

## Interaction between two polyelectrolyte brushes

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We report molecular dynamics simulations on completely charged polyelectrolyte brushes grafted to two parallel surfaces. The pressure  $\Pi$  is evaluated as a function of separation  $D$  between the two grafting planes. For decreasing separation,  $\Pi$  shows several regimes distinguished by their scaling with  $D$  which reflects the different physical nature of the various regimes. At weak compression the pressure obeys the  $1/D$  power law predicted by scaling theory of an ideal gas of counterions in the osmotic brush regime. In addition we find that the brushes shrink as they approach each other trying to avoid interpenetration. At higher compressions where excluded volume interactions become important, we obtain scaling exponents between  $-2$  at small grafting density  $\rho_a$  and  $-3$  at large  $\rho_a$ . This behavior indicates a transition from a brush under good solvent condition to the melt regime with increasing grafting density.

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Macromolecules carrying ionic groups, so-called polyelectrolytes, play an important role in biology, materials science, and soft matter research. Polyelectrolyte brushes consist of charged polymers densely end-grafted to surfaces of various geometries [1–3]. The interactions between polyelectrolyte brushes that are grafted to two apposing surfaces have recently received a lot of attention in experiments [4–6] and simulations [7,8]. These interactions are important, e.g., in stabilization of dispersions against flocculation. Polyelectrolyte brushes attached to surfaces rubbing across an aqueous medium provide means of efficient lubrication [6]. Inspired by biology, there are also efforts to reduce mechanical wear by using biolubrication [9]. In addition to previous simulation studies, in this communication we report different scaling regimes that can be clearly separated in the behavior of disjoining pressure at decreasing separation between the two brushes. The different physical nature of the various regimes is discussed.

The basic behavior of polyelectrolyte brushes can be understood with simple scaling arguments. In the so-called osmotic brush regime where all counterions are trapped inside the brush, the equilibrium brush height  $h$ , is determined by the balance between counterion osmotic pressure and chain elasticity. Finally the brush height becomes independent of grafting density  $\rho_a$  [10],

$$h_0 \sim Na f^{1/2}, \quad (1)$$

where  $N$  is the chain length,  $a$  is the monomer size, and  $f$  is the degree of ionization. On the other hand, the thickness of the counterion layer is given by [11]

$$H_0 \sim h_0 + \frac{3}{2} \lambda_{GC}, \quad (2)$$

where the Gouy-Chapman length reads  $\lambda_{GC} = 1/(2\pi\lambda_B N f \rho_a)$  and the Bjerrum length  $\lambda_B$  sets the strength of Coulomb in-

teraction. For a typical fully charged brush,  $\lambda_{GC}$  is of the order of 1 Å or less. Thus the counterions are completely confined inside the brush. Nevertheless, recent experiments [11,12] as well as simulations [11,13] indicate a weak increase of brush height with grafting density. This behavior can be understood by an extended scaling approach that treats the finite volume of the polymers within a free volume approximation. In the so-called nonlinear osmotic brush regime the equilibrium height becomes [11]

$$h \sim Na \frac{f + \sigma_{\text{eff}}^2 \rho_a}{1 + f}, \quad (3)$$

with  $\sigma_{\text{eff}}$  being an effective diameter of the polymer chains. Note that the dependence on  $\rho_a$  arises because of the nonlinear entropy due to the reduced volume available for counterions. This scaling prediction qualitatively captures the slowly increasing brush height as observed in simulations and experiment. The corresponding thickness of the counterion layer reads

$$H \sim h + \frac{3}{2} \frac{\lambda_{GC}}{1 - \eta}, \quad (4)$$

where  $\eta = \rho_a \sigma_{\text{eff}}^2 Na / h$  is the degree of close-packing in the brush. Note that within the scaling approach both  $h$  and  $H$  are evaluated by using a box density profile. The real profiles, however, can exhibit pronounced tails which might be responsible for remarkable interaction between brushes also at separations larger than  $h$  or  $H$ .

