Colloid Stabilization by Long Grafted Polymers

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ABSTRACT: Two colloidal particles, each with f long polymers grafted to it, experience an effective mutual repulsion in a good solvent. The effective interaction potential depends logarithmically on the separation between the particles, with a universal coefficient depending on the functionality f. We deduce this coefficient for f = 1 and 2 using results of des Cloizeaux for interior correlations within a self-avoiding walk. For $f \gg 1$ we deduce that this coefficient varies as $f^{3/2}$, using the semidilute scaling properties of the polymeric "corona" around a colloidal particle. We show that the repulsive interaction arising from the polymers can be sufficient to stabilize a dispersion of colloidal particles, despite their inherent tendency to precipitate owing to van der Waals attractions. The repulsions also give rise to a peak in the scattering structure factor S(q) for concentrations near the overlap concentration c^* . We show that the height of this peak scales as $f^{3/2}$ and predict a macrocrystalline phase for c near c^* and for sufficiently large f.

I. Introduction

One common means of stabilizing large particles in a solution is by the attachment of polymers to the particles.¹ In good solvents, the polymers avoid one another, and this tends to keep the large particles apart. One may distinguish two general ways in which the polymers may be fastened to a particle. (1) The simplest is $a dsorption:^2$ the surface is constituted so as to attract the monomers. The overall attraction may easily be made strong enough to bind a polymer irreversibly to the surface while leaving most of the monomers away from the surface, where they may serve as a repelling buffer. The adsorption method, while simple to realize experimentally, may not have the desired effect of repulsion. Indeed, adsorbed polymers may as easily produce a strong attraction as a repulsion.^{1,3} (2) An alternative attachment method is grafting. Here, a polymer is irreversibly chemically attached to a surface, e.g., at the end of the polymer chain. The chain is chosen to repel both the surface and other chains. In order to achieve this, the medium must be a good solvent for the polymer and must have a lower surface energy than the polymer against the particle surface. Such grafted chains produce an unambiguous repulsion between the particles. The chain conformations and the form of this repulsion when the polymers are short and numerous have been studied theoretically.^{4,5} On the experimental side, a very similar case of adsorbed block copolymers (one end adsorbing on the surface and the other end repelling the surface) has recently been investigated.⁶

Let us briefly review this case of polymers grafted to a *flat* surface (Figure 1). We are interested in effects specific to high molecular weight; accordingly we assume that the local concentration of monomers is small enough that detailed packing and interaction effects are unimportant. Alexander and de Gennes⁴ have argued that if the mean distance between grafting points, D, is less than the radius of gyration of the unattached polymer in good solvent, $R_0 = N^{3/5}a$, then, the chains will be stretched by the excluded volume repulsions between them. (Here, N is the degree of polymerization of the individual chains and "a" is a typical monomeric dimension.) Their scaling considerations⁷ yield a brush thickness, L

$$L/a = N(a/D)^{2/3}$$
 (I.1)

for $D < R_0$. Note (i) the linearity in N, which is typical

of stretched chains, and (ii) the proper crossover to excluded volume dimensions as the grafting density diminishes, $D \rightarrow R_0$. de Gennes⁵ considered the force between two parallel brushes whose grafting surfaces are separated by a distance h. For h > L, the force is exponentially small while for h < L, the disjoining pressure, II, is dominated by the osmotic pressure of the confined chairs, giving⁸

$$\Pi/T = D^{-3}(L/h)^{9/4} \tag{I.2}$$

For a curved surface, with radius of curvature, b, large compared with the brush thickness, L, the force is weakly perturbed from (I.2) and may be evaluated in a Derjaguin-like approximation.¹

In this study, we focus on the complementary regime, where the chains extend far beyond the diameter of the particle. (Colloidal stabilization by these long chains is probably rare in practice.) Since this regime concerns many long polymers attached to a common center, it has also been studied in the context of copolymer micelles^{9,10} and many-armed star polymer.¹¹⁻¹³ It is generally appreciated that excluded volume effects are magnified by the large number of arms and that as a result, a solution of micelles or stars may form a crystalline or glassy macrostructure. The present treatment focuses on the effective *interaction* between the stars. We find a surprising logarithmic dependence of the effective interaction on the particle separation. The coefficient of the logarithm is related to universal critical exponents¹⁴ of the self-avoiding walk problem.

