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Binding of Long Flexible Chains to a Rodlike Macromolecule

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ABSTRACT: A phase transition can occur if long flexible chains are attracted to a rodlike macromolecule, and an analytical calculation is given of the weak binding of flexible polycations to a sufficiently stiff polyanion. The rodlike polyelectrolyte is highly charged whereas the flexible coils are only weakly charged. In a rough approximation, excluded-volume effects are neglected. The diffusion equation for the distribution function of the flexible chains is solved in the WKBJ approximation. At a certain salt concentration, a bound state appears. At lower ionic strengths the density profile of long chains surrounding the rodlike macromolecule is calculated for the case of weak binding when the adsorbed sheath is rather thick. The bound layer collapses dramatically with only a slight decrease in the ionic strength.

Introduction

A particularly appealing approach to the theory of adsorption of flexible chains to surfaces was initiated by de Gennes[1] and Lifschitz.[2] de Gennes explicitly used Edwards' analogy[3] between the configurations of a chain and the possible Feynman paths of a nonrelativistic particle, whereas Lifschitz employed an integral equation for the partition function directly. In the limit of weak adsorption the treatments are equivalent. In that case, the distribution function of the chain is determined by a diffusion equation with fields arising externally and from excluded-volume effects. This equation is solved with the help of physically plausible boundary conditions. Useful recent papers bearing on this technique include ref 4–10, thorough reviews having been given by Freed,[11] Lifschitz,[12] and de Gennes.[13] It must be observed that de Gennes[14] has criticized the application of the self-consistent field theory to this specific problem. From an experimental viewpoint, a number of interesting applications to the theory of particulate dispersions have been surveyed by Vrij.[15]

Here we want to study the interaction of a rodlike or sufficiently stiff macromolecule with long flexible chains. This system has a pronounced asymmetry similar to that of small ions surrounding a polyion. Thus it is physically reasonable to regard the stiff macromolecule as the adsorbing surface. If the macromolecule is rather long, it must be described by, say, a wormlike chain model, and appreciable bridging of the flexible chains might occur between its various sections. Accordingly, the statistical theory is complicated because of both the inherent complexity of stiff-chain theory[16] and the difficult winding problems likely to exist.[17,18] At the other extreme, the stiff macromolecule is at most several persistence lengths long so what remains is the much more modest behavior of a flexible chain in a field with cylindrical symmetry.

To be specific, we investigate the weak binding of long, flexible polycations of low charge density, to a highly charged, rodlike polyanion. We incorporate electrostatic interactions since results without adjustable parameters are obtained which might be verified experimentally. It is safe to disregard local electrostatic stiffening[19] if the flexible coil has a linear charge density of, say, one elementary charge per 20 Å. Neglect of the excluded-volume effect is not allowed, but its influence does not seem to be too severe at low enough polymer concentrations. A possible candidate for the polyanion is double-stranded DNA which has a persistence length of about 600 Å. Even though its linear charge density is high, the persistence length is practically constant in the range of ionic strengths appropriate to weak binding.

Our formulation follows closely ref 1–13. The main differences with other work are as follows: (1) The electrostatic field in the vicinity of the central rodlike polyelectrolyte is rather high. In spite of this, a region of weak binding can still be distinguished. (2) It is more difficult forcing a flexible chain into a tube than into a layer of comparable thickness, due to the larger decrease in entropy. This in turn partly counterbalances the higher electrostatic potential. (3) The electrostatic field is continuous so we cannot introduce a cutoff as is rather arbitrarily done in the neutral-polymer case. Nevertheless, we can attempt a solution in the spirit of the quantum-mechanical analogy.[1] If a bound state occurs, we are posed with a turning-point problem that is amenable to analysis by WKBJ methods. Using the uniformly valid Langer approximation which is well-known to workers in semiclassical mechanics,[20] we derive the condition for the appearance of a bound state. At the same time, the density profile of weakly bound chains is calculated as a function of the ionic strength, this being the basic independent variable experimentally.

