Colloid Stabilization with Grafted Polyelectrolytes

P. Pincus

Materials Department, University of California, Santa Barbara, California 93106

Received August 20, 1990; Revised Manuscript Received December 5, 1990

ABSTRACT: We consider the structure of a surface with a fairly dense array of polyelectrolytes end-grafted to it. A simple theory for the scaling properties of the corona thickness, counterion distribution, and disjoining pressure between opposing layers is presented, which makes contact with previous numerical studies. We show that by distributing the charges on a macromolecule the interlayer force is considerably less sensitive to Debye screening by added electrolytes. This provides the physical basis for the importance of polyelectrolytes in colloid control in polar solvents. The flat layer studies are extended to the case of small (spherical) colloidal particles. Finally some speculations are made concerning the role of grafted polyelectrolytes on contributing to the bending energies of flexible membranes.

I. Introduction

The stabilization of colloids by adsorbed[1] and end-grafted polymers[2] in nonpolar solvents has been well investigated both experimentally and theoretically in recent years. In this situation, a generally accepted picture for the effects of macromolecules on modifying the forces between solid surfaces is used. In polar solvents, ionic macromolecules are often used for the control of colloidal properties. On the other hand, fundamental understanding of this situation has still not become established. There have been a few force balance experiments with adsorbed polyelectrolytes.[3] The Wageningen group has carried out some numerical studies of the mean-field equations[4] in this case. More recently, two groups[5,6] have theoretically investigated polyelectrolytes that are end-grafted to solid surfaces. These studies provide numerical solutions of the electrostatic mean-field equations (Boltzmann–Poisson equation) coupled to polymer elasticity for polyions grafted to flat surfaces. The aim of this work is to provide simple analytic scaling laws that are approximations to these results and to give extensions to the case of spherical colloidal particles. Finally we speculate on the contributions of grafted polyions to the curvature elasticity of flexible membranes.

It would seem at first that, in polar solvents where charge separation is possible, it is sufficient to attach ionic groups to the surface of the particles that need to be kept from flocculating, sedimenting, or creaming. Indeed charged lattices[7] even form ordered colloidal crystals under the influence of the repulsive Coulombic interactions between the charged surfaces.[8] Although, in principle, this method is effective, in practice, it is not often used because of the extreme sensitivity to dissolved salts or other electrolytes. The range of the repulsive interaction is given by the Debye screening length κ^{-1} where $\kappa^2 = 4\pi nl$; n is the concentration of dissolved monovalent charged ions, and the Bjerrum length, l, is given by $l = e^2/\epsilon T$ where e is the electronic charge, ϵ is the dielectric constant of the solvent, and T is the temperature in energy units.[9] While there is no formal difficulty in including multivalent species in the Boltzmann–Poisson theory, the screening lengths become sufficiently short that the point ion approximation is seriously in error.[10,11] For dilute monovalent moieties, the point ion approximation seems to be, at least semiquantitatively, reasonable. (For water where the Bjerrum length is approximately 6 Å, a 1 mM electrolyte corresponds to a Debye length of about 100 Å. Thus even modest concentrations of salt provide strong screening of the repulsive interparticle Coulombic interaction.) As a rough guideline,[12] the range of the repulsive interaction should scale with the particle dimension in order to stabilize colloids against aggregation under the influence of van der Waals attractions. Since many applications of colloids involve situations where it is difficult to control ionic strengths at the millimolar level, it is necessary to find methods that are less sensitive to Debye screening. This is the principal motivation for using macromolecules.

With charged macromolecules the stabilization is achieved with a combination of electrostatic and steric interactions. The polyions used may be moderate-sized ionic surfactants such as oleic acid or higher molecular weight polyelectrolytes. In this paper, we discuss the particular case of polyelectrolytes that are end-grafted to a solid surface. The end grafting may be achieved by covalently bonding the polymer to the surface with a chemically active end group. Prepolymerized molecules may thus be attached to an appropriately prepared surface, or the polymerization may even be initiated and carried out in situ. Alternately, the grafting topology may be obtained by adsorbing block copolymers with one block (possibly even nonpolar) that adsorbs on the surface, with a polyelectrolyte as the other block, e.g., polystyrene/polystyrenesulfonate. Such copolymers may be simply viewed as macrosurfactants.

Despite the importance of polyelectrolytes to colloid and emulsion control in aqueous solvents, why has relatively little work been done in this area? Part of the reason may be understood by contrast with our present level of knowledge concerning neutral polymers in nonpolar solvents at interfaces. In this case[12-16] our understanding of the surface properties relies on the foundation of the excellent level of current theory of semidilute polymer solutions.[17]

On the other hand, in spite of some efforts,[18-20] bulk polyelectrolyte solutions have eluded any well-established theoretical picture that unifies the available empirical data. This lacuna has significantly retarded the development of the theory of charged polymers at interfaces. Our point of view, as well as that of the previous related studies of Miklavic and Marčelja[5] and Misra, Varanasi, and Varanasi[6] is that, for at least the case of end-grafted polyions, the existing familiarity with charged double-layer surfaces obviates a detailed understanding of the properties of polyelectrolyte solutions. Let us begin by reviewing the Boltzmann–Poisson theory for charged flat surfaces in the absence of polymers.[21] Consider a flat solid surface of charge (negative) density Σ^{-1} in contact with a polar solvent, e.g., water. We assume that the neutralizing monovalent counterions are arranged in the solvent

