Explicit Solvent Simulations of Friction between Brush Layers of Charged and Neutral Bottle-Brush Macromolecules

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ABSTRACT: We study friction between charged and neutral brush layers of bottle-brush macromolecules using molecular dynamics simulations. In our simulations the solvent molecules were treated explicitly. The deformation of the bottle-brush macromolecules under shear were studied as a function of the substrate separation and shear stress. For charged bottle-brush layers, we study effect of the added salt on the brush lubricating properties to elucidate factors responsible for energy dissipation in charged and neutral brush systems. Our simulations have shown that for both charged and neutral brush systems the main deformation mode of the bottle-brush macromolecules is associated with the backbone deformation. This deformation mode manifests itself in the backbone deformation ratio, $\alpha$, and shear viscosity, $\eta$, to be universal functions of the Weissenberg number $W$. The value of the friction coefficient, $\mu$, and viscosity, $\eta$, are larger for the charged bottle-brush coatings in comparison with those for neutral brushes at the same separation distance, $D$, between substrates. The additional energy dissipation generated by brush sliding in charged bottle-brush systems is due to electrostatic coupling between bottle-brush and counterion motion. This coupling weakens as salt concentration, $c_s$, increases resulting in values of the viscosity, $\eta$, and friction coefficient, $\mu$, approaching corresponding values obtained for neutral brush systems.

1. INTRODUCTION

Interactions between surfaces covered with grafted polymer chains (brushes) play an important role in adhesion, friction, and lubrication. Brush covered surfaces can withstand normal loads larger than 0.1 MPa and at the same time can reduce the sliding friction coefficient below $10^{-2}$.\(^{8-23}\) The best known example of brush lubrication is the low friction between opposing articular cartilage surfaces of human joints. Interaction between cartilage surfaces is mediated by brush-like polyelectrolyte layers of glycoproteins, in which a large number of sugar chains are bound along the polymer backbone. The human joints such as hips and knees have remarkably low friction coefficient $\mu$ in the range $0.001-0.03$ and can withstand pressures of the order of ten atmospheres.\(^{24-28}\) Some synthetic brush coatings can emulate lubricating properties observed in natural joints in the interval of physiological pressure loads.\(^{22}\) There are several working hypothesis that were put forward to explain the low friction between charged brushes: (i) electrostatic interactions between ionized groups and counterions, (ii) osmotic pressure of counterions, and (iii) a hydration layer surrounding charged groups in brush interpenetration zone.

During the last 20 years, numerous theoretical\(^{29-33}\) and computational\(^{33-48}\) studies attempted to pinpoint the exact mechanism responsible for low lubrication between brushes. It was confirmed for charged brush layers that the osmotic pressure of counterions and electrostatic interactions between charged monomers reduce interpenetration between brush layers and low friction between sliding brushes.\(^{47,48}\) The value of the friction coefficient between charged (polyelectrolyte) brushes could be an order in magnitude lower than the corresponding friction coefficient between neutral brush layers.\(^{47,48}\) However, the majority of simulations were performed without explicit solvent thus completely eliminating solvent effect on brush lubricating properties. There are only few computer simulations\(^{33,33,49}\) that considered effect of explicit solvent on the friction between brush layers of the linear chains. These simulations have shown that inclusion of the explicit solvent results in quantitative changes in the brush behavior in comparison with implicit solvent simulations.\(^{33}\)

In this paper we present results of the molecular dynamics simulations of interaction between layers made of neutral and charged bottle-brush macromolecules as a function of the brush grafting density, brush separation and shearing force. The simulations were performed with explicit solvent that introduced hydrodynamic coupling between brush and...
surrounding solvent. Comparison between charged and neutral brush systems allowed us to elucidate the role of the electrostatic and polymer—solvent interactions on brush lubricating properties. The rest of the paper is organized as follows. In section 2, we describe our model of the bottle-brush macromolecules and simulation procedure. In section 3, we illustrate how electrostatic interactions influence bottle-brush deformation under shear, brush layer interpenetration and their effect onto friction coefficient between brush layers. Finally, in section 4, we discuss our result.

