Adsorption of Flexible Polymers on Small Colloids: Complexes and Gels

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Summary: We describe adsorption of neutral flexible polymer chains onto small colloids that can be covered by one chain. We discuss the structure of star-shaped complexes and their abundance in dilute solution. In semi-dilute solution similar complexes form crosslinks between chains and cause gelation.

Keywords: adsorption; colloids; gels

Introduction

Mixing colloids and polymers is a common process in the preparation of complex materials[1]. Many shearthining fluids in paints and food industry are essentially such mixtures, at or out of equilibrium. Long polymers are also sometimes used to promote protein crystallisation from solution[2].

Adding polymers to a colloid solution is a versatile way of controlling the stability of the suspension, as has been shown by extensive fundamental experimental research. There are to main classes of systems depending on the sign of polymer/colloid interaction.

In the case of repulsive polymer/colloid interaction the polymers induce an effective so-called depletion interaction between the colloids. Early studies describe large colloids as compared to the polymer size (or polymer correlation length in solution). In the fifties Osawa[3] presented a theory for the depletion interaction in mixtures of small and large colloids, later this was extended to colloid/polymer mixtures with proper account of the polymer structure by Joanny et al.[4] Since the phase diagram of this system was considered more closely merely by the liquid state theorists[5]. Many experimental data were also produced, among others in the group of Poon and

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Pusey (Edinburgh)[6]. The equilibrium properties of repulsive systems with large colloids seem rather well understood. Recent work also explains some rather generic non-equilibrium properties.

The opposite limit of small colloids was first addressed in a seminal paper by de Gennes[7], who recognised that the interactions are weak, as it is easy to incorporate a small colloid in a polymer coil. Recently the colloid/polymer and colloid/colloid interactions were carefully analysed in a field theoretical approach by Eisenriegler and co-workers[8]. They stress that colloid/colloid interactions induced by the polymer are long ranged and saturate at contact, they further show that the variations of the colloid/colloid virial coefficient are non-monotonic with polymer concentration[9]. Recent work by Sear[10] and by Fuchs[11,12], the later using integral equation methods, describe the phase diagram of such mixtures in Mean-Field, Erukhimovich is currently developing a field theoretical description with some of the present authors and it seems that we are close to a widely accepted description.

Systematic experimental studies of the adsorbing case were undertaken twenty years ago by Cabane[13].The understanding of polymer adsorption on flat surfaces was initiated earlier by Silberberg[14] and de Gennes[15]. An early model by Alexander[16] applies these ideas to the case of large spheres. A systematic description of curvature effects for adsorption on a single sphere is proposed by Birshtein and Borisov[17] for ideal chains and Marques and Joanny[18] for excluded volume chains, the latter also address surface fractality. Subsequently Aubouy et al.[19] stressed that a sphere of radius R small enough to be covered by less than one chain of contour length N will carry two long polymer tails, with a size of order N. Following this idea a small sphere satisfies $R^{d-1}<N$. Recently Semenov[20] proposed a more detailed model for the adsorption on a flat surface rationalising the numerical findings by the Dutch group[21] that the adsorption layer decomposes into an inner sublayer dominated by loops and an outer one dominated by tails. He finds a crossover distance : $z^* = N^{1/d-1}$. As in earlier work the overall layer thickness (cut off length for tails) is essentially fixed by the bulk chemical potential. The small sphere criterion by Aubouy thus corresponds to a radius where loops start feeling curvature.

Here we focus on the case of such small adsorbing colloids[22]: One chain adsorbed on a colloid has two large tails with a size fixed by the overall contour length N. In the presence of many chains a small colloid may nonetheless carry two or more chains giving rise to a star-shaped complex. We calculate the abundance of such complexes in dilute solution. In semi-dilute solution similar polymer crosses form on a colloid, these act as effective crosslinks that percolate on the gelation line.

