Figure 8. Calculated $(5 \times \sqrt{3})$ LEED pattern.[33]

species derived from the phosphate buffer are not present on the surface.

As the potential is made more positive than −0.4 V, the expected electrodesorption of Cs^+ ions is borne out by the data in Figures 3 and 5. In addition, Θ_I increases while Θ_{Cs} decreases. The absence of counter cations at the interface and the data afforded by the XPS experiments indicate that the iodine species which exist on the surface under these conditions is zerovalent. The zerovalency of the surface iodine and the fact that the increase in Θ_I is coincident with the emergence of the first anodic peak in the cyclic voltammogram in Figure 6 lead to the conclusion that formation of the new superlattice is via an oxidative chemisorption (anodic deposition) reaction. The $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern observed here is typical for adlattices formed from the adsorption of halogens on the (111) surface plane of transition metals.[5,6,21,26-31] The interfacial structure generally proposed for this particular

LEED pattern involves the adsorption of one-third of a monolayer of halogen atoms ($\Theta_I \sim 0.33$) in which each halogen atom is situated in the 3-fold sites. Such a structure, drawn to atomic dimensions, is depicted in Figure 7b. It is essential to note in this figure that the I atoms are not fully close-packed; that is, enough space is still available on the $Au(111)(\sqrt{3} \times \sqrt{3})R30°$–I adlayer for additional iodine chemisorption.

Coincident with the appearance of the second anodic peak in the voltammetric curves (Figure 6) are: (i) a still further increase in Θ_I to 0.4, and (ii) a change from a $(\sqrt{3} \times \sqrt{3})R30°$ to a $(5 \times \sqrt{3})$ LEED pattern (Figure 4c). The latter is also frequently observed on the (111) planes of transition metals exposed to halogens,[21,28-31] but is occasionally mislabeled as a $(\sqrt{3} \times \sqrt{3})R30°$ "split pattern" because of the characteristic groups of spots at the $\sqrt{3}$ positions and the absence of other fractional-order beams (Figure 8). A structure that contains a combination of $\sqrt{3}$ and (12×12) symmetry elements has previously been assigned, erroneously, to this particular LEED pattern.[31] Figure 7c shows one structure that is consistent with the LEED and AES data. This structure is formed by (i) forcing some of the I atoms originally present in 3-fold sites into less ideal sites, and (ii) compacting the $(\sqrt{3} \times \sqrt{3})R30°$ structure in one dimension. Three domains are formed of this structure, each rotated by 120°. The result of the compression is the formation of a close-packed, albeit slightly distorted, hexagonal structure. Under these conditions, saturation chemisorption of I atoms, limited by van der Waals dimensions, is reached.

At still more positive potentials, such as at 0.4 V, additional iodine atoms forced into the already space-limited interfacial layer only leads to the formation of molecular iodine which is evolved into the solution as $I_2(aq)$. This, of course, represents the anodic part of the reversible $I_2(aq)/I^-(aq)$ redox couple. At considerably higher potentials, the I(ads) atoms and the $I_2(aq)$ molecules are all oxidized to $IO_3^-(aq)$ ions.

The results and conclusions of the present study closely parallel those for iodide/iodine at $Pt(111)$[5] which, in the area of electrochemical surface science, is a fundamentally significant trend.

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Electrostatic Forces between Charged Surfaces in the Presence of a Polyelectrolyte Chain

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We have derived the self-consistent field equations describing the configurational statistics of an infinitely long polyelectrolyte chain confined between two charged macroscopic surfaces. We were able to obtain an analytic solution of the linearized SCF equations in the limit of the ground-state dominance. This permits us to investigate the connection between the polyelectrolyte conformation and the intersurface forces for different values of the parameters describing the system. The most important characteristics of the interaction free energy is a region of intersurface separations where the interactions are attractive. We show that the onset of attraction is connected with a conformational transition of the confined chain.

Introduction

The study of electrostatic interactions between macroscopic surfaces with fixed charges immersed in an aqueous electrolyte has been extensive in the past, and the understanding reached on the theoretical level is usually subsumed under the heading of the DLVO theory.[1] In this framework the electrostatic interactions

between macroscopic bodies are broken into two disjointed contributions. First of all there is a contribution that has its origin

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in the creation of double layers close to the charged surfaces. Their existence is due to the interplay of entropic effects, which favor homogeneous distribution of mobile charges, and electrostatic attraction between the charges on the surfaces and their counterions in the aqueous environment, described on the level of the Poisson–Boltzmann equation. This contribution to the total force between the surfaces is repulsive if the surfaces bear charges of the same sign. The second contribution is attractive, irrespective of the charges on the surfaces, and has its origin in the fluctuations (thermodynamic as well as quantum mechanical) of the local electrostatic fields in the dielectric media involved. It is usually referred to as the van der Waals–Lifshitz interaction.

In the present work we shall be concerned with a model system that presents a substantial variation on the s.c. primitive model, taken as a starting point of the DLVO theory. It is composed of two charged, impenetrable surfaces with an infinitely polyelectrolyte chain spanning the region between them. The statistical mechanics of a single polyelectrolyte chain in the bulk has been worked out on different levels of approximations starting from the seminal work of Richmond.[2] On the other side the problem of a confined (neutral) polymer, first addressed by Dolan and Edwards[3] and independently by Richmond and Lal,[4] is also well worked out, and the forces between confining surfaces have been studied in detail.[5] The present problem is closely connected to these two and has been, to our knowledge, first approached by Åkesson et al.[6] In their case it is only the connectivity of the polyelectrolyte chain that separates their model system from the counterion-only case where the intersurface space contains only mobile counterions. In spite of this similarity the intersurface forces bear almost no resemblance to the latter case and show a pronounced region of attraction totally absent in the former case (at least on the Poisson–Boltzmann level).