For concreteness, we take the particles to be spherical balls of radius b. We idealize the polymers as self-avoiding walks of N steps on a lattice of spacing $a \ll b$. On each ball, f of these polymers are grafted; i.e., f points are chosen with uniform spacing around the ball, and a polymer is attached to each. Each of these hairy balls has a partition function Z_0 , which is the number of mutually avoiding configurations of the f polymers. We denote the average radius of gyration of the assembly as R.

If two hairy balls are separated by a displacement r < R, the total number of configurations Z(r) of the system is reduced because of mutual self-avoidance; i.e., $Z(r) < Z_0^2$. This effect is the basis of the repulsion between the balls. In a large lattice sparsely filled with such balls at random positions, a dilute dispersion, the probability P(r)that two balls are at a displacement r is given by P(r) =



Figure 1. Polymer chains grafted to a flat surface. The circular "blobs" have a diameter D equal to the lateral spacing of the chains on the surface. Each blob contains predominantly monomers of a single chain.

 $P(\infty)Z(r)/Z_0^2$. Here $P(\infty)$ is simply the concentration of balls. Since Z(r) decreases progressively as r decreases, close approaches are suppressed. One may view this suppression as arising from a repulsive interaction, U(r), a potential of mean force, defined by

$$P(r)/P(\infty) = \exp[-U(r)/T]$$
(I.3)

Our interest here is in how this repulsion depends on the chain length N and on the number of polymers per ball, f, in the regime where the polymers are very large compared to the size b of a ball.

In section II, we discuss these osmotic forces between a pair of particles and derive the structure of the potential of mean force. Colloidal stabilization requires that this effective repulsive potential balances the ubiquitous van der Waals attraction, V(r), between the spheres. This competition is considered in section III. Section IV is devoted to some comments concerning a suspension of hairy balls at a finite concentration. In particular, we calculate the osmotic pressure and predict a peak in the scattering (neutron or X-ray) structure factor in the concentration range where the hairs are starting to overlap.

II. Potential of Mean Force

There are two limits where we may readily deduce the potential of mean force between a pair of hairy balls. (i) In the small-f limit where there are only one or two polymers per sphere, we show that the interaction is related to certain critical exponents of the excluded volume problem. (ii) In the opposite limit of large f, we may discuss how U(r) depends upon f by extending the Alexander-de Gennes⁴ results for polymers grafted to a flat surface.

Let us first consider the case f = 1. As we are interested in discusses $r \gg b$, it is convenient to treat the polymeric hairs as N' blobs of radius b. If the ends of two such polymers are fixed at a separation b, the result is essentially a similar polymer of length 2N'. Its partition function Z(b)scales with N' just like any self-avoiding chain¹⁵

$$Z(b) \propto (2N')^{\gamma-1} \tau^{2N'} \qquad (\text{II.1})$$

Here the exponent $\gamma \approx {^7/_6}$ is a critical exponent of the excluded volume problem, and the "effective coordination number" τ depends on the detailed construction of the polymer. From this Z(b), we may infer the form of P(r), with r = b:

$$P(r)|_{r=b} \equiv Z(b) / Z_0^2 \propto (2N')^{\gamma - 1} \tau^{2N'} / (N'^{\gamma - 1} \tau^{N'})^2 \propto N'^{1 - \gamma}$$
(II.2)

The r dependence of P(r) can now be inferred by scaling arguments. First, P(r) must approach $P(\infty)$ if r is of the



Figure 2. Two colloidal particles of radius b, each with a long polymer grafted to it. Excluded volume repulsion between the polymers results in an effective repulsion between the colloidal particles.

order of the chain size R. This radius scales with N according to the Flory exponent $\nu \ (\approx^3/_5)$; i.e., $R \ \propto \ N^{\nu}$. Now, assuming that P(r) has the scaling form

$$(r) = P(\infty)\Phi(r/R) \tag{II.3}$$

where $\Phi(x)$ is an unknown function that must agree with P(b) (eq II.2) as $x \to b/R$. This implies that

$$\Phi(x) \propto x^{(\gamma-1)/\nu} \qquad (II.4)$$

for x < 1. The colloidal stabilization arises because the local concentration of monomers near a given sphere is reduced. For this case of a single hair, this reduction is by a factor $P(b)/P(\infty) \propto \Phi(b/R) \approx N'^{-1/6}$. The potential of mean force (eq I.3) between two such single-haired balls (Figure 2) is then

$$U(r)/T \approx \left[(\gamma - 1)/\nu \right] \ln \left(R/r \right) \tag{II.5}$$

Note the weak logarithmic dependence on separation of the spheres for R > r > b.