0024-9297/91/2224-2912$02.50/0

according to the Boltzmann distribution. At this point, we specialize the case of no added electrolyte and neglect the contribution of water ionization to the Debye screening. The Boltzmann–Poisson (BP) equation is the mean-field description of the spatial counterion distribution. It is obtained by combining Poisson's equation of electrostatics, div $\vec{D} = 4\pi e\rho$ where $\vec{D}$ is the electric displacement, with the Boltzmann weighting for the counterion density, i.e., $\rho = \rho_0 e^{-e\Phi/T}$ where ρ_0 is a constant determined by global charge neutrality and $\Phi(\vec{r})$ is the potential at the point $\vec{r}$. It is convenient to use dimensionless variables: $\phi \equiv e\Phi/T$ for the potential and $z \equiv x/\lambda$ for the length scale where x is the perpendicular distance from the surface into the solvent and the Guoy–Chapman length is $\lambda \equiv \Sigma/2\pi l$. In terms of these variables, the BP equation is

$$\mathrm{d}^2\phi/\mathrm{d}z^2 = 4\pi l\lambda^2\rho_0 e^{-\phi} \tag{I.1}$$

This second-order nonlinear differential equation is solved by the counterion distribution

$$\rho = [2\pi l(x + \lambda)^2]^{-1} \tag{I.2}$$

Note that the counterions are effectively localized to within a distance λ from the charged surface. Indeed, it is useful to consider the counterions as an ideal gas confined to a sheath of thickness on the order of the Guoy–Chapman length. The Guoy–Chapman length is itself the Debye screening length associated with the mean counterion density in the sheath. Given the counterion distribution, properties such as the contribution of the double-layer interactions to the disjoining pressure between two identical parallel surfaces separated by a distance $2h$ may be easily derived.[21] The physics of this situation may be simply understood by noting that the midplane between the surfaces is a symmetry plane on which the electric field must vanish. Therefore, the only contribution to the pressure across this plane arises from the mixing entropy of the counterions. If $h \gg \lambda$, this disjoining pressure, Π, is then given by $\Pi = T\rho(h) \simeq T/2\pi lh^2$. For $h < \lambda$, the pressure becomes $\Pi \simeq T/\Sigma h$. In both limits, the pressure effectively competes with the attractive van der Waals force per unit area, which is given by[21] $\Pi_{\mathrm{vw}} = -A/(4h^3)$ where A is the Hamaker constant, which depends on the contrast in the dielectric function between the solids and the solvent and is quite generally on the order of T, i.e., an ambient thermal energy. Thus charged surfaces are stabilizing against aggregation and flocculation under the influence of dispersion attractive forces. However, as previously mentioned, this electrostatically induced repulsive interaction is easily screened by dissolved electrolytes. The use of ionic macromolecules greatly reduces this sensitivity, effectively coverting the exponential screening to a weaker power law behavior. As we shall see, this effect is associated with the entropic polymer elasticity.

In order to understand the role of elasticity for macromolecules grafted to interfaces, we shall briefly review the principal points for the situation of end-grafted neutral polymers in contact with a good solvent.[14-16] The planar geometry is sketched in Figure 1. We consider the simple case of monodisperse polymers of degree of polymerization N with a mean grafting density[22] d^{-2} and with an excluded volume v per monomer. The polymers are extended in the form of a brush of thickness L, which is determined by balancing the excluded-volume repulsion tending to swell the chains against the entropic polymer elasticity. In mean-field theory, the osmotic pressure P corresponding to a local monomer concentration c is $P = (1/2)vc^2T$. If a Gaussian polymer has an end-to-end length L, it stores an elastic energy $(1/2)kL^2$, where the elastic constant k for a random-walk chain is $k \simeq (Na^2)^{-1}T$ (a is a monomer dimension). Then, assuming that all the grafted chains are stretched an identical length L, static equilibration is governed by

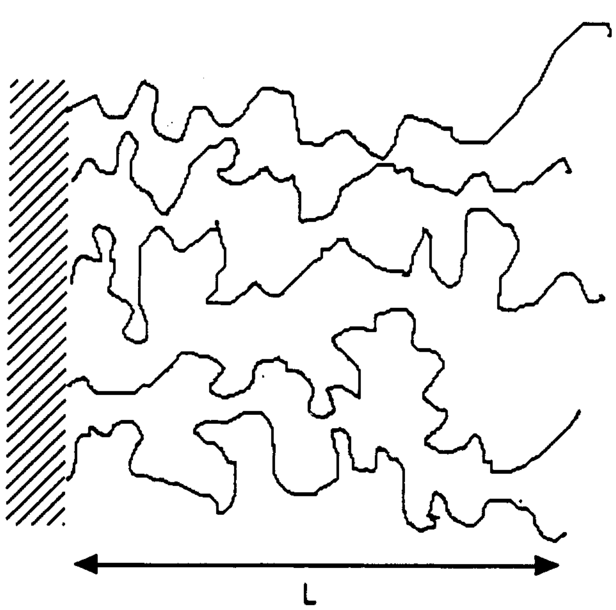

Figure 1. Sketch of the structure of a relatively dense grafted polymer brush. The brush height is L.

$$P = kL/d^2 \tag{I.3}$$

If the monomers are uniformly distributed through the brush region, $c = N(Ld^2)^{-1}$. The equilibrium condition, (I.3), then determines the brush thickness to be

$$L = Na(v/2ad^2)^{1/3} \tag{I.4}$$

This result is consistent with Alexander's[14] more sophisticated scaling discussion. The disjoining pressure between opposing identical brushes is exponentially small for $h > L$ but becomes equal to the appropriate osmotic pressure P when the brushes are pushed against one another. Then

$$\Pi = P = (1/2)vc^2T \sim vN^2T/(d^4/h^2) \tag{I.5}$$

This brush-induced pressure is of longer range[23] than the attractive van der Waals force, and, thus, if the grafting density is sufficiently large, it provides a barrier against adhesion in the dispersion-mediated minimum near contact.

Subsequently, Hirz[24] numerically solved the mean-field equations for this situation, but relaxing the assumption of a flat monomer distribution and the constraint that all free ends be at the same distance, L, from the surface. She found a parabolic profile but with the overall brush thickness obeying the Alexander scaling structure (I.4). This was rationalized analytically by Milner, Witten, and Cates (MWC)[15] in terms of a WKB approximation to the Edwards analogy between polymers and the motion of a quantum mechanical particle.[17] Much of the physics of the Hirzian profile may be understood in terms of the following simple argument.[25] The mean-field free energy per unit area, γ, of a grafted layer may be expressed as

$$\gamma/T = \int \left[\frac{1}{2}vc^2(x) + \frac{1}{2}(k/T)x^2\Psi(x) - \mu c(x) \right] \mathrm{d}x \tag{I.6}$$

The first two terms in the integral, respectively, represent the excluded-volume energy and the polymer stretching energy, where $\Psi(x)$ is the concentration of free ends at x from the surface; μ is a Lagrange multiplier to fix N monomers per chain. The problem is to determine $\Psi(x)$.

