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Polymer adsorption on colloidal particles

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Résumé. — Nous considérons l'adsorption de polymères sur des particules colloïdales, sphériques et cylindriques, dont les dimensions sont comparables au rayon de gyration des chaînes des polymères. L'adsorption a lieu lorsque « l'énergie d'adhésion » par monomère excède un certain seuil. Pour une particule colloïdale ce seuil s'accroît d'un montant inversement proportionnel à son rayon. En outre, les interactions répulsives entre les monomères limitent le nombre des monomères attachés à une particule donnée. Ainsi, il existe un degré de polymérisation caractéristique N^* proportionnel à la surface de la particule. Pour $N < N^*$ une chaîne peut recouvrir complètement une particule donnée; pour $N \geq N^*$, une chaîne de polymère est décorée par des particules colloïdales comme un collier de perles.

Abstract. — We consider the adsorption of polymers on colloidal particles — spheres and cylinders — whose dimensions are comparable to solution polymer radii of gyration. Adsorption occurs if the « sticking energy » per monomer exceeds a certain threshold. For a colloidal particle, this threshold increases by an amount inversely proportional to its radius. In addition, the repulsive interactions between monomers limit the number which may be attached to a given particle. Thus, there is a characteristic degree of polymerization, N^* , proportional to the surface area of the particle. For $N < N^*$, one chain may completely clothe a given particle; for $N \geq N^*$, a polymer chain is decorated by the colloidal particles like beads on a necklace.

1. Introduction.

Colloidal particles in nonpolar solvents are often maintained dispersed by means of adsorbed polymers [1]. Polymeric steric stabilization against aggregation requires [1, 2] that : 1) the solid particle provides an adsorbing substrate for the polymer; 2) the polymer is *irreversibly* adsorbed; 3) the solvent is « good » for the polymer; i.e., the solvent mediated polymer segment-segment interactions are strongly repulsive. A considerable body of literature exists relating to the interaction of polymers with a flat surface [1, 3-10] and the interaction between solid surfaces in the presence of polymer solutions [11-13]. An excellent review article by Vincent [1] provides a relatively up-to-date view of the status of the field.

The purpose of the present study is to investigate the modifications that arise when the polymer adsorption is onto small colloidal particles rather than large, flat surfaces. Many of these modifications have been discussed *via* scaling laws by Alexander [14] in the

context of adsorption onto micelles. We shall consider adsorption onto both spherical and cylindrical colloidal particles in good and theta solvents. There are two basic effects. The colloidal surface is less accessible to the polymer than is a flat surface so that the chain must deform more to achieve the same degree of adsorption. Further, for the case of spherical adsorbates, the localization of an adsorbed chain to a finite volume of space leads to high excluded volume energies which limit the molecular weight of a completely adsorbed chain. We denote this maximum degree of polymerization by N^* and call it the *adsorbance capacity*. Both of these effects become important for radii of curvature, b , smaller than the radius of gyration R_g of the isolated chain. Typically then we are concerned with colloidal particles smaller than about $10^{-1} \mu$. In the present study, we limit ourselves to single chain properties where the major effects already become apparent. Furthermore, we utilize only a simple mean field treatment for the excluded volume interactions. Thus, in good solvents, while our results probably yield a correct qualitative picture, we should not expect precise coefficients or even exponents.

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These excluded volume effects are rather different for spherical, cylindrical and planar surfaces. Polymers adsorbed onto a planar surface are generally confined to a thickness D called the extrapolation length [8], whose magnitude is nearly independent of molecular weight and of excluded-volume interactions [9]. The osmotic excluded-volume pressure is relieved by the chain swelling *along* the surface. The resulting loss of entropy is compensated by increasing the number of surface contacts [10]. A similar « escape along the surface » may occur for long cylinders. The cylinders may be needle-shaped inorganic solids, rigid biopolymers like DNA [16] or viruses, or even aggregates of spherical particles [16-18]. The essential requirement is that their axial length L exceeds the polymer radius R_g . For spheres, this escape along the surface is not possible. Instead, there is a limiting molecular weight, the adsorption capacity N^* , above which the adsorption energy is unable to balance the swelling pressure.

