\text{eq}}\}]$, is a decreasing function of the polymerization index of the chains. This means that the interface will always lower its energy by replacing the polymer chains present by longer ones. We thus predict preferential adsorption of the longest chains.

These predictions do not hold in the concentrated regime, as detailed in Sec. IV. The crucial point is that “free” chains are always present inside the interfacial layer whenever the concentration is high. By “free” chains, we mean chains that are not in direct contact with the surface. These “free” chains decrease the loop density due to space filling reasons. The net result is a decrease in the interfacial free energy. In this section, we consider an interfacial layer made of monodisperse N -chains in the presence of a melt of monodisperse P -chains, and we compare two situations: (a) $N \gg P$, and (b) $N \ll P$. In the absence of interpenetration, the former situation would be favored, as explained in Sec. II. We show that the presence of “free” chains dramatically affects this conclusion, and indeed situation (b) is favored. Hence we predict preferential adsorption of shorter chains in the concentrated regime [point (iii)].

In Sec. V, we consider the equilibrium properties of thin polymer films [point (iv)]. We explain that a film made of

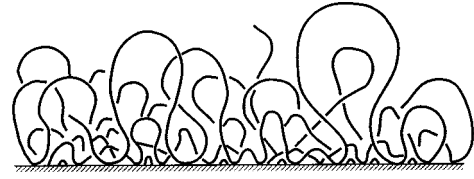


FIG. 1. Sketch of a polymer layer.

long chains (N monomers) which is confined [i.e., whose thickness (h) is below the natural extension of one chain ($R_G \sim N^{1/2}$)] is equivalent to a layer of shorter chains (n_c monomers, with $h \sim n_c^{1/2}$) at equilibrium. Then, the same physical process that favors the presence of long chains at the interface in the dilute regime, now favors high values of n_c , hence high values of h . This can be written in terms of an effective “disjoining pressure,” which tends to thicken the film, and thus enhance dewetting.

In the following discussion, we concentrate on scaling relations, and all numerical factors will be omitted.

II. SCALING DESCRIPTION OF A POLYMER LAYER: THE AGR APPROACH

In this section, we consider an arbitrary layer consisting of overlapping polymer chains, as depicted in Fig. 1. For simplicity, we assume that the chains are strongly attracted to the surface, so that the immediate vicinity of the interface is saturated with monomers. Formally, this is when the number of loops or tails per unit area (S_0) is of the order of $1/a^2$, a being the size of the monomer [note that $S_0 = S(1)$]. It is reasonable to argue that this occurs when the energetic gain for a monomer in direct contact with the surface is of the order of T , the thermal energy (hence this assumption is not incompatible with the hypothesis that the adsorption is reversible [26,27]). In practice, this situation is the most common case. We consider initially the case of an athermal solvent, i.e., a “good” solvent characterized by an excluded volume parameter $v \cong a^3$ [25]. As we will see, this is a generic case. In this section, we follow closely the presentation of Ref. [22]. The reader may refer to this article for a detailed discussion of the hypothesis or the calculations.

In a simplified view, we can visualize each loop of $2n$ monomers as two independent tails of n monomers each, and assume that all the tails behave in a like manner. The behavior of all the different tails is therefore described by a single trajectory $n(z)$, where n is the arc length parameter, and z the spatial position: all n th monomers of any tail (having more than n monomers) are situated at the same height z above the surface.

At this stage, an important tool is the loop density profile, defined in Eq. (1). It is easy to prove in particular that the average distance between tails at an altitude z , $D(z)$, scales as $S(n)^{-1/2}$, and the monomer density obeys $\dot{z}\phi(z) \sim S(n(z))$ (\dot{z} denotes the derivative of z with respect to n). Following Refs. [28] and [29], we argue that the tails behave independently at a scale lower than D , and stretch away from the surface at a scale larger than D , in order to reduce two-body repulsive interactions. This can be written as

$$\frac{\partial z}{\partial n} \cong a(a^2 S(n))^\nu, \quad (2)$$

where $\nu=1/3$. It is useful to picture each tail as a string of subunits, called ‘‘blobs’’ [25], whose size D increases with z . In this terminology, Eq. (2) expresses the fact that (a) the string is linear, and that (b) inside one blob, the chain segment is a three-dimensional self-avoiding walk.