In our approach to the problem of a confined polyelectrolyte chain immersed in an electrolyte solution we shall try to remain as close to the Poisson–Boltzmann approach to a confined electrolyte as possible. We shall formulate the appropriate partition function in a form of a field theory similar to the one used in the case of a confined Coulomb fluid.[7] We showed for this case that the saddle-point configuration of the local electrostatic fields corresponds to the solution of the Poisson–Boltzmann equation. Using the saddle-point ansatz in the presence of the confined polyelectrolyte chain will naturally lead to a generalization of the Poisson–Boltzmann equation where the statistical averages over the polymeric degrees of freedom will be included in a self-consistent manner. The equations derived by this procedure will be quite close to those used in the SCF treatment of the polymer-excluded volume and indeed represent a variation on the SCF equations for the electrostatic excluded-volume problem derived by Kholodenko and Beyerlein.[8] To solve this new set of coupled self-consistent equations, we shall introduce a linearization approximation by completely ignoring the effects of the electrostatic stiffening of the polyelectrolyte chain.[9] This will permit us to obtain an analytically solvable equation for the polyelectrolyte Green's function and the interaction free energy in the ground-state dominance limit. We shall perform a detailed investigation of the behavior of the interaction free energy as a function of the dimensionless intersurface separation. We shall also draw some conclusions on the connection between the polyelectrolyte conformation and the intersurface forces, specifically, we shall demonstrate that the onset of attractive forces between the charged surfaces is connected with a conformational transition of the
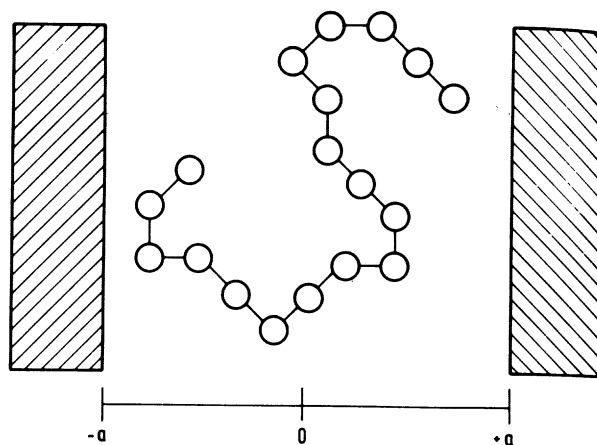
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Figure 1. Model system. Two charged surfaces (surface charge density σ) at a separation $2a$ with an infinitely long polyelectrolyte chain (charge per bead τ) between. The dielectric constant ϵ is supposed to be the same in all regions of the space. The boundary surfaces represent an impenetrable barrier to the polyelectrolyte.

confined polyelectrolyte chain. A connection with the previous work on the problem will be established and commented upon.

In this contribution, in accord with the previous work on the subject,[6] we shall confine ourselves to a model system characterized by smeared surface charges and a dielectric constant assumed to be uniform throughout the system. The presence of discrete surface charges and/or dielectric discontinuities (image forces) is known to lead to different *quantitative* variations in the statistical properties of the charged system[19,20] but rarely has any qualitative effect.

Theory

The polyelectrolyte is modeled as a free-flight chain with charge τ per bead of length l, with a total contour length equal to Nl. The polyelectrolyte chain is confined between two impenetrable surfaces separated by $2a$, each carrying a surface charge density σ, Figure 1. The sign of the charges on the polymer is opposite to the sign of the fixed charges on the walls. All the electrostatic interactions are mediated by a Coulomb potential of the form $u(r,r') = {}^1/_4\pi\epsilon\epsilon_0|r - r'|$, being a solution of the Poisson equation $-\epsilon\epsilon_0\nabla^2 u(r,r') = \delta(r - r')$, where ϵ is the dielectric constant and $\delta(r)$ is the Dirac δ function. The configuration part of the Hamiltonian can be written in a discretized form:

$$H = \frac{3kT}{2l^2}\sum_i (R_{i+1} - R_i)^2 + \frac{1}{2}\sum_{i,j}\tau^2 u(R_i,R_j) - \frac{1}{2}\tau^2\sum_i u(R_i,R_i)$$

(1)

Indexes i and j run over all polymer beads. In what follows we shall strictly use a continuum representation of the Gaussian chain that amounts to the following formal replacement: $\sum_i (R_{i+1} - R_i)^2 \to \int_0^N (dR(n)/dn)^2\, dn$, where $R(n)$ now stands for the coordinate of the nth bead along the polymeric chain. The electrostatic potential acting on the polyelectrolyte charges between two infinite charged walls is a constant and can be disregarded. This does not mean that the magnitude of the surfaces charges is irrelevant since the system as a whole has to remain electroneutral in order that a stable thermodynamic state can be reached. As is usual in the case of Poisson–Boltzmann type theories the electroneutrality enters the discussion through the boundary condition for the mean potential (vide eq 14).

The configurational part of the partition function now follows as[10]

$$\Xi = \int_{[R]} e^{-\beta H} \mathcal{D}R(n)$$

(2)

where β is the inverse thermal energy, $\beta^{-1} = kT$. The integration

(10) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley and Sons: New York, 1987.

measure in the above equation is defined as $\mathcal{D}R(n) = d^3R(1)$ $d^3R(2)...d^3R(N)$.