We shall first demonstrate these results in terms of simple scaling arguments [19]. We represent the polymer chain as an ideal random flight of N segments, each of average length « a ». Thus the chain has an average size $R_0 \approx aN^{1/2}$. We represent the adsorbing surface as a thin layer of thickness « a ». Monomers within the adsorbing layer have their free energy reduced by an amount $\varepsilon k_B T$. (We drop the Boltzmann constant k_B in the following discussion.) After de Gennes [19, 20], we write the free energy of an adsorbed polymer as :

$$F_0/T \cong \varepsilon Nf + (R_0/D)^2 \quad (1.1)$$

where T is the temperature, f is the fraction of monomeric units in contact with the surface, and D is the confinement thickness. The first term represents the free energy gained by the adsorbed chain *via* surface contacts; the second term is the cost in entropic elastic energy for deformation of the coil to increase the number of surface contacts. We may estimate the adsorbed fraction f by assuming that the monomers are uniformly distributed in space. For a planar surface (Fig. 1), this gives $f \approx (a/D)$. Then optimizing the free energy (Eq. (1.1)) with respect to D yields $(a/D) \cong \varepsilon$. Indeed recent developments [9, 10] lead us to believe that this result for the extrapolation length retains meaning even in good solvents where both the sticking and elastic terms are strongly modified.

For restricted surfaces, the elastic energy of (Eq. (1.1)) is unchanged (D still represents the thickness of the confinement layer), but the adsorption term is

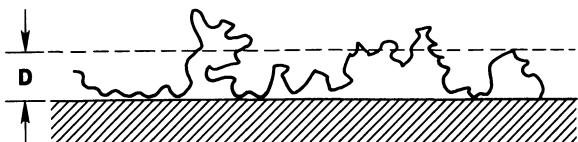


Fig. 1.

modified. For long cylinders ($L \gg R_g$) and spheres of radii b , the monomeric contact fraction f can again be estimated :

$$f \cong \begin{cases} 2ba/[(b+D)^2 - b^2] & \text{cylinders} \\ 3b^2a/[(b+D)^3 - b^3] & \text{spheres} \end{cases} \quad (1.2)$$

For both cases, upon minimizing the free energy with respect to the extrapolation length, D , we find a finite D only if the sticking energy exceeds a threshold value ε_t with $\varepsilon_t \sim a/b$. Typically, the attraction is a Van-der-Waals interaction with $\varepsilon \sim 10^{-1}$. Then the radius b must be several times as long as a segment length « a » — several tens of angstroms — to attain adsorption. Particles too small to adsorb will not be stabilized. Particles well above this minimum size have $D \ll b$, so that the adsorbed polymer forms a thin coating on the particle. In the next section a more detailed investigation of the single chain adsorption is carried out. We show that this threshold effect is somewhat modified for cylinders. In the limit $\varepsilon < \varepsilon_t$, we find weak adsorption with $D \sim b \exp(\varepsilon_t/\varepsilon)$.

As mentioned earlier, excluded volume repulsions should inhibit adsorption on spherical particles. Within the framework of a simple meanfield Flory approximation, we augment the free energy (1.1) by adding interaction terms derived from second and third virial terms,

$$F_{int}/T = \int [1/2 vc^2 + \frac{1}{6} wc^3] d^3r \quad (1.3)$$

where c is the mean concentration of segments in a coil, $v = g_2 a^3$ arises from the second virial coefficient of two isolated segments, $w = g_3 a^6$ ($g_3 \sim 1$) derives from the third virial coefficient, and the integral is over the volume occupied by the polymer chain. For good solvents ($g_2 \sim 1$), the excluded volume dominates; in the θ regime ($g_2 \ll 1$), the three body term becomes relevant. For good and θ solvents, respectively, we may then estimate the perturbation caused by F_{int} , up to numerical constants