Formation of colloid/polymer complexes

Adsorption on a flat wall

The standard model for the adsorption of a long neutral chain onto a flat wall was proposed twenty years ago by de Gennes. It starts from the remark that the local polymer/polymer correlations in the adsorption layer should be the same as in a homogeneous solution at the local concentration c(z), with z the distance from the wall. The local correlation length[23] in the layer is then given by $\xi = c^{-\nu/(\nu d-1)}$ with ν the swelling (Flory) exponent and d the dimension of space. Inside the adsorption layer of thickness λ the only characteristic lengthscale is the distance to the wall, the local correlation length $\xi(z)$ is thus proportional to z. Hence the celebrated power law profile:

$$c(z) \propto z^{\frac{-(\nu d-1)}{\nu}}$$

where the exponent is approximately —4/3.The fast decay of this profile indicates that the adsorbance Γ is dominated in the strong adsorption limit, this approach does not need to discuss the detailed structure of the layer in terms of loops and tails as done by the Dutch group. It is nontheless possible to deduce the loop distribution under the assumption that loop-monomers dominate over tail-monomers. Each loop of size larger than n feels up a correlation volume of radius z at heights up to n^{ν}. The loop-size distribution $D(n)$ can thus be rewritten in terms of the correlation disk-density at height z :

$$\int_{z^{1/v}}^{\infty} D(n')dn' = \frac{1}{z^{d-1}}$$

The loop-size distribution obtains by differentiation: $D(n) = n^{-v(d-1)-1}$. The loop-size distribution is used as a measure of the loop partition function Z_l. The tail partition Z_t function is linked to the loop partition by considering that a loop of size n can be build by connecting two tails of size $n/2$ initially within reach of each other :

$$Z_l = Z_t^{\,2} n^{1-\gamma} \frac{n^{v(d-1)}}{n^{vd}}$$

the second factor stands for loosing two free chain ends, the last one is a geometric factor specifying that the tails are within reach (here we make no difference between n and $n/2$ as the prefactor remains unknown). This relation is rather general and does not imply loop-monomer dominance. Assuming loop-monomer dominance, Z_l is known and Z_t can be deduced :

$$Z_t = n^{\frac{-v(d-2)+\gamma}{2}-1}$$

This partition function in turn determines the chain end distribution: $c_e \propto z^{-\beta/v}$ where β is the order parameter exponent linked to the previous critical exponents by the general relation: $2\beta = vd - \gamma$.

The tail-monomer concentration can in turn be calculated from the tail partition function; due to the slow decay of the tail partition function integral is actually dominated by the upper bound. About $2\Gamma/N$ ends are located beyond any distance z from the wall., any of this tails fills a correlation volume at any distance, hence the tail monomer profile $c_t(z)$ is given by :

$$c_t(z) = \frac{\Gamma}{2N} z^{\frac{1}{v}-1}$$

Comparing the tail-monomer profile to the loop-monomer profile show that the loop-monomer dominance assumption fails for $z = z^* \approx N^{\frac{1}{d-1}}$.

At larger distances, tail-monomers dominate over loop-monomers and build up de Gennes power law profile. Each correlation volume is then filled by one tail starting further from the wall, this sets the end point concentration to $c_e(z) = z^{-d}$. Reverting the arguments in the loop-monomer dominance regime it is now possible to get the tail partition function, loop partition function and loop-monomer profile.

$$Z_t = N^{\frac{\gamma+\nu d}{2\nu(d-1)}} n^{-1-\nu(d-1)} \qquad Z_l = N^{\frac{\gamma+\nu d}{\nu(d-1)}} n^{-1-\gamma-\nu(2d-1)} \qquad c_l(z) = N^{\frac{\gamma+\nu d}{\nu(d-1)}} z^{\frac{-2\nu d+1-\gamma}{\nu}}$$

Note the strong power law decrease of the loop-monomer concentration beyond z^*, with an exponent close to —6 for 3-D excluded volume statistics.

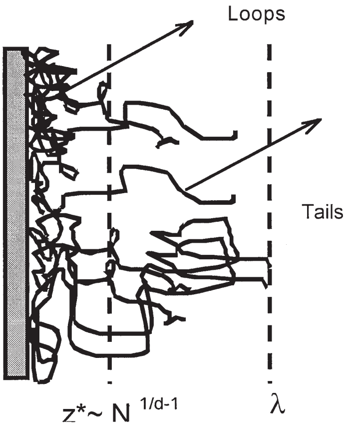

Fig. 1 Structure of the adsorbed layer in terms of loops and tails. z* is the crossover distance from the wall and λ is the thickness of the adsorbed layer

Adsorption Regimes

To put the small spheres in some general context, we first briefly discuss the various adsorption regimes encountered when the sphere radius is decreased [24].