If the function S is known, these results are enough to completely characterize the layer. For example, if we have a polymer ‘‘brush’’ (i.e., monodisperse N chains attached by their ends to a repulsive surface [30]), with σ chains per unit surface, the loop density profile is a step function:

$$S(n) \cong \sigma, \quad 1 \leq n \leq N. \quad (3)$$

Integrating Eq. (2), e.g., gives the thickness of the ‘‘brush’’: $L \cong aN(a^2\sigma)^{1/3}$.

To discuss situations where S is not known, we estimate the interfacial free energy per unit surface (\bar{F}). In general, \bar{F} can be split into a contribution that describes the interactions between the monomers and the surface (\bar{F}_S), and a contribution from the layer (\bar{F}_L), comprising the effect of the deformation of the loops and the repulsive interactions between the monomers:

$$\bar{F}[\{S\}] \cong \bar{F}_S(S_0) + \bar{F}_L[\{S\}]. \quad (4)$$

Here, we are working in the limit where the monomer density in the immediate vicinity of the surface is constant ($S_0 = 1/a^2$); and in this situation, the term \bar{F}_S is irrelevant to the structure of the layer. When studying wetting properties of polymer films, this term is important, but until this is discussed in Sec. V we will equate \bar{F} with \bar{F}_L . From Ref. [22], for a layer at equilibrium, we may write

$$\begin{aligned} \bar{F}_L[\{S\}] \cong & \frac{T}{a^2} \int_1^N \{k(a^2 S(n))^\beta \\ & + (-a^2 \dot{S}(n)) \ln(-a^2 \dot{S}(n))\} dn, \end{aligned} \quad (5)$$

with $\beta=11/6$. In Eq. (5), k is a numerical factor of the order of unity. The first term accounts for both the elastic free energy of the loops and the loop-loop repulsion. This contribution may be evaluated by assuming that each blob contributes an energy of order T to the free energy (the well-known ‘‘ T per blob’’ ansatz [25]). An alternative way to reach the same result is to realize that the AGR approach is a local description of the layer in terms of polymer ‘‘brushes.’’ This is clear from Eq. (3), where we see that S can be understood in terms of a local grafting density. The osmotic contribution to the free energy in the case of an arbitrary layer is thus a generalization of the results found for a polymer ‘‘brush’’ [28,29]: $\bar{F}_B \cong N(a^2\sigma)^{11/6}T/a^2$ (athermal solvent). Formally, we can state the following relationship:

$$\begin{aligned} & \frac{T}{a^2} (a^2\sigma)^{11/6}N \quad (\text{‘‘brush’’}) \\ & \rightarrow \frac{T}{a^2} \int_1^N (a^2 S(n))^{11/6} dn \quad (\text{arbitrary layer}). \end{aligned} \quad (6)$$

It is important to realize that Eq. (5) correctly accounts for intraloop correlations, but neglects interloop correlations. This is because the repulsive interactions between the loops are calculated at their mean position. In that sense, we have treated the set of loops at a mean-field level. The second term in Eq. (5) is an estimate of the entropy of the set of loops.

We may then evaluate S for a layer at equilibrium. Minimizing \bar{F}_L over S gives

$$S_{\text{eq}}(n) \cong \frac{1}{a^2 n^\alpha}, \quad 1 \leq n \leq N, \quad (7)$$

with $\alpha=(\beta-1)^{-1}=6/5$. As explained above, finding the characteristics of the layer is now a simple task. For example, the extension of the layer is $aN^{3/5}$, and the volume fraction decreases as $z^{-4/3}$. These are the same results as those obtained by de Gennes in a completely different manner [31], and they were also successfully compared with experimental data [5]. The AGR approach, however, has one advantage: it provides a simple model for the physical processes involved in these systems. It is clear from Eq. (5) that the equilibrium structure results from a compromise between entropy and repulsive loop-loop interactions.