$$F_{int}/T \cong \begin{cases} g_2 N^2 a^3/(b^2 D) & \text{good solvent} \\ g_3 N^3 [a^3/(b^2 D)]^2 & \theta \text{ solvent} \end{cases} \quad (1.4)$$

where we have used the strong adsorption result $c \sim N/(b^2 D)$. Combining (1.4) with (1.1) ($F = F_0 + F_{int}$), we note that for sufficiently high molecular weight the influence of F_{int} becomes dominant and reduces the adsorption energy strongly. Indeed, by minimizing F with respect to the molecular weight and D , we find its optimum value N^* for adsorption on a given size particle :

$$N^* \cong \begin{cases} (\varepsilon/g_2) (b/a)^2 & \text{good solvent} \\ g_3^{-1/2} (b/a)^2 & \theta \text{ solvent} \end{cases} \quad (1.5)$$

Note that 1) the adsorbance capacity N^* , scales with the surface area of the colloidal particle and 2) for θ solvents it is independent of the sticking energy ε . Thus the surface area per monomer is of order « a ». To understand this, we may re-derive N^* by setting the interaction and the elastic energies equal. Both of these have the same D dependence. Thus N^* is independent of D . It is also independent of ε , since this enters only through the surface term. This result requires $D \ll b$.

We expect that polymeric steric stabilization of colloidal dispersion will be optimum for $N \cong N^*$. For $N \gg N^*$, the polymer should envelop the particle with a coverage corresponding to $N \simeq N^*$ and then continue its random walk trajectory, attaching to other particles (Fig. 2) like beads on a necklace. Indeed, this is precisely the picture that has emerged for the interaction between micelles and polymers in aqueous solution from a detailed neutron scattering study by Cabane and Duplessix [21]. In general, this situation will reduce the polymer solubility in the dispersions and consequently be detrimental to stabilization.

In the next section, we shall refine these ideas in the framework of a self-consistent field approach.

2. Self-consistent fields.

A natural approach for describing a polymer chain in an inhomogeneous environment is provided by the self-consistent field method formalized by Edwards [22] and reviewed by de Gennes [20, 23]. For slow spatial variations, it is demonstrated that the statistical weight for a polymer to proceed from a point \mathbf{r}' to \mathbf{r} in N steps, $G_N(\mathbf{r}, \mathbf{r}')$ is given by the solution of a Schrödinger like equation,

$$-\frac{\partial G}{\partial N} = - (a^2/6) \nabla^2 G + [U(\mathbf{r})/T] G \equiv \mathbf{H}G \quad (2.1)$$

where $U(\mathbf{r})$ is an external potential (which in a mean field sense may also include internal interactions). This $G_N(\mathbf{r}, \mathbf{r}')$ may be expressed in terms of the eigenfunctions $\psi_m(\mathbf{r})$ of the operator \mathbf{H} :

$$G_N(\mathbf{r}, \mathbf{r}') = \sum_m \psi_m^*(\mathbf{r}') \psi_m(\mathbf{r}) e^{-N\omega_m} \quad (2.2)$$

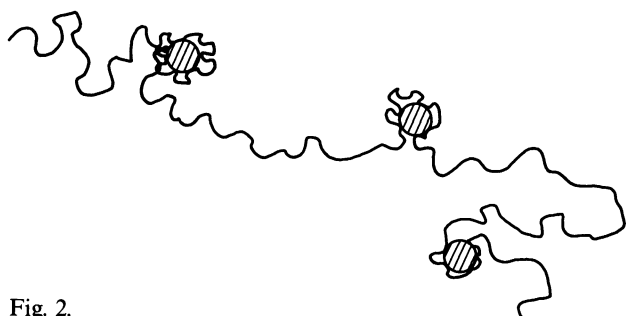


Fig. 2.