We shall now proceed by introducing the Hubbard–Stratonovich transformation for the pair interactions, reducing them to effective one-particle interactions with auxiliary field ϕ (see ref 7 for details):

$$\exp\{-\tfrac{1}{2}\beta\sum_{ij}\xi^2 u(r_i,r_j)\} =$$

$$\Delta(\beta)\int_N \mathcal{D}\phi(\mathbf{r}) \exp\{-\tfrac{1}{2}\beta\sum_{ij}\phi(r_i)u^{-1}(r_i,r_j)\ \phi(r_j) + i\beta\sum_i\xi\phi(r_i)\}$$

(3)

where $\Delta(\beta) = (2\pi)^{N/2}(\det \beta u^{-1}(r,r'))^{1/2}$ and $\mathcal{D}\phi(r) = \lim_{n\to\infty} d\phi(r_1)$ $d\phi(r_2)...d\phi(r_n)$. Though the Hubbard–Stratonovich transformation has been written in a discretized form, it is straightforward to get its continuum representation, amounting to a formal replacement $\sum_r\phi(r_r) \to \int \phi(r)\ d^3r$. The inverse of the pair interaction potential has been defined in a standard manner:

$$\int u^{-1}(\mathbf{r},\mathbf{r}')\ u(\mathbf{r}',\mathbf{r}'')\ d^3\mathbf{r}' = \delta(\mathbf{r} - \mathbf{r}'')$$

(4)

Clearly for the Coulomb potential $u^{-1}(\mathbf{r},\mathbf{r}') = -\epsilon\epsilon_0\delta(\mathbf{r} - \mathbf{r}')\nabla^2$.

The Hubbard–Stratonovich transformation permits us to write the pair interactions in an effective one-particle form, remaining with the following compact form of the partition function:

$$\Xi = \Delta(\beta)e^{U_p(N)}\int\int \langle G_\phi(\mathbf{R},\mathbf{R}';N)\rangle_\phi\ d^3\mathbf{R}\ d^3\mathbf{R}'$$

(5)

where $U_p(N) = {}^1\!/_2\beta e_0^2 N u(\mathbf{R},\mathbf{R})$ is the electrostatic self-energy of the polyelectrolyte chain. $G_\phi(\mathbf{R},\mathbf{R}';N)$ is obtained in the standard form of a Wiener integral:

$$G_\phi(\mathbf{R},\mathbf{R}';N) = \int_{\mathbf{R}(0)=\mathbf{R}'}^{\mathbf{R}(N)=\mathbf{R}} \mathcal{D}R(n)\ \exp\left(-\frac{3}{2l^2}\int_0^N\left(\frac{dR(n)}{dn}\right)^2 dn\right.$$
$$\left. + i(\beta\tau)\int_0^N \phi(R(n))\ dn\right)$$

(6)

and is clearly nothing but the Green's function of a Gaussian polymer chain in an external field.[10] A representation of the polyelectrolyte partition function similar to eq 5 has already been derived by Kholodenko and Beyerlein[8] in the case of a screened Coulombic potential. Furthermore, since $u(\mathbf{r},\mathbf{r}')$ is a solution of the Poisson equation, we can use its inverse in a continuous version of eq 3 to obtain the following form for the ϕ average in eq 5:

$$\langle...\rangle_\phi = \int \mathcal{D}\phi(\mathbf{r})(...)e^{-(1/2)\beta\epsilon_0\int(\nabla\phi)^2 d^3\mathbf{r} - i\beta\int\phi\sigma d^2\mathbf{r}}$$

$$= \int \mathcal{D}\phi(\mathbf{r})(...)e^{-\beta H_\phi}$$

(7)

where the action in the last line of the above equation is nothing but the electrostatic free energy evaluated at imaginary values of the charges; therefore

$$H_\phi = F_{el}(ie) = {}^1\!/_2\epsilon\epsilon_0\int (\nabla\phi)^2\ d^3\mathbf{r} + i\oint \phi\sigma\ d^2\mathbf{r}$$

(8)

We can now take into account all the above developments and derive the final expression for the partition function eq 5:

$$\Xi = \Delta(\beta)e^{U_p(N)}\int \mathcal{D}\phi(\mathbf{r})e^{-\beta S_\phi}$$

(9)

where the action in the above equation can be put into the form

$$S_\phi = H_\phi - kT \ln\left(\int\int G_\phi(\mathbf{R},\mathbf{R}';N)\ d^3\mathbf{R}\ d^3\mathbf{R}'\right)$$

(10)

This concludes our formal developments. Clearly the partition function eq 9 cannot be evaluated explicitly since the action in the functional integral is highly non-Gaussian due to the implicit dependence of the polymeric Green's function on the local potential. We therefore use the saddle-point method to obtain the equilibrium profile of ϕ. Standardly the saddle-point is defined as a solution of (see Ref 11 for details):

$$\delta S_\phi/\delta\phi(\mathbf{r}) = 0$$

(11)

We shall not write down this functional derivative explicitly at this stage. To evaluate it, one needs the following identity, which can be derived directly from the representation of the Green's function eq 6 as a solution of a diffusion type equation,[12] viz.

$$[\delta/\delta\phi(\mathbf{r})]\ln\left(\int\int G_\phi(\mathbf{R},\mathbf{R}';N)\ d^3\mathbf{R}\ d^3\mathbf{R}'\right) = i\beta\tau\rho_\phi(\mathbf{r})$$

(12)

where $\rho_\phi(\mathbf{r})$ is the polymer segment density evaluated at point $\mathbf{r}$:

$$\rho_\phi(\mathbf{r}) = \frac{\int\int d^3\mathbf{R}\ d^3\mathbf{R}' \int_0^N dn\ G_\phi(\mathbf{R},\mathbf{r};N-n)\ G_\phi(\mathbf{r},\mathbf{R}';n)}{\int\int d^3\mathbf{R}\ d^3\mathbf{R}'\ G_\phi(\mathbf{R},\mathbf{R}';N)}$$

(13)

The functional derivative eq 11 now decouples into two terms: a volume contribution that amounts to a modified Poisson equation and a surface contribution in a form of a boundary condition, expressing the electroneutrality of the system. It is straightforward to see that the boundary condition demands that the saddle-point ϕ be pure imaginary. Making thus the substitution $\phi \to i\phi$, one remains with the following saddle-point equations:

$$\epsilon\epsilon_0\nabla^2\phi(\mathbf{r}) = -\tau\rho_\phi(\mathbf{r}) \qquad -\epsilon\epsilon_0\ \partial\phi/\partial n = \sigma$$