As is usual in scaling laws, another solvent condition is characterized by a different set of exponents. Table (8) gives the exponents that describe the cases of ‘‘theta’’ solvents and melts (i.e., no solvent present). The change in the value of the exponents corresponds to a change in the nature of the repulsive loop-loop interactions, and these are listed in table (8):

	α	ν	β	Origin of the repulsion	
‘‘Good’’	6/5	1/3	11/6	Two-body interactions	(8)
‘‘Theta’’	1	1/2	2	Three-body interactions	
Melt	1/2	1	3	Induced stretching	

The case of a melt deserves a special comment, however. What is described is a layer made of polymer chains without any solvent. This means that the penetration of the layer by other ‘‘free’’ polymers is not allowed, as they would play the role of a solvent. Indeed, it is easy to show that Eq. (2) with $\nu=1$ leads to a volume fraction in monomers from adsorbed chains which is a step function: $\phi(z)=1$, if $a \leq z \leq aN^{1/2}$ and $\phi(z)=0$ instead. This analysis is thus not appropriate for describing the interface of a bulk melt of chains. We return to this problem in Sec. IV.

Perhaps the most interesting consequence of the AGR analysis (which was not emphasized in Ref. [22]) is that the behavior of the layer is consistent with the hypothesis that the loops are independent. This is clearly not obvious. Consider, for definiteness, an interfacial layer made of N -chains in a ‘‘good’’ solvent in the dilute regime. One adsorbed chain can be treated as a succession of loops of different sizes. In our language, a ‘‘train’’ (i.e., a segment of chain made of adsorbed monomers) is a succession of loops of one monomer. We do not distinguish between loops and tails. If this chain was isolated on the surface, we would expect that two adjacent loops would be strongly correlated. What this analysis suggests is that in the limit where many chains are present at the interface and overlap, these are not correlated. This is very much reminiscent of what happens in three-dimensional melts where the long range excluded-volume

interactions are screened by the overlapping from other chains [25]. In both of these cases two adjacent units [monomers in three-dimensional (3D) melts, loops in 2D dense layers] behave as if they were independent. However, further work in this direction is needed before we can establish a complete analogy.

III. PREFERENTIAL ADSORPTION IN THE DILUTE REGIME

The basic experiment is described as follows: a solution containing a mixture of two polymer chains differing only in length is exposed to an attractive surface. Both the adsorption isotherm of the mixture and the adsorbed amount of each component is measured (by, e.g., gel permeation chromatography). In the plateau region of the adsorption isotherm, the data show that the longest chains are adsorbed, and the shortest chains remain in solution. In this section, we would like to propose an explanation for this preferential adsorption based on the AGR approach.

We consider an adsorbed layer in equilibrium with a dilute solution. If the concentration of the solution is sufficiently low, "free" chains do not penetrate into the layer. This is because any "free" chain in the layer pays a penalty because of the repulsive interactions with the adsorbed chains. It is reasonable to argue that whenever the concentration of the bulk is below the overlapping threshold, this penalty is prohibitive, and the "free" chains can be taken as absent. In this limit, the scaling description of the layer presented in the first section is appropriate, and we may calculate the interfacial free energy $\bar{F}_L[\{S_{eq}\}]$. Combining Eqs. (5) and (7), we find that

$$\bar{F}_L[\{S_{eq}\}] \cong \bar{F}_0 + B_1 \frac{T}{a^2 N^{6/5}} (\ln N + C_1), \quad (9)$$

where \bar{F}_0 is a constant of order T/a^2 , and B_1 and C_1 are numbers of order unity. (The precise values of these constants depend on the various prefactors of order unity that we omitted, and are not relevant.) Figure 2 displays the variations of $\bar{F}_L[\{S_{eq}\}]$ with respect to N . This function shows a maximum for $N \cong e^{-C_1}$, and is a decreasing function of N for larger values of N . Since e^{-C_1} is of order unity, the interfacial free energy is a decreasing function of the index of polymerization of the chains at every values. This means that the interface would always lower its free energy by re-

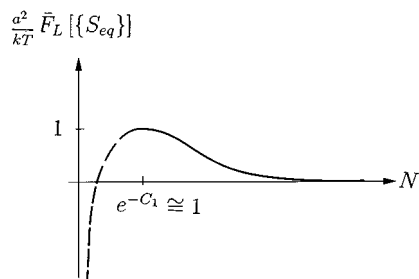


FIG. 2. Variations of the interfacial free energy (per unit area) as a function of the index of polymerization of the chains (N) for an adsorbed layer in equilibrium in the dilute regime.

placing the polymer chains present by longer ones. This is possible when the bulk solution is a mixture of chains of different lengths.

