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Molecular Dynamics Studies of Anchored Polyelectrolytes

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SUMMARY: We study polyelectrolytes end-grafted to a surface in a model which includes counterions explicitly and treats the full long-range Coulomb interaction. For strongly charged polyelectrolytes the counterions are localized inside the brush and electroneutrality is satisfied locally. Under these conditions, we find that the brush thickness is linearly proportional to the chain length and the grafting density. The counterion distribution is strongly inhomogeneous, and counterion condensation can be observed although the Bjerrum length is smaller than the average bond length. Varying the Bjerrum length we find a non-monotonic behaviour of the brush height. Counterion diffusion is anisotropic, and is enhanced at higher grafting densities. For partially charged polyelectrolytes we obtain a crossover from quasi-neutral behaviour to the strongly charged behaviour reported above.

Introduction

Polyelectrolyte brushes - charged polymers densely end-grafted to a surface - are important in several respects. They are a subject on which there is now a substantial body of theoretical work, following the successful earlier work on uncharged brushes. In recent years there have been several experiments on polyelectrolyte brushes, including polyelectrolytes end-grafted to a solid surface and charged amphiphilic diblock-copolymers in free-standing black films or at the air/water interface. Charged brushes are an efficient means for preventing colloids in polar media from flocculation. However, both in experiment and in theoretical work, polyelectrolytes are an challenging subject with many unresolved problems. In this situation, computer simulations are a promising tool to validate theoretical models, and to probe quantities and regimes which are not easily observable experimentally.

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Model and method

We use stochastic molecular dynamics to study the system in equilibrium. The equation of motion for particle i at position $\mathbf{r}_i(t)$ is the Langevin equation,

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla_i U - m\Gamma \frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i(t), \qquad (1)$$

where m is the mass of the particles, and Γ is a friction constant which couples the particles to a heat bath. The system is held at thermal equilibrium by a Gaussian random force $\mathbf{W}_i(t)$, which is coupled to Γ by the fluctuation-dissipation relation. The potential energy U has four contributions: (i) a repulsive Lennard-Jones term modeling the good solvent situation, (ii) a bonding potential between neighbouring monomers along the chains treated as a nonlinear spring, (iii) a repulsive wall potential preventing the particles (monomers and counterions) from crossing the anchoring surface, and (iv) the bare Coulomb interaction between all charged particles. The implementation of the long-ranged Coulomb interaction requires special care. To calculate the conditionally convergent Coulomb sum over all periodic images we use a technique proposed by Lekner1) and modified by Sperb2). The polymer chains are anchored to the grafting surface by means of an uncharged end segment. The anchor segments are fixed and form a square lattice with lattice spacing $d = \rho_a^{-1/2}$, where $\rho_a = M/L^2$ is the grafting density with M being the number of chains in the simulation box and L is its planar length. Some simulations are also done with randomly grafted chains. In the case of completely charged polyelectrolytes we have studied systems with $M = 6$, 9 and 36 chains each containing an uncharged anchor monomer and $N = 50$, 30 or 20 charged monomers. Due to electroneutrality there are $M \times N$ counterions. The temperature was set to $k_B T = 1.2\epsilon$ measured in Lennard-Jones energy units ϵ. The choice of parameters of the bonding potential gives an average bond length of $a = 0.98\sigma$ where σ is the Lennard-Jones radius. The length scale for our simulation is set by the Bjerrum length λ_B, which gives the distance between two elementary charges at which their electrostatic interaction equals the thermal energy. For water it is 7.14Å at room temperature. If not stated otherwise we choose $\lambda_B = 0.70\sigma$ so that σ is about 9.8Å. Thus the average bond length a is approximately 9.6Å and the dimensionless Manning ratio is $\lambda_B/a = 0.74$, i.e., below the condensation limit for a fully stretched chain. Our mesoscopic model should be viewed as a coarse-grained representation of a flexible polyelectrolyte such as NaPSS with a monomer length of 2.5 Å. The charge separation a

implies a fraction $f \approx 1/4$ of charged monomers, similar to previous numerical work on polyelectrolyte solutions. The grafting densities studied range from $\rho_a\sigma^2 = 0.02$ to 0.14. This interval covers the typical range for experimental studies. The contour lengths of the chains varies from about 20nm to 50nm, comparable to experimental systems.