(14)

where $\mathbf{n}$ is the local normal of the boundary surfaces. Furthermore the polymer segment density is obtained from eq 13 with the Green's function eq 6 satisfying[10]

$$\left[\frac{\partial}{\partial N} - \frac{l^2}{6}\nabla^2 + (\beta\tau)\phi(\mathbf{R})\right]G_\phi(\mathbf{R},\mathbf{R}';N) = \delta(\mathbf{R} - \mathbf{R}')\ \delta(N)$$

(15)

Relations eqs 13–15 represent the self-consistent field equations[12] for a polyelectrolyte confined between two charged walls. Equation 14 could also be viewed upon as a Poisson–Boltzmann equation for the polyelectrolyte chain, where the average local number density at position $\mathbf{r}$, $\rho_\phi(\mathbf{r})$, is given as a polymer configurational average $\rho_\phi(\mathbf{r}) = \langle e^{-\beta\tau\phi(\mathbf{r})}\rangle$. This expression is rather more complicated than in the case of absent connectivity (counterion-only system[1]), where $\rho_\phi(\mathbf{r}) = e^{-\beta e\phi(\mathbf{r})}$. The SCF equations relate in a rather nondirect manner to the polyelectrolyte Poisson–Boltzmann approximation (PPB), set forth by Åkesson et al.[6] The major difference with respect to this work is in the treatment of the statistical average over the polyelectrolyte configurations, which is done explicitly in our case, eqs 6 and 13, in contrast to a seminumerical procedure exploited in ref 6. To avoid confusion, we shall refer to our approximation scheme as the single-chain Poisson–Boltzmann approximation for polyelectrolytes (SC-PBP).

Linearization of the SCF Equations

In what follows we shall reduce the basic set of SCF equations to a form appropriate for our model system in the thermodynamic limit, defined by the following limiting procedure, $N \to \infty$, $S \to \infty$ (in this order), where S is the area of the bounding surfaces, while $N/S = $ constant. The order of both limits is important since it prevents trapping of the chain in the vicinity of a single surface. The trapping of the chain with unsymmetric distribution of the polymer beads between the surfaces would be present only if finite size effects (finite N) or physical adsorption of the chain on one of the surfaces would play a role in the behavior of the system. In this article we disregard such possibilities and concentrate only on the generic electrostatic effects in the thermodynamic limit ($N \to \infty$, $S \to \infty$). In this limit we also assume that the basic quantities of the model do not depend on transversal coordinates (x,y).

The thermodynamic limit, defined above, now leads to the following normalization of the segment density, derivable from eq 13:

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$$\int_{-a}^{+a} \rho_\phi(z) \, dz = N/S \qquad (16)$$

Additionally we also introduce the ground-state dominance ansatz for the Green's function in the limit $N \rightarrow \infty$, leading to the following representation:

$$G_\phi(\mathbf{R},\mathbf{R}';N) = G_\phi(z,z';N) \approx \psi(z) \, \psi(z')e^{-E_N N} \qquad (17)$$

Furthermore we shall define the monomer density as $\rho_\phi(z) = (N/S)\psi^2(z)$, so that the proper normalization of $\psi(z)$ can be obtained as $\int_{-a}^{+a}\psi^2(z) \, dz = 1$. In view of this definition we can write the solution of eq 14 for the mean potential in the form

$$\phi(z) = -\frac{\tau}{\epsilon\epsilon_0}\frac{N}{S}\int_{-a}^{+a}|z - z'|\psi^2(z') \, dz' \qquad (18)$$

It is quite straightforward to establish that the boundary condition eq 14 reduces to $\tau N/S = \sigma$ if the polyelectrolyte chain and the surfaces bear charges of opposite sign. If this equality holds, the system will remain overall electrically neutral. We now use the solution eq 18 as a closure relation for the equation determining the Green's function of the polymeric chain, i.e., eq 15. In the ground-state dominance this equation reduces to the following closed equation for $\psi(z)$:

$$\frac{l^2}{6}\frac{d^2\psi(z)}{dz^2} + E_N\psi(z) + \frac{\beta\tau\sigma}{\epsilon\epsilon_0}\int_{-a}^{+a}|z - z'|\psi^2(z') \, dz' \, \psi(z) = 0$$
$$(19)$$

with an additional boundary condition that $\psi(z)$ has to vanish at the impenetrable surfaces, $z = \pm a$. The above equation clearly has the form of a one-dimensional Hartree equation, where the range of the potential is the same as the dimensions of the system. This makes it quite difficult to solve in general since the potential cannot be approximated by its zeroth Fourier component.[15] We therefore have to resort to a different way of approaching eq 19.

Since we need only even solutions of eq 19, we can delimit ourselves to the region $z > 0$, while demanding that $d\psi/dz(z=0) = 0$. In this region we can derive the following alternative form of the last term in eq 19:

$$V(z) \, \psi(z) = \int_{-a}^{+a}|z - z'|\psi^2(z') \, dz' \, \psi(z) =$$
$$z\psi(z) + 2\int_0^{a-z}u\psi^2(u + z) \, \psi(z) \, du \qquad (20)$$

This representation allows us to linearize equation eq 19 by keeping only the first term on the right-hand side of eq 20. This linearization should work quite well whenever z is close to the boundaries of the system where we have

$$\left.\frac{dV(z)}{dz}\right|_{z=a} = 1 \qquad \left.\frac{d^2V(z)}{dz^2}\right|_{z=a} = 0 \qquad (21)$$

Also, it is in this regime that $V(z)$ is largest and therefore the linearized solution should not be far from the exact one (at least if the electrostatic coupling in the system is small). The linearization procedure would fail most dramatically in the vicinity of $z = 0$, where we can derive the following approximate form:

$$V(z) \approx \langle z \rangle + \psi^2(z=0)z^2 + \dots \qquad (22)$$

where we introduced the average position of the chain as $\langle z \rangle = 2\int_0^a u\psi^2(u) \, du$.