A correct approach is that given by MWC.[15] However, a crude approximation may be obtained by guessing that $\Psi(x) \approx c(x)/N$; i.e., the concentration of free ends scales with the monomer concentration. This is a reasonable approximation[15] in the outer extremities of the brush but quite poor near the surface. However, since the energetics is controlled by the highly extended chains, this ansatz gives quite good results. Now setting $\delta\gamma/\delta c(x) = 0$, we obtain

$$c(x) = v^{-1}\left[\mu - \frac{1}{2}(x/Na)^2\right] \qquad \text{(I.7)}$$

where $\mu = [(3/2\sqrt{2})(v/d^2a)]^{2/3}$ and the brush thickness is consistent with Alexander scaling, $L = Na(3v/d^2a)^{1/3}$. The free energy associated with this profile is intermediate between the Alexander[14] and MWC[15] results. The overall Hirzian parabolic form is clearly evident.

In the next section, we combine the PB equation with the approximate schemes for treating neutral grafted polymers to obtain analytic expressions for the thickness and forces between polyelectrolyte brushes. Section III is devoted to an extension of these ideas to the case of polyelectrolytes grafted to small spherical particles. Finally the concluding remarks include some speculations on the contribution of grafted polyelectrolytes to the curvature elasticity of flexible membranes.

II. Polyelectrolytes Grafted to Flat Surfaces

In this section, we consider the situation of a planar surface to which is end-grafted a concentration d^{-2} of ideally flexible polymers, each containing N monomeric units. We assume that a fixed fraction f of the monomers possesses an ionic group, e.g., sulfonate or carboxylate. (To be explicit, we suppose that the charges fixed to the chain are negative.) This charge fN per chain is neutralized by an equal number of counterions as well as a possible concentration c_s of monovalent salt molecules, e.g., NaCl. For simplicity, we only consider the electrostatic interactions. This is in contrast to the previous studies,[5,6] which also include excluded-volume repulsions. Since our point of view is to elucidate the role of the Coulombic forces, we do not wish to encumber the results with extraneous parameters. Furthermore, since the organic backbones of the polyelectrolytes are typically insoluble in water, it would seem more appropriate to use a negative excluded-volume-type interaction[26,27] in addition to the electrostatics. We plan to do so in a later publication.

The approach of Miklavic and Marčelja[5] and Misra et al.[6] is to apply the full WKB method of Milner et al.[15] augmenting the excluded-volume interaction with electrostatics using the linearized Debye–Hückel (DH) and Poisson–Boltzmann approximations, respectively. We shall demonstrate that, in contrast to the situation discussed in the Introduction of charged surface plus counterions without macroions, for the present case of grafted polyelectrolytes, the DH approximation is sufficient because the degree of freedom of chain stretching self-adjusts the electrostatic potential to be less than $\approx T$.[28] In order to carry this out, we follow the basic outlines of Misra et al.[6] i.e., combining the PB equation with entropic polymer elasticity. However, as we have seen in the Introduction for the case of neutral polymers, it may be necessary to solve the complete WKB equations in order to obtain an excellent physical picture for the structure of the brushes and their interactions. We have then investigated this system at various levels: (i) assuming an Alexander step function monomer profile; (ii) allowing the profile to self-adjust but with the ansatz that the free end concentration is given by $c(x)/N$, as is done in the Introduction for uncharged grafted chains; (iii) by a simple force balance assuming the counterions form a constrained ideal gas. The first two methods are carried out in the Appendix and serve to justify the force balance approach discussed in this section. As we shall see later, the results are also consistent with those of Miklavic and Marčelja.[5]

No Added Electrolyte. We first consider the situation in the absence of added electrolyte, i.e., the negatively charged polyions grafted to the surface with their monovalent neutralizing small counterions, e.g., Na$^+$. As is clear from the discussion of the PB equation for a charged interface in the Introduction, the dominant effect of electrostatics is to preserve local charge neutrality at the expense of the entropy of mixing of the counterions, which is increased if they can explore larger volumes. Defining ξ as the distance scale over which a test charge is neutralized,[29] we identify two possible regimes, namely $L \geq \xi$ and $L \leq \xi$. In fact, the latter one corresponds to most physical situations. Assuming that $L \geq \xi$, the brush thickness is determined by a balance between the swelling effect of the counterion entropy and the chain elasticity. In this regime the role of the electrostatics is to establish the neutralization length ξ but is not explicitly involved in determining the global brush thickness because neutrality is quite local. Then, L may be found in a similar manner to the derivation of (I.4), i.e., using $P = kL/d^2$ where now P is the counterion osmotic pressure $P = fcT$, where we have used the local neutrality condition to identify the counterion concentration with the monomer concentration, c. With the use of the step function concentration profile, this immediately yields

$$L \simeq f^{1/2}Na \qquad \text{(II.1)}$$

The neutralization length ξ is then given by the Debye screening length associated with the counterion concentration, fc. This results in

$$\xi \simeq d(a/4\pi l f^{1/2})^{1/2} \qquad \text{(II.2)}$$

Consequently, the condition $L \geq \xi$ applies unless $Nf^{3/4} \leq d(4\pi la)^{1/2}$. The result (II.1) is valid except for weakly charged polymers and low grafting densities. Note that the chains are highly stretched for finite charging and, furthermore, the brush thickness is independent of the grafting density.

In the opposite limit, $L \ll \xi$, the counterion distribution extends beyond the brush. Then, viewed from afar, the brush resembles a simple charged surface of charged density, fN/d^2. The length ξ is given by the Guoy–Chapman length λ corresponding to this charge density, $\xi \simeq d^2/2\pi lNf$. The counterion swelling pressure on the polymers is reduced by the fraction remaining (eq I.2) within the brush region, L/ξ. The force balance is then given by

$$P \simeq fc(L/\xi)T \simeq kL/d^2 \qquad \text{(II.3)}$$

which immediately yields

$$L \simeq 2\pi l N^3(fa/d)^2 \qquad \text{(II.4)}$$

This properly crosses over to (II.1) when $\xi = L$. Note the unusual N^3 molecular weight variation of the brush thickness as well as its dependence on grafting density. This regime only exists for low charge densities, $f \ll 1$; for $f \simeq 1$, $\xi \geq L$ implies grafting densities such that $d \geq R_g$, which is outside the high grafting density regime.