Within the AGR approach, the interpretation of this effect is quite straightforward: the longer the chains, the greater is the selection of accessible sizes for the loops. Thus the entropy of the layer increases with N due to the increase in the number of possible arrangements of loops on the surface. Equation (4) with $\bar{F}_L[\{S\}]$ given by Eq. (9) is an expression that can be proposed for the surface tension of adsorbed chains from dilute solutions. Unfortunately, we are not aware of any experimental data for this quantity. These would provide a quantitative verification of the ideas presented in this section.

Many of the experimental studies of preferential adsorption involve exposing an adsorbed layer made from short chains to a solution of long chains and observing the kinetics of exchange [21]. A very interesting consequence of the above analysis is that the state of the layer is no longer given in terms of chain density, but in terms of loop density. (This is of course a consequence of the fact that there is no correlation between two different loops, as explained in Sec. II.) For example, the equilibrium state requires, on average, a certain number of loops of n monomers ($1 \leq n \leq N$), but it does not matter if these are segments of chains of N or P monomers, with $n < P, N$. This means that the same state of equilibrium might be achieved with monodisperse or polydisperse chains, provided that the global distribution of loops is that of the least overall free energy. In particular, a small fraction of short chains could well be present at equilibrium in a layer exposed to a solution of long chains. Signs of this effect might be evident in the experiments of Ref. [11] where it is observed that the displacement of short chains by longer ones is never complete. Current work is being carried out in this direction.

IV. PREFERENTIAL ADSORPTION IN THE CONCENTRATED REGIME

The crucial feature in the high concentration regime is that "free" chains (i.e., chains that are not in direct contact with the surface) are always present in the layer. Our purpose in this section is to show that this effect is responsible for preferential adsorption of shorter chains. A complete theoretical model for preferential adsorption from a concentrated solution implies a careful examination of the organization of a polydisperse solution in the presence of an interface, and is a formidable task. Here, we wish to enlighten the physical processes involved, and so we simplify the problem. Firstly, we restrict our attention to melts only. Secondly, we consider an interfacial layer made of *monodisperse* N -chains in the presence of a melt of *monodisperse* P -chains. Our strategy is to compare the two following situations: (a) where the adsorbed chains are longer ($N \gg P$), and (b) where the adsorbed chains are shorter ($N \ll P$). This is performed by the AGR approach which gives a very crude picture for the interfacial layer in the concentrated regime, but plausibly retains the essential physics.

The situation (a) is discussed first. To estimate the loop distribution profile of the layer, it is useful to remember the relation between the "brush" and the arbitrary layer [see Eq.

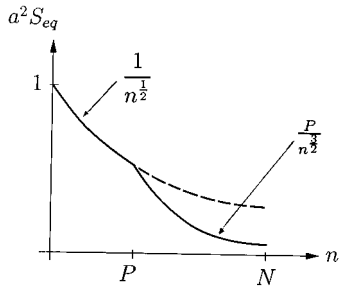


FIG. 3. Variations of the loop density profile S (see text) as a function of the index of polymerization of the chains (N) for an adsorbed layer in equilibrium with a melt of shorter chains (P monomers per chain).

(6)]. For a “brush” immersed in a solvent of high molecular weight (i.e., a solvent made of polymer chains), the osmotic contribution to the free energy (per unit area) is [32] $\bar{F}_B \cong N(a^2\sigma)^{5/3}P^{-2/3}T/a^2$. (Strictly, this last result is only valid at the limit $N \ll P^2$, but it is sufficient to consider this limit without loss of generality.) In this case, the free energy (per unit area) may then be written as

$$\bar{F}_L[\{S\}] \cong \frac{T}{a^2} \int_1^N \{kP^{-2/3}[a^2S(n)]^{5/3} + [-a^2\dot{S}(n)]\ln[-a^2\dot{S}(n)]\} dn. \quad (10)$$

Minimizing Eq. (10) with respect to S gives $S_{\text{eq}}(n) \cong P/(a^2n^{3/2})$.