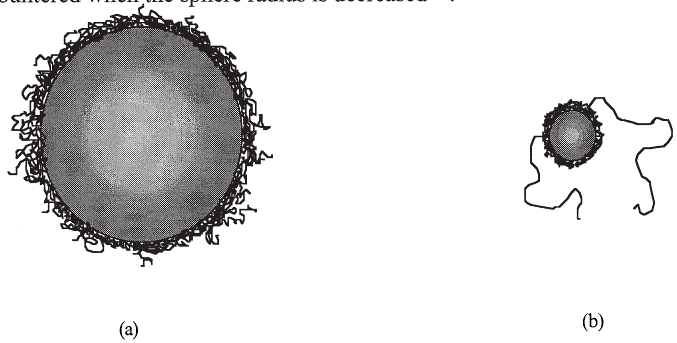

Fig. 2 Adsorption of polymers onto colloidal particles: large sphere (case a) small sphere (case b).

As long as the radius remains larger than the layer thickness the system stays in the flat regime. For somewhat smaller spheres, the layer is cut by the curvature in the sense that only a few chain sections dangle beyond a distance 2R from the colloid centre, this is best seen from de Gennes' self-similar construction. Shorter tails (and loops) still do not feel the curvature and can be described by the flat layer arguments. At even smaller colloid radii, $R<z^*$, the loops in turn feel the curvature. As argued previously the colloid is then covered by one chain with two long tails of size of order N where monomers in excess are stored.

Polymer/colloid star-shaped complexes

Depending on the stoechiometry of the polymer/colloid mixture, different complexes are expected.

If colloids are in excess, one chain wraps several colloids building a necklace. Though the single chain state is the preferred one if polymer is in excess, some colloids will accommodate a small number of chains building star-shaped complexes. In the following we will mainly comment on star-shaped complexes (a generalisation to necklace arms in the case of colloid excess is rather straightforward).

The abundance of those complexes is fixed by a balance between extra interactions of the branches and some entropy gain. At large scale a star-shaped complex has the properties of a star-polymer with polydispersed arms. Duplantier[25] gave a general expression for the partition of a polymer of any topology. This expression generalises the one for linear chains

$$Z_G = N^{\gamma_G}.$$

The new susceptibility exponent γ_G for an arbitrary connected graph G is constructed from vertex exponents, entering the star description, and depends on the number of independent closed loops. For symmetric star-polymers with all p arms identical, the expression reduces to $Z = N^{\gamma_p - 1}$. The exponent γ_p is the same for $p = 1$ and $p = 2$ (these both values of p describe a linear chain), it goes through a (formal) maximum between $p = 1$ and $p = 2$ and decreases as a power-law at high p in accordance with the Daoud and Coton blob model $\gamma_p \propto -p^{d/(d-1)}$where d is the dimension of space. The exponents γ_p are exactly known in 2-D, in 3-D only a low order ε-expansion is known.

For a star with polydispersed arms all of different size ranging from the smallest N_1 to the largest N_p the partition function can be constructed step by step: Let first all p arms have the smallest size N_1, the partition Z is $N_1^{\gamma_p -1}$, let now grow all chains but one to the next size N_2 , Z becomes $N_1^{\gamma_p -1} N_1^{\gamma_{p-1} -1} / N_1^{\gamma_{p-1} -1}$, in the next step, all outer chains but one grow to the next size N_3 and so on. As a result:

$$\mathrm{Z_p} = \mathrm{N}_1^{\gamma_p - \gamma_{p-1}} \mathrm{N}_2^{\gamma_{p-1} - \gamma_{p-2}} \cdots \mathrm{N}_{p\text{-}1}{}^{0} \mathrm{N}_p^{\gamma_1 - 1}$$