2. SIMULATION DETAILS

We performed molecular dynamics simulations of interactions between grafted layers of the charged and neutral bottle-brush macromolecules with explicit solvent. For charged bottle-brush systems counterions and salt ions were included explicitly. The bottle-brush macromolecules were modeled by chains of Lennard-Jones (LJ) particles (beads) with diameter \( \sigma \). Each bottle-brush macromolecule consisted of a main chain with the degree of polymerization \( N = 97 \) and side chains with the degree of polymerization \( m = 21 \) (see Figure 1). (The bottle-brush model is similar to the one used in our simulations of the bottle-brush layers.\(^47,50,51\)) There were total 31 side chains per each bottle-brush macromolecule that corresponds to every third monomer of the main chain to have a side chain attached to it. For charged bottle-brush macromolecules only side chains were charged with the fraction of the charged monomers \( f = 1/3 \) corresponding to every third monomer carrying a negative electrical charge, \( -e \). There were two substrates per simulation box located at \( z = 0 \) and \( z = L_z \) (see Figure 2). A substrate consisted of four layer lattice of beads each composed of 80 \( \times 70 \) beads with diameter \( \sigma \). It had symmetry of the hexagonal closed-packed (HCP) lattice with lattice constant equal to \( \sigma \). The number \( N_B = 6 \) and 21 of the bottle-brush macromolecules was grafted to a substrate corresponding to brush grafting density, \( \rho_g \), equal to 1.24 \( \times 10^{-3} \sigma^{-2} \) and 4.33 \( \times 10^{-3} \sigma^{-2} \). The height of the space between substrates, \( D \), was varied between 30 \( \sigma \) and 140 \( \sigma \). The top substrate with grafted bottle-brush layer was allowed to move along \( y \)-direction to model shear.

All particles (beads) in the system interacted through truncated-shifted Lennard-Jones (LJ) potential:

\[
U_{\text{LJ}}(r_{ij}) = \begin{cases} 
4\varepsilon_{ij} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \left( \frac{\sigma}{r_{cut}} \right)^6 & r \leq r_{cut} \\
0 & r > r_{cut}
\end{cases}
\]

where \( r_{ij} \) is the distance between \( i \)-th and \( j \)-th beads, and \( \sigma \) is the bead diameter chosen to be the same regardless of the bead type. The cutoff distance \( r_{cut} = 2^{1/6} \sigma \) was selected for all pair wise interactions. The interaction parameter \( \varepsilon_{ij} \) was equal to \( k_BT \) for all interactions, where \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature.

The connectivity of monomers into bottle-brush macromolecules was maintained by the finite extension nonlinear elastic (FENE) potential\(^2\):

\[
U_{\text{FENE}}(r) = -\frac{1}{2} k_{spring} R_{\max}^2 \ln \left( 1 - \frac{r^2}{R_{\max}^2} \right)
\]

with the spring constant \( k_{spring} = 30 k_BT/\sigma^2 \), and maximum bond length \( R_{\max} = 1.5 \sigma \). The repulsive part of the bond potential was represented by the truncated-shifted LJ potentials with \( \varepsilon_{ij} = k_BT \) and \( r_{cut} = 2^{1/6} \sigma \). In our simulations we have excluded \( 1 \sim 2 \) LJ-interactions such that monomers connected by a bond only interacted through the bonding potential. The particles forming substrates were connected by harmonic springs with the spring constants

\[
U_{\text{harm}}(r) = \frac{1}{2} k_h (r - r_0)^2
\]

where \( k_h = 1000 k_BT/\sigma^2 \), and \( r_0 = \sigma \).

