Scaling Description of a Colloidal Particle Clothed with Polymers

M. Aubouy† and E. Raphaël*,‡

Groupe Matière Condensée aux Interfaces, Département de Recherche Fondamentale sur la Matière Condensée, UMR 5819 (CEA-CNRS-Univ. J. Fourier), 17 rue des martyrs, 38054 Grenoble cedex 9 France, Laboratoire de Physique de la Matière Condensée, URA No. 792 du CNRS, Collège de France, 11 place Marcelin Berthelot, Paris 75005 France

Received November 5, 1997; Revised Manuscript Received March 30, 1998

ABSTRACT: We present a scaling approach to describe an arbitrary polymer layer coating a colloidal particle. Our analysis is based on a description of the layer in terms of loops and tails. Within a simple scaling model for the behavior of the loops and tails, we are able to relate the features of the interface to the "loop density profile" $\tilde{S}(n)$, defined as the number of loops and tail having more than n monomers on the particle. Our theory predicts (as functions of $\tilde{S}$) the variations of the monomer density inside the layer, the extension, the adsorbance, and the effective free-energy of the polymer coating, for various solvent conditions ("good" solvent, Θ solvent or melt). In all cases, the key parameter which controls the influence of the curvative on the structure of the interface appears to be R/L, where R is the radius of the bare particle and L is the extension that the same layer would have on a flat surface (by same layer, we mean a layer characterized by the same "loop distribution profile" S). As an illustration of our approach, we consider the situation where polymer chains adsorb reversibly on colloidal particles. Both quantitative and qualitative new results are obtained for this problem.

1. Introduction

Controlling the stability of colloidal suspensions is of primary importance in many industrial applications such as painting and surface coating.[1] Without any special treatment, a colloidal suspension has an inherent tendency to precipitate owing to van der Waals attractions. There is a well-known remedy for this which consists of adding polymers to the solution. This is because, in some favorable cases, these polymers build a layer around the particles which resists compression and can thus keep the solid grains apart.

In flat geometries, the equilibrium structure of these polymer layers have been the subject of numerous studies, and they are quite well understood (the references by Fleer et al.[2] and by de Gennes[3] provide an overview of the field). Both scaling and self-consistent field (SCF) type of theories have been used to describe three specific situations: (a) polymer "brushes" (polymer chains end-attached to a repulsive surface);[4] (b) reversibly adsorbed polymer layers;[5] (c) irreversibly adsorbed polymer layers.[6] There is a reasonable agreement between the theoretical predictions and the experimental data for each of these situations.[7−9]

Concerning spherical geometries, the situation is quite different. The influence of the curvature on the structure of polymer layers have been mainly investigated for grafted chains. This is because amphiphilic diblock-copolymers self-organize quite commonly into spherical micelles composed of polymer segments end-attached to a "small", solidlike, core. These objects, which are extensively studied for their industrial importance, may be described in terms of grafted polymer layers on spherical particles. A very elegant theoretical description of this problem was achieved by Daoud and Cotton.[10] This model was experimentally confirmed by many authors (see, for example, Biver *et al.*[11]). Other types of polymer layers on curved interfaces have been studied theoretically (irreversible adsorption;[12] reversible adsorption[13,14]), but experimental data are rather scarce (see, however, Ou-Yang et al.[15] and Cosgrove et al.[16]).

Recently, a new scaling approach has been proposed by Aubouy Guiselin and Raphaël (AGR) to model an arbitrary polymer layer in flat geometries.[17] The basic idea is to describe the layer as a population of loops and tails of different sizes. (By loop, we mean a chain segment between two adsorbed monomers which does not touch the surface.) The layer is then treated as a statistical ensemble of these objects. In this approach, the main tool is a function S designated as the "loop density profile", and defined such that

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

Within some approximations, the characteristics of the layer, such as the extension or the effective free energy, may be written as functionals of S. The behavior of the layer is then easily obtained. This approach has proved to be successful in modeling the equilibrium properties of adsorbed layers.[18] Furthermore, the "loop density profile" appeared to be a powerful tool to undersand many other features of these interfaces, such as preferential adsorption, wetting properties, etc., as shown by Aubouy.[19]

Our aim in this article is to generalize the AGR approach to spherical geometries. As in the planar case, we show that any polymer layer on a spherical particle, whatever the solvent conditions, can be very simply described in terms of its "loop density profile" and that this function in turn appears to be the correct tool for studying these interfaces. This is done in three steps.

We first give a general description of an arbitrary polymer layer on a spherical particle (section 2). It is assumed that (a) the polymer chains are homogeneous, linear, flexible, and monodisperse (N monomers per chain) and that (b) the chain density at the interface is

† UMR 5819. E-mail: aubouy@drfmc.ceng.cea.fr.
‡ Collège de France. E-mail: elie@ext.jussieu.fr.