By linearizing the self-consistent interaction potential in eq 19, we have essentially excluded effects like electrostatic stiffening of the chain (see ref 9) from subsequent discussion. With this linearization ansatz eq 19 becomes

$$\frac{l^2}{6}\frac{d^2\psi(z)}{dz^2} + E_N\psi(z) + \frac{\beta\tau\sigma}{\epsilon\epsilon_0}z\psi(z) = 0 \qquad (23)$$

with the boundary conditions

$$\frac{d\psi}{dz}(z=0) = 0 \qquad \psi(z=a) = 0 \qquad (24)$$

This equation is now in the form of an eigenvalue problem allowing a solution in terms of Airy's functions.[13] Clearly for positive eigenvalues we have to choose the largest E_N satisfying the boundary conditions eq 24. On the contrary, in the case of bound states corresponding to $E_N < 0$, we have to obtain a solution of the boundary conditions corresponding to the smallest energy eigenvalue.

Results

To write down the solution of the linearized equation determining the spatial profile of the polyelectrolyte density distribution, we first introduce the dimensionless variables

$$y = \frac{6E_N}{l^2\lambda_B^{2/3}} \qquad x = \lambda_B^{1/3}z \qquad (25)$$

where $\lambda_B = 6\beta\tau\sigma/l^2\epsilon\epsilon_0$, and in terms of which an even solution of eq 23 can be obtained as

$$\psi(z) = \psi(y + x) \sim Ai(-y - x) - \frac{Ai'(-y)}{Bi'(-y)}Bi(-y - x) \qquad (26)$$

Where Ai, Bi, Ai', and Bi' stand for the two linearly independent solutions of the Airy equation and their derivatives. To obtain a normalized solution, we would have to divide the above expression by the square root of $\int_0^a\psi^2(z) \, dz$, which can be obtained directly from eq 23 in the form

$$\int_0^a \psi^2(z) \, dz = \lambda_B^{-1/3}\left[\left(\frac{d\psi}{dx}(y + x_0)\right)^2 - y\psi^2(y)\right] \qquad (27)$$

where $x_0 = \lambda_B^{1/3}a$. The eigenvalue $y(x_0)$ is now obtained from the secondary boundary condition eq 24, leading to

$$\frac{Ai(-y - x_0)}{Bi(-y - x_0)} = \frac{Ai'(-y)}{Bi'(-y)} \qquad (28)$$

Clearly the energy eigenvalue depends on a single parameter, x_0, and can be written in terms of a universal function $y = y(x_0)$ in the scaling form $E_N = (l^2/6)\lambda_B^{2/3}y(\lambda_B^{1/3}a)$. We shall postpone for now the numerical solution of eq 28 and shall first try to obtain some analytic estimates. Also we note that the scaling form of E_N remains valid even in the case of the full nonlinearized equation eq 19.[18]

At small intersurface separations, corresponding to $x_0 \ll 1$, the steric constraints at the boundary surfaces will exclude all the polyelectrolyte configurations that would tend to cross the borders of the system at $z = \pm a$. This would lead to large, entropically driven repulsion corresponding to large, positive E_N. In this limit the boundary condition eq 28 would reduce to the following approximate form:

$$\tan\left(\frac{2}{3}y^{3/2} + \epsilon_N^{1/2}a + \frac{1}{4}\frac{\lambda_B}{\epsilon_N^{1/2}}a^2 + \dots + \frac{\pi}{4}\right) =$$
$$-\cot\left(\frac{2}{3}y^{3/2} + \frac{\pi}{4}\right) \qquad (29)$$

that in turn leads to the energy eigenvalue

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$$E_N \approx \frac{l^2}{6}\left[\left(\frac{\pi}{2}\right)^2\frac{1}{a^2} - \frac{1}{2}\lambda_B a\right] \tag{30}$$

Clearly the first term in the above approximation for the energy eigenvalue, which is the same as in the case of a neutral confined Gaussian chain,[3,4] is dominant in the small-a regime, and the electrostatic interactions enter only as a first-order perturbation. At small intersurface separations we are therefore dealing with an effectively discharged system, where the eigenenergy is due purely to steric exclusion at the borders of the confining region.

In the limit of large intersurface spacings, $x_0 \gg 1$, the boundary condition eq 28 suggests that y and x_0 should be two large equivalents of opposite sign. We therefore assume that the solution of the boundary condition in this limit is given by the ansatz $y = -x_0 + \Delta$, obtaining for Δ

$$Ai(-\Delta)/Bi(-\Delta) \approx -\tfrac{1}{2}e^{-(4/3)x_0^{3/2}} \tag{31}$$

Clearly in the regime $x_0 \gg 1$, Δ has to be close to ai_0, the first zero of Ai defined by $Ai(-ai_0) = 0$. We therefore obtain for the eigenenergy in the lowest order approximation valid in this regime of intersurface spacings

$$E_N \approx (l^2/6)[-\lambda_B^{1/3}a + ai_0 - \tfrac{1}{2}C(ai_0)e^{-(4/3)\lambda_B^{1/2}a^{3/2}}] \tag{32}$$

where we substituted $C(ai_0)$ for the quotient $|Bi(-ai_0)/Ai'(-ai_0)|$. As we shall see in the next section, the first term in the square brackets of the above equation is cancelled by the electrostatic self-energy in the expression for the total free energy, leaving only the exponential dependence on the intersurface spacing. What is more important is that in this regime of x_0 the eigenenergy is negative, meaning, that we are dealing with bound states, where most of the chain is concentrated close to the boundary surfaces. Segments of the chain that are not localized close to the surfaces, due to the electrostatic attraction between polymer and surface-bound charges, act as bridges driving the attraction between the surfaces.[6] We shall verify this statement by an explicit calculation of the monomer density distribution in the next section.

