Interactions between planar stiff polyelectrolyte brushes

Aaron Wynveen and Christos N. Likos
Institute for Theoretical Physics II: Soft Matter, Heinrich-Heine-Universität Düsseldorf, D-40225 Düsseldorf, Germany

(March 25 2009; published 31 July 2009)

Molecular-dynamics simulations were performed for two opposing flat surfaces sparsely grafted with rigid polyelectrolyte chains whose lengths are smaller than their persistence lengths. The resulting force-distance dependence was analyzed theoretically in terms of two separate physical mechanisms: the pressure arising from osmotically active counterions trapped within the brush and the work required to bend the brush chains under confinement, which can be accurately characterized by a ground-state theory of rigid polymer buckling. These contributions are of the same magnitude and should be distinguishable in experiments of double-stranded DNA brushes.

DOI: 10.1103/PhysRevE.80.010801 PACS number(s): 82.35.Rs, 82.20.Wt, 82.70.Dd, 87.10.Tf
respectively the complete elliptic integrals of the first and second kinds, with the same accessible system volume, $D_{\text{chain}}$, giving a total pressure $\Pi = \Pi_{\text{osm}} + \Pi_{\text{chain}}$. Being that sparse brushes of stiff chains are completely interpenetrating \cite{31}, as opposed to studies of brushes with flexible PEs and/or with large grafting densities, this latter contribution is realized when chains make contact with the opposite wall, i.e., when $D < L$.

This component to the total force may be determined by calculating the bending energy of a buckled inextensible chain \cite{32,33},

$$V_{\text{bend}} = \frac{B}{2} \int_0^L ds \left( \frac{dz}{ds} \right)^2,$$

where $B$ is the bending rigidity modulus and $\mathbf{t}(s)$ is the tangent vector to the contour at contour length $s$. This must be minimized subject to the condition that the ungrafted end of the chain lies at the opposite wall without penetrating it, that is $\int_0^L \mathbf{t}(s) \cdot d\mathbf{z}/D = 0$ where $\mathbf{z}$ is the unit vector perpendicular to the brush wall. The chain conformation minimizing the bending energy is found by solving the corresponding Euler-Lagrange equations, which are given in Refs. \cite{33,34}. However, in contrast to the very similar solutions with the boundary conditions of a chain clamped at both ends \cite{33,34}, we determine solutions for a chain that is free at its ungrafted end. The solution takes different forms about a critical distance \cite{34} $D^*/L = 2E(1/2)/K[1/2] = 1 - 0.4569\ldots$ (where $K[m]$ and $E[m]$ are the complete elliptic integrals of the first and second kinds, respectively): (i) when $D > D^*$, the chain’s curvature is finite throughout its contour length becoming zero only at its free end; and (ii) when $D < D^*$, a segment of length $(1 - D/D^*)L$ at the end of the chain lies flat against the opposing surface. For the latter, the shape of the chain up to this flat segment has the same form, with the contour location $s$ rescaled by $D/D^*$, as the chain conformation when $D = D^*$.

Once the chain conformation is known, the bending energy and the force between the brushes due to bending of the chains may be found:

$$F_{\text{bend}}(D) = \begin{cases} \pi B D^* / 2 L D^2 & \text{if } D < D^*, \\ K^2[m] B / L & \text{if } D^* < D < L, \end{cases}$$

where $m$ is a solution to $2E[m]/K[m] = 1 - D/L$. At $D = L$, when the chains first contact the opposite wall, the force jumps abruptly from zero to a finite value, $K^2(0)B/L^2 = (\pi/2)^2 B/L^2$. The chain contribution to the total pressure is thus given by $\Pi_{\text{chain}} = \alpha F_{\text{bend}}$.