S0024-9297(97)01637-9 CCC: $15.00 © 1998 American Chemical Society
Published on Web 05/30/1998

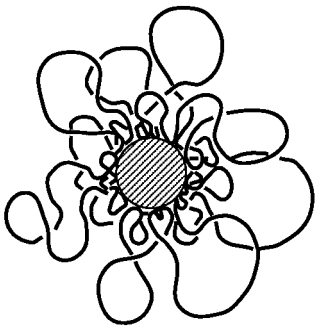

Figure 1. Sketch of a spherical particle clothed with polymers.

high enough that the different coils overlap. Three solvent conditions are considered: "good" solvent (athermal for simplicity), Θ solvent, and melt (i.e. no solvent whatsoever).

We then estimate the effective free-energy of the layer (section 3).

In section 4, we illustrate our approach on the example of a colloidal particle coated with reversibly adsorbed polymer chains. We show that the clothed particle can be pictured as follows: (a) an inner region made of overlapping loops and tails which build a self-similar structure (the self-similar region) surrounded by (b) few loops or tails which emerge from the self-similar layer and behave as isolated chains (the "mushroom" region). The relative importance of these two regions depends on the size of the particle, R, and the length of the chains, N.

In all of what follows, we will omit all the various order−unity prefactors which may appear, and we will concentrate on scaling relations.

2. Description of an Arbitrary Polymer Layer

In this section, we consider a spherical particle of radius R coated with a arbitrary polymer layer, as depicted in Figure 1. The layer is characterized by the "loop density profile" S defined in (1). It is convenient however to consider a slightly different "loop density profile": $\tilde{S}$, defined as follows

$\tilde{S}(n)$ is the total number of loops or tails having more than n monomers on the particle (2)

Of course, we have

$$\tilde{S}(n) = 4\pi R^2 S(n) \tag{3}$$

Note that $\tilde{S}$ and S do not have the same dimensionality. We will see that the external radius of the coated particle, R_c, the variations of the volume fraction of monomers, ϕ, and the adsorbance, $\tilde{\Gamma}$ (the total amount of material carried by the particle), can all be simply expressed as functions of $\tilde{S}$.

We assume that (a) each loop of $2n$ monomers can be visualized as two separate "pseudo-tails" of size n each (and from now on, we shall make no distinction between tails and pseudo-tails) and that (b) the behavior of all the different tails is described by a single trajectory $n(r)$, where n is the arc length parameter, and r the spatial position: all nth monomers of any tail (having more than n monomers) are situated at the same distance r from the center of the particle. These assumptions have been discussed in great detail.[17] Since the spherical geometry does not introduce any special feature, the reader may refer to this reference.

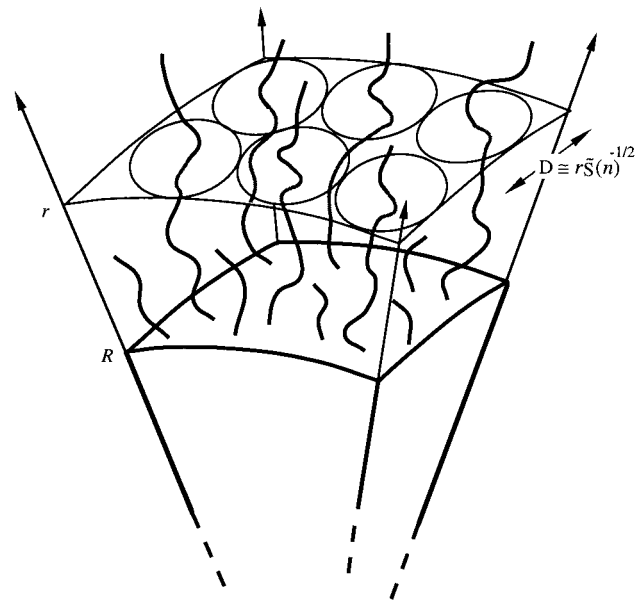

Figure 2. Sketch of the pseudo-tails. At a given distance r from the center of the particle, the average distance between pseudo-tails is $D(r) \cong r\tilde{S}(n(r))^{-1/2}$.

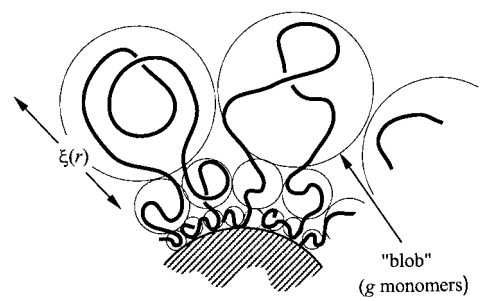

Figure 3. Drawing of the layer. By analogy with a semidilute solution, the layer can be pictured locally as a close packing of subunits, called "blobs", whose size $\xi(r)$ is of the order of the mean distance between tails (good solvent conditions).

With these assumptions, we can relate the average distance between two "pseudo-tails" $D(r)$ at a distance r to the average number of "pseudo-tails" having more than n monomers $\tilde{S}(n)$ (see Figure 2):

$$D(r) \cong r\tilde{S}(n(r))^{-1/2} \tag{4}$$

The conservation of monomers can be written as

$$\phi(r) \cong \frac{a^3\tilde{S}(n(r))}{r^2\dot{r}} \tag{5}$$

where we have set $\dot{r} = \mathrm{d}r/\mathrm{d}n$, a being the size of the monomer. Finally, the adsorbance is obtained by counting the total number of monomers:

$$\tilde{\Gamma} \cong \int_1^N \tilde{S}(n)\,\mathrm{d}n \tag{6}$$

Equations 4−6 are purely geometrical, and up to this point, no mention of the behavior of the polymer chains is required. We now specify the solvent conditions.