Formalism

We view the stiff macromolecule as a uniformly charged cylinder of radius a and length l ($l \gg a$, $l \leq O(L_p)$, where L_p is the persistence length of the stiff polyelectrolyte). Its center line is the z axis in our Cartesian coordinate system (r: xyz). Later on we use cylindrical coordinates ($\rho = (x^2 + y^2)^{1/2}$, φ, z). In the vicinity of the rod, we have a flexible chain of contour length $L = NA$ which consists of N Kuhn segments, each of length A. First, we want to evaluate the partition function $G_N(\mathbf{r}, \mathbf{r}')$ (or equivalently, the distribution function) of this coil when its first segment is fixed at $\mathbf{r}'$ and its Nth link ar $\mathbf{r}$.

However, a topological problem appears whenever the cylinder is rather long. The chain with its ends fixed will be wound around the rod a certain number of times, this number being a constant for large l if the coil takes on all possible configurations. In other words, $G_N(\mathbf{r}, \mathbf{r}')$ depends on a topological constraint.[17,18] Here, it is to be understood that a sum over all winding numbers has been taken because we are interested in smoothed density profiles only. This particular problem will crop up in other situations. One might then employ the analysis of Inomata and Singh,[21] who have included interactions in Edwards' entanglement calculation.

The cylinder exerts a certain potential $\varphi(\mathbf{r})$ on every segment of the chain. One can derive an integral equation for $G_N(\mathbf{r}, \mathbf{r}')$.[1,2,5,12] Under certain conditions, the long chain is relatively weakly bound. Accordingly, the adsorbed sheath is thick, the density varies smoothly, and the integral equation reduces to the following diffusion equation:[31]

$$\partial G_N(\mathbf{r}, \mathbf{r}')/\partial N - \tfrac{1}{6}A^2\nabla_r^2 G_N(\mathbf{r}, \mathbf{r}') + (e^{\varphi(\mathbf{r})/k_BT} - 1)G_N(\mathbf{r}, \mathbf{r}') = 0 \quad (1)$$

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Here, k_B is Boltzmann's constant and T is the temperature.

The partition function $G_N(\mathbf{r}, \mathbf{r}')$ is a Green function since it satisfies the condition

$$\lim_{N \to 0} G_N(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{2}$$

Hence it can be expressed as a bilinear expansion in terms of a complete, orthogonal set of eigenfunctions $f_k(\mathbf{r})$ with corresponding eigenvalues λ_k[22]

$$G_N(\mathbf{r}, \mathbf{r}') = \sum_k f_k(\mathbf{r}) f_k(\mathbf{r}') e^{-\lambda_k N} \tag{3}$$

$$\tfrac{1}{6} A^2 \nabla_{\mathrm{r}}{}^2 f_k(\mathbf{r}) + (1 - e^{\varphi(\mathrm{r})/k_B T}) f_k(\mathbf{r}) + \lambda_k f_k(\mathbf{r}) = 0 \tag{4}$$

If the segments are attracted to the cylinder, the potential $\varphi(\mathbf{r})$ is negative and when it is strong enough, a bound state should appear. A negative eigenvalue $\lambda_0 = -\mu$ separates from the otherwise positive spectrum. The ground-state eigenfunction $f_0(\mathbf{r})$ dominates whenever the flexible coil is long enough.[1]

$$G_N(\mathbf{r}, \mathbf{r}') \simeq f_0(\mathbf{r}) f_0(\mathbf{r}') e^{\mu N} \tag{5}$$

The equations are valid only if the chains are weakly bound. Therefore, we confine ourselves to a single negative eigenvalue. The boundary conditions for adsorption are[1]

$$\lim_{\rho \to a} f_0(\mathbf{r}) = 0 \tag{6}$$

$$\lim_{\mathbf{r} \to \infty} f_0(\mathbf{r}) = 0 \tag{7}$$

Equation 6 implies that the chain is strongly repelled at the surface of the cylinder. As is shown in ref 1, the segment distribution $n(\mathbf{r})$ may be derived from $G_N(\mathbf{r}, \mathbf{r}')$

$$\begin{aligned} n(\mathbf{r}) &= Z_N{}^{-1} \sum_{M=1}^{N} \int\int \mathrm{d}\mathbf{t}\, \mathrm{d}\mathbf{s}\; G_{N-M}(\mathbf{t}, \mathbf{r}) G_M(\mathbf{r}, \mathbf{s}) \\ &\simeq N f_0{}^2(\mathbf{r}) \end{aligned} \tag{8}$$

with the unconstained partition function defined by

$$Z_N = \int\int \mathrm{d}\mathbf{s}\, \mathrm{d}\mathbf{t}\; G_N(\mathbf{s}, \mathbf{t}) \tag{9}$$