Let us first consider the simpler case where only one chain wraps the colloid. Only $n_a = 4\pi\Gamma R^2$ monomers go into small loops covering the surface of the colloid the energy gain upon adsorption of the small loops is $F_a \approx 4\pi R^2$ in thermal energy units, in case of strong adsorption. These small loops are almost of monomeric size and the small-loop layer ressembles a 2-D melt, the partition fuction of the small loop strand is described by $n_a^{\gamma_a -1}$ with γ_a the susceptibility exponent for a 2-D melt[26]. For chains such that the two tails are only of length $n_t = R^{1/\nu}$ the partition function of the two uncorrelated tails is the same as on a flat surface, of order $n_t^{\gamma - \nu - 2}$. All together the partition function reads in this case $Z_a = R^2 n_a^{\gamma_a -1} n_t^{\gamma - \nu - 2} e^{F_a} = Z_{a,0} e^{F_a}$ where R^2 stands for the choice of the starting point of one tail on the colloid. On the other hand for a very long chain wraping the colloid, the partition function of the complex scales with the chain size as for a free chain $Z_0 = N^{\gamma -1}$. Imposing a smooth crossover between the two limits at $N = n_t$, we get the partition function of the one chain complex ;

$$Z_1 = Z_{a,0} n_t (N / n_t)^{\gamma} e^{F_a}$$

When q chains wrap around the small colloid, a 2q-star shaped complex obtains. Let us characterise each chain by the smallest of its two arms (the largest is essentially its complement to N) and let again N_1 be the smallest of these $p = 2q$ arms (all by definition smaller than $N / 2$).

The partition function of the complex can be obtained in a way similar to Z_1, as a result $Z_q = n_a{}^{q-1} Z_{a,0}{}^q e^{F_a} I_t(q)$ where the small loop contribution is explicit and the first factor stands for the ways to chose the lengths of the q adsorbed loop sequences (throughout q is assumed not to be a large number). The last factor stands for the configuration integral of the large tails :

$$I(q) = \int_{n_t}^{N/2} dN_q \left(\frac{N_q}{n_t}\right)^{\gamma_{q+1}-\gamma_q} \left(\frac{N-N_q}{n_t}\right)^{\gamma_q-\gamma_{q-1}} \cdots \int_{n_t}^{N_2} dN_1 \left(\frac{N_1}{n_t}\right)^{\gamma_{2q}-\gamma_{2q-1}} \left(\frac{N-N_1}{n_t}\right)^{\gamma_1-1}$$

The value of $I(q)$ strongly depends on whether the integrals are dominated by the lower boundary.

After the general shape of the $\gamma_p(p)$ plot, the slope $\gamma_p'(p)$ becomes very negative at high p, there is a value p^* of p where $\gamma_{p-1} - \gamma_p$ becomes smaller than —1.

Let us first suppose that there are not many chains so that $2q < p^*$ in that case the lower boundary can be shifted to zero in all integrals and :

$$I(q) \propto N^q \left(\frac{N}{n_t}\right)^{\gamma_{2q}-1} \qquad (2q < p^*)$$

The chains in the star-shaped aggregate adopt mainly symmetric configurations.

In the very opposite case $q > p^*$, where there are many chains in one aggregate, all integrals are dominated by the lower boundary and:

$$I(q) \propto n_t{}^q \left(\frac{N}{n_t}\right)^{\gamma_q-1} \qquad (q > p^*)$$

The chains adopt dissymmetric configurations with only one long tail per chain (this would be expected from Daoud and Coton blob model).

In the intermediate regime $q < p^* < 2q$

$$I(q) \propto n_t{}^q \left(\frac{N}{n_t}\right)^{\gamma_{p^*}-1+p^*-q} \qquad (q < p^* < 2q)$$

There are essentially p^* long tails. Note that the intermediate regime crosses over smoothly with the previous ones.

In the following we focus on small p-values corresponding to symmetric aggregates wich are more aboundent.

Star-shaped complexes at equilibrium in dilute solution

At very small colloid densities ρ, and in dilute polymer solutions, each chain complexes at most one particle. One colloid can adsorb more than one chain, let ρ_q be the density of colloids bound to q chains. The complex densities ρ_q are given by the mass action law:

$$\rho_q / \rho_0 = \frac{Z_q}{Z_0{}^q} \left(\frac{c}{N} \right)^q$$

with c the monomer concentration. When F_a is large there are almost no free colloids and most particles are bound to a single chain $\rho \approx \rho_1$. High-q agregates are rare and the only important agregates are thos with two chains; their density is: :

$$\rho_2 = \rho c n_a Z_{a,0} n_t{}^{\gamma - \gamma_a} N^{\gamma_4 - 2\gamma + 1}$$

Inserting approximate values of the critical exponents we get $\rho_2 = \rho c R^{2.7} N^{-0.6}$.