In a similar manner, in the case when two hairs are attached to each ball, we can relate the behavior of P(r)to previously identified polymer exponents.¹⁶ des Cloizeaux¹⁴ has treated P(r) for two monomers spaced a distance of order N along a single chain. He finds $P(r) \propto r^{\theta}$, where θ is another approximately known critical exponent ($\theta \approx$ 0.8 in three dimensions). The same power law describes P(r) when the monomers in question are on different chains.¹⁶ By the same reasoning employed in the singlehair case, P(r) also describes two hairy balls for R > r >b. This again results in a logarithmic potential of mean force with the prefactor in (II.5) replaced by θ , i.e., an approximate doubling of the interaction for a given separation.

We now turn to the limit of many hairs per ball. The surface area per hair, $4\pi b^2/f$, is now a small fraction of the area of the sphere. The distance *D* between adjacent hairs on the surface is then of order $bf^{-1/2}$. We denote the ratio $D/b \ll 1$ by β . The situation is now similar to polymers on a flat surface.⁴ The local environment is that of a semidilute polymer solution with correlation length¹⁵ ξ much smaller than the end-to-end radius of a hair. This regime many be treated along the lines of the Daoud-Cotton¹¹ study of many-armed star polymers. Globally, each hair is stretched out radially away from the chain so that the lateral separation between hairs at a distance rfrom the center is always of order βr . As usual in a semidilute solution, $\xi(r) \approx \beta r$.

It is useful to visualize this semidilute region using a blob picture; i.e., we partition space into spherical blobs of radius $\xi(r)$ (Figure 3). The surface of the sphere is covered by f blobs. Above this lies a second shell of f blobls, each $1 + \beta$ times larger than those in the first shell. The blobs in each subsequent shell are expanded by the same factor. This continues until all the monomers are contained in the shell structure. The radius of the sphere plus its corona Macromolecules, Vol. 19, No. 10, 1986



Figure 3. Daoud-Cotton conception of a many-haired ball. In this (two-dimensional) example the number f of grafted polymers is 20 and their molecular weight is such that the number S of shells is 5. The blobs drawn on the picture are constructed as described in the text. Because of excluded volume effects, each blob contains predominantly monomers of a single chain.

of polymers is then determined by this construction. Within a blob, the polymer resembles a self-avoiding walk which gives a number g of monomers per blob of order $g \approx (\xi/a)^{1/\nu}$. The resulting monomer concentration profile is then

$$c(r) \approx fg(r)[4\pi r^2 \xi(r)]^{-1}$$

 $\approx (ab/Dr)^{4/3} a^{-3}$ (II.6)

The overall radius R is then fixed by counting the total number of monomers in the corona

$$fN = \int 4\pi r^2 c(r) dr$$

$$\approx (b/D)^{4/3} (R/a)^{5/3}$$
(II.7)

or

$$R/R_0 \approx (b/D)^{2/5} \tag{II.8}$$

The overall radius scales with hair molecular weight like a polymer swollen in a good solvent but with an enlarged effective monomer size arising from the local crowding near the core. The total number of shells, S, may also be easily calculated by noting that the number of monomers per chain per shell is g(r)

$$N = (D/a)^{1/\nu} (1 + x + x^2 + ... + x^S)$$

= $(D/a)^{1/\nu} (x^{S+1} - 1)/(x - 1)$ (II.9)

where $x = (1 + \beta)^{1/\nu}$. For $D/b \ll 1$, S becomes

$$S \approx \nu(b/D) \ln [N(D/b)(a/D)^{1/\nu}]$$
 (II.10)

While the number of shells grows linearly with b (for fixed D), it increases only logarithmically with the hair molecular weight.