The integral of $n(\mathbf{r})$ over all space outside the rod must give the total number of links

$$\int_{\rho \geq a} \mathrm{d}\mathbf{r}\; n(\mathbf{r}) = N \tag{10}$$

an equation which shows the normalization of the eigenfunction.

As we noted earlier, we disregard all excluded-volume effects; i.e., the chains behave ideally. If there are n_F chains in the solution, n_B, the number of coils bound to the cylinder, is derived from the equality of the chemical potentials in the respective phases[1,4]

$$n_B / Z_N = n_F / V \tag{11}$$

where V is the volume of the system.

Uniformly Valid Approximation

Next, we specify the potential further. The chains and macromolecules are immersed in a 1:1 electrolyte solution of concentration n and with dielectric constant D. The Debye–Hückel screening length κ^{-1} is given by

$$\kappa^2 = 8\pi Q n \tag{12}$$

if an excess of salt is present in comparison with the (local) segment density. Here, Q is the usual Bjerrum length equal to q^2/Dk_BT, with q the elementary charge. A number of theories[23-26] give the electrostatic potential exerted by the uniformly charged cylinder when its charge spacing is smaller than Q. It can be written as $-B\psi(\kappa\rho)$ for $\rho \geq a$, where ψ is dimensionless and B is a positive factor with dimension energy per charge which may have a slight κ and a dependence. Furthermore, we suppose that every segment of the flexible chain possesses one positive elementary charge q. If A is sufficiently long, say of order 20 Å, we can neglect electrostatic stiffening effects and in a rough approximation, excluded-volume interactions. The potential exerted on each segment becomes

$$\varphi(\mathbf{r}) = -qB\psi(\kappa\rho) \tag{13}$$

We now assume that the ground-state eigenfunction is cylindrically symmetrical. Hence we need to solve the following eigenvalue problem as can be seen from eq 4

$$\epsilon^2 \frac{1}{u} \frac{\mathrm{d}}{\mathrm{d}u} u \frac{\mathrm{d}f_0(u)}{\mathrm{d}u} + (1 - e^{-\beta\psi(u)} - \mu) f_0(u) = 0 \tag{14}$$

with boundary conditions

$$f_0(\alpha) = 0 \tag{15}$$

$$f_0(\infty) = 0 \tag{16}$$

For convenience, we have introduced the dimensionless parameters $u = \kappa\rho$, $\alpha = \kappa a$, $\beta = qB/k_BT$, and $\epsilon^2 = A^2\kappa^2/6$. At this stage, let us note that a must be of order A or larger in order that eq 14 remains meaningful.

With the help of the substitution $u = e^w$, eq 14 is transformed into an expression suitable for the application of WKBJ techniques. At first sight, the substitution $f_0(u) = u^{-1/2} g(u)$ would seem to work too. When this is done and the WKBJ method is used, mathematical subtleties appear similar to those encountered in applying the WKBJ approximation to the radial Schrödinger equation. This point is discussed by Berry and Mount[20] and it seems that the first replacement is the only one worthwhile. Equation 14 becomes

$$\epsilon^2\, \mathrm{d}^2 f_0 / \mathrm{d}^2 w - R(w) f_0 = 0 \tag{17}$$

where

$$R(w) = e^{2w}(\mu + e^{-\beta\psi(e^w)} - 1) \tag{18}$$

and with boundary conditions $f = 0$ at $w = \ln \alpha$ and $f(\infty) = 0$.