For a "good" solvent, different chains repel and, by analogy with a semidilute solution, the layer can be pictured locally as a close packing of subunits, called

"blobs",[20] whose size is of the order of the mean distance between "pseudo-tails" (Figure 3): $\xi(r) \cong D(r)$. At a scale smaller than ξ, "the pseudo-tails" are self-avoiding and the number of monomers, g, inside one subunit is $(\xi/a)^{5/3}$ (for simplicity reasons, we have considered the athermal limit where the excluded volume parameter $v \cong a^3$). At a scale larger than ξ the "pseudo-tails" are stretched away from the surface and thus $\mathrm{d}n/g \cong \mathrm{d}r/\xi$. Combining the above relations, we find that

$$\dot{r} \cong a\,\frac{\tilde{S}(n)^{\nu}}{(r/a)^{2\nu}} \tag{7}$$

where

$$\nu = {}^{1}/_{3} \quad (\text{"good" solvent}) \tag{8}$$

It is important to realize that (7) is only valid in the limit where the different loops and tails are stretched away from the surface. This is a reasonable assumption as soon as the loops or tails overlap because the two polymer segments repel each other. However, this is an important hypothesis to be kept in mind. We shall come back to this point in Section 4, with a specific example. Substituting (7) into (5), we obtain

$$\phi(r) \cong \frac{(a^2\tilde{S}(n))^{1-\nu}}{(r/a)^{2(1-\nu)}} \tag{9}$$

Equations 7 and 9 allow the determination of the characteristics of the layer. In particular, integrating formally (7) reveals the extension of the layer to be a simple functional of the loop density profile:

$$R_c \cong R\left(1 + \frac{\int_1^N \tilde{S}^{\nu}(m)\,\mathrm{d}m}{(R/a)^{2\nu+1}}\right)^{1/(2\nu+1)} \tag{10}$$

At this point, it is useful to introduce the extension, L, that a layer *characterized by the same "loop distribution profile"*, S, would have on a flat surface. This quantity is[17]

$$L = a\int_1^N (a^2 S(m))^{\nu}\,\mathrm{d}m = a\left(\frac{a^2}{4\pi R^2}\right)^{\nu}\int_1^N \tilde{S}^{\nu}(m)\,\mathrm{d}m \tag{11}$$

and thus

$$R_c \cong R\left(1 + \frac{L}{R}\right)^{1/(2\nu+1)} \tag{12}$$

Note that from a practical point of view, L is a known quantity in most cases. This is because, as explained in the Introduction, our understanding of flat polymer layers is satisfying. Equation 12, which expresses the extension of the coating as a function of R and L, is quite interesting. First, it gives the radius of the coated particle for all the possible values of R, even in the intermediate regimes which may be relevant in practical cases. Second, it clearly shows the limits of the different physical regimes. From the "layer's point of view", it is important to know, for a given particle and a given type of layer, whether the curvature of the particle is relevant for the structure of the layer ("spherical regime"), or not ("flat" regime). Alternatively, one might be primarily interested in the particle. It is then important to know whether the particle is "large" or "small" with respect to a given type of layer. Whatever the point of view adopted, (12) shows that the natural parameter is R/L, where R is the radius of the bare particle and L is the extension that the same layer (by same layer, we mean a layer characterized by the same "loop distribution profile" S) would have on a flat surface. For $R \gg L$, the curvature is not relevant. This is the "large" particle limit. A Taylor expansion of (12) leads to $R_c - R \cong L$. As was expected, in this limit we recover the result valid for flat layers (11). For $R \ll L$, however, we find that

$$R_c \cong a\left(\int_1^N \tilde{S}^{\nu}(m)\,\mathrm{d}m\right)^{1/(2\nu+1)} \tag{13}$$

This is the "small" particle limit, where the curvature is relevant.

Let us consider an example, namely, the case of f chains (N monomers) grafted on a particle of radius R, where the surface is repulsive for the polymers. The loop distribution profile $\tilde{S}$ is

$$\begin{aligned}\tilde{S}(n) &= f \quad \text{for } 1 \le n \le N \\ &= 0 \quad n \ge N\end{aligned} \tag{14}$$

For that particular layer, the limit between the "spherical" and the "flat" regime is given by the comparison of R and

$$L = \int_1^N S^{1/3}(m)\,\mathrm{d}m \cong aN\left(\frac{fa^2}{4\pi R^2}\right)^{1/3} \quad (\text{"good" solvent}) \tag{15}$$

which is the well known result of Alexander and de Gennes for the extension of a layer made of grafted polymer chains on a flat surface.[21,22] Moreover, in the limit where $R \ll L$, the radius of the coated particle scales as

$$R_c \cong af^{1/5}N^{3/5} \tag{16}$$

We thus reach the same result obtained by Daoud and Cotton for star polymers (in the limit of $R \to a$, the description corresponds to a star polymer with f branches).[10]