Within the scaling approach [10] the disjoining pressure of two overlapping polyelectrolyte brushes grafted to surfaces separated by a distance  $2D$  is given by the osmotic pressure of the counterions. Considering them as ideal gas one has

$$\Pi_0 \sim k_B T f N \rho_a / D. \quad (5)$$

Taking into account the finite volume of polymers in the free volume approximation mentioned above the osmotic pressure becomes

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$$\Pi \sim \frac{\Pi_0}{1 - \eta}. \quad (6)$$

Note that for compressed brushes, the packing fraction is determined by separation  $D$  and not by the unperturbed brush height  $h$ . Using expressions based on Eq. (6) the stress profiles obtained by surface force measurements of interacting polyelectrolyte brushes could be well fitted [5].

For large separations  $D \gg h$ , interacting polyelectrolyte brushes were predicted to behave as highly charged interfaces with disjoining pressure given by the Poisson-Boltzmann expression  $\Pi = k_B T / (2\pi\lambda_B D^2)$  [7,10]. However, no electrical double-layer forces have been observed experimentally [4,5]. This can be explained by the small Gouy-Chapman lengths of typical polyelectrolyte brushes. Due to the strong electrostatic interaction between brush and counterion layer polyelectrolyte brushes appear electroneutral also on local length scales.

In this communication we present molecular dynamics simulations of interacting polyelectrolyte brushes. Reducing the separation between the two brushes both interpenetration and growing repulsion is obtained. Varying grafting density and separation the disjoining pressure is shown to exhibit different scaling regimes, one of which is dominated by counterion osmotic pressure.

The model used is that earlier applied for single brush simulations [14]. Both brushes consist of  $M=36$  freely jointed bead-spring chains of length  $N+1=31$  which are anchored by one uncharged end to an uncharged planar surface at  $z=0$  or  $z=2D$ , respectively. Within the simulation box of size  $L \times L \times 2D$  the grafting density is given by  $\rho_a = M/L^2$ . The chains are assumed to be in a good solvent modeled by a purely repulsive short-range interaction that is described by a shifted Lennard-Jones potential  $U_{LJ}$ . Along the chains, beads are connected by a finitely extensible nonlinear elastic (FENE) bond potential  $U_{\text{bond}}$ . With our choice of parameters we obtain an average bond length  $b \approx \sigma$  where  $\sigma$  is the Lennard-Jones parameter. All particles except the anchor segments are exposed to a short-ranged repulsive interaction  $U_{\text{wall}}$  with the grafting surface at  $z=0$  and  $z=2D$ , respectively.

For completely charged chains ( $f=1$ ), due to electroneutrality there are  $2 \times M \times N$  monovalent counterions which are treated as individual, nonbonded particles of the same size as monomers. All charged entities interact with the bare Coulomb interaction  $u_{\text{Coul}}(r) = k_B T q_i q_j \lambda_B / r$  with  $q_i$  and  $q_j$  being the corresponding charges in units of elementary charge  $e$  and the Bjerrum length is set  $\lambda_B = \sigma$ . To treat the long ranged Coulomb interaction we use the so-called MMM method suggested by Strebel and Sperb [15] and modified by Arnold and Holm [16] for systems which are periodic in two dimensions only.

The numerical integration of the equations of motion is performed by means of the velocity Verlet algorithm with a time step  $\delta t = 0.008 \tau_{LJ}$  where the Lennard-Jones time is given by  $\tau_{LJ} = (m\sigma^2/\epsilon)^{1/2}$ . Using a Langevin thermostat with damping constant  $\Gamma = 0.5 \tau_{LJ}^{-1}$  the system is simulated at constant temperature  $k_B T = 1.2\epsilon$  (with  $\epsilon$  being the Lennard-Jones energy). The simulations are started with straight chain con-