The WKBJ solution we employ is formally exact in the limit $\epsilon \to 0$. However, it is known to work extremely well if ϵ is somewhat smaller than $O(R(w))$.[27,30] For instance, in comparison with Wiegel's exact calculation,[5] the WKBJ approximation for the appearance of a bound state is in error by only 1%. If a bound state exists, $\mu > 0$ and the function $R(w)$ has a first-order zero at $w = w_0$ ($u_0 = e^{w_0}$)

$$\mu = 1 - e^{-\beta\psi(e^{w_0})} \tag{19}$$

Moreover, since ψ decreases monotonically, at least in the approximations existing in the literature,[23-26] $R(w) < 0$ if $w < w_0$ and $R(w) > 0$ if $w > w_0$. When eq 17 is interpreted as a Schrödinger equation, w_0 is the classical turning point of first order. Classically, a particle with energy $-\mu$ moving in the potential trough will be confined to the region $\ln \alpha \leq w \leq w_0$. Quantum mechanically, the bound particle has a nonzero probability of being in the classically forbidden region $w > w_0$. This follows from the Schrödinger equation: to the left of w_0, f_0 exhibits oscillatory behavior;[32] to the right it must decay monotonically to zero. The first-order WKBJ solution which is uniformly valid in the region $w \geq \ln \alpha$, even at the turning point w_0, is the Langer approximation given by[20,27]

$$f_0 \simeq 2\pi^{1/2} E \left(\frac{3}{2\epsilon} S_0\right)^{1/6} [R(w)]^{-1/4} \operatorname{Ai} \left[\left(\frac{3}{2\epsilon} S_0\right)^{2/3}\right] \tag{20}$$

where the action is defined as $S_0 = \int_{w_0}^{w} R^{1/2}(v)\, \mathrm{d}v$, Ai signifies the Airy function, E is a normalization constant and the boundary condition eq 16 has been used.

Bound State

It may be verified by using the leading term in the asymptotic expansion of the Airy function[27,28] that eq 20 reduces to

$$f_0(u) \simeq Eu^{-1/2}(\mu + e^{-\beta\psi(u)} - 1)^{-1/4} \times \exp\left[-\frac{1}{\epsilon}\int_{u_0}^{u} (\mu + e^{-\beta\psi(v)} - 1)^{1/2}\,\mathrm{d}v\right] \quad (21)$$

if $u \gg u_0$, where we have switched back to the u variable again. Likewise, if $u \ll u_0$, it can be shown that[33]

$$f_0(u) \simeq 2Eu^{-1/2}(1 - e^{-\beta\psi(u)} - \mu)^{-1/4} \times \sin\left[\frac{1}{\epsilon}\int_{u}^{u_0} (1 - e^{-\beta\psi(v)} - \mu)^{1/2}\,\mathrm{d}v + \frac{\pi}{4}\right] \quad (22)$$

The potential ψ decays so rapidly that eq 21 can be fruitfully approximated by

$$f_0(u) \simeq \frac{E}{u^{1/2}\mu^{1/4}}e^{-u\mu^{1/2}\epsilon^{-1}} \quad (23)$$

or

$$f_0(\rho) \simeq \frac{E}{(\mu^{1/2}\kappa\rho)^{1/2}}e^{-6^{1/2}\mu^{1/2}\rho A^{-1}} \qquad (\kappa\rho \gg 1)$$

This form is readily derived from the original differential equation. Thus, it is verified that the WKBJ solution correctly predicts the occurrence of a bound state when $\mu > 0$. However, such a state appears only if the boundary condition at the surface of the rod can be met. In the WKBJ approximation, this will happen if the potential has a long enough range for the Airy function to have a zero. In the case of slightly bound chains, only the first zero η_1 is of interest

$$\mathrm{Ai}\,(\eta_1) = 0$$

$$\eta_1 \simeq -2.338$$

Therefore, the flexible chain will be captured whenever the Debye radius is larger than κ_1^{-1} given by the implicit equation

$$\int_{\kappa_1 a}^{\infty} (1 - e^{-\beta(\kappa_1)\psi(v)})^{1/2}\,\mathrm{d}v = \left(\frac{2|\eta_1|^{3/2}}{3.6^{1/2}}\right)A\kappa_1 = 0.973A\kappa_1 = CA\kappa_1 \quad (24)$$