It is also interesting to consider power-laws distributions of the form $\tilde{S}(n) \sim n^{-\alpha}$, where the exponent α satisfies the double inequality $0 \le \alpha < 1$. Scaling analysis of (10) leads to

$$R_c \cong R\left(1 + C\frac{N\,(\tilde{\Gamma}/N)^{\nu}}{(R/a)^{2\nu+1}}\right)^{1/(2\nu+1)} \tag{17}$$

where C is a numerical factor of order unity. In particular, in the spherical regime

$$R_c \cong a\,(\tilde{\Gamma}/N)^{\nu/(2\nu+1)}\,N^{1/(2\nu+1)} \tag{18}$$

This means that the size of the coated depends only on the amount of polymer carried and not on the particular form of the loop distribution function. Consider for example two identical small particles A and B. Particle A is coated with grafted chains, while particle B is coated with chains irreversibly adsorbed from a melt. We impose the condition that the two particles carry the same amount of material $\tilde{\Gamma}$. As

explained above, the coating of particle A is characterized by a loop distribution $\tilde{S}$ which is constant. This amounts to $\tilde{S}(n) \sim n^{-\alpha}$, which the value $\alpha = 0$. As explained by Aubouy et al.,[12] the coating of particle B is characterized by $\tilde{S}(n) \sim n^{-1/2}$. Both situations satisfy the double inequality $0 \leq \alpha < 1$, and thus the radius of the two coated particles are comparable, within a numerical factor, although the inner structure of the layers are very different.

As is usual with scaling laws, other solvent conditions are characterized by a different set of exponents. The results are displayed in Figure 4, and details of the calculations are given in Appendix 1. The difference in the value of the exponents relates to a difference in the nature of the repulsive loop−loop interactions.

3. Energetics

We now estimate the effective free energy, F, of the layer. By analogy with the planar situation, we have at equilibrium[17]

$$F \cong \gamma_0 4\pi R^2 - \gamma_1 \tilde{S}_0 + T \int_1^N \left\{ k \left(\frac{r(n)}{a}\right)^2 \left(\frac{\dot{r}(n)}{a}\right)^\beta + \tilde{S}_0 \left(-\frac{\tilde{S}'(n)}{\tilde{S}_0}\right) \ln\left(-\frac{\tilde{S}'(n)}{\tilde{S}_0}\right) \right\} \mathrm{d}n \quad (19)$$

where $\tilde{S}_0 = \tilde{S}(1)$ is the total number of tails or loops on the particle (note that $\tilde{S}_0$ is also the total number of monomers in direct contact with the surface), and k is a numerical factor of order unity. The quantity $\tilde{S}'$ denote the derivative of $\tilde{S}$ with respect to n.

The two first terms in (19) describe the interactions between the monomers and the surface. Here, γ_0 is the bare solid/liquid surface tension and γ_1 is the solid/polymer surface tension. (Note that these quantities do not have the same dimensionality in (19)).

The third term is the osmotic contribution to the free energy, which accounts for the repulsive interactions between tails and loops. For an athermal solvent, this repulsion is due to two-body interactions. At equilibrium, one can estimate the corresponding energy by integrating the osmotic pressure over the entire layer: $F_{\mathrm{osm}} \cong \int_R^{R_c} \Pi_{\mathrm{osm}}\, \mathrm{d}V$. Making use of Des Cloiseaux's law, which relates the osmotic pressure to the volume fraction of monomers[20]

$$\Pi_{\mathrm{osm}} \cong T\phi^{9/4} \quad (20)$$

we find

$$F_{\mathrm{osm}} \cong T \int_R^{R_c} \phi(r)^{9/4} r^2\, \mathrm{d}r \quad (21)$$

which may be written as a functional of r only ((7), (8), and (9))

$$F_{\mathrm{osm}} \cong T \int_1^N \left(\frac{r(n)}{a}\right)^2 \left(\frac{\dot{r}(n)}{a}\right)^\beta \mathrm{d}n \quad (22)$$

with

$$\beta = {}^{11}/_{2} \quad (\text{“good” solvent}) \quad (23)$$

Equation 22 is still valid for a Θ solvent or a melt, but with different values for β (cf. Figure 4): $\beta = 6$ (Θ solvent) and $\beta = 3$ (melt). See Appendix 2 for details.

solvent conditions	ν	β	origin of the repulsion
"good"	1/3	11/2	two-body interactions
Θ	1/2	6	three-body interactions
melt	1	3	induced stretching

Figure 4. Different solvent conditions characterized by different sets of exponents. (See text for details.)

The last term represents the entropy which accounts for how many arrangements of the layer can exist for a given loop distribution.