where the ψ_m satisfy

$$-\omega_m \psi_m = \mathbf{H}\psi_m.$$

The local monomer concentration $c(\mathbf{r})$ can be expressed in terms of the ψ_m . If the chain occupies a fixed volume, the ground state ψ_0 dominates for sufficiently large N and $c(\mathbf{r})$ becomes :

$$c(\mathbf{r}) = N |\psi_0(\mathbf{r})|^2 \quad (2.3)$$

where ψ_0 is the normalized ground state eigenfunction. This approach does a better job in treating the configurational entropy in an inhomogeneous environment than the cruder approximation of the introduction. Odijk [15] has applied this method to investigate polyelectrolyte complexes formed by the binding of a flexible polycation to a rod-like polyanion. Our interest here is in the relatively different situation of nonpolar solvents where the dominant interactions are local dispersion forces rather than Coulombic effects.

For the adsorbed polymers of interest here, the eigenfunction equation, 2.2-1/2, takes the form :

$$(a^2/6) \nabla^2 \psi_0(\mathbf{r}) + \varepsilon a \delta(|r - b|) \psi_0(\mathbf{r}) = \omega_0 \psi_0(\mathbf{r}). \quad (2.4)$$

For example, for a planar surface [17], the local surface attraction leads to the boundary condition :

$$-\psi^{-1} \left(\frac{d\psi}{dx} \right) \Big|_0 = \kappa \equiv 6 \varepsilon/a. \quad (2.5)$$

The exterior solution to (2.4) is then $\psi \propto e^{-\kappa x}$ with $\omega_0 = -(\kappa a)^2/6$. It is then natural to identify the extrapolation length D with κ^{-1} . In the asymptotic limit of high molecular weight ($N \rightarrow \infty$), polymers are adsorbed onto a flat surface for arbitrarily small binding energy ε in the absence of interactions. For finite molecular weight a certain minimum value of κ is necessary to obtain ground state dominance and irreversible adsorption. In practice this implies $\kappa R \gtrsim 2.4$ or $\varepsilon \gtrsim 10^{-3}$ for $N \simeq 2 \times 10^5$.

For the cases of interest here, cylindrical needles and spherical grains, the boundary condition (2.5) remains with x being replaced by the appropriate radial coordinate r . The solution of (2.4) and (2.5), then yields the conformation of an adsorbed *ideal* (no interactions) polymer chain. For spheres, we find :

$$\psi(r) = \psi(b) (b/r) e^{-k(r-b)} \quad (2.6)$$

with

$$k = (6 \omega_0/a^2)^{1/2} = \kappa - b^{-1}. \quad (2.7)$$

Adsorption requires $kR \gtrsim 1$. Hence, using equation (2.7) and the definition of κ , we obtain $\varepsilon > \varepsilon_0 [1 + (b/R_0)]$, where $\varepsilon_0 \equiv a/(6b)$. This is in agreement with the discussion following (1.2). For $\varepsilon \gg \varepsilon_0$, the localization length $D (\simeq \kappa^{-1})$ approaches the planar surface value.

The polymer-cylinder interaction is more delicate. The appropriate solution of (2.4) is the modified Bessel function $K_0(kr)$ which asymptotically behaves as :

$$K_0(z) \xrightarrow{z \rightarrow \infty} z^{-1/2} e^{-z}.$$

For small z , $K_0(z) \sim -\ln z$.

The boundary condition (2.5) yields the eigenvalue equation for k

$$\left. \frac{d \ln K_0(z)}{dz} \right|_{z=kb} = \kappa/k. \quad (2.8)$$

For strong coupling, $\kappa b \gg 1$, $k \simeq \kappa$ and the adsorption is as on a flat surface. In the weak coupling limit, $\kappa b < 1$, (2.8) becomes :

$$kb = \exp[-(1/\kappa b)].$$

The adsorption condition $kR > 1$, yields :

$$\varepsilon > \varepsilon_0 (\ln R_0/b)^{-1} \quad (2.9)$$

which for practical purposes ($R_0 \gtrsim b$) is in agreement with the predictions made on the basis of the simple energy balance arguments of the last section.