However, a solvent of high molecular weight is expelled from the layer if the local tail density is too high, as shown by de Gennes [29]. This means that there is a region near the solid surface where the P -chains do not penetrate. In this region, we expect that the results obtained for an adsorbed melt (quoted in Sec. II) should be valid, and accordingly $S \sim n^{-1/2}$. Requiring that the loop density profiles cross over gives the final result:

$$S_{\text{eq}}(n) \cong \begin{cases} \frac{1}{a^2n^{1/2}} & \text{for } 1 \leq n \leq P \quad (\text{“dry” region}) \\ \frac{P}{a^2n^{3/2}} & \text{for } P \leq n \leq N \quad (\text{“wetted” region}). \end{cases} \quad (11)$$

Equation (11) already contains a lot of physics. First, it is important to realize that the penetration of the P chains inside the layer results in a decrease in the loop density. This is clear from Fig. 3, where the loop density profile is plotted: in the absence of interpenetration, we would expect $S_{\text{eq}}(n) \cong 1/a^2n^{1/2}$ for $1 \leq n \leq N$ [see Eq. (7)]; this function corresponds to the dashed line. The physical origin of this effect is that the number per unit surface of loops or tails diminishes when they are surrounded by P chains due to space filling reasons. Moreover, the loop density profile in the wetted region is an increasing function of P : $S_{\text{eq}} \sim P$. This means that the shorter the chains, the stronger this effect. Secondly,

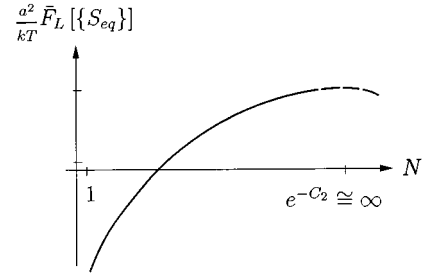


FIG. 4. Variations of the interfacial free energy (per unit area) as a function of the index of polymerization of the chains (N) for an adsorbed layer in equilibrium with a melt of shorter chains (P monomers per chain).

as the index of polymerization of the solvent is increased, the “free” chains are progressively expelled from the layer: $S_c \sim P^{-1/2}$.

In fact, Eq. (11) also gives the answer to what happens in case (b). Since total expulsion of the solvent occurs for $P = N$, longer “free” chains do not penetrate the layer. This has two consequences. First, in the limit $P \gg N$, which describes case (b), the loop density profile is simply given by $S_{\text{eq}}(n) \cong a^{-2}n^{-1/2}$ for $1 \leq n \leq N$. Secondly, for $P > N$, the structure of the interfacial layer is not affected by P . In particular, the interfacial free energy in the limit $P \gg N$ is that when $P = N$. Thus, within the AGR approach, it is sufficient to compare the interfacial free energies at the two following limits: (a) $N \gg P$, and (b') $N = P$.

We may now evaluate the interfacial free energy in case (a). Combining Eqs. (5) and (11), we find that

$$\bar{F}_L[\{S_{\text{eq}}\}] \cong \bar{F}'_0 + B_2 \frac{kT}{a^2N^{3/2}}(\ln N + C_2), \quad (12)$$

where \bar{F}'_0 , B_2 , and C_2 are constants with respect to N . Although almost exactly the same function appears in Eq. (9), the dependence of $F_L[\{S_{\text{eq}}\}]$ on N in Eq. (12) is dramatically different. This is because C_2 is *not* of order unity: $C_2 \sim -P^{2/3}$ (in the limit $P \gg 1$), and the maximum, $N_m \cong e^{-C_2}$, is now shifted to unattainable values of N (for typical values of P). As shown in Fig. 4, the relevant part of the curve is an increasing function with respect to N . This means that the limit when $N \gg P$ [case (a)] has a free energy higher than when $N = P$ [case (b')], which itself, as explained above, has the same free energy as in the limit $N \ll P$ [case (b)].

Perhaps this result may be best understood if we imagine the following experiment: an interfacial layer made of monodisperse N -chains is put in the presence of a melt of shorter P -chains. What we have compared previously is the situation (a) where the N -chains remain adsorbed, and the situation (b'), where the N -chains are replaced by the shorter ones. In the thermodynamical limit where the volume of the sample is infinitely large, if desorption of N chains occurs, they spread throughout the bulk, and from the point of view of the surface, they vanish. Our analysis shows that the situation (b') is favored. We therefore conclude that there is preferential adsorption of the shorter chains.