For densely grafted brushes in the osmotic regime \cite{13,14,35}, nearly all counterions are confined within the brushes. If the density of the counterions at a brush wall corresponds to a fraction $f$ of the average density of counterions within the entire brush, the osmotic pressure at separations $D < 2L$ is given by \cite{22}

$$\Pi_{\text{osm}} = \alpha f \Pi_{\text{ideal}} = \frac{f k_B T N a}{D(1 - \eta)}^{-1},$$

where the term in the brackets is a correction for the excluded volume fraction $\eta = \pi a^2 L\sigma / D$ of the chains within the brush. Assuming that the counterion density within the brush was uniform, $f$ would be unity. This assumption, however, is not valid for the sparse brushes we consider. For a finite charged line, the electrostatic potential near the center of the line is nearly twice that near its end, and thus, the counterion population is much less at the grafted wall than in the center of the brush. This argument can be recast in terms of counterion condensation on the strong (having a Manning parameter $\xi > 1$ \cite{36}) PE chains. Although any finite PE would lose all its counterions under infinite dilution, studies \cite{37-41} demonstrate counterion condensation on finite chains in the semidilute regime of our brushes. Furthermore, it was shown that fewer counterions condense at the ends of the chain than at the center \cite{38}, so for simplicity, based on this study, we approximate that the counterion density at the brush wall is half its average value, $f = 1/2$.

We have also determined the osmotic pressure contribution by mapping the sparse brush problem onto a two-dimensional (2D) cell model for infinite charged rods \cite{42,43} (see Fig. 1). Here we assume that the pressure at the cylindrical cell boundary of the PE chain is equivalent to the pressure at the brush walls. Indeed, Antypov and Holm \cite{41} demonstrated that for the finite cylindrical cell which provides the lowest free energy in a system of rodlike PEs and fully neutralizing counterions, the average counterion den-
sity, and hence the osmotic pressure, at the lateral cell wall is the same as that at the ends of the cell. Although our system is quite different from theirs [41], and we employ a cylindrical cell with a geometry defined by the distance between the brush walls and by the grafting density, we find that such a treatment yields another means by which to obtain the osmotic pressure contribution while also providing a quantitative comparison of the counterion distributions about the brush chains.

For our problem, we assume the chains in each cell are fully neutralized by the counterions in our closed (periodic) system, and so the electrostatic interaction between brushes is quite weak before the chains begin to interdigitate at $D = 2L$. Hence we solve the nonlinear Poisson-Boltzmann equation

$$\nabla^2 \varphi(r) = -4 \pi n_c \exp[\kappa T \varphi(r)],$$

where $\beta = (k_B T)^{-1}$, with the boundary conditions

$$a(\partial \varphi / \partial r)|_{r=a} = 2e/(eb) \quad \text{and} \quad R_s(\partial \varphi / \partial r)|_{r=R_s} = 0,$$

which has been solved analytically in previous works (see, e.g., Refs. [25,35,42,43]) and which may be modified if full neutralization of the line charges is not assumed [40]. Here $r$ is the radial coordinate, $e$ is the unit charge, $n_c$ is the average counterion concentration, $a$ is the effective radius of the chain, and, again, $b$ is the distance between unit charges along the chain. The original brush system is then translated into this 2D formulation by scaling the radius of the cell with a geometry fixed by the distance between the brush walls and by the grafting density, we find that such a treatment yields another means by which to obtain the osmotic pressure contribution while also providing a quantitative comparison of the counterion distributions about the brush chains.

The distribution of the counterions’ short-distance (less than $0.02 \pi \bar{a}^2$) and long-distance (less than $0.032 \pi \bar{a}^2$) chain contributions, Eq. (1), relative to their values at $D/L = 3.4$, is given by the dashed lines (red) and squares (blue) for these separations, where $R_s = \sqrt{D}/(2 \pi \bar{L} \bar{a})$ (Fig. 1).