The polymer contribution to the free energy per ball, F, is then given by T per blob¹⁵ multiplied by the number of blobs fS

$$F \approx \nu T f^{3/2} \ln \left[N(D/b)(a/D)^{1/\nu} \right]$$
 (II.11)

If now two such balls are brought within a distance of order



Figure 4. Schematic plot of net interaction potential U(r) between two colloidal particles stabilized with long grafted polymers, showing the net effect of van der Waals attraction and the logarithmic repulsion discussed in the text.

b of each other, the bulk of the system is similar to a single ball with 2f hairs. Then, using (II.11), we find that the increase in free energy, ΔF , in this process is $\Delta F \approx F$. This ΔF is exactly the potential U(r) defined in (I.3). The N dependence of the probability P(b) is again a power law:

$$\begin{array}{l} P(b)/P(\infty) \approx \\ \exp(-\Delta F/T) \approx (N/f^{1/2})^{-\nu\theta(f)} (D/a)^{\theta(f)} \propto N^{-\nu\theta(f)} \ (\text{II.12}) \end{array}$$

where $\theta(f) \approx f^{3/2}$. The scaling argument of (II.3) gives the power law form for P(r) (cf. (II.4))

$$P(r)/P(\infty) \approx (r/R)^{\theta(f)}$$
 (II.13)

where R is the overall ball radius given in (II.8). For many hairs (large f), the suppression of close encounters is very strong. Nevertheless, the potential of mean force only increases logarithmically with N.

The behavior of $\theta(f)$ seen here sheds an instructive sidelight on des Cloizeaux's original treatment. His values of θ for small f are based on an expansion in ϵ , the dimension of space minus 4. To lowest order in ϵ one finds that $\theta \propto \epsilon f^2 + \mathcal{O}(\epsilon^2 f^4)$. Our deviation of $\theta(f)$ for large f gives $\theta(f) \propto f^{d/(d-1)}$ in d-dimensional space, so that $\theta \propto \epsilon^3 f^{4/3}$ in four dimensions. This contrasts with the leading behavior in ϵ for fixed f, and gives an insight about how the domain of validity of the ϵ expansion must shrink as f grows.

III. Steric Stabilization

The stability of colloidal suspensions requires a repulsive force to balance the van der Waals attraction, V(r), which always obtains between like objects. For spheres separated by a distance $r (\gg b)$, V(r) is given by

$$V(r) = -A(b/r)^6$$
(III.1)

where A is the Hamaker constant,¹ which depends on the polarizabilities of both solid particles and solvent. The potential of mean force U(r) associated with the "hair-hair" repulsions discussed in section II leads to the logarithmic form

$$U(r) = \nu \theta(f) T \ln (R/r)$$
(III.2)

The net effective potential E(r) = V(r) + U(r) is sketched in Figure 4. Stabilization requires first that the maximum in the potential energy E_{max} exceeds T so that the probability of one particle having enough thermal energy to penetrate into the inner minimum is small. Second, the depth, Δ , of the secondary minimum must be small relative to T, to prevent flocculation into tenuous aggregates.



Figure 5. Schematic plot of reduced osmotic pressure $\Pi(Tc)$ vs. monomer concentration c. For large functionality f an increasingly steep rise appears near the overlap concentration c^* .

Since the position of the maximum, r_{max} , obeys $r_{max} \ll R$, we can write

$$E_{\rm max}/T \approx \nu \theta(f) \ln \left(R/r_{\rm max} \right)$$
 (III.3)

Thus for many-haired balls $(f \gg 1)$ the barrier is sufficiently high to prevent aggregation provided that

$$R \gg b(6A/(T\nu\theta))^{1/6}$$
(III.4)

where R is given in (II.8). Even systems with large Hamaker constants may be protected against aggregation with long grafted chains.

The secondary minimum occurs in the vicinity of the corona edge $(r \approx R)$ where the potential of mean force, U(r), is falling exponentially toward zero. Then, using (II.8), we find

$$\Delta \approx V(R) = -A(b/R)^6 \approx -A(b/R_0)^6 f^{-6/5}$$
 (III.5)

For $A \approx T$, the secondary minimum is shallow compared to T if the individual hair radius of gyration is much larger than the ball or if there are sufficiently many hairs. In general, stabilization may be obtained with either many short hairs or a few long ones.