Completely charged polyelectrolytes

The average thickness of the brush $\langle z_m \rangle$ and of the counterion layer $\langle z_{ci} \rangle$ can be measured by taking the first moment of the corresponding density profiles $\rho_m(z)$ and $\rho_{ci}(z)$, respectively. These heights are shown in Fig. 1. For brushes of length 30 and 50, we find that the brush thickness scales linearly with grafting density ρ_a[3]. For length 20 at high grafting, the chains are overstretched and the relation $\langle z \rangle \propto \rho_a$ breaks down. Our findings disagree with the accepted scaling law for charged brushes in the osmotic regime, which predicts $h \propto Nbf^{1/2}$, independent of the grafting density[4,5]. We believe that the disagreement is caused by the assumption that the counterions inside the brush form an ideal gas, which is only reasonable for $f \ll 1$. If one studies the counterion properties, one finds in fact a strongly inhomogeneous density distribution as a result of counterion condensation. Recently it has been shown that the presence of condensed counterions can change the solvent quality from good to poor[6]. Note that the results shown in Fig. 1

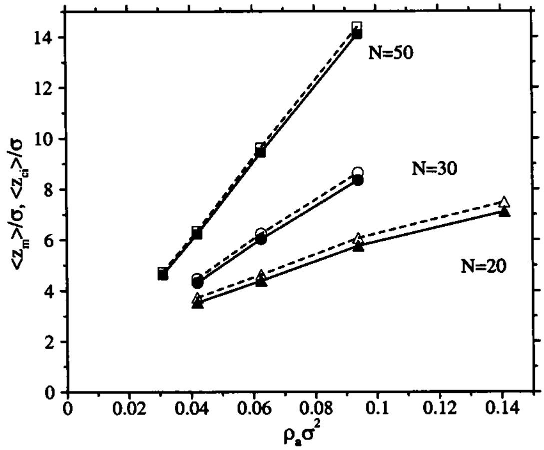

Figure 1: Average thickness of polyelectrolyte layer $\langle z_m \rangle$ (filled symbols) and average counterion height $\langle z_{ci} \rangle$ (empty symbols) versus anchoring density ρ_a.

are based on simulations of $M = 9$ chains. A comparison with recent results of systems with $M = 36$ chains indicates finite size effects resulting in different absolute values of the heights. However, the same scaling behaviour is maintained. From the monomer and counterion profiles it is evident that at average all the counterions are inside the brush, i.e., charge neutrality is satisfied locally. To estimate the amount of local screening and counterion condensation, we show the polyelectrolyte-ion pair distribution $P(r)$ in Fig. 2 for two different counterion sizes. $P(r)$ is normalized according to $2\pi \int_0^\infty r dr P(r) = 1$, where r is the separation between ion center and closest polyelectrolyte bond. Due to both Coulomb interaction and steric effects there occurs a strong localization of counterions close to polyelectrolyte charges. The peak heights at $\sigma = 1$ and $\sigma = 0.4$, respectively, depend on the grafting density, with the lowest ρ_a showing the strongest increase. In a very rough manner, this trend can be explained by introducing an effective Manning ratio $\xi_{\text{eff}} = N\lambda_{\text{B}}/2\langle z_m \rangle$, where we assume rigid rods in the z-direction with a rescaled line charge density $N/2\langle z_m \rangle$. In this rod model, counterion condensation occurs, and the fraction of condensed counterions increases for lower grafting densities. The motion of the counterions can be traced with the mean square (MS) displacement $|\mathbf{R}(0) - \mathbf{R}(t)|^2$. The motion of the counterions in z-direction is bounded due to the anisotropy of the brush. It reaches a plateau which is roughly $(\langle z_{\text{ci}} \rangle / 2)^2$ when the correlation with the initial z-value is lost. Fig. 3a shows the perpendicular MS motion of counterions and confirms that the long-time limit indeed approaches $(\langle z_{\text{ci}} \rangle / 2)^2$ to within about 10%. The short- and