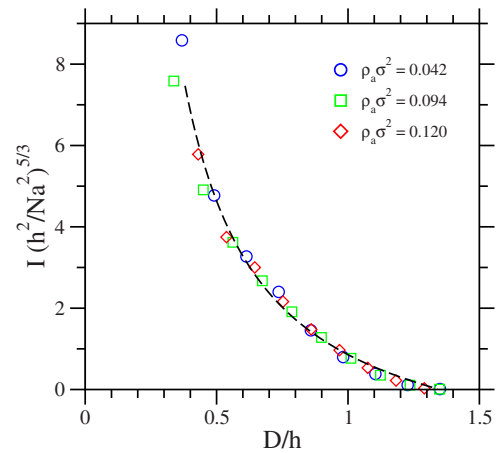


FIG. 1. (Color online) Interpenetration  $I$  between two brushes rescaled with stretching parameter  $(h^2/Na^2)$  to the power of  $-5/3$  plotted as a function of separation  $D$  rescaled with the theoretically predicted single brush height  $h$  (see Eq. (3)) at varying grafting density  $\rho_a$ . The dashed line shows a phenomenological fit (see the text).

figurations and a line of neighboring counterions. The starting separation  $D$  is chosen large enough that the brushes do not overlap. After equilibration  $D$  is reduced by a very small amount at each time step. Subsequent measurements at selected values of  $D$  run over times from  $2000\tau_{LJ}$  to  $3000\tau_{LJ}$ , depending on grafting density. This is much longer than configurational relaxation times of the polyelectrolyte chains which are typically a few hundred  $\tau_{LJ}$ .

As the brushes are approaching two processes occur: interpenetration and compression. The amount of interpenetration can be quantified in several ways. Murat and Grest [17] introduced the quantity  $I(D)$  defined by

$$I(D) = \int_D^{2D} \rho_1(z) dz / \int_0^{2D} \rho_1(z) dz, \quad (7)$$

where  $\rho_1(z)$  is the contribution of one of the brushes to the overall density and  $z$  is the distance from the grafting surface of that brush. In general we observe that with growing grafting density the interpenetration is slightly enhanced at large distances  $D$  because of an increased stretching of the brushes while at short distances it is reduced due to the higher density inside the brushes. For uncharged polymer brushes it has been shown that  $I(D)$  has the scaling form  $I(D) \sim (Na^2/h^2)^{2/3} x^{-4/3} (1-x^3)$ , where  $x = D/h$  [17]. Note that the relation  $h^2/Na^2$  is a measure of stretching. Simulation data on uncharged brushes confirm this scaling law reasonably well. For polyelectrolyte brushes, however, after such a rescaling we do not succeed with a master plot. Obviously the scaling behavior is changed reflecting the nonparabolic density profile of polyelectrolyte brushes. Assuming that the stretching parameter  $h^2/Na^2$  is still the appropriate scaling variable, we obtain the best collapse of the simulation data with a scaling  $I(D) \sim (Na^2/h^2)^{5/3}$ . The corresponding plot is shown in Fig. 1. To calculate the theoretical brush height  $h$  in the nonlinear osmotic regime we use exactly the same pa-

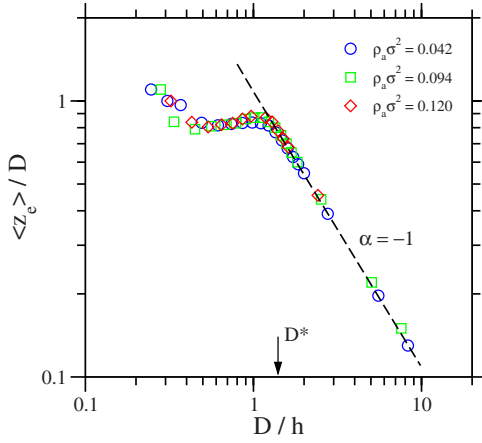


FIG. 2. (Color online) Relation between endpoint height  $\langle z_e \rangle$  and separation  $D$  as a function of  $D$  rescaled with the theoretically predicted single brush height  $h$  (see Eq. (3)) at varying grafting density  $\rho_a$ .