We are now in position to derive the behavior of the disjoining pressure between two opposing surfaces with grafted polyelectrolytes. For the dominant regime, $L \geq$

ξ, there are two domains: (a) large separation $h \geq L$; (b) compressed brushes, $h \leq L$. At large separations (a), the system behaves as highly charged interfaces and the disjoining pressure is that given in the Introduction, $\Pi = T(2\pi l h^2)^{-1}$. When the brushes are compressed (b), Π is given by the counterion osmotic pressure, $P = fcT$, where the monomer concentration is $c = N/d^2h$. Then we obtain

$$\Pi \simeq fNT/d^2h \qquad \text{(II.5)}$$

This result for the grafted polyelectrolytes exceeds that of (I.5) for neutral chains at the same grafting density and molecular weight.[30] In the neighborhood where the brushes start to overlap, $h \approx L$, there is a jump in the disjoining pressure of order $\Delta\Pi \simeq f^{1/2}T/d^2a$, which occurs over the screening length ξ. As for neutral polymers, this sharp increase in the disjoining pressure occurs because of the elastic energy stored in the stretched chains, which is converted to an interplanar force as the brushes are compressed.

We now turn to a consideration of the disjoining pressure in the weak charging limit where $\xi \geq L$. Again there are two regimes delimited by h/ξ. For $h > \xi$, we recover the standard charged interface result, $\Pi \simeq T(2\pi l h^2)^{-1}$. In the opposite limit, $h < \xi$, we find that the disjoining pressure is given by (II.5). However, there is now a smooth crossover at $h \approx \xi$. While the formal expressions in this case are similar to those in the strong charging regime, it is important to note that the pressures are numerically much weaker.

For the remainder of this paper, for simplicity we shall restrict our attention to the dominant regime of highly charged polyelectrolytes where $\xi \leq L$. In particular, we shall assume $f = 1$. It is now clear how to relax this constraint in order to obtain more complete formulas allowing for different degrees of neutralization.

Added Electrolyte. Technologically the most important aspect of colloid stabilization with polyelectrolytes is the fact that the disjoining pressure is much less sensitive to Debye screening with added electrolytes than simply charged surfaces. Let us suppose that in addition to the grafted polyelectrolytes there is a finite concentration, c_s, of monovalent completely ionized salt molecules. This corresponds to a Debye screening length κ_s^{-1}. It is important to recognize that the electrolyte plays a central role in determining the brush structure *only* when its concentration is sufficiently large that the corresponding Debye length κ_s^{-1} becomes comparable to the neutralization length ξ. Thus, for example, when $\kappa_s\xi \ll 1$, the only effect of the electrolyte is in the outer fringes, $x \geq L$ of the brush where the counterion concentration becomes equivalent to that of the salt. Then for two opposing brushes and for $\kappa_s h \geq 1$, the disjoining pressure decays exponentially to zero, $\Pi \simeq T(\kappa^2/2\pi l)e^{(-\kappa h)}$. This appropriately crosses over to the standard charged surface result in the range $L \leq h \leq \kappa_s^{-1}$. In fact, except for perturbative corrections of order $\kappa_s h$, the entire structure of the profile and disjoining pressure remain unaffected by Debye screening when $\kappa_s h \leq 1$. Therefore, in the weak screening limit $\kappa_s\xi \leq 1$, the added electrolyte only cuts off the disjoining pressure just as it would for a charged interface, as discussed in the Introduction.

What happens as the salt concentration increases and $\kappa_s\xi \geq 1$? Note that the critical dimension in determining the parameter $\kappa_s\xi$ is the mean distance between grafting sites d (eq II.2). Thus, the higher the grafting density, the less sensitive is the system to added electrolytes. As c_s increases, we expect that the Debye screening reduces the counterion osmotic pressure, which stretches the polymers. In the presence of salt, Witten and Pincus[20] have suggested that the osmotic pressure of a semidilute polyelectrolyte solution is given by

$$P \simeq cT(\kappa_0/\kappa)^2 \qquad \text{(II.6)}$$

where κ_0 is the Debye length associated with the counterions alone and $\kappa^2 \equiv \kappa_0^2 + \kappa_s^2$. Then in the limit $\kappa_s \gg \kappa_0$, the osmotic pressure scales as $P \simeq c^2T/2c_s$. This is of the form of the mean-field expression for the osmotic pressure in the presence of short-range repulsive forces,[17] with an effective excluded volume per monomer $v \simeq 4\pi l/\kappa_s^2$. The crossover from linear to quadratic dependence on the monomer concentration, as salt is added, is consistent (to within scaling corrections) with the experimental observations.[31] Using (II.6) for the osmotic pressure, we again balance it against the polymer entropy loss on expanding. This is

$$P \simeq cT(\kappa_0/\kappa)^2 \simeq LT[N(ad)^2]^{-1} \qquad \text{(II.7)}$$

which in the strong screening limit, $\kappa_s\xi \geq 1$, yields

$$L \simeq Na(2ad^2c_s)^{-1/3} \qquad \text{(II.8)}$$

Note the characteristic Alexander scaling form of the brush thickness with $L \propto d^{-2/3}$. The central result is, however, that the brush collapses with increasing salt concentration, but only as a relatively weak power law, $c_s^{-1/3}$. An interpolation formula for the structure of the crossover between the weak and strong screening limits is easily obtained by using the complete WP osmotic pressure (eq II.6).

The disjoining pressure for strong screening has three different regimes of spatial scales. For $h \geq L$ (eq II.8), the screening is exponentially strong and the disjoining pressure weakens as $e^{-\kappa_s h}$. There is an intermediate regime $L \geq h \geq h^*$ where the disjoining pressure is given by the strong screening limit of (II.6) and is

$$\Pi \simeq (1/2)(T/c_s)(N/d^2h)^2 \qquad \text{(II.9)}$$

The disjoining pressure remains a power law in h, which is still of longer range than the van der Waals attraction. When the interplanar spacing becomes smaller than

$$h^* \simeq N(2d^2c_s)^{-1} \qquad \text{(II.10)}$$

the counterion distribution is sufficiently compressed that its concentration exceeds $2c_s$ and the disjoining pressure crosses over into the regime described by (II.5). Thus throughout the strong screening regime, a power law dependence of the disjoining pressure on interplanar spacing is maintained with a crossover from h^{-1} behavior at small separations to h^{-2} at larger spacings, with a final abrupt drop to small values at $h \approx L$. This functional form for the Π–h curve is given in Figure 2, and the numerical values approximately coincide with Figure 4 of the study by Miklavic and Marčelja.[5]

This result, that the effect of Debye screening on the disjoining pressure between two polyelectrolyte grafted surfaces is greatly diminished by the polymer elasticity, is the central result of this work. While this is implicitly included in the previous calculations,[5,6] the present simple approach underscores the operating physical principles.