Chain Conformation and Intersurface Forces

In this section we shall evaluate the total free energy and pressure of the system through a numerical solution of the boundary condition eq 28. Furthermore we shall investigate the spatial profile of the monomer density distribution in the confined region. First of all we note that at the saddle-point in the ground-state dominance limit the free energy can be obtained in the form

$$F = -kT \ln \Xi = kTE_N N - \tfrac{1}{2}\epsilon\epsilon_0 \int (\nabla_\phi)^2 d^3r - \oint \phi\sigma d^2r \tag{33}$$

where the last two terms clearly represent the electrostatic self-energy of the system. In the plane-parallel geometry, using also the linearization ansatz of eq 20, we can reduce the surface density of the free energy to the following simple expression:

$$\frac{F}{S} = kTE_N\frac{N}{S} + \frac{\sigma^2}{\epsilon\epsilon_0}a$$

$$= \frac{\sigma^2}{\epsilon\epsilon_0\lambda_B^{1/3}}(y(x_0) + x_0) \tag{34}$$

where in the last line we took account of the electroneutrality condition, $\tau N/S = \sigma$. $y(x_0)$ is of course the solution of the boundary condition eq 28, and the exact dependence of the free energy on x_0 is given in Figure 2. We observe that the total free energy is always positive with a well-developed minimum at $x_0 = x_m$. To understand the emergence of this minimum, we note a relation that can be derived directly from the boundary condition eq 28, i.e.

$$(y' + 1) = yy'\left(\frac{Bi(-y - x_0)}{Bi'(-y)}\right) \tag{35}$$

where y' stands for the derivative of y with respect to x_0. Therefore it follows that the free energy has a minimum exactly at the point
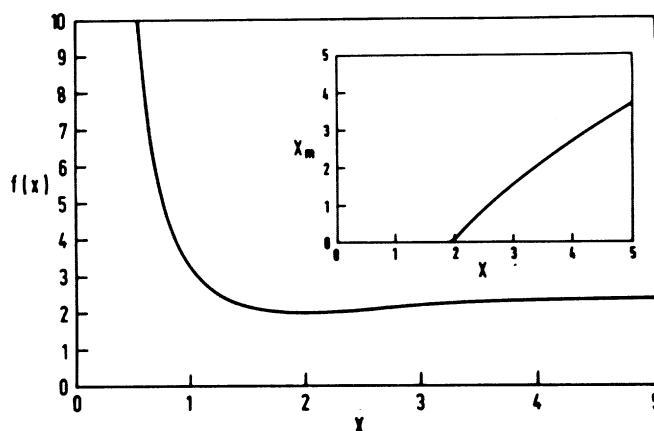

Figure 2. Dimensionless free energy eq 34, $f(x_0) = y(x_0) + x_0$, as a function of dimensionless separation $x_0 = \lambda_B^{1/3}a$. The dimensionless free energy has a minimum at $x_0 = x_m = 1.986$, where $y(x_m) = 0$ and approaches a constant value for $x_0 \rightarrow \infty$. The inset shows the position of the maximum of the monomer density distribution $\rho(x) \sim \psi^2(x)$ as a function of the intersurface separation. At $x_0 = x_m$ there is a transition from a unimodal to a bimodal distribution, characterized by the fact that its maximum is displaced from the origin.
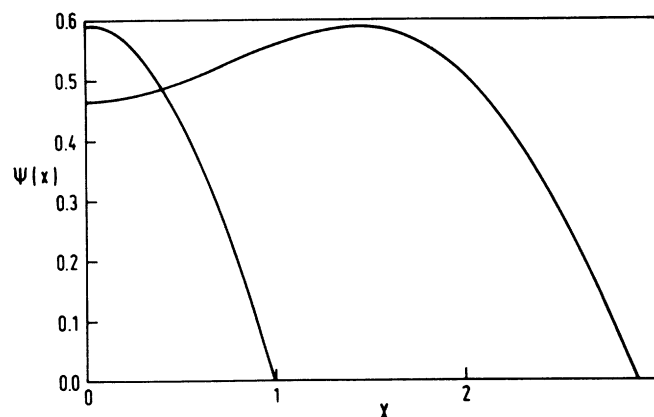

Figure 3. Form of $\psi(x)$ for $x > 0$, with the monomer density given as $\rho(x) \sim \psi^2(x)$, for two values of intersurface separation: $x_0 = 1$ and $x_0 = 2.9$. In the first case we have a unimodal distribution, with most of the chain concentrated close to the middle of the intersurface space, and in the second case a bimodal distribution, where the chain segments remain in the vicinity of the charged surfaces, leaving a depleted region in the middle of the intersurface space.

where $y(x_0)$ crosses the abscissa, i.e., at $y(x_m) = 0$. By a numerical investigation we obtain $x_m \approx 1.986$. This value of x_0 has another interesting interpretation that we elucidate in what follows.

Let us ask ourselves where does the monomer density distribution have a maximum. If this maximum is at $x_M = x_M(x_0)$, than we should have $d\psi/dx\,(x_M) = 0$, leading to

$$\frac{Ai'(-y(x_0) - x_M)}{Bi'(-y(x_0) - x_M)} = \frac{Ai'(-y(x_0))}{Bi'(-y(x_0))} \tag{36}$$

Clearly one solution of this equation, in view of the first boundary condition of eq 24, is always $x_M = 0$, stable for $x_0 \rightarrow 0$. However on increasing the value of the intersurface spacing, we obtain that exactly at x_m the solution $x_M = 0$ becomes unstable, and a new branch develops for $x_0 > x_m$, characterized by $x_M \neq 0$. The details of this transition are shown in the inset of Figure 2. The form of the monomer density, Figure 3, for $x_0 < x_m$ and $x_0 > x_m$ indicates that at $x_0 = x_m$ we have a transition from an extended polymer configuration characterized by a unimodal distribution (where most of the chain is concentrated near the middle of the intersurface region) to a surface-bound configuration characterized by a bimodal distribution (with most of the chain confined in a region close to the surfaces).