4. Reversible Adsorption of Polymer Chains on a Colloidal Particle

We will now use the above general procedure to model reversible adsorption of polymer chains on colloidal particles. This situation is relevant for numerous experiments where a set of polymer chains is put in the presence of an assembly of colloidal particles.[1] Our aim is to describe the structure of the layer around the particles; hence, we only consider the limiting case of isolated colloids and dilute solutions of polymers. We assume thermodynamic equilibrium, which is fair with true reversible adsorption. Finally, for simplicity reasons, we assume that the surface is saturated with monomers: $\tilde{S}_0 = 4\pi R^2/a^2$.[23]

The structure of the layer is given by the equilibrium “loop distribution profile”, obtained by minimization of the free energy, (19). It is convenient to rewrite this free energy as a function of r only: combining (19) and (7), we find

$$F \cong R^2 T \int_1^N \left\{ k \left(\frac{r(n)}{R}\right)^2 \left(\frac{\dot{r}(n)}{a}\right)^{11/2} + \left[-\frac{\partial}{\partial n}\left(\left(\frac{r(n)}{R}\right)^2 \left(\frac{\dot{r}(n)}{a}\right)^3\right)\right] \ln\left[-\frac{\partial}{\partial n}\left(\left(\frac{r(n)}{R}\right)^2 \left(\frac{\dot{r}(n)}{a}\right)^3\right)\right]\right\} \mathrm{d}n \quad (24)$$

(we consider the case of an athermal solvent, $\beta = {}^{11}/_{2}$, without lost of generality). Note that we have dropped the first two terms of (19) since these terms are constant (remember that by assumption, $\tilde{S}_0 = 4\pi R^2/a^2$). We now minimize the function in (24) with respect to r.

Self-Similar Region. (This is a region characterized by the following in-equality: $R \leq r \leq 2R$.) Let us consider the structure of the layer close to the solid surface: $r(n) = R + h(n) \ll R$. To the first order in h/R, we find

$$r_{\mathrm{eq}}(n) \cong R + an^{3/5} \quad (25)$$

The equilibrium “loop density profile” close to the solid surface is then obtained from (7)

$$\tilde{S}_{\mathrm{eq}}(n) \cong \frac{(R + an^{3/5})^2}{a^2 n^{6/5}} \quad 1 \leq n \leq (R/a)^{5/3} \quad (26)$$

and the volume fraction of monomers is obtained from (5):

$$\phi(r) \cong \left(\frac{r - R}{a}\right)^{-4/3} \quad R < r \leq 2R \quad (27)$$

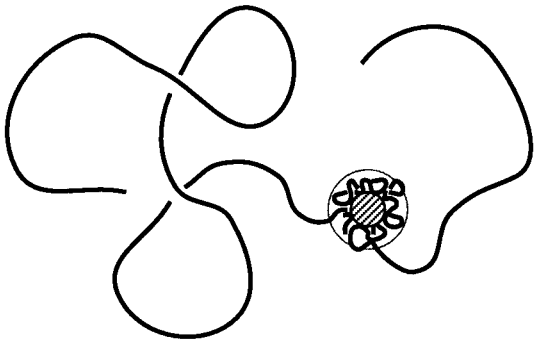

Figure 5. Polymer chains reversibly adsorbed on a spherical colloid. When the solid particle is very "small", i.e. for $R < aN^{1/2}$, very few chains are sufficient to fully cover the surface. The gray circle indicates the limits of the self-similar region (its radius is $2R$, where R is the radius of the bare particle).

The physical interpretation of these results is quite clear. Close to the solid surface, the curvature of the surface is not relevant and we recover the self-similar structure of layers made of polymer chains reversibly adsorbed on flat surfaces. In particular, (27) shows that the volume fraction of monomers scales as $z^{-4/3}$, where $z = r - R$ is the altitude.[5,17]

"Mushrooms" Region. What is the structure of the layer above the self-similar region: $r \geq 2R$? First, it is important to realize that the general formalism described above is not valid when $r > 2R$. This is because the spherical cap of radius $2R$ is the limit below which the different loops do not overlap. One can easily estimate the number, η, of loops or tails emerging from the spherical cap of radius $2R$. By definition in (2), we have $\eta = \tilde{S}_{eq}(n(2R))$, where $n(2R)$ is the arc-length parameter at a distance $2R$ from the center of the particle. From (25), we get $n(2R) \cong (R/a)^{5/3}$ and thus (26)

$$\eta \cong 4 \tag{28}$$

The precise value of η is not relevant since we have omitted various prefactors of the order of unity. However, (28) tells us that the loops or tails which emerge from the spherical cap of radius $2R$ are not numerous enough to overlap.

This means that the self-similar region is surrounded by few loops or tails which emerge from the inner layer. These loops or tails protrude into the solvent and behave as isolated chains. By analogy with the situation where chains are end-attached on a repulsive surface at low grafting density, we call these loops or tails "mushrooms".[22]

Relative Importance of the Two Regions. So far, we have pictured the particle coated with reversibly adsorbed polymer chains as follows: (a) an inner region ($R < r \leq 2R$) made of overlapping loops and tails which build a self-similar structure surrounded by (b) few loops or tails which emerge from the self-similar layer ($r \geq 2R$) and behave as isolated chains. It is important to determine the relative importance of these two regions. This depends on the size of the particle, R, and the length of the chains, N.