IV. Osmotic Pressure and Structure Factor

In this section, we consider the situation where the suspension contains a finite concentration, c_b , of manyhaired balls. Our main results in this regime were discussed in a separate note.¹⁷ The Daoud-Cotton scaling arguments are extended to allow a calculation of the scaling regimes of the osmotic pressure, II. In particular, we find a sharp increase in II at the concentration $c_b^* (\approx T^{-3})$ where the coronas begin to overlap. This crossover in the concentration dependence of the osmotic pressure is predicted to provoke a peak in the neutron scattering structure factor near $qR \approx 1$ (q is the scattering wavevector) for c_b in the vicinity of c_b^* .

In the dilute limit, $c_b \ll c_b^*$, the osmotic pressure corresponds to a dilute gas

$$\Pi = Tc_{\rm b} \tag{IV.1}$$

For semidilute solutions, $c > c_b^*$, the hairs entangle and locally resemble a semidilute linear polymer solution where the osmotic pressure is given by¹⁵

$$\Pi = T\zeta^{-3} \tag{IV.2}$$

where $\zeta/a = (ca^3)^{-3/4}$, with c being the average monomer concentration; i.e., $c = Nfc_b$. This semidilute formula should remain valid as c_b decreases until c_b^* , where we find $\Pi(c_b^*) = f^{3/2}Tc_b^*$. This is a factor $f^{3/2}$ larger than the osmotic pressure calculated from (IV.1). This implies a relatively rapid change in $\Pi(c)$ in the neighborhood of the overlap concentration (Figure 5). As the functionality, f, increases, the jump at c^* becomes larger. Many-haired balls resemble hard spheres.

The jump in the osmotic pressure in the vicinity of c^* implies a sharp decrease in the osmotic compressibility with increasing concentration in the same region. Thus at c^* , the "quasi-hard sphere"-like resistance to compression translates to a weak neutron scattering amplitude in the forward direction. We now argue that this relative incompressibility engenders a peak in the neutron scattering structure factor S(q) with scattering wavevector $q \approx R^{-1}$.

Consider first a dilute solution of hairy balls. The forward scattering structure factor per unit monomer concentration¹⁸, S(0), is then simply¹⁵ S(0) = Nf. This is related to the osmotic compressibility $[c(\partial \Pi/\partial c)]^{-1}$ by

$$S(0) = T(\partial \Pi / \partial c)^{-1}$$
 (IV.3)

For finite but small q (qR < 1), we are in the normal Guinier range where S(q) decreases with q^2 and gives the corona radius of gyration, which scales like R. For larger scattering wavevectors, we are probing the internal blob structure of the corona, which is essentially the square of the Fourier transform of the global monomer density distribution $[c(r) \propto r^{-4/3}]$. The main point that we need here is that the dilute system structure factor is a monotonically decreasing function of q.

For a finite concentration of balls near c^* where the osmotic pressure jumps, we find $\partial \Pi / \partial c \approx T f^{1/2} / N$ or using (IV.3)

$$S(0) \approx N f^{-1/2} \qquad (IV.4)$$

The strong reduction in the forward scattering amplitude arises because concentration fluctuations are greatly suppressed near the "hard sphere" packing volume fraction. On the other hand, for qR > 1, we should recover the single-chain structure factor. In particular, S(q) for $qR \approx$ 1 is given by Nf as discussed in the preceding paragraph. For qR > 1, S(q) decreases with increasing q. This implies the existence of a peak in the scattering structure factor in the vicinity of $q \approx R^{-1}$ of relative amplitude $S(q=R^{-1})/S(0) \approx f^{3/2}$. In principle, this provides an experimental method to determine the average ball functionality and corona radius.

V. Concluding Remarks

In this paper, we have considered the interactions between spherical solid particles with flexible polymers end-grafted to them. The potential of mean force associated with the hairs in good solvents is found to be a logarithmic function of the interparticle separation and polymer molecular weight. The prefactor is proportional to $f^{3/2}$. Thus if one's aim is to stabilize the particles against flocculation with the minimal amount of polymer, it is clearly more efficient to use numerous shorter hairs rather than few very long ones.