III. Porcupines: Polyelectrolytes Grafted to Small Colloidal Particles

The ideas discussed in the last section will now be applied to polyelectrolytes grafted to finite-size colloidal particles. We concentrate on the specialized case of small spherical particles, Figure 3. By "small", we mean that the char-

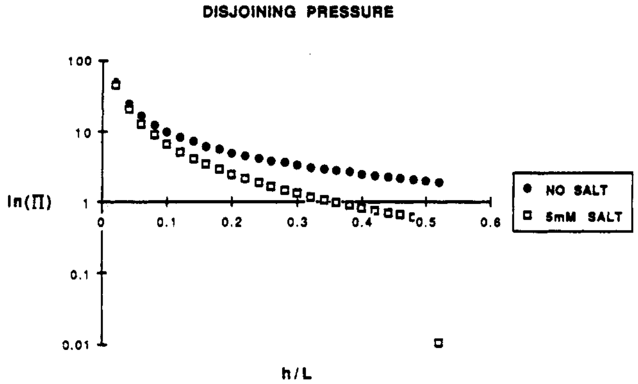

Figure 2. Logarithm of the disjoining pressure between two identical polyelectrolyte brushes plotted as a function of the surface separation normalized to the brush height for fully extended chains. The filled squares are for no added electrolyte while the open squares are for 5 mM monovalent salt. The pressure is in arbitrary units. The parameters used for this calculation are $L_0 = 10^4$ Å, $d = 10^3$ Å, and $f = 1$.

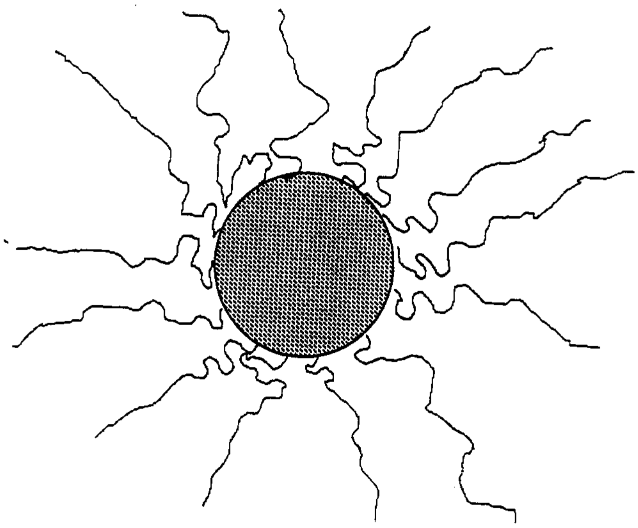

Figure 3. Sketch of a porcupine, i.e., a polyelectrolyte brush on a small spherical particle. In the absence of salt, the chains become stiffer in their regions, which are more distant from the surface.

acteristic particle dimension b is much smaller than the corona thickness R. If $b \gg R$, the Deryagiun[21] approximation immediately provides the force between two particles whose surfaces are separated by a smallest distance $2h$ in terms of the planar results of the last section. We assume spherical particles for convenience, but our analysis may be readily generalized to other shapes.

Let us briefly review this hairy ball topology for the case of grafted neutral polymers in a good solvent. If there are g homogeneously distributed hairs per particle, several groups[32,33] have applied scaling arguments to show that the coronal thickness, R, is given by

$$R \approx g^{1/5}N^{3/5}a \qquad \text{(III.1)}$$

Localization of the ends of the surface of the sphere provides an additional outward excluded-volume pressure, which provides the extra swelling, the $g^{1/5}$ factor, when compared to isolated chains.[17]

Subsequently the scaling analysis was extended[34] to ascertain the force between particles separated by a distance h, Figure 4. It was found that the scaling form from the force in the limit $R \gg h \gg b$ is given by

$$F \simeq qg^{3/2}T/h \qquad \text{(III.2)}$$

where q is a numerical constant of order unity.

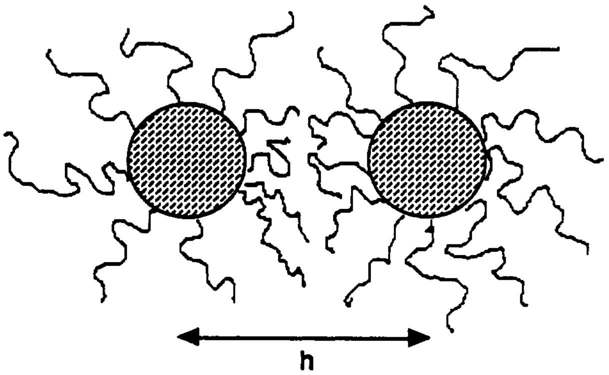

Figure 4. Sketch of two colloidal particles, which are interacting via compression of their respective brushes.

It is useful to understand these results before considering the corresponding polyelectrolyte case. The corona dimension is simply given by a Flory argument, balancing the osmotic pressure against the polymer elasticity

$$P = (1/2)c^2a^3T \simeq kRg(4\pi R^2)^{-1} \qquad \text{(III.3)}$$

where we have taken the excluded volume v to be given by a^3. Crudely assuming that the monomer concentration has its average value $Ng(4/3\pi R^3)^{-1}$, (III.3) immediately yields the Daoud–Cotton scaling form (eq III.1) to within an unknown numerical coefficient of order unity. This is an example of the typical behavior that a Flory-type force balance yields overall polymer dimensions that are consistent with scaling. However, for other properties, it is generally necessary to go beyond the naive mean-field approximation. In particular, the monomer concentration profile, $c(r)$, has a scaling[32,33] structure with $c(r) \propto r^{-4/3}$. Then, in terms of the local osmotic pressure, $P(r)$, the interparticle force may then be obtained by integrating the normal component of the osmotic pressure, $P_n(r)$, over the symmetry plane