Let us estimate the amount of material, $\tilde{\Gamma}$, carried by the particle: $\tilde{\Gamma} = \tilde{\Gamma}_{inn} + \tilde{\Gamma}_{much}$, where the first (second, respectively) term is the contribution from the inner layer ("mushrooms" region, respectively). From (6) and (26), we have

$$\tilde{\Gamma}_{inn} \cong 5\,(R/a)^2 + (R/a)^{5/3} - 5\,(R/a) - 1 \tag{29}$$

The mushroom region is made of few, e.g., δ, loops or tails which emerge from the inner region. The arc-length coordinate $n(2R)$ is $(R/a)^{5/3}$. The maximal size of the "mushrooms" is thus $N - (R/a)^{5/3}$ monomers. One can crudely estimate

$$\tilde{\Gamma}_{much} \cong (N - (R/a)^{5/3})\,\delta \tag{30}$$

Depending on the relative values of R and N, we distinguish three regimes.

(1) When $R < aN^{1/2}$, the dominant contribution to $\tilde{\Gamma}$ is $\tilde{\Gamma}_{much}$, and the material located in the inner region can be neglected. This corresponds to the situation where the solid particle is very small and very few chains are sufficient to fully cover the surface (Figure 5). In that limit, the adsorbance scales as

$$\tilde{\Gamma} \sim N \tag{31}$$

The particle is a perturbation for the chain and the size of the coated particle is thus on the order of the natural extension of one isolated chain:

$$R_c \cong aN^{3/5} \tag{32}$$

Note however that the whole approach assumes that the size of the particle, R, is larger than a the monomer size (the Kuhn length) of the chain.

(2) When $aN^{1/2} < R < aN^{3/5}$, most of the material is located in the inner region, $\tilde{\Gamma} \sim \tilde{\Gamma}_{inn}$, but few loops or tails protrude into the solution (Figure 6). In this regime

$$\tilde{\Gamma} \sim (R/a)^2 \tag{33}$$

The size of the coated particle can be estimated from the maximal size of the "mushrooms" as

$$R_c \cong 2R + a\,(N - (R/a)^{5/3})^{3/5} \tag{34}$$

(3) In the limit where $R > aN^{3/5}$, the "mushroom" region vanishes as can be deduced from (30). This is also the limit where the curvature is not relevant (Figure 7): the radius of the bare particle, R, is larger than the extension that a layer made of versibly adsorbed polymers would have on a flat surface, $L \cong aN^{3/5}$.[17] In this regime, we reach the results for planar geometries. Equation 25 leads to $R_c \cong R + aN^{3/5}$. The adsorbance scales as $\tilde{\Gamma} \sim (R/a)^2$.

An important observable for the problem of reversible adsorption is the adsorbance per unit of solid surface, Γ: $\Gamma = \tilde{\Gamma}/4\pi R^2$ (see Figure 8). In the absence of curvature (dashed line), this quantity is independant of the index of polymerization of the adsorbing chains: $\Gamma \cong a^{-2}$.[17] For spherical particles (full line), the variations of Γ with respect to the length of the chains, N, are quite different. Qualitatively, we see that the adsorption is enhanced by the effect of the curvature. This may be interpreted in purely topological terms. Qualitatively, the enhancement is effective as soon as we are in the spherical regime ($N \gg (R/a)^{5/3}$), but there is a third regime ($N \gg (R/a)^2$) characterized by a well-defined behavior for Γ: $\Gamma \sim N/(R/a)^2$. We emphasis that we have not considered the possibility that a single chain "bridge" several colloids. However, these effects

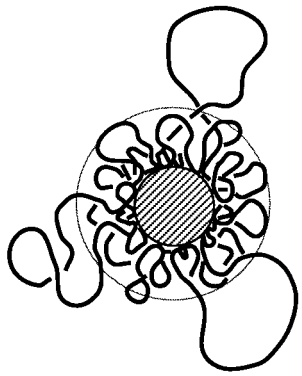

Figure 6. Polymer chains reversibly adsorbed on a spherical colloid. In the limit where $aN^{1/2} < R < aN^{3/5}$, most of the material is situated in the inner region, but few loops or tails protrude into the solution. The gray circle indicates the limits of the self-similar region (its radius is $2R$, where R is the radius of the bare particle).

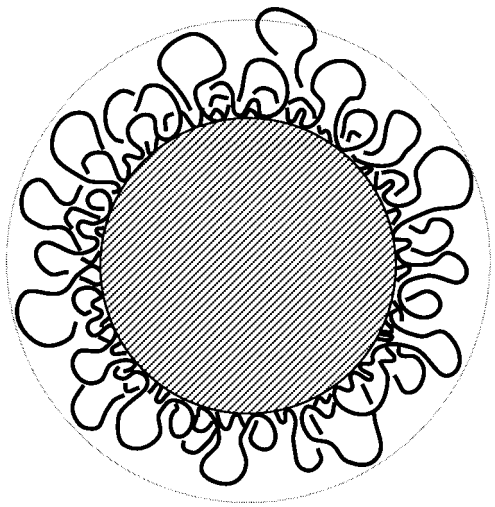

Figure 7. Polymer chains reversibly adsorbed on a spherical colloid. When the particle is "large", i.e. for $R > aN^{3/5}$, the curvature of the solid surface is not relevant. All the material is located in the self-similar region whose extension is $aN^{3/5}$ (gray circle).