The upper limit corresponds to $\mu = 0$. The eigenvalue $-\mu$ is derived from the condition

$$\int_{\kappa a}^{u_0} (1 - e^{-\beta(\kappa)\psi(v)} - \mu)^{1/2}\,\mathrm{d}v = CA\kappa \quad (25)$$

with

$$1 - e^{-\beta(\kappa)\psi(u_0)} = \mu$$

In the case of weak binding, only one negative eigenvalue must appear, so the Debye radius has an upper bound, $\kappa > \kappa_2$, the latter being given by

$$\int_{\kappa_2 a}^{\infty} (1 - e^{-\beta(\kappa_2)\psi(v)})^{1/2}\,\mathrm{d}v = \left(\frac{2|\eta_2|^{3/2}}{3.6^{1/2}}\right)A\kappa_2 \quad (26)$$

with

$$\mathrm{Ai}\,(\eta_2) = 0$$

$$\eta_2 \simeq -4.09$$

Application to a Specific Potential

There have been several attempts[23-26] to derive the electrostatic potential of a uniformly charged cylinder in an excess salt solution, the most convincing treatment being due to Fixman.[26] His investigation shows that the potential satisfies the nonlinear Poisson–Boltzmann equation reasonably well. However, a uniformly valid solution has not yet been presented, except at low charge densities. The approximate "limiting law" potential due to Manning[23] is often used in analytical work and is given by[34]

$$\psi(v) = K_0(v)$$

$$\beta(\kappa) = 2 \quad (27)$$

with $K_0(v)$ the usual zero-order Bessel function.[28] The numerical Poisson–Boltzmann solution differs only to logarithmic order from this approximation. It may be noted that the Manning potential underestimates the Poisson–Boltzmann potential near the surface of the cylinder whereas it overestimates the other results at vast distances from the rod.[26] In the intermediate range, which is needed to explain a large number of physical phenomena, the Manning potential still retains reasonable accuracy.

Thus, with this choice, the phase transition occurs at the Debye radius κ_1^{-1} obtained from

$$I(0) \equiv \int_0^{\infty} (1 - e^{-2K_0(v)})^{1/2}\,\mathrm{d}v \simeq CA\kappa_1 + \tfrac{1}{2}a\kappa_1(1 - Fa^2\kappa_1^2)^{1/2} + \tfrac{1}{2}F^{-1/2}\arcsin F^{1/2}a\kappa_1 \quad (28)$$

to a good approximation whenever $a\kappa_1 \lesssim {}^1/_2$. We have used the first term[28] Fv^2 of the expansion of $\exp(-2K_0(v))$ for small v, where F equals $({}^1/_2e^{\gamma})^2 \simeq 0.793$. In this manner, the left-hand side of eq 28 conveniently becomes implicitly dependent on κ_1. Likewise, the eigenvalue is derived from

$$I(\mu) \equiv \int_0^{u_0} (1 - e^{-2K_0(v)} - \mu)^{1/2}\,\mathrm{d}v \simeq CA\kappa + \tfrac{1}{2}(1 - O(\mu))[a\kappa(1 - Fa^2\kappa^2)^{1/2} + F^{-1/2}\arcsin F^{1/2}a\kappa] \quad (29)$$

with

$$\mu = 1 - e^{-2K_0(u_0)}$$

We are interested in small μ values but a Taylor expansion of $I(\mu)$ is impossible, for the integral is not analytic in the variable μ. However, an asymptotic expansion proves feasible, as we will now show. The gist of our method is that small μ values should be determined by the tail of the potential, which in turn is dominated by an exponential function.