At higher colloid densities one chain carries many colloids and forms a necklace agregate, necklaces in turn form a small fraction of decorated star-shape complexes; these will not be discussed here.

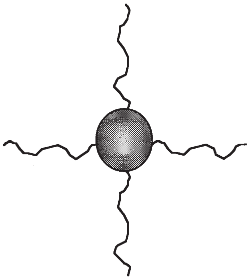

Fig.3 Star-shaped complex (q=2, p=4)

Gelation in semi-dilute solution

Above the overlap concentration $c^* = N^{1-d\nu}$ of polymer coils, the polymer form a temporary network of meshsize ξ the correlation length of polymer concentration fluctuations or concentratton blob size. Properties of such solutions of long, strongly overlapping chains are essentially insensitive to the chain length,. This is in particular true for the density of colloids linked to two blobs. To ensure a smooth crossover at c^* the density ρ_2 in the semi-dilute should be of the form $\rho_2 = \rho n_a Z_{a,0} n_t^{\gamma-\gamma_a} c^{\alpha}$ with $\alpha = 1 + \frac{2\gamma - \gamma_4 - 1}{3\nu - 1}$. Where less than one colloid per correlation volume is assumed.

On the gelation line the number of crosslinks due to colloid complexation is of order one, this locates the gelation line at:

$$\rho_g \approx \frac{n_t^{\gamma_4-\gamma}}{N n_a Z_{a,0}} c^{-\left(\frac{2\gamma-\gamma_4-1}{3\nu-1}\right)}$$

As we ignore prefactors throughout, our rough criterion for gelation is sufficient. Inserting critical exponents we obtain: $\rho_g = c^{-0.8} R^{-2.7} N^{-1}$. For long chains, there is indeed less than one colloid per polymer mesh for strongly overlapping polymer solutions.

Concluding Remarks

In this short note we present scaling results for mixtures of polymers and small adsorbing spheres. Special attention is payed to star-shaped complexes that form by adsorption of several (typically two) chains on the same colloid in dilute polymer solution with polymer in large excess. In our previous letter[22] we had no occasion to discuss the derivation of the partition function in details. It is shown that partition function of complexes comprising only a few adsorbed chains are dominated by configurations where chains have symmetric long tails. In contrast if many long chains are forced on a colloid the partition function is dominated by dissymmetric configuration where each chain only contributes one long tail in accordance with results of the Daoud and Coton star-model. The cross over between different regimes can be expressed in term of the vertex exponents introduced by Duplantier[24]. The abundance of complexes is calculated as a function of colloid radius, chain length and concentrations.

Semi-dilute solutions are described as a transient network of entangled chains by the standard concentration-blob model. Here again one colloid has some probability to link to different chains. The abundance of colloids bearing polymer crosses does not depend on chain length in the strongly overlaping regime and is obtained here from a simple cross over argument (a different argument is used in ref. 22). Beyond a critical average number of crosslinks per chain, the solution undergoes a percolation transition and forms, in that sense, a gel. The transition is located at vanishing colloid density for very long, strongly overlaping, chains. This validates *a posteriori* our assumption that there is less than one colloid per polymer mesh. This assumption is relaxed in ref.22.

Our theory is restricted to scaling arguments, it seems difficult to describe the subtle correlations between star-arms at low (finite) number of arms in more details. Also are more detailed Mean-Field theories not well suited here, they are space-dimension independent an obscure the new physics introduced by curvature(for example the criteria $\Gamma R^2 = N$ and $R = z^* \approx N^{1/3}$ are not equivalent and a spurious regime opens).

From a practical point of view the assumption of flexible chains may not always hold at the level of the colloid radius. The description of a single stiff macromolecule wrapping a colloid is available[27] (also in the charged case[28]). A description of complexes involving several chains should be possible even in the case of semi-flexible chains at least at the scaling level. In addition to the latex particles, silica colloids, or micelles used in previous experiments it should be possible to use fullerenes or modified fullerenes as model colloids[29,30].