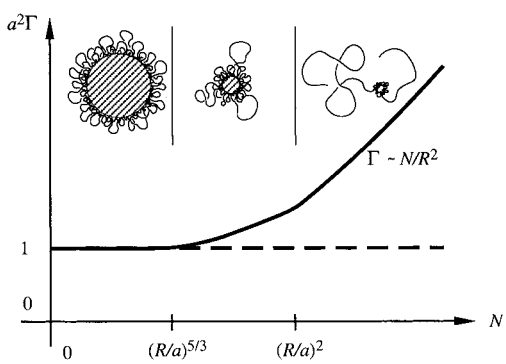

Figure 8. Reversible adsorption of polymer chains on an isolated spherical colloid. Variation of the adsorbance per unit of solid surface, Γ, with respect to the index of polymerization of the chain, N. For comparison, we displayed the result for planar surfaces (dashed line).

should be relevant for high concentrations of particles and large values of the dimensionless quantity $N/(R/a)^2$.

Comparison with the Results of Marques and Joanny. Finally, it is interesting to compare our picture for reversible adsorption on colloids with that of Marques and Joanny who have studied the same problem (under semidilute conditions) using Widom–Cahn–de Gennes type of argument.[13] Essentially, they show that the layer may be decomposed into three regions:

The first region is close to the solid surface ($R < r \leq 2R$, a self-similar layer made of overlapping chains. In this region, the volume fraction decreases as $z^{-4/3}$, where z is the altitude.

The second is a region where the loops still overlap, but the "loop density profile" varies as $\tilde{S}(n) \sim n^{-7/3}$ ($2R < r \leq \sqrt{\xi R}$, where ξ is the correlation length of the semi-dilute solution).

The third is a region where the volume fraction ϕ decreases exponentially ($\sqrt{\xi R} < r \leq \xi$).

Both approaches give the same result concerning the structure of the layer close to the solid surface, but they disagree about the structure of the layer in the region where the curvature is relevant. Whereas we find a "mushroom" type of structure, Marques and Joanny still treat the layer as made of overlaping loops. However, as explained above, the number of loops and tails which participate to the layer in the region $r \geq 2R$ is of the order of unity, and these loops or tails do not overlap.

5. Concluding Remarks

In this article, we have presented a complete scaling theory of an arbitrary polymer layer coating a colloidal particle. Basically, we have described the behavior of the polymer in terms of a statistical ensemble of tails and loops. Both formally and with the specific example of reversible adsorption, we showed that the main features of this interface may be simply expressed as functionals of a "loop distribution profile" $\tilde{S}$, which appears to be an effective tool for studying these interfaces. Our description is, of course, based on a certain number of approximations and simplifications. Since these are similar in this study and in Aubouy et al.,[17] which deals with the planar situation, we shall not comment on them (see also Aubouy[19]). Instead, we would like to discuss some directions for future work.

As explained in the introduction, polymers are useful in stabilizing colloidal suspensions because the interaction between colloidal particles is modified when they are coated by polymer chains. It is thus important to study the interaction between two clothed particles.[24,25] This program was initiated in the spirit of the AGR approach for irreversibly adsorbed polymer chains.[12] However, some assumptions of this study are unrealistic. An interesting continuation of the present work would be to consider the interaction between particles coated with an arbitrary layer. We hope that our description may provide a good framework to deal with large perturbation of the layer.

Concerning reversible adsorption of polymers on colloidal particles, we have focused on the single particle case. It would be interesting to consider the case where many solid particles are present and where a single chain is able to "bridge" several colloids.[14,26,27] This is the limit when the particles are very small and/or the polymers very long. A closely related situation was achieved by Cabane *et al.* with polymers and micelles.[28] These experiments showed several interesting regimes including the gellike behavior of the assembly.

In all this work, we have only considered simple (homogeneous) polymer chains on simple (hard) colloidal particles. However, our theory might be adapted to describe situations involving more complicated polymer

or colloidal architectures. Consider for example a multiblock copolymer made of two incompatible sequences A and B. In the presence of a selective solvent (e.g., "good" for the sequences A and "bad" for the sequences B), we expect that the chain self-organizes into a spherical micelle where the A blocks protrude into the solvent and the B blocks form a dense core. If the A sequences are not monodisperse in size, the resulting object would probably be very similar to a polymer layer made of polydisperse tails and loops lying on a spherical colloidal particle. Indeed, some of the structures obtained with telechelic polymers ("flowers")[29] or statistical block copolymer ("kikus")[30] can be compared to those displayed in Figures 1 and 5.

Acknowledgment. We are grateful to Pierre-Gilles de Gennes, Olivier Guiselin, Mohamed Daoud, and Frans Leermakers for useful discussions. Tom Waight is acknowledged for a critical reading of the manuscript.