$$F = \int P_n(r)\, dS \qquad \text{(III.4)}$$

The scaling form for the osmotic pressure[17] is $P \simeq c^{9/4}a^{15/4}T$. The proportionality constant in the self-similar profile, $c(r) \propto r^{-4/3}$, is given by the sum rule on the total number of monomers, $Ng = \int 4\pi c(r)\, r^2\, dr$. Then the force is determined from (III.4) by

$$F \simeq \int 2\pi g^{3/2}Tr^{-3}\cos\theta\, y\, dy \qquad \text{(III.5)}$$

where $\cos\theta$, Figure 4, is the projection normal to the bisecting plane. Because the particles are assumed to be very small, the self-similar profile persists into the regime, $R \gg h$, and (III.5) then reproduces the Witten–Pincus scaling form (eq III.2). It is useful to note for later reference that if we has used the mean-field form for the osmotic pressure, $P \simeq (1/2)c^2a^3T$, instead of the scaling form, the repulsive interparticle force from (III.4) would have been

$$F \simeq g^{4/3}T(h^{2/3}a^{1/3})^{-1} \qquad \text{(III.6)}$$

This is qualitatively similar to the Witten–Pincus form (eq III.2) but with slightly different exponents.

For the case of polyelectrolyte chains grafted to a spherical colloidal particle, when there is no added electrolyte, the polymers will be found to be strongly stretched radially, resembling the quills of a porcupine. In order to determine R, we must again equate the stretching force deriving from the concentration entropy against the polymer elasticity. However, in the geometry here where the particles have a finite surface area, all the counterions are not bound to the surface as in the onedimensional planar case discussed in section II; i.e., a fraction of the counterions are thermally dissociated from the grains. Therefore, a distant test charge experiences an electrostatic potential from a sphere of effective charge Z^*. It has been demonstrated[35] that $Z^* \simeq R/l$ to within logarithmic corrections, which depend on the volume fraction of colloidal particles. If the polymers are strongly stretched, $R \simeq Na$, which implies that $Z^*/Z \approx a/lg$ (with logarithmic corrections) which is extremely small when there is a large number of grafted hairs. The majority of the counterions are then bound to the neighborhood of the particle and are therefore available to swell the polymers. The now familiar procedure of balancing forces then yields the scaling form $R \simeq Na$. A more detailed calculation following the procedures outlined in the Appendix corroborates this result.

There are two regimes for the force between two particles separated by a distance h. For $h \geq R$, the interactions behave as for charged colloidal particles[7,35] with a Yukawa type potential discussed in the Introduction. For $h \leq R$, we follow the method used above for neutral grafted polymers, i.e., integrate the normal pressure over the symmetry plane. In this case, however, the pressure is dominated by the counterions, $P = \rho(r)T$. The approximate charge neutrality for $Z^* \ll Z$ yields $\rho(r) \approx c(r) \simeq A/r^2$, where the proportionality constant A is determined by the condition that there are Ng monomers attached to the particle. The r^{-2} dependence of the concentration profile derives from the strongly extended nature of the chains. Performing the integrals as above, in the limit $R \gg h \gg b$, we obtain the unusual result that the force is

$$F \simeq gT/2a \tag{III.7}$$

i.e., a force that is effectively independent of the interparticle spacing. This repulsive interaction between two colloidal particles when the brushes are compressed is generally much stronger than the van der Waals attractions and provides a high barrier against segregation in the primary minimum; as is usually the case, stabilization against flocculation in the secondary minimum[21] is assured for $R \geq b$.

In the presence of salt, the Witten–Pincus form for the osmotic pressure (eq II.6) is used in the force balance. As expected, this produces a corona thickness of the Daoud–Cotton form (eq III.1)

$$R \simeq (g/c_s a^3)^{1/5} \tag{III.8}$$

The force between two particles is again computed by integrating the osmotic pressure over the symmetry plane, yielding

$$F \simeq g^{4/3}(\kappa h)^{-2/3}/a \tag{III.9}$$

Comparing this to (III.6) and (III.2), we are led to speculate that if a proper scaling theory had been done (rather then the mean-field approximation), (III.9) might well have the form

$$F \approx g^{3/2}(\kappa a)^{-3/4}/h \tag{III.10}$$

It is again clear that the effect of Debye screening on leading to a "salting out" effect is weak in comparison to the situation without flexible polyions.

IV. Concluding Remarks

This paper has been devoted to a consideration of the interactions between surfaces to which have been end-grafted polyelectrolytes. For flat surfaces, our studies may be viewed as providing a transparent physical interpretation for previous numerical results.[5,6] The principal important result is that, in contrast to charged interfaces where in the presence of salt there is exponential Debye screening, the disjoining pressure associated with the polyelectrolytes only weakens as a power law in the electrolyte concentration. This provides the key to understanding the role of polyions in the control of colloid stability in aqueous and other polar solvents.

These ideas were then applied to the case of very small colloidal particles. Expressions for the forces deriving from the polyelectrolyte coronas between these particles were derived. By comparing to the more well-understood situation of neutral polymers grafted to spherical particles, we conclude that while these results may be qualitatively correct, the power laws on spacing, ionic strength, etc., may be incorrect in detail. It is clear that further studies should focus on constructing a consistent scaling picture.

In recent years there has been considerable interest in solutions and suspensions of more-or-less flexible membranes. Such membranes may be classified as liquid or solid (tethered) depending upon whether the internal topological organization of the elementary building blocks is invariant. The tethered membrane is predicted to have a crumpling transition[36] from an asymptotically flat to a random structure. The flat phase of the tethered membranes will have a strong tendency to flocculate[25] and will require stabilizers to prevent sedimentation, which, in polar environments, could be provided by grafted polyelectrolytes.

The physics of self-assembled fluid membranes is dominated by bending energies[37] because the largest interactions lead to a nearly constant area per surfactant, which greatly reduces the importance of surface tension. It is therefore of interest to compute the contribution of grated polymers to the resistance of a flat membrane against bending. The free energy per unit area, F_c, for bending a membrane with local radius of curvature r is given by

$$F_c = (1/2)K/r^2 \tag{IV.1}$$

where K is the bending constant, which has dimensions of an energy. The contribution to K of neutral brushes has been calculated by several groups,[38] who find that K scales as $N^3(a/d)^{14/3}T$ and $N^3(a/d)^5T$ in mean field and scaling, respectively. The structure of these results are easily obtained in terms of the scaling relation that $K \approx F_0L^2$ where F_0 is the free energy per unit area of the flat grafted layer. The difference between the two results derives from the slightly different exponents on the grafting density dependence of F_0 for mean-field and scaling theories.