Again, the physical origin of this effect is clear: in the absence of interpenetration, the situation (a) would be fa-

vored because the entropy of the set of loops increases with the length of the chains, as explained in Sec. III. But this effect competes with the penetration of the solution, which decreases the loop density. The latter effect favors the situation (b) [or (b')], and is eventually responsible for the behavior of the layer.

Our analysis is of course based on a rather crude picture for the penetration of the “free” chains. We clearly expect penetration of the “free” chains whatever their length, not only in the limit where it is shorter than that of the adsorbed chains [33]. However, we argue that this is not important as long as we adhere to the qualitative conclusions. As explained above, preferential adsorption in the concentrated regime results from a competition between entropy (which favors the adsorption of the longest chains), and penetration of the concentrate solution, which—in effect—favors the adsorption of the shortest chains. Crucially, the AGR approach systematically *underestimates* the penetration of the “free” chains, as is clearly shown in Sec. II. We therefore expect that our conclusion that this effect dominates the behavior of the layer should be strengthened by a more accurate description, rather than ruled out.

V. DEWETTING OF ULTRATHIN POLYMER FILMS

Previous discussions have dealt totally with free interfacial layers. For a long time, this was the only subject of experimental study. Very recently, however, an interesting new class of experiments has appeared that investigates the properties of ultrathin polymer films. These are polymer films whose thickness (h) is below the natural extension of one chain (R_G), and may be considered as being constrained interfacial layers. In most cases, they are dried spin-coated polymer solutions.

A standard experimental method in the study of ultrathin polymer films involves applying a sudden change in temperature to the film and then observing the relaxation of the film to the new equilibrium state [18]. One important result is that ultrathin films may dewet surfaces that thick films would wet. In this section, an explanation for this phenomenon is proposed in terms of the AGR approach, relating this feature to those discussed above.

Our starting point is the interfacial free energy of an ultrathin film, which may be written as

$$\bar{F}_L \cong \frac{T}{a^2} \int_1^N \{k[a^2 S(n)]^3 + [-a^2 \dot{S}(n)] \ln[-a^2 \dot{S}(n)]\} dn. \quad (13)$$

Equation (13) is a modification of Eq. (5) now accounting for the fact that the layer is in a dry state (i.e., no solvent whatever), and thus $\beta=3$ [see table (8)]. (Note that there should be an additional factor of 2 in Eq. (13) to account for the two sides of the ultrathin film). It is important to realize that although Eq. (13) for dry ultrathin films is formally identical to the free energy proposed for interfaces of melts, it has a sounder basis. This is because in the limit $h < R_G$, all the chains touch the surface, and therefore we do not have any “free” chain inside the layer. Turning to the loop distribu-

tion profile, the confinement provides a constraint on S : so that the thickness is h . Specifically, S must be such that [Eq. (2) with $\nu=1$]

$$\int_1^N a^3 S(n) dn = h \quad (14)$$

is satisfied. As usual, this may be accounted for by minimizing $\bar{F}_L - \mu \int_1^N a^2 S(n) dn$, where μ is a Lagrange multiplier. The net result is the loop distribution profile S_{eq} for the ultrathin film:

$$S_{\text{eq}}(n) \cong \begin{cases} \frac{1}{a^2 n^{1/2}} & \text{for } 1 \leq n \leq n_c \\ \frac{e^{-(n-n_c)/n_c}}{a^2 n_c^{1/2}} & \text{for } n \geq n_c, \end{cases} \quad (15)$$

where the parameter n_c obeys

$$h \cong a n_c^{1/2}, \quad (16)$$

as may be found by imposing the requirement (14). From Eq. (15), we see that the loop density profile is unperturbed [see Eq. (7) with $\alpha=1/2$] until the size of the loops becomes comparable with h , when it drops abruptly. The precise shape of this cutoff is not important. Essentially, Eqs. (15) and (16) show that the loop density profile of a layer of N chains confined to a thickness h is that of a free layer of n_c chains, with n_c corresponding to the largest size available: h . In other words, the sole effect of confining a polymer film is to prepare a layer that has the equilibrium structure of a free layer, but with a lower value for the index of polymerization. With this in mind, we are able to understand the behavior of ultrathin films in terms of the equilibrium properties of free interfacial layers. The remarkable feature is that, although we are dealing with melts, there is no interpenetration with “free” chains. Therefore we expect that the properties of these dense interfaces should be similar to those of interfacial layers in the dilute regime, and not the concentrated regime. In particular, the same physical process that favors the presence of long chains at the interface in the dilute regime now favors high values of n_c , and hence high values of h .