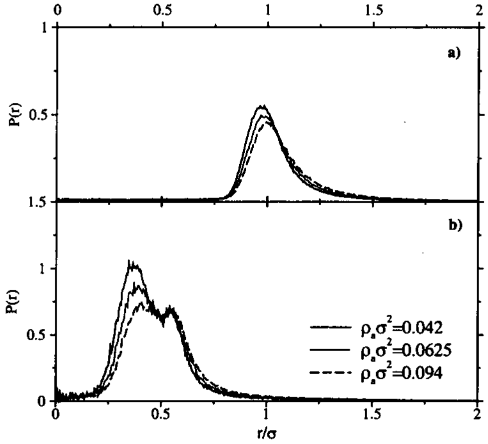

Figure 2: Counterion-polyelectrolyte distribution $P(r)$ for ion size $1.0\,\sigma$ (a) and $0.2\,\sigma$ (b).

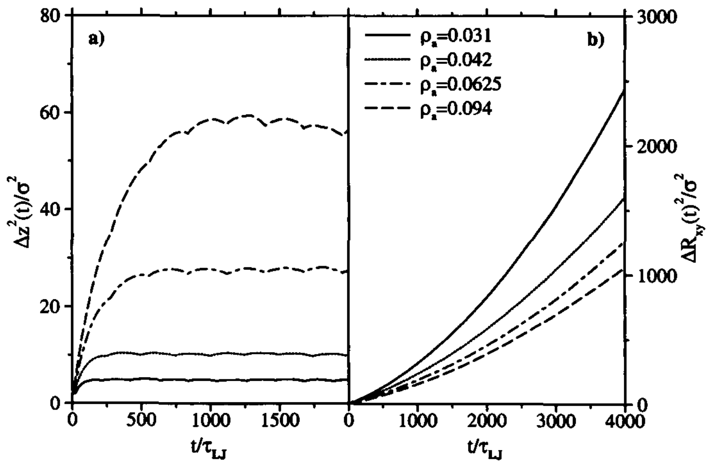

Figure 3: Counterion diffusion perpendicular (a) and parallel (b) to the grafting surface.

long-time behavior of the perpendicular MS displacement is given by

$$\langle |z(t) - z(0)|^2 \rangle = \begin{cases} 2D_z t & \text{for} \quad t \ll \tau_P, \\ (\langle z_{\text{ci}} \rangle /2)^2 & \text{for} \quad t \gg \tau_P, \end{cases} \tag{2}$$

where D_z is the corresponding diffusion constant. The plateau time τ_P gives the time scale for which the ions cross a distance of the order of the brush thickness. It is the crossover time between diffusive motion and constant MS displacement at long times and can be estimated with $\tau_P \approx \langle z_{\text{ci}} \rangle^2 / 8D_z$. The long-time perpendicular MS displacement shows oscillations with a constant period τ_{osc}. A study of the autocorrelation function of the endpoint height of the chains reveals that τ_{osc} represents the time scale for height fluctuations of the grafted polyelectrolytes to which the counterions are closely coupled. At times larger than τ_P, the planar component $\mathbf{R}_{xy}$ dominates the diffusive motion of the counterions. The corresponding planar MS displacements are shown in Fig. 3b. Ion diffusion is considerably enhanced for increasing grafting density; this is consistent with our results on counterion condensation, where we found that the fraction of free (uncondensed) counterions is larger at higher grafting density. For free diffusive motion, with the parameters used in the simulation a diffusion constant $D_{\text{free}} = k_B T / m\Gamma = 2.4\sigma^2/\tau_{\text{LJ}}$ is expected. The measured planar diffusion constants are 3 – 6 times lower, allowing an rough estimate of the fraction of condensed counterions: according to the lateral diffusion data, 64% (for $\rho_a \sigma^2 = 0.094$) to 84% (for $\rho_a \sigma^2 = 0.031$) of the counterions are condensed.