We now turn to a consideration of the role of grafted polyelectrolytes in increasing the resistance to curvature and its modification by Debye screening. However, in order to confront this problem, it is necessary to understand the contribution of the electrostatic interactions to the curvature energy of a charged membrane. This problem has recently attracted a great deal of attention,[39] and the result is surprisingly complex, depending on the three lengths: λ, κ, and h. These authors find that the electrostatic part of the bending energy, K_e, is given by $K_e \approx (h/l)T$ in the absence of salt and for $h > \lambda$; $K_e \approx (\kappa l)^{-1}T$ for $h > \kappa^{-1} > \lambda$; $K_e \approx T/\kappa^3\lambda^2 l$ in the Debye–Hückel region, $h > \lambda > \kappa^{-1}$. Using these results, we may speculate on the part K_g of the bending constant of a membrane associated with grafted polyelectrolytes.

In the limit of no added electrolyte, i.e., $\kappa \rightarrow 0$, there are two regimes depending upon the interplane spacing, h. In the limit $h \rightarrow \infty$, the long-range nature of the unscreened

Coulombic interaction dominates, and we recover the result for a charged membrane in the Guoy–Chapman region, $K_g \approx (h/l)T$. However, for smaller values of h, the internal pressure of the brush is the dominant contribution leading to $K_g \approx N^3(a/d)^2T$, with the N^3 dependence characteristic of brushes but varying linearly with the grafting density (in contrast to the case of neutral brushes). This crosses over to the Guoy–Chapman result for $h/L \simeq (l/a)(L/d)^2$.

In the presence of electrolyte, we expect that Debye screening will decouple different membranes when $\kappa h \geq 1$ and there will exist an intermediate regime with $K_g \approx T/(\kappa l)$ only for $h \geq \kappa^{-1} \geq (l/a)L^3/d^2$. For stronger screening, we suggest that the free energy density is derived from (II.6) to yield, for $\kappa\xi \geq 1$, $k_g \approx N^3(a/d)^{2/3}(c_sd^3)^{-4/3}$. This is of the general form of the bending energy for neutral grafted chains discussed above but exhibiting a power law softening with added electrolyte. In the future, it is likely that membrane systems with flexible charged groups will be studied and we hope that these speculations can provide a basis for exploring the relevant undulatory modes.

Acknowledgment. I acknowledge important discussions with J.-F. Joanny, L. Leibler, J. Klein, and T. Witten. This study was supported in part by a SURS grant from IBM and the U.S. DOE DE-FG03-87ER45288. I express my appreciation to the Indian Institute of Science, Bangalore, for their hospitality during March 1990 when much of the work for this paper was accomplished.

Appendix

In this Appendix, we sketch out how the results of section II may be derived by free energy optimization assuming either a step function monomer profile or a self-adjusting profile (as done in the Introduction for neutral polymers). In order to simplify the presentation, we consider the situation in the absence of added electrolyte.

We first look at the structure of the grafted electrolyte brush in analogy with the Alexander method for neutral brushes; i.e., we assume a step function profile of undetermined thickness L for the monomer distribution of concentration $c = Nf/Ld^2$ for $x \leq L$ and $c = 0$ for $x \geq L$. The BP equation (eq I.1) becomes

$$\mathrm{d}^2\phi/\mathrm{d}x^2 = 4\pi l[c(x) - \rho_0 e^{-\phi}] \tag{A.1}$$

where the second term in the brackets represents the counterion distribution. With the step function form for the polymer concentration profile, the dimensionless electrostatic potential in the region, $x > L$, is given by

$$\phi(x) = 2 \ln [e^{\phi_L/2} + (x - L)/\xi] \tag{A.2}$$

where $\phi_L = \phi(L)$ and $\xi = (2\pi l\rho_0)^{-1/2}$. This is the Guoy–Chapman solution to the BP equation for a charged interface at $x = L$ with surface potential ϕ_L. The solution to (A.1) in the exterior region, $x > L$, for which the electric field is continuous at $x = L$ is given implicitly by

$$2x/\xi = \int_0^{\phi} (e^{-\phi} - 1 + \phi/\phi_L)^{-1/2}\,\mathrm{d}\phi \tag{A.3}$$

The potential ϕ_L is simply related to the monomer and counterion concentration scales by $\phi_L = \rho_0/c$. Then (A.3) may be viewed (at $x = L$) as an eigenvalue equation for determining ρ_0. It is clear that $\phi_L \leq 1$. There are two limiting cases: (i) $\phi_L \ll 1$; (ii) $\phi_L \approx 1 - \epsilon$, where $\epsilon \ll 1$.

Case i applies to weakly charged polyelectrolytes, $f \ll 1$. Then, (A.3) yields $\phi_L \simeq L/\xi$, which immediately shows that $\xi \geq L$ in this case as discussed in section II. Indeed, the explicit expression for ξ in terms of c is identical with that given in section II, $\xi \simeq \Sigma/2\pi l$.

Case ii is appropriate for more strongly charged polyelectrolytes, and (A.3) becomes

$$\sqrt{2}(L/\xi) \approx \ln\left[\frac{\phi_L}{2(1-\phi_L)}\right] \tag{A.4}$$

Then we find that $\epsilon \approx (1/2)e^{\sqrt{2}(L/\xi)}$ and ξ is given by (II.2).

It remains to determine the brush height L, which arises from a balance of the counterion pressure against the polyion elasticity. This may be formally accomplished by minimizing the sum of the electrostatic and elasticity contributions to the free energy. The free energy density associated with the electrostatics is

$$f_{\mathrm{es}} = \frac{1}{2}e\rho(x) + \Phi(x) + \rho_+(x) \ln \rho_+(x)\ T \tag{A.5}$$

where $\rho(x)$ is the local density of all monovalent charged moieties and ρ_+ is the local counterion concentration. The total interfacial energy, γ, is

$$\gamma = \int_0^{\infty} \left[f_{\mathrm{es}} + \frac{1}{2}k(L/d)^2 \right] \mathrm{d}x \tag{A.6}$$

where the second term in the integral is the stretching energy of the chains. Minimization of γ with respect to L gives the results derived in section II by more elementary force balance arguments.