[1] Napper DH, *Polymeric Stabilization of Colloidal Dispersion* (Academic Press, 1983); Russel WB, Saville DA, and Schowalter WR, *Colloidal Dispersions* (Cambridge University Press, Cambridge UK, 1989).

[2] Kulkarni AM, Chaterjee AP, Schweizer KS, and Zukoski Phys. Rev. Lett. **83** , 4554 (1999).

[3] Asakura S., Osawa F., J. Chem. Phys. **22** 1255 (1954).

[4] J.F.Joanny, L.Leibler, P.G.De Gennes, J. Polym. Sci. Polym. Phys. **17**,1073 (1979).

[5] M. Fuchs, K. Schweizer, Journal of Physics-Condensed Matter. 14, 239 (2002).

[6] A. Moussaid, W.C.K. Poon, P.N. Pusey, M.F. Soliva, Phys. Rev. Lett. **82**, 225 (1999).

[7] P.G.De Gennes C. R. Acad. Sc. Paris B **288**, 359 (1979).

[8] A. Hanke, E. Eisenriegler, S. Dietrich, Phys. Rev. E **59**, 6853 (1999).

[9] E.Eisenriegler, J. Chem. Phys. **113,** 5091 (2000).

[10] Sear R. , Phys. Rev. Lett. **86**, 4696 (2001); preprint 2002.

[11] M. Fuchs, K. Schweizer, Europhysics Letters **51**, 621 (2000);
M. Fuchs, K. Schweizer, Phys. Rev. E **64**,(2001).

[12] I.Y. Erukhimovich et al. In preparation.

[13] B. Cabane, R. Duplessix, J. Phys. France **48**, 651 (1987);
F.Lafuma, K.Wong , B.Cabane, J. Coll. Int. Sci **143**, 9 (1991);
K.Wong, P.Lixon, F.Lafuma, P.Lindner, O.Aguerre Charriol, B.Cabane, J. Coll. Int. Sci **153**,55 (1992);
K.Lindell and B.Cabane, Langmuir **14**, 6361 (1998).

[14] A. Siberberg, J. Phys. Chem. **66**, 1872 (1962); **66**, 1884 (1962).

[15] P.G. De Gennes, Macromolecules **14**, 1637 (1981); **15**, 492 (1982)

[16] S. Alexander, Journal de Physique **38**, 977 (1977).

[17] T.M. Birshtein, O.V. Borisov, Polymer **32**, 916 (1991).

[18] C. Marques, J.F. Joanny, J. Phys. France **94**, 1103 (1988).

[19] M. Aubouy, E. Raphael, Macromolecules **31**, 4357 (1998).

[20] A. N. Semenov et al. *Theoretical and Mathematical Models in Polymer Research,* Ed. A. Grosberg.

[21] G. Fleer, M. Cohen Stuart, J. Scheutjens, T. Cosgrove, B. Vincent,
Polymers at interfaces, (Chapman and Hall, London 1993).

[22] A. Johner, J-F Joanny, S. Diez Orrite, J. Bonet Avalos, Europhys. Lett. **56**, 549 (2001).

[23] P.G. De Gennes, *Scaling Concepts in PolymerPhysics*
(Cornell University Press, Ithaca, 1985).

[24] Silvia Diez Orrite, PhD Thesis, 2002.

[25] B. Duplantier, J. Stat. Phys. **54**, 581 (1989).

[26] A.N. Semenov (private communication), There are actually two cases, the strict 2-D case where the susceptibility exponent is non-trivial and the case where crossings are allowed (by means of small loops) where the mean-field susceptibility exponent applies. Here we should set $\gamma_a = 1$, unlike in our previous publications.

[27] H. Schiessel,RF Bruinsma, WM. Gelbart, Journal of Chemical Physics. **115**, 7245 (2001).

[28] K.K. Kunze, R.R. Netz, Phys. Rev. Lett. **85**, 4389 (2000).

[29] Y. Ederl , C. Mathis, Macromolecules **30**,2546, 1997.

[30] Larissa S. Litvinova, Veniamin G. Ivanov, Maxim V. Mokeev and Vladimir N. Zgonnik
Mendeleev Commun. 193 (2001).