In conclusion we can say that as the eigenenergy crosses the abscissa, the character of the monomer density distribution changes
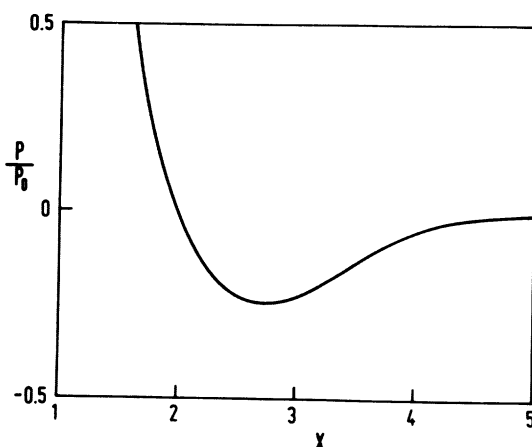
Figure 4. Pressure as a function of the dimensionless intersurface separation eq 37 with $p_0 = \frac{1}{2}\sigma^2/\epsilon\epsilon_0$. Exactly at $x_0 = x_m$ the force has a turning point going from repulsion to attraction. The turning point in the force curve corresponds to the transition from the unimodal to the bimodal distribution of the polymer segments between the walls.

drastically and a transition from a monomodal to a bimodal distribution of the polymer segments sets in. This transition is quite similar to the coil–stretch transition in the bulk, studied by Mansfield,[14] which is accomplished by varying the strength of an external field stretching the polymer. This field would in our case correspond to electrostatic interactions between the charges on the polymeric chain and those fixed on the two bounding surfaces. It has been argued[14] on the basis of an analogy with thermodynamics that the coil–stretch transition in the bulk can be of the first as well as of the second order. The latter possibility appears to be true also for the transition presented in this work.[18]

Let us now turn our attention to the forces acting between the surfaces in the presence of an intervening polyelectrolyte chain. It is quite straightforward to derive the pressure in the dimensionless form:

$$p = -\frac{1}{2}\frac{\partial}{\partial a}\left(\frac{F}{S}\right)$$
$$= \frac{1}{2}\frac{\sigma^2}{\epsilon\epsilon_0}\left(-\frac{dy}{dx_0} - 1\right) \qquad (37)$$

where again $y = y(x_0)$ is the solution of the boundary condition eq 28. Using the normalized form of $\psi(x)$, which we can obtain by implementing in its definition eq 27, we can derive after some substantial algebra that

$$\frac{dy}{dx_0} = -\frac{2}{\lambda_B}\left(\frac{d\psi}{dz}(z=a)\right)^2 \qquad (38)$$

and therefore obtain the pressure in an alternative form, valid in the frame of the linearization procedure of eq 20:

$$p = \frac{1}{2}\frac{\sigma^2}{\epsilon\epsilon_0}\left(\frac{2}{\lambda_B}\left(\frac{d\psi}{dz}(z=a)\right)^2 - 1\right) \qquad (39)$$

The dependence of pressure on x_0 is displayed in Figure 4 and can be given in an explicit form for the two limiting cases

$$\lim_{a\to 0} p \approx \frac{\sigma^2}{\epsilon\epsilon_0\lambda_B}\left(\left(\frac{\pi}{2}\right)^2\frac{1}{a^3} + \frac{1}{4}\lambda_B\right)$$

$$\lim_{a\to\infty} p \approx -\frac{1}{2}\frac{\sigma^2}{\epsilon\epsilon_0}\lambda_B^{1/6}C(ai_0)a^{1/2}e^{-(4/3)\lambda_B^{1/2}a^{3/2}} \qquad (40)$$

The pressure is therefore repulsive at small separation with a dominant steric term (the system is effectively discharged) and is attractive at large intersurface spacings of an approximately exponential form.

In connection with the above form of the pressure, eq 39, a few remarks are in order. It is well known that in the Poisson–Boltzmann theory, dealing with mobile ionic charges without any

connectivity between them, the pressure acting between the confining surfaces can be expressed through the contact theorem in the form[1]

$$p = kT\rho(a) - \frac{1}{2}\frac{\sigma^2}{\epsilon\epsilon_0} \qquad (41)$$

where $\rho(a)$ is the density of confined ions right at the confining surfaces. In the mean field (saddle-point[7]) approximation the first term of the above relation is always larger than the second, leading to repulsive forces for all values of the intersurface spacing. The Poisson–Boltzmann contact theorem eq 41 clearly does not make sense in the polyelectrolyte case because the connectivity of the chain fixes the value of the monomer density at the excluding surface to zero, i.e., $\rho(a) = 0$. Since the new polymer contact theorem, eq 39, has been derived by taking account of the linearization approximation, its general validity remains yet to be determined.[18] It has, however, a nice property that (at least in the linearized regime) it remains valid for any value of the electrostatic coupling λ_B.

Discussion

In this work we have developed a general formalism describing the conformation of a charged polymeric chain confined between two oppositely charged, impenetrable walls. In spirit the formalism is quite close to the SCF approach amply used in the analysis of the excluded volume interactions of polymers in the bulk.[10,12] The main difference lies in the fact that in our case the pair potential is Coulombic, whereas it is approximated by a δ function in the excluded volume case.