A somewhat more refined approach, which is intermediate between that used by Misra et al.[6] and the step profile ansatz of the last few paragraphs of this appendix, is to follow the simple method of the Introduction, which yields a Hirzian parabolic profile for neutral polymer brushes. By analogy to (I.6), we write an expression for the interfacial free energy where the polyelectrolyte profile is allowed to adjust

$$\gamma = \int_0^{\infty} \left[f_{\mathrm{es}} + \frac{1}{2}kx^2\Psi(x)\ T - \mu c(x)\ T \right] \mathrm{d}x \tag{A.7}$$

where the electrostatic free energy density is given by (A.5) and the other terms have the same meaning as in (I.6). With the approximation that the concentration of polyelectrolyte ends at x, $\Psi(x)$, is given by the monomer concentration $c(x)$, the distributions of polymer and counterions are determined from the coupled Euler–Lagrange equations derived from $\delta\gamma/\delta\rho_+ = \delta\gamma/\delta{=}0$. The solutions of these equations provide explicit profiles, which may be compared with the numerical results in refs 5 and 6. Furthermore, it is straightforward to demonstrate that the results are in agreement with the scaling relations of section II.

References and Notes

(1) Patel, S. S.; Tirrell, M. *Annu. Rev. Phys. Chem.* **1989**, *40*, 597.

(2) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.

(3) These experiments have been reviewed in ref 1.

(4) Papenhuizen, J.; van der Schee, H. A.; Fleer, F. J. *J. Colloid Interface Sci.* **1985**, *104*, 540.

(5) Miklavic, S. J.; Marčelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.

(6) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 5173.

(7) Sood, A. *Solid State Physics*; Ehrenreich, H., Turnbull, G., Eds.; Academic Press: New York, 1990; p 443. An excellent general reference on colloidal crystals.

(8) The appropriate interparticle potential is of the form of a screened Coulombic interaction, or Yukawa potential, $V(r) = V_{0\mathrm{e}}{-}kT$ where V_0 depends on the surface charge and the inverse Debye screening length k^{-1} is proportional to the concentration of neutralizing counterions.

(9) We assume throughout that all dissolved small ions are monovalent in order to simplify the expressions.

(10) Wennerstrom, J. *J. Chem. Phys.* **1984**, *79*, 2221.

(11) Kjellander, R.; Marcelja, S. *Chem. Phys. Lett.* **1986**, *127*, 402. Kjellander, R.; Marcelja, S. *J. Phys. Chem.* **1986**, *127*, 402.

(12) Pincus, P. *Lectures on Thermodynamics and Statistical Mechanics: XVII Winter Meeting on Statistical Physics*; Gonzalez, A. E., Varea, C., Eds.; World Publishing Company: Singapore, 1988.

(13) de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637.

(14) Alexander, S. *J. Phys. Paris* **1977**, *38*, 983.

(15) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1989**, *5*, 413. (b) Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610. (c) Skovortsov, A. M.; Pavlushkov, I. V.; Gortimov, A. A.; Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A. *Vysokomol. Soedin.* **1988**, *A30*, 1615.

(16) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.

(17) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(18) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. Paris* **1976**, *17*, 1461.

(19) Odijk, T. *Macromolecules* **1979**, 412, 688.

(20) Pincus, P.; Witten, T. *Europhys. Lett.* **1987**, *3*, 315.

(21) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1985.

(22) Throughout this paper we assume that the grafting density is sufficiently high that the mean spacing, d, is smaller than the characteristic dimension. This implies that the local polymer concentration is in the semidilute (or denser) range.

(23) This is a mean-field result, and various exponents are inconsistent with more accurate scaling. In particular, for this case of a good solvent, the osmotic pressure scales as $c^{9/4}$ not the mean field c^2. This then implies that $\Pi \propto h^{-9/4}$. Throughout this paper we ignore these subtle distinctions and are content to apply the effective field approximation. In fact, since we use the PB equation, which is itself a mean-field approximation, it might well be inconsistent to employ more accurate exponents for other factors.

(24) Hirz, S. J. *Modeling of Interactions Between Adsorbed Block Copolymers.* M.S. Thesis, University of Minnesota, Minneapolis, MN, 1988.

(25) Pincus, P. *Phase Transitions in Soft Condensed Matter*; Riste, T., Sherrington, D., Eds.; Plenum Publishing: New York, 1989.

(26) Davis, R. M.; Russel, W. B *J. Polym. Sci.* **1986**, *B24*, 511.

(27) Joanny, J. F.; Leibler, L. *J. Phys. Paris* **1990**, *151*, 545.

(28) Joanny, J. F. Private communication.

(29) For the PB solution of a charged surface in the absence of salt, $\epsilon = \lambda$. In the usual linear DH theory, $\kappa\lambda \approx 1$.

(30) This is easily seen by taking the ratio of (I.5) to (II.5) and noting that $v/d^2h \leq 1$ and $N/f \geq 1$.

(31) See for example: Wang, L.; Bloomfield, V. A. *Macromolecules* **1990**, *23*, 804.

(32) Daoud, M.; Cotton, J. P. *J. Phys. Paris* **1982**, *43*, 531.

(33) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453.

(34) Witten, T. A.; Pincus, P. A. *Macromolecules* **1986**, *19*, 2506.

(35) Alexander, A.; Chaikin, P. M.; Grant, P.; Morales, G. J.; Pincus, P.; Hone, D. *J. Chem. Phys.* **1984**, *80*, 5776.

(36) An excellent view of the current status of membrane physics is to be found in: *Statistical Mechanics of Membranes and Surfaces*, Proceedings of the Jerusalem Winter School; Nelson, D. R., Piran, T., Weinberg, S., Eds.; World Scientific: Teaneck, NJ, 1989.

(37) Helfrich, W. *Z. Naturforsch.* **1973**, *28A*, 693. (b) Helfrich, W. *J. Phys. Paris* **1986**, *47*, 321.

(38) Cantor, R. *Macromolecules* **1981**, *14*, 1186. (b) Milner, S. T.; Witten, T. A. *J. Phys. Paris* **1988**, *49*, 1951.

(39) Pincus, P.; Joanny, J.-F.; Andelman, D. *Europhys. Lett.* **1990**, *11*, 763 and references therein.