parameter setting  $\sigma_{\text{eff}}^2 = 2\sigma^2$  earlier applied to study the dependence of the brush height on grafting density [11] and the distribution of free ions in polyelectrolyte brushes [14]. This choice corresponds to an approximate two-dimensional square-lattice packing of monomers and counterions on two interpenetrating sublattices. In this way we get  $h = 16.3, 17.8, 18.6$  for  $\rho_a = 0.042, 0.094, 0.12$ , respectively. At small distances  $D$  we observe the asymptotic scaling  $I(D)(h^2/Na^2)^{5/3} \sim (D/h)^{-3/2}$ . On the other hand, there is no interpenetration at large distances  $D > D^* \approx 1.35h$ . Combining these two features into a phenomenological fitting function, finally we find  $I(D) \sim (Na^2/h^2)^{5/3} x^{-3/2} [1 - (x/x^*)^2]$  (see the dashed line in Fig. 1). Thus we observe a reasonable master plot of interpenetration  $I(D)$  also in the case of polyelectrolyte brushes. Compared to uncharged brushes  $I(D)$  decays a bit slower at large distances which might be due to longer tails of the density profiles.

To study the compression of the brushes in Fig. 2 we plot the average end-point height  $z_e$  rescaled with separation  $D$  vs the separation rescaled with the theoretically predicted brush height in the nonlinear osmotic regime given in Eq. (3). Figure 2 allows three conclusions: (i) As long as the compression is not too large, i.e., at  $D \geq 0.5 \times h$  the influence of the varying grafting density is captured by the nonlinear osmotic brush behavior. (ii) At large separations  $D > D^* \approx 1.35 \times h$  the brush height remains almost constant, i.e., Fig. 2 exhibits a purely  $1/D$  behavior. (iii) Before overlapping at  $D = h$  the chains of the two brushes begin to contract. Such a behavior is well known for dilute polyelectrolyte solutions.

To have a better understanding of the interactions between the two brushes we calculate the pressure at each separation  $D$  which can be directly obtained from

$$\Pi = \frac{N_{\text{tot}}}{V} (k_B T + \langle w \rangle), \quad (8)$$

with  $\langle w \rangle$  being the pressure virial per particle,

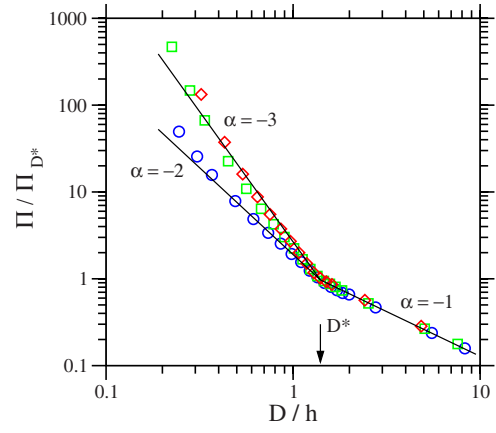


FIG. 3. (Color online) Log-log plot showing pressure  $\Pi$  vs separation  $D$  at grafting density  $\rho_a = 0.042\sigma^{-2}$  (circles),  $0.094\sigma^{-2}$  (squares),  $0.120\sigma^{-2}$  (diamonds) where  $D$  is rescaled with the single brush height in the nonlinear osmotic regime  $h$  and  $\Pi$  with the pressure at the particular separation  $D^*$ .