Appendix 1

In this appendix, we will show that (7) still holds for other solvent conditions, but with different values of ν: $\nu = {}^1/_2$ (Θ solvent) and $\nu = 1$ (melt). Under all of these solvent conditions, each tail or loop (a) can be pictured as a linear string of non-overlapping "blobs" of size $\xi(r)$ (formally, we have $\mathrm{d}n/g \cong \mathrm{d}r/\xi$, where g is the number of monomers inside one "blob") and (b) behave as if it was isolated at a scale smaller than $\xi(r)$. The difference comes from the nature of the repulsive interactions between the chain segments, which affects the statistical behavior of the tails at a scale smaller than ξ.

For a Θ solvent, the repulsion between the segments is a three-body interaction:[20] $g \cong (\xi/a)^2$ and $\xi(r) \cong D(r)$. Combining (4) with the above relations, we reach (7) with $\nu = {}^1/_2$.

For a melt, the chains are gaussians and the repulsion between the segments is induced by the stretching of the chains at constant volume fraction:[31] $g \cong (\xi/a)^2$ and $\phi(r) = 1$. Combining the above relations with (4) and (5), we find that (7) is still valid with $\nu = 1$.

Appendix 2

In this appendix, we show that (22) still holds for other solvent conditions, but with different values of β: $\beta = 6$ (Θ solvent) and $\beta = 3$ (melt). The result for a Θ solvent is obtained by considering the appropriate scaling law for the osmotic pressure. Since three-bodies interactions are dominant, (20) should be replaced by[20] $\Pi_{\mathrm{osm}} \cong T\phi^3$.

In melt conditions, we calculate the elastic energies of the tails and loops (at equilibrium, the elastic contribution to the free energy is equal, within a numerical factor, to the osmotic contribution)

$$F_{\mathrm{osm}} \cong F_{\mathrm{el}} \cong \int_1^N (-\tilde{S}'(n))\, E_n \mathrm{d}n \qquad (35)$$

where $E_n \cong T \int_1^n (\dot{r}/a)^2\, \mathrm{d}n$ is the elastic energy of a tail of n monomers. After some manipulation, it is easily confirmed that the elastic contribution to the free energy is given by (22) with $\beta = 3$.

References and Notes

(1) Napper, D. In *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.
(2) Fleer, G. J.; Cohen Stuart, M.; Scheutjens, J.; Cosgrove, T., Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993.
(3) de Gennes, P. G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.
(4) Milner, S. T. *Science* **1991**, *251*, 905.
(5) de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637.
(6) Guiselin, O. *Europhys. Lett.* **1992**, *17*, 225.
(7) Auroy, P.; Auvray, L.; Léger, L. *Phys. Rev. Lett.* **1991**, *66*, 719.
(8) Auvray, L.; Cotton, J.-P. *Macromolecules* **1987**, *20*, 202.
(9) Cohen-Addad, J. P. *Polymer* **1989**, *30*, 1820.
(10) Daoud, M.; Cotton, J. P. *J. Phys.* (*Paris*) **1982**, *43*, 531.
(11) Biver, C.; Hariharan, R.; Mays, J.; Russel, W. B. *Macromolecules* **1997**, *30*, 1787.
(12) Aubouy, M.; Di Meglio, J. M.; Raphaël, E. *Europhys. Lett.* **1993**, *24*, 87.
(13) Marques, C. M.; Joanny, J. F. *J. Phys. Fr.* **1988**, *49*, 1103.
(14) Pincus, P.; Sandroff, C. J.; Witten, T. A., Jr. *J. Phys.* **1984**, *45*, 725.
(15) Ou-Yang, D.; Gao, Z. *J. Phys. II Fr.* **1991**, *1*, 1375.
(16) Cosgrove, T.; Griffiths, P. C.; Lloyd, P. M. *Langmuir* **1995**, *11*, 1457.
(17) Aubouy, M.; Guiselin, O.; Raphaël, E. *Macromolecules* **1996**, *29*, 7261.
(18) Fleer, G. J.; Leermakers, F. A. M. *Curr. Opin. Colloid and Interface Sci.* **1997**, *2*, 308.
(19) Aubouy, M. *Phys. Rev. E* **1997**, *56*, 3370.
(20) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1985.
(21) Alexander, S. *J. Phys. Fr.* **1977**, *38*, 983.
(22) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(23) It has been argued by Pincus *et al.*[14] that for very small particles the critical "stricking energy" above which the solid surface is fully covered with monomers is a function of the particle size. In the present paper, we do not consider this effect.
(24) Witten, T. A.; Pincus, P. *Macromolecules* **1986**, *19*, 2509.
(25) Scheutjens, J.; Fleer, G. J. *Macromolecules* **1985**, *18*, 1882.
(26) Alexander, S. *J. Phys.* (*Paris*) **1977**, *38*, 977.
(27) Chaplain, V.; Janex, M. L.; Lafuma, F.; Graillat, C.; Audebert, R. *Colloid Polym. Sci* **1995**, *273*, 984.
(28) Cabane, B.; Duplessix, R. *J. Phys.* **1987**, *48*, 651.
(29) Semenov, A. N.; Joanny, J.-F.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 1066.
(30) de Gennes, P.-G. *Isr. J. Chem.* **1995**, *35*, 33.
(31) Aubouy, M.; Fredrickson, G. H.; Pincus, P.; Raphaël, E. *Macromolecules* **1995**, *28*, 2979.

MA971637E