Comparisons of the counterion concentration about a chain between this implementation of the cell model and simulations for different brush separations are shown in Fig. 2. Although the cell model is a mean-field theory and the change in brush separation is modeled solely by changing the location of the chain boundary, the larger amplitude at the chain surface and the initial decay near the chains of the counterion density with decreasing $D$ is well described by the cell model without taking into account the counterion correlation effects underlying counterion condensation at the surface of the strong PE chains. Via the argument that the average counterion distribution at the cell boundary is the same at the end of the cell (the brush wall here) [41], the cell model predicts an osmotic pressure between the brushes of $\Pi_{\text{osm}} = n_c k_B T \ln[\beta \varphi(R_s)].$

Results of the simulation and theory are presented in Fig. 3 for the two different chain lengths. As predicted by the theory for bending of stiff chains, the pressure jumps at the location $D/L = L$. We find that a slightly larger bending rigidity modulus $B$ is required to fit the chain contribution to the pressure of the brushes with smaller $(N=30$ monomer) chains, resulting from an effective larger persistence length for these shorter brushes associated with the discreteness of the chains. The force resulting from chain bending constitutes a larger share of the total force for shorter chains as well.

For the osmotic counterion contribution, we assumed that the number of counterions within the brush remained constant as $D$ was varied. This assumption, confirmed by the simulations, is based on theory demonstrating that the osmotic coefficient, and hence the net charge, of a brush was invariant to a change in the cell size enclosing the brush [23]. Again, the counterion density at the brush wall, providing the osmotic pressure, is less than the average density within the brushes.

FIG. 2. (Color online) The distribution of the counterions’ shortest distance to a (bent) brush chain averaged over the entire length of a chain. Simulation results are shown for the $N=50$ monomer chain at brush separations of $D/L = 0.44$ (circles), $D/L = 0.88$ (squares), and $D/L = 1.76$ (crosses). The corresponding cell model calculations of the radially dependent counterion densities (lines) for these separations, where $R_s = \sqrt{D}/(2 \pi \bar{L} \bar{a})$, are also illustrated. Inset: The radial distribution of the counterions about only the grafted ends of the chains for $N=30$ (circles) and $N=50$ (squares) for $D/L = 0.44$, demonstrating the larger population of the counterions at the brush wall for the shorter chains.

FIG. 3. (Color online) Simulation and theory results for the pressure between brushes as a function of their separation for the $N=50$ ($N=30$, inset) monomer chains. The total pressure ($\times$ symbols), relative to their values at $D=2L$, and the contribution only due to the chains (circles) for the simulations are shown. The bending contribution, Eq. (1), is given by the dashed (blue) line with $B=3.0 \times 10^{-28}$ J m ($B=3.4 \times 10^{-28}$ J m, inset). The sum of this contribution and that due to the counterions is shown by the dash-dot (red) ($\Pi_{\text{chain}} + \Pi_{\text{osm}}^\text{idb}$) and solid (black) ($\Pi_{\text{chain}} + \Pi_{\text{osm}}^\text{cell}$) lines. The dotted vertical line indicates where the bending behavior changes ($D^* = L$).
brush, and so \( f \) in Eq. (2) was approximated as being 1/2. In the cell model, the chain’s charge in the interior of the brush is judged to be neutralized by the counterions, which has also been ascertained from simulations, and so no fitting parameters are required. For the shorter chains at close confinement, the infinite chain (2D) approximation of the cell model underestimates the counterion contribution to the overall pressure since finite-size effects for the smaller chains become more important. Here, proportionately larger sections of the ungrafted ends of a brush are compressed against the opposite brush wall, increasing the average counterion density, and hence osmotic pressure, at the wall (see inset of Fig. 2).

In summary, simulations and a theoretical treatment have been completed for sparse brushes of short PE chains with finite rigidity. Unlike densely grafted brushes of flexible PEs, the force between the brushes investigated here not only arises from the osmotic stress of compressed counterions within the brush but also results from the work required to bend the rigid chains. The contribution to the total force arising from chain bending is of the same order as this osmotic term and may even dominate it at increased confinement as the bending contribution scales as \( 1/D^2 \). Interestingly enough, this is the same law as the simple compression mechanism put forward in Ref. [5], demonstrating the insensitivity on the precise form of chain deformation. Our analysis offers a unique quantitative description of the interactions between PE brushes with rigid chains that may be exploited, e.g., for statistical mechanical studies of multibrush systems and/or for their many physical applications, such as colloidal stabilization and lubrication, as well as control of electrical conductivity of nanoparticle films [44].

We thank Sven van Teeffelen for useful discussions. A.W. thanks the Alexander von Humboldt Foundation for financial support.