$$\langle w \rangle = -\frac{1}{3N_{\text{tot}}} \left( \sum_{i=1}^{N_{\text{tot}}-1} \sum_{j=i+1}^{N_{\text{tot}}} \langle \nabla U'_{ij} \cdot \mathbf{r}_{ij} \rangle - \langle U_{\text{Coul}} \rangle \right), \quad (9)$$

where  $N_{\text{tot}}$  is the total number of particles,  $V = L^2 \times 2D$  is the volume of the simulation box. To properly account for the long-range nature of the Coulomb interaction the virial in Eq. (9) is subdivided into contributions from the short-range part of the interaction potential ( $U' = U - U_{\text{Coul}}$ ) and the electrostatic contribution [18]. For large separation, the resulting pressure behavior can be well fitted by Eq. (6) which also captures qualitatively the strong increase of  $\Pi$  at small  $D$ . At intermediate  $D$ , however, the behavior observed in the simulations is different from that predicted by Eq. (6). This might be an indication that in this range the osmotic pressure is not dominated by the contribution of the free counterions. In Fig. 3 we plot the pressure  $\Pi$  as a function of separation  $D$  rescaled with the brush height  $h$ , which captures the weak dependence on grafting density. In fact at  $D > D^*$ , we find the behavior of an ideal gas of counterions  $\Pi \sim 1/D$ . In agreement with experimental findings [4,5] we do not observe any significant indication of double-layer interactions. On the other hand, there occurs clearly different behavior at  $D < D^*$ . At low grafting density the pressure obeys a  $\Pi \sim 1/D^2$  power law. With growing grafting density, however, the scaling is considerably changed and the pressure exhibits a  $\Pi \sim 1/D^3$  dependence. For very small separations, packing effects come into play and obviously the pressure does not follow a power law.

Assuming that at moderate compression  $D < D^*$  the disjoining pressure is dominated by the excluded-volume interaction of monomers the leading terms of the corresponding virial expansion read

$$\Pi/k_B T \sim \frac{\nu}{2} (N\rho_a/D)^2 + \frac{w}{6} (N\rho_a/D)^3, \quad (10)$$

with  $\nu$  and  $w$  being the second and third virial, respectively. Thus under good solvent conditions the pressure is predicted

to scale as  $\Pi \sim 1/D^2$ . For  $\theta$  conditions or in the melt regime, i.e., at  $\nu=0$ , the third order term governs the pressure and its scaling is changed to  $\Pi \sim 1/D^3$ . Hence the simulation results indicate that at moderate compression the disjoining pressure between two polyelectrolyte brushes is dominated by steric interactions and undergoes a transition from good solvent behavior to the melt regime with growing grafting density. Note that in previous single brush simulations a similar continuous transition with increasing grafting density was obtained in the scaling of the chain size in lateral directions with respect to chain length  $N$  [13].

In summary, we have studied the interaction between two opposing polyelectrolyte brushes by molecular dynamics simulations. We have shown the existence of different scaling regimes in disjoining pressure with decreasing separation between brushes which are governed either by the osmotic pressure of counterions or by the excluded volume of polymers. At large separations  $D > D^* \approx 1.35 \times h$  there is no interpenetration and the brush height  $h$  remains almost constant while the disjoining pressure is growing as  $\Pi \sim 1/D$ ,

the behavior expected due to counterion osmotic pressure. In this regime a weak increase of pressure with growing grafting density is captured by the behavior of the brush height in the nonlinear osmotic regime. We do not observe any indication of double-layer interactions which is in agreement with the small Gouy-Chapman lengths less than  $0.1\sigma$  for the systems simulated. Note that for evaluating the pressure by means of Eq. (8), we assume a homogeneous system. For large  $D$ , obviously this is a crude approximation. Therefore we can not exclude a modified pressure dependence due to inhomogeneities in  $z$ -direction. For separations below  $D^*$ , first the brushes try to reduce overlapping and interpenetration by contraction. The pressure shows a behavior expected in the excluded-volume-dominated regime. With increasing grafting density we observe a transition from good solvent behavior  $\Pi \sim 1/D^2$  to  $\Pi \sim 1/D^3$  expected in the melt regime.

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