We first observe that some number ω of order unity exists such that $\exp(-2K_0(v))$ can be approximated by the leading asymptotic term[28] $1 - (2\pi/v)^{1/2}\exp(-v) \equiv 1 - H(v)$ for values of v larger than ω. Hence, it follows that

$$I(0) - I(\mu) = \int_0^{\omega} [(1 - e^{-2K_0(v)})^{1/2} - (1 - e^{-2K_0(v)} - \mu)^{1/2}]\,\mathrm{d}v + \int_{u_0}^{\infty} H^{1/2}(v)\,\mathrm{d}v + \int_{\omega}^{u_0} [H^{1/2}(v) - (H(v) - \mu)^{1/2}]\,\mathrm{d}v \quad (30)$$

The resulting integrals can now be simplified

$$\int_0^{\omega} [(1 - e^{-2K_0(v)})^{1/2} - (1 - e^{-2K_0(v)} - \mu)^{1/2}]\,\mathrm{d}v = O(\omega\mu) \quad (31)$$

$$\int_{u_0}^{\infty} H^{1/2}(v)\,\mathrm{d}v = \left(\frac{2\pi}{u_0}\right)^{1/4} e^{-u_0/2} \int_0^{\infty} \frac{e^{-t/2}}{(1 + t/u_0)^{1/4}}\,\mathrm{d}t = 2\mu^{1/2}\left[1 - O\left(\frac{1}{u_0}\right)\right] \quad (32)$$

$$\mu \rightarrow 0$$

The order term in eq 32 is to be understood in an asymptotic sense.

An asymptotic series for the integral on the right-hand side of eq 30 can be derived in the following way:

$$\int_{\omega}^{u_0} [H^{1/2}(v) - (H(v) - \mu)^{1/2}]\,\mathrm{d}v = \mu \int_{\omega}^{u_0} \frac{\mathrm{d}v}{H^{1/2}(v) + (H(v) - \mu)^{1/2}} = \mu^{1/2} \int_{0}^{u_0-\omega} \frac{(1 - t/u_0)^{1/4} e^{-t/2}\,\mathrm{d}t}{1 + (1 - e^{-t}(1 - t/u_0)^{1/2})^{1/2}} = \mu^{1/2}\left[\pi - 2 - 2e^{-1/2(u_0-\omega)} - O(e^{-(u_0-\omega)}) - O\left(\frac{1}{u_0}\right)\right] \quad (33)$$

$$\mu \rightarrow 0 \qquad u_0 \rightarrow \infty$$

In eq 32 and 33, the limit is taken in such a way that $\mu = (2\pi/u_0)^{1/2} \exp(-u_0)$. The eigenvalue is determined by combining eq 28–33[36]

$$[CA + a(1 - Fa^2\kappa_1^2)^{1/2}](\kappa_1 - \kappa) = \pi\mu^{1/2} \quad (34)$$

$$\mu \rightarrow 0$$

If $a = O(A)$, we can write the surprisingly simple result for the thickness d of the bound layer, using eq 23[36]

$$d \simeq (\kappa_1 - \kappa)^{-1} \simeq \frac{\kappa_1^{-2}}{\kappa^{-1} - \kappa_1^{-1}} \quad (35)$$

Once the coil is bound, it collapses drastically when the salt concentration is slightly decreased.

Distribution Functions

To proceed further, we replace eq 20 by the form strictly valid at large distances. Investigation of the Airy function shows that this is reasonable. Approximate expressions for various quantities are found starting from the ground-state eigenfunction

$$f_0(\mathbf{r}) \simeq \left(\frac{\xi}{\pi l \rho}\right)^{1/2} e^{-\xi\rho} \quad (36)$$

which is normalized as

$$\int_{-l/2}^{l/2} \mathrm{d}z \int_0^{2\pi} \mathrm{d}\varphi \int_a^{\infty} \rho\,\mathrm{d}\rho\, f_0^2(\mathbf{r}) = 1 \quad (37)$$

The characteristic decay length ξ^{-1} is given by $\xi \equiv 6^{1/2}\mu^{1/2}A^{-1}$ and it must not be larger than L_p. Equation 8 yields the segment distribution function

$$n(\mathbf{r}) = \frac{\xi N}{\pi l \rho} e^{-2\xi\rho} \quad (38)$$

$$\int_{-l/2}^{l/2} \mathrm{d}z \int_0^{2\pi} \mathrm{d}\varphi \int_a^{\infty} \rho\,\mathrm{d}\rho\, n(\mathbf{r}) = N$$