The adsorbance capacity N^* , associated with spherical grains, where escape along the surface is topologically forbidden, may be estimated by treating the segment-segment interactions (1.3) in perturbation theory. For a good solvent, where the two body interactions dominate, the energy shift per monomer $\Delta\omega$ is given by :

$$\Delta\omega \cong 1/2(v/N) \int \phi^2(r) d^3r. \quad (2.10)$$

Substituting (2.3) and (2.6) and performing the integration, we obtain, in the strong adsorption limit $\kappa b \gg 1$,

$$\Delta\omega \cong (3/(4\pi)) N g_2 \varepsilon (a/b)^2. \quad (2.11)$$

A similar first order perturbation calculation for a θ solvent yields :

$$\Delta\omega = 1/2(\varepsilon/\pi)^2 g_3 N^2 (a/b)^4. \quad (2.12)$$

The similarity to (1.4) is evident. The corresponding adsorbance capacity therefore retains the form given in (1.5). Minimizing $\omega_0 + \Delta\omega$ with respect to N gives :

$$N^* = \begin{cases} (4\pi\varepsilon/g_2) (b/a)^2 & \text{good solvent} \\ 2\pi g_3^{-1/2} (b/a)^2 & \theta \text{ solvent.} \end{cases} \quad (2.13)$$

Typically [7], $\varepsilon \approx 10^{-1}$ and $a \approx 5 \text{ \AA}$; thus for 50 \AA particles the corresponding adsorbance capacity is

$N^* \sim 10^2$. Hence in order to optimize colloid stabilization by means of polymeric additives, the molecular weight should be tuned to the particle dimensions.

3. Discussion.

We have examined polymer adsorption onto colloidal particles with a particular view toward pointing out some significant differences relative to the case of a planar surface. i) Even for ideal chains of high molecular weight $R \gg b$, the irreversible adsorption necessary for steric stabilization requires a minimum sticking energy per monomer $T\varepsilon_0 \sim (a/6b)T$ relative to that of a flat surface. ii) Both for good and theta solvents, the intramolecular repulsions impose a maximum molecular weight for complete adsorption, $N^* \propto b^2$. For practical situations with small colloidal particles or micelles, high molecular weights $N > N^*$, are unfavorable for stabilization.

These calculations have been performed in a mean field approximation. We expect that more subtle effects associated with scaling behaviour and special surface exponents in good solvents should not make qualitative changes. Similarly, our results do not depend critically on our assumption of weak coupling, $\varepsilon < 1$. In the opposite limit of *saturated* adsorption, with a fixed coverage of monomers, one can show that again $N^* \sim b^2$.

To explore experimentally how molecular weight, particle dimension and sticking energy affect the adsorption behavior of polymers, a technique is required which allows adsorbed species to be detected, even in the presence of a bulk fluid. Furthermore, the technique should permit adsorption to be detected on both planar and curved surfaces. Some preliminary experiments suggest that surface-enhanced Raman scattering (SERS) [24] could be an illuminating probe. We have recently carried out adsorption studies with aqueous solutions of 4- and 2-polyvinyl pyridine (PVPYR). Strong SERS signals were readily observed when 4-PVPYR was allowed to adsorb onto silver electrodes (planar surfaces) and small aggregates of $\sim 50 \text{ \AA}$ gold colloidal particles. That adsorption of 2-PVPYR could be seen only on the electrode surface suggests a smaller sticking energy per monomer unit for the 2-PVPYR than the 4-PVPYR resulting in a smaller N^* as indicated by equation (2.13). Since the pyridine polymer is expected to attach to the metal surface *via* the ring nitrogen, steric considerations would dictate a smaller ε for the 2-PVPYR as well.

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