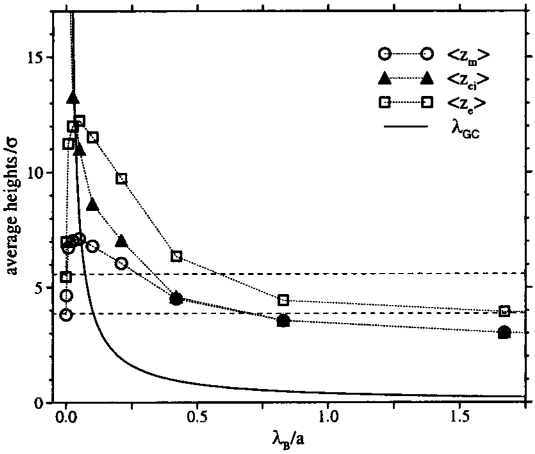

Figure 4: Average thickness of polyelectrolyte layer $\langle z_m \rangle$, average counterion height $\langle z_{ci} \rangle$ and average height of endpoints $\langle z_e \rangle$ and Guoy-Chapman length $\lambda_{GC} = (2\pi\lambda_B N \rho_a)^{-1}$ versus Bjerrum length λ_B $(N = 20, \rho_a = 0.02\sigma^{-2})$. The dashed lines indicate $\langle z_m \rangle$ and $\langle z_e \rangle$ of identically grafted uncharged chains.

Variation of the Bjerrum length

Varying λ_B we find a non-monotonic behaviour of the brush thickness[7)]. Fig. 4 shows the dependence of several characteristic heights in the limit of small grafting density where no brush structure is obtained for uncharged chains as well as at $\lambda_B \gtrsim a$. Remarkably, already at moderate interaction strength $\lambda_B/a \gtrsim 0.5$ polyelectrolyte mushrooms appear to be more compact than neutral ones. Reducing λ_B we obtain a stretching up to about 2/3 of contour length before the brush is again collapsing when λ_{GC} exceeds $\langle z_{ci} \rangle$.

Partially charged polyelectrolytes

Fig. 5 shows the ρ_a-scaling of the brush height at various fractions of charged monomers. At small f one obtains a behaviour consistent with the quasi-neutral limit $\langle z_m \rangle \propto \rho_a^{1/3}$ while electrostatic effects overwhelm steric repulsion at large f, giving a tendency to linear scaling known from completely charged systems. Similarly to the behaviour at large λ_B, in the limit of small ρ_a the chains become more and more collapsed for increasing f. A systematic study of the dependence of brush properties on charge fraction f is under progress.

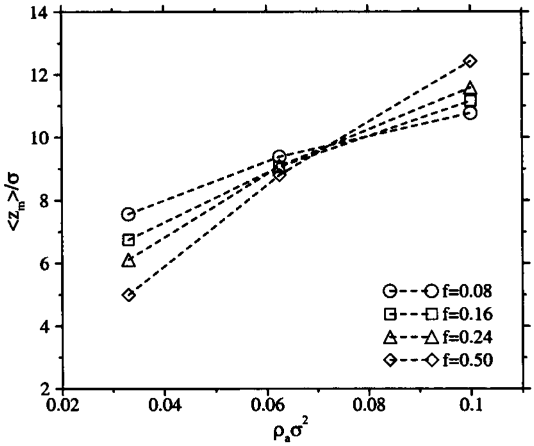

Figure 5: Average thickness of polyelectrolyte layer $\langle z_m \rangle$ versus anchoring density ρ_a at different fraction f of charged monomers($N = 50, \lambda_B/a = 0.74$).

Acknowledgments

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