We evaluate the partition function from eq 5, 9, and 10

$$Z_N = \int \mathrm{d}\mathbf{s} \int \mathrm{d}\mathbf{t}\, f_0(\mathbf{s}) f_0(\mathbf{t}) e^{\mu N} = \pi^2 l \xi^{-2} e^{\mu N} \quad (39)$$

The number of bound chains is calculated with the help of eq 11

$$n_B = \pi^2 C_F l \xi^{-2} e^{\mu N} = \tfrac{1}{6}\pi^2 C_F l A^2 \mu^{-1} e^{\mu N} \quad (40)$$

where C_F is the number of free chains per unit volume. This result is physically obvious.[35] The entropy of the coils decreases when we force them into tubes of length l and diameter ξ^{-1}. On the other hand, there is a decrease in the free energy due to adsorption, amounting to $\mu k_B T N$ per chain.

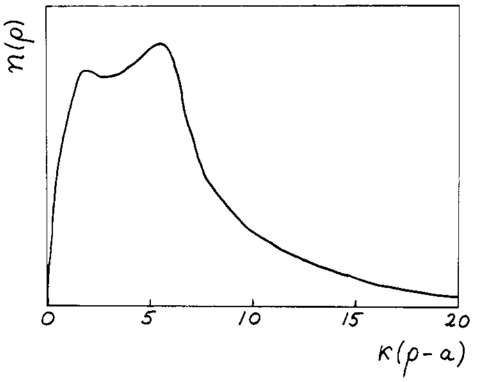

Figure 1. Density profile $n(\mathbf{r}) = f_0^2(\rho)$ (in arbitrary units), pertaining to the example considered in the Discussion, with $f_0(\rho)$ calculated from eq 20.

Discussion

It might be useful to apply the results to a specific calculation to see what orders of magnitude are involved. Let the flexible coils consist of 1600 Kuhn segments, each 25 Å long, each segment bearing one positive charge. The stiff macromolecule is 1000 Å long and 16 Å thick. The solution has a dielectric constant $D = 78.5$ (H_2O at 25 °C), so from eq 12, the Debye radius can be expressed as $\kappa^{-1} = 3.04n^{-1/2}$ (Å) if n is given in mol/L. The integral $I(0)$ of eq 28 has the approximate value 2.36. Therefore, by iteration we find $\kappa_1^{-1} = 13.53$ Å; i.e., the chains are bound at a 1:1 salt concentration of 0.0505 M. If the concentration is reduced to 0.045 M ($\kappa^{-1} = 14.33$ Å), the bound chains collapse, the bound layer decreasing in thickness from 1000 to about 250 Å. The former value is the root-mean-square extension length, $N^{1/2}A$, whereas the latter value is $\xi^{-1} = A6^{-1/2}\mu^{-1/2}$ with $\mu = 0.001667$ calculated from eq 34. (The approximate thickness can also be estimated from eq 35.) The density profile pertaining to the concentration 0.045 M is shown in Figure 1.

We are certain the ground-state dominates because $\exp(\mu N) \simeq 14.4$ is much larger than unity. The turning point occurs at $u_0 \simeq 6.4$, i.e., at a distance of 92 Å from the cylinder, and this is smaller than ξ^{-1} as it should be. With the aid of eq 40, we derive that, on the average, one chain is bound to the stiff macromolecule, when the concentration of coils is one chain per 10^{10} Å^3. Finally, the excluded-volume parameter approximately equal to $QA^{-3}\kappa^{-2}N^{1/2}$ is of order unity. Hence, excluded-volume effects will not modify the results appreciably in this case.

We stress again one of the limitations of this work. The diffusion eq 1 is valid only if $G_N(\mathbf{r}, \mathbf{r}')$ varies smoothly. This is certainly not true near the surface of the cylinder, which implies that, for instance, eq 28 is an approximate condition. Equation 34, on the other hand, depends to a large extent on the long range of the electrostatic potential. Thus, the eigenvalue will not be crucially affected by the detailed properties of the inner bound layer in the case of weak binding.