To be more quantitative, we can estimate the interfacial free energy of the film, $\bar{F}_L[\{S_{\text{eq}}\}]$ [Eqs. (13) and (15)]:

$$\bar{F}_L[\{S_{\text{eq}}\}] \cong \bar{F}_0'' + B_3 \frac{T}{a^2 n_c^{1/2}} (\ln n_c + C_3), \quad (17)$$

where \bar{F}_0'' is a constant of order T/a^2 , and B_3 and C_3 are numbers of order unity. Here, we have used a simplified version of Eq. (15), specifically, $S_{\text{eq}}(n) \cong n^{-1/2}$, if $1 \leq n \leq n_c$; and $S(n)=0$ instead. This avoids unnecessary complications. As expected, the result of Eq. (17) is very similar to the results found for the case of a dilute solution [see Eq. (9) and Fig. 2]. The function \bar{F} decreases with n_c . In our case, however, n_c does not correspond to a topological constraint, but is related to a physical variable: h . This means that there is a effective force that tends to modify the film thickness. Combining Eqs. (17) and (16), we find that

$$\bar{F}_L \cong \bar{F}_0'' + 2B_3 \frac{T/a}{h} [\ln(h/a) + C_3/2]. \quad (18)$$

We thus identify an effective long range ‘‘disjoining pressure’’ [34]:

$$\Pi = - \frac{\partial \bar{F}_L}{\partial h} \cong 2B_3 \frac{T/a}{h^2} [\ln(h/a) + C_3/2 - 1],$$

$$h \leq R_G \cong aN^{1/2}, \quad (19)$$

which tends to thicken the film when its thickness is below the natural extension of the chains. We thus understand qualitatively that the film dewets the surface when its thickness becomes less than the gyration radius of the chains.

Let us compare our theoretical prediction with the experimental data of Zhao *et al.* The system of Ref. [18] is a polyethylene propylene (PEP) film, spin coated onto a silicon surface. For this system, the interactions between the monomers and the surface reduce to the spreading parameter: $\bar{F}_S \cong (\gamma + \gamma_{SL} - \gamma_{SV})$, with $\gamma, \gamma_{SL}, \gamma_{SV}$, the surface tension of the polymer, the solid-polymer, and solid-vapor interfacial tensions, respectively (here, the quantity \bar{F}_S is the negative of the macroscopic spreading parameter). Note that the long range van der Waals interactions are not relevant for $h \geq 4$ nm. We thus find that the total free energy per unit area may be written as

$$\bar{F} \cong (\gamma + \gamma_{SL} - \gamma_{SV}) + \bar{F}_0'' + B_3 \frac{T}{ha} [\ln(h/a) + C_3/2],$$

$$h \leq R_G \cong aN^{1/2}. \quad (20)$$

Even without knowing the precise value of the numerical factors in Eq. (20), it is clear that the behavior of the system will be dominated by the contribution from the layer (\bar{F}_L). This is because the contribution from the interaction with the surface (\bar{F}_S) is purely composed of van der Waals interactions, and is of the order of 10^{-3} J m $^{-2}$; whereas \bar{F}_L is of the order of $T/a^2 \cong 10^{-1}$ J m $^{-2}$. As a consequence, the system will ‘‘lock’’ at the highest possible value for h : R_G . This is in very good agreement with the data of Ref. [18]. The above analysis, however, is based on the hypothesis that the layer is incompressible. It may well be that this is not a realistic assumption [35].