We further predict that there is a fairly sharp jump in the osmotic pressure at c^* , which, in turn, leads to a peak in the neutron scattering structure factor. Together, the peak amplitude and position yield structural data relating to the actual number of grafted hairs per ball and the extent of swelling of the polymeric corona. This swelling itself is predicted on the basis of scaling considerations parallel to those used for star polymers. Indeed, most of the results of this paper may be taken over to the case of stars if the core radius is properly defined.

A corollary of the strong peak in the structure factor is the prediction that a solution of hairy balls or stars at c^* should crystallize into an ordered steric colloidal crystal. Applying the empirical Verlet criterion that simple fluids order when the peak in the structure factor reaches approximately 3-4, we would expect crystallinity with only a few hairs. Of course, a glassy phase might intervene and mask the order but nevertheless we would predict a definite shear modulus for small shear rates.

Acknowledgment. We are very pleased to acknowledge important discussions with Dr. M. Cates.

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Kinetics of Polymer Degradation

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ABSTRACT: Explicit size distributions for polymers undergoing degradation are found for systems where the rate of bond scission depends on total chain length as well as on the position of the bond within the chain. Previously, the only model solved explicitly was the case of purely random bond scission (by Montroll and Simha). A new model is solved where chain bonds break preferentially in the center with a parabolic probability distribution, F(x,y) = xy. Here F(x,y) is the rate of fragmentation of polymers length x + y into chains of length x and y. A ternary breakup model with equal bond reactivity is also solved. The general solution is given for the case where the rate of breakup is proportional to the total chain length raised to a power α , $F(x,y) = (x + y)^{\alpha}$. When $\alpha < -1$ it is found that mass is not conserved because of a cascading breakup rate as the fragments get smaller. The long-time scaling behavior of the models is studied and found to differ for the different models. Discrete models corresponding to $\alpha = -2$ and -3 are also solved and help to show the "shattering" transition is a spontaneous breakup of a fraction of the system into monomers.

I. Introduction

Polymer chains undergo degradation (depolymerization) through a variety of mechanisms, including shear action,^{1,2} chemical attack.³ and nuclear, ultraviolet, and ultrasonic irradiation.^{4,5} It is of great interest to predict theoretically the evolution of the size distribution during such processes. For that purpose, two approaches have been used. One has been through the use of statistical and combinatorial arguments, as first used by Kuhn,⁶ Mark and Simha,⁷ and Montroll and Simha⁸ to solve the equireactivity model, in which polymer bonds break randomly and independently. The second approach has been through a kinetic equation for depolymerization. Such an equation was first introduced by Blatz and Tobolsky⁹ (in combination with polymerization) and solved for the case of size-independent polymerization and fragmentation rates. The kinetic equation of fragmentation was also studied by Jellinek and White¹⁰ and Saito.¹¹ Others who have considered the problem of depolymerization kinetics include Charlesby,¹² Nanda and Pathria,¹³ Simha and Wall,¹⁴ and Simha, Wall, and Blatz.¹⁵ Demjanenko and Dušek¹⁶ have recently considered the problem of random degradation in conjunction with cross-linking. In all these works, explicit solutions were found for only the case where the breakup rate is a constant, or all bonds break with equal probability, which is essentially the model first solved by Montroll and Simha 46 years ago. The equireactivity assumption is analogous to Flory's model of chain polymerization where all bonds are equally probable.¹⁷

In many polymer systems, however, the breaking of bonds does not occur randomly but depends upon the position of the bond within the chain and/or the total chain length. Experimental studies on systems undergoing degradation through shear,¹⁸ elongation,¹⁹ or irradiation⁴ have found that the bonds in the center of the chains break preferentially to those at the ends. For many systems, it has been proposed that the breakage rate along the chains is a truncated Gaussian distribution.^{4,20,21} One would also like to be able to understand the depolymerization kinetics of these systems. Since the equations are linear, the discrete form of the fragmentation equation can be solved in principle for any breakup function.^{10,20} Yet there have been no cases other than equireactivity where an explicit solution has been found, and other solutions have been obtained only numerically with computers. We note that a form of unequal scission has been considered in detail by Amemiya²² in connection with cross-linking kinetics. In his models, inhomogeneity was introduced by having