On the practical side, it is rather obvious that there are a large number of problems. For instance, various excluded-volume and specific interactions will influence the results. A difficult problem is how to prevent aggregation or bridging of the flexible chains between different rods. However, theoretically, one expects that once the complexes consisting of flexible chains bound to the stiff macromolecules are formed, they will be stabilized in view of the "entropic repulsion" between the respective bound layers. The first technique that comes to mind for monitoring the complexes is dynamic light scattering, which has been applied to a diverse variety of systems.[29] It might be possible to verify eq 34 by measuring the translational diffusion coefficient of the complexes as a function of the ionic strength.

From an experimental point of view, our calculation rather severely restricts the range of values of the experimental parameters. More complex situations are of more practical interest. Hopefully, our results may be extended to other cases, a scaling approach being perhaps the most feasible extension.

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(30) This is necessary only in those regions where $R(w)$ varies markedly. In the other regions, ϵ may be much larger than $|R(w)|$.
(31) Wiegel[5] derives an integral equation and then eq 1 by using the condition that the density profile varies sufficiently smoothly; i.e., $|\partial G/\partial \mathbf{r}|A \ll 1$. We note, however, that eq 1 cannot be exact for $\rho \to a$ since the boundary condition eq 6 implies that $G_N(\mathbf{r}, \mathbf{r}')$ varies markedly near the surface of the cylinder. As we remark in the Discussion, eq 28 cannot then be taken too literally, but the physically interesting collapse, as expressed by eq 34 and 35, is almost independent of the behavior of G_N near the surface.
(32) The ground-state eigenfunction f_0 "oscillates" for about half a period only and, of course, it has no nodes.
(33) In eq 22, 24, and 25, the integrand is related to the term $(-R(v))^{1/2}$. The negative sign arises because $S_0 = \int_{w_0}^{w} R^{1/2}(v)\,dv = e^{3\pi i/2}\int_{w}^{w_0}(-R(v))^{1/2}\,dv$. Hence, ${S_0}^{2/3}$ is negative so one needs the asymptotic behavior of Ai for negative arguments. See, e.g., ref 27.
(34) Even in the Manning approximation, one should perhaps use $\beta(\kappa) = 2[\kappa a K_1(\kappa a)]^{-1}$, where K_1 is the first-order modified Bessel function of the second kind. We have set $\kappa a K_1(\kappa a) \simeq 1$ whereas in the example of the Discussion, it is about 0.8. However, eq 27 is more in line with the Poisson–Boltzmann results in the region of physical interest. Moreover, our model is approximate anyway—we assume a uniform dielectric constant, a uniform charge density, etc.—so at this stage, errors of about 20% are not really severe.
(35) Equation 40 can be obtained by a mean-field argument. This is explained in ref 14 for the case of a polymer adsorbed onto a plane surface.
(36) Equations 34 and 35 are valid only when κ does not differ too much from κ_1; i.e., the binding should be weak and the thickness should be much larger than the segment length.

Technique of High-Concentration Tagging in Small-Angle Neutron Scattering: R_g for Bulk Polystyrene[†]

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ABSTRACT: A demonstration of the use of high-concentration deuterated polymer samples at the new University of Missouri Research Reactor small-angle neutron scattering spectrometer is presented. Bulk polystyrene samples with 30 and 70% deuteration are measured for two molecular weights. The data are expressed as the sum of a single-chain factor $S_s(Q)$ and a total scattering factor $S_T(Q)$. It is found that $S_T(Q)$ is zero within experimental error.

Introduction

It has been customary in small-angle neutron scattering (SANS) measurements on polymer systems to use samples in which a few percent or less of the polymer molecules are "marked" by deuteration.[1,2] This is to avoid the effects of chain–chain interference and follows older methods of spectroscopy. As pointed out by us for bulk polymers,[3] and recently generalized to polymer solutions,[4] it is very useful to decompose the scattering cross section into a self-term, $S_s(Q)$, and a total scattering term, $S_T(Q)$. Because of a different dependence on concentration for the coefficients of $S_s(Q)$ and $S_T(Q)$, it is possible to subtract

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