Finally, it is very interesting to compare our theoretical explanation for the behavior of the layer to that which was proposed by Zhao *et al.* in Ref. [18]. These authors suggest that a term should be added to \bar{F}_S in order to account for the confinement of the chains. From a scaling consideration, they arrive at

$$\bar{F} \cong (\gamma + \gamma_{SL} - \gamma_{SV}) + (\pi^2/6)nT \left[\left(\frac{R_G}{h} \right)^2 - 1 \right],$$

$$h \leq R_G \cong aN^{1/2}, \quad (21)$$

where n is the number of chain per unit area. This leads to an equilibrium thickness that is lower than R_G . From a quantitative point of view, the correction for confinement in Eq. (21) is smaller than that in Eq. (20) because it is a penalty of

the order of T per chain, whereas in our analysis we obtain a penalty of the order of T per loop (there is approximately one loop per site a^2). It is important to realize, however, that the two approaches are qualitatively very different. This is because in our approach, the chain is not the relevant object to be considered. As explained in Sec. II, there is no correlation between two different loops and thus the idea of a connection between different loops is not relevant. Indeed, in all of our analysis, the index of polymerization of the chain only appears as an upper limit for the size of the loops. From our point of view, we can say that there is no penalty due to chain confinement simply because the idea of chains is no longer relevant.

VI. CONCLUDING REMARKS

The above analysis provides a framework for a general understanding of the behavior of polymers at interfaces. Four different experimental situations were examined, corresponding to the special features of interfacial polymer layers. In each case, we have been able to propose a simple theoretical explanation in terms of a single approach—namely, the AGR approach. Essentially, we find that dense polymer layers behave as a thermodynamical ensemble of loops. Our analysis was restricted to (a) ‘‘simple’’ situations, (b) equilibrium situations, (c) dense layers, and (d) mainly qualitative discussions, but we hope that it may provide some insight into the full problem.

The analysis presented in this article is clearly a first step towards a complete theory for polymers at interfaces. Two lines of study are of particular interest. The first is to consider the semidilute regime. This is the situation between the dilute regime, where the longer chains adsorb preferentially, and the concentrated regime, where shorter chains adsorb preferentially. One important task is to identify the crossover region. Then we might understand the behavior of a solution in the whole range of concentrations. The second line of study is to consider the equilibrium state of the layer in the presence of a polydisperse solution. In this article, we suggest that preferential adsorption from polydisperse solutions does not necessarily imply that the equilibrium state of the interfacial layer is monodisperse (i.e., made with only one type of chain). This may be of some relevance when dealing with very polydisperse solutions, such as bidisperse mixtures.

All our discussions are based on the assumption of thermodynamic equilibrium. For ultrathin films, it is a constrained equilibrium, but the state of the system is always assumed to be independent of the sample history. In some cases, this might be an unrealistic assumption. For example, the inner part of the layer consists of adsorbed segments of chains in a dense state. In fact, some experiments of Cohen-Stuart [37] suggest that this inner layer may be in a glassy state. Then, we may be rather far from equilibrium. However, we emphasize that many features of interfacial polymer layers can be understood in terms of equilibrium properties, although at first they seem to be the result of irreversible processes. This is particularly true for kinetics, as shown by Scheutjens and Fleer [21], and more recently by Semenov and Joanny [36]. The AGR approach may serve as a basis for

a kinetic theory of polymers at interfaces that would include scaling exponents [38,39].

We have only considered dense layers where different chains overlap. This is crucial, as explained in Sec. II, because it is certainly related to the assumption that the loops are not correlated with one another. One might be led to think that this remark suggests the use of a mean-field type of treatment for this problem, and not necessarily scaling. The complication that arises with interfacial layers is that although the set of loops may (apparently) be treated at a mean-field level, the loops themselves are objects that cannot be correctly described with the same theories (at least in good solvent condition). Besides, one important following step in this theory concerns situations where the surface is not saturated with chains, as assumed in this paper. In this regime, only scaling theories should account correctly for interloop correlations [40].

That the AGR approach, as outlined above and described in detail in Ref. [22], is able to give quantitative predictions

was shown by studying the equilibrium structure of an adsorbed layer. The conclusions of de Gennes [7] were reached in a completely different manner, and these were successfully confronted with experiments [5]. Moreover, in Sec. V, we compared the results of our theory with the experimental data and the agreement was quite good. This gives us confidence in the quantitative predictions that could be obtained from the AGR approach.

We emphasize that the ideas presented in this paper may be very simply adapted or generalized to meet other solvent conditions or other geometries.

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