To solve the general equations describing the monomer density distribution between the walls, we had to introduce a linearization ansatz, eq 19, which reduced a Hartree type equation to a simple eigenvalue problem. In this framework we showed that forces between the surfaces can be either attractive or repulsive, depending solely on the dimensionless separation between the walls, x_0. Furthermore the change from repulsion to attraction at $x_0 = x_m$ is accompanied by a conformational transition of the polymeric chain, which can be characterized as a continuous transition of the monomer density distribution from a unimodal to a bimodal form. We were able to obtain asymptotic forms for the free energy as well as the total force acting between the surfaces when the intersurface separation is either very small or very large. The pressure acting between the walls was shown to be determined by a special form of the "contact condition" (usually used in the frame of the Poisson–Boltzmann theory of the electrostatic forces between charged surfaces with intervening freely mobile ionic charges), connecting the derivative of ψ at the boundary surfaces with forces acting between them. The conclusions reached in this work point to the view that the properties of a confined polyelectrolyte chain are due to an interplay of entropic effects, stemming from the steric exclusion at the bounding surfaces, and electrostatic forces that promote soft binding of the chain to the oppositely charged surfaces. This differs from the PB case, where steric exclusion of ions at the surfaces does not lead to depletion layers close to the surfaces.

Though the general theory developed in section II is quite close to the self-consistent treatment of the excluded-volume effect, the final results bear almost no resemblance to this case. The interaction of two surfaces, where the intervening space contains a polymeric chain with excluded-volume interactions, was discussed by Wiegel.[15] In this case the Hartree type equation, eq 18, reduces to a form quite similar to a one-dimensional Landau–Ginzburg equation.[17] An approximate analysis of the solutions of this equation points to the conclusion that forces between the surfaces are always repulsive and the pressure behaves asymptotically as $p \sim a^{-2}$. A model system that bears some similarity to the confined polyelectrolyte case was studied by Chan et al.[16] These authors considered a confined polymer chain where interaction with the surfaces is described by a finite adsorption energy. Depending on the magnitude of the adsorption energy the intersurface force can be either repulsive or attractive; however, it has no turning points, being of the same sign for all values of the

intersurface spacing. Our system therefore behaves as if the "adsorption energy", stemming from an effective electrostatic attraction between the charges on the surfaces and on the polymeric chain, would be a function of the intersurface spacing, varying in magnitude as the separation between the surfaces is changed.

Recently Åkesson et al.[6] studied a problem that is quite close to the one presented in this work. There are, nevertheless, important differences concerning the treatment of the steric exclusion at the walls that manifest themselves most ostensibly in the form of the "contact theorem", eq 41, used by these authors. As already stated above, this form of the "contact theorem" is not applicable when there is real steric exclusion (as indeed is the case for our model system) acting at the walls, since it reduces the monomeric density at the walls to zero. However the interaction energy used by Åkesson et al.[6] contains no such terms, and the Poisson–Boltzmann contact theorem appears to be valid for their case only inasmuch as it describes a situation where "in essence the underlying chain is able to penetrate into the aggregate". This difference in the treatment of steric exclusion at the surfaces precludes a quantitative comparison of our results with theirs. The differences, as expected, are most clearly seen in the monomeric density profile, which in our case always displays a minimum right at the wall, whereas in their case it is often largest at the wall (Figures 2–6 of ref 6). Qualitative differences in the dependence of pressure on the intersurface separation are much less pronounced, and an attractive region is observed in both systems. Let us just add that in our case there does not seem to be any indication that the pressure could become repulsive again at very large separations.

Though our model system is admittedly highly idealized due to the absence of other mobile charges in the bathing solution (such as counterions or ions generated by dissolution of salts), the study of more complex ionic systems involving polyelectrolytes and salts[18] shows that it displays all the generic features that are present even in these more realistic cases. It is therefore a valid limiting case, the behavior of which can be recovered even in more realistic model systems.

The problem of interactions between charged surfaces with an intervening polyelectrolyte chain is of a far greater complexity than one would naively expect on the basis of our experience with the Poisson–Boltzmann equation.[1] From the theoretical side it is indeed quite fascinating since it leads to a common ground for the application of different methods amply used by the molecular force and the polymer community.

Structural Evidence for π Complexes in Catalytically Active Y Zeolites with o-, m-, and p-Xylene

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The structures of Yb,Na–Y zeolites containing sorbed perdeuterated xylenes have been studied for two different xylene converages at 5 K by powder neutron diffraction. The space group is *Fd3m*. The ytterbium ions are located in the sodalite cage on position I′ or in the hexagonal prism on position I. The sodium ions are all located on position II′ in the six-ring window shared by the sodalite and the supercages. The molecules are located in the supercage, the plane of the aromatic ring being perpendicular to the ⟨111⟩ axis with short contacts to the Na$^+$ cations on II′. The para and ortho isomers are statistically disordered with respect to the 6-fold axis of the ring, and are equally distributed over these orientations, whereas *m*-xylene molecules occupy only three of these orientations due to interactions of the methyl groups with the framework oxygens. A second crystallographic site was found occupied by the para and ortho isomers at low coverages. It is the less favored one: the molecules are at longer distances from the Na$^+$ cations and at no distance shorter than 0.32 nm from the framework. Even at high coverages this second site is less occupied. Not all the adsorbed molecules, however, can be located in the high-coverage samples. The powder diffraction pattern appears to indicate a liquidlike phase of xylenes within the cavities.

Introduction

Synthetic Y zeolites can be converted into active catalysts by exchanging the residual sodium cations with rare earth cations,[1] thereby improving the activity of the zeolite in reactions like the isomerization/disproportionation of xylenes[2] or the disproportionation of trimethylbenzenes.[3] These reactions take place in the channels and cavities of the zeolite framework in which molecules smaller than the pore openings (for zeolite Y ca. 0.74 nm)[4] can be adsorbed.

The diffusion and sorption of aromatic molecules in faujasite-type zeolites have been the subject of many studies. Diffusion

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