In the case of charged bottle-brush layers interaction between any two charged beads (charged monomers, counterions and salt ions) with charge valences \( q_i \) and \( q_j \), and separated by a distance \( r_{ij} \), was given by the Coulomb potential

\[
U_{\text{Coul}}(r_{ij}) = k_B T \frac{q_i q_j}{r_{ij}}
\]

where \( l_B = e^2/\varepsilon k_BT \) is the Bjerrum length, defined as the length scale at which the Coulomb interaction between two elementary charges \( e \), in a dielectric medium with the dielectric constant \( \varepsilon \), is equal to the thermal energy \( k_BT \). In our simulations, the value of the Bjerrum length \( l_B \) was set to 1.0 \( \sigma \). This value of the Bjerrum length was selected to avoid effects associated with the counterion condensation.

The particle–particle–particle–mesh (PPPM) method\(^55\) with GPU acceleration\(^54\) implemented in LAMMPS\(^55\) with the sixth order charge interpolation scheme and estimated accuracy 10\(^{-5}\).

![Figure 1. Snapshot of the bottle-brush macromolecule.](Image)
was used for calculations of the electrostatic interactions between all charges in the system. Because PPPM is implicitly periodic in all directions, artificial periodicity in the z-direction was removed by extending the PPPM mesh with empty volume along z direction by 3Lz and removing dipole interslab interactions.56

In our simulations, the top substrate was subjected to a constant shear stress, σz (see Figure 2). This was achieved by applying a constant shear force f, acting on each bead forming the top layer of the substrate. These simulations were performed to obtain the relationship between the substrate velocity and magnitude of the shear stress.

To preserve hydrodynamic modes and maintain a constant temperature during simulations we used substrates as heat sinks. In particular we applied Langevin thermostat along the vorticity direction (x-axis)57 and z-direction to the two middle layers of the top and bottom substrates. The equations of motion of beads belonging to these substrate layers were

\[
m \frac{d\vec{v}_i(t)}{dt} = \vec{F}_i(t) - \xi (v_i(t)\vec{e}_x + v_i(t)\vec{e}_z) + \vec{F}_i^{\text{R}}(t)
\]

where \(\vec{F}_i(t)\) is a deterministic force acting on the i-th bead with mass m moving with velocity \(\vec{v}_i(t)\), the stochastic force \(\vec{F}_i^{\text{R}}(t)\) had only x and z-components with zero average value \(\langle \vec{F}_i^{\text{R}}(t) \rangle = 0\) and ξ-function correlations \(\langle \vec{F}_i^{\text{R}}(t)\vec{F}_i^{\text{R}}(t') \rangle = 4\xi k_B T \delta(t - t')\)

where friction coefficient \(\xi = 0.143 m / \tau_{ij}\) and \(\tau_{ij}\) is the standard Lennard-Jones time \(\tau_{ij} = \sigma (m / \epsilon_{ij})^{1/2}\), \(\vec{e}_x = (1,0,0)\) and \(\vec{e}_z = (0,0,1)\) are unit vectors. The mass m was set to unity for all particles.

For all other beads in a system (solvent, bottle-brush monomers, counterions, salt ions and beads belonging to the first and fourth layers of the substrates) the equations of motion were

\[
m \frac{d\vec{v}_i(t)}{dt} = \vec{F}_i(t)
\]

Since only deterministic forces, \(\vec{F}_i(t)\), were included into the equation of motion (eq 6) the momentum and energy were conserved during bead collisions (interactions). This preserved hydrodynamic modes in the solvent/bottle-brush complex fluid between substrates.

The velocity-Verlet algorithm with a time step \(\Delta t = 0.005 \tau_{LJ}\) was used for integration of the equations of motion (eq 5 and 6). All simulations were performed using LAMMPS with GPU acceleration.54,55,58

Simulations were performed using the following procedure: at the beginning of each simulation run, the main and side chains of the bottle-brush macromolecules were in a fully extended conformation with the main chain pointing along the z-direction and side chains were randomly oriented in the x–y plane. In the case of the charged systems neutralizing monovalent counterions, salt ions and solvent particles were uniformly distributed over the volume of the simulation box. (For neutral systems only solvent particles were uniformly distributed over the simulation box.) The size of the simulation box along the x and y directions were kept constant and equal to \(L_x = 70 \sigma\) and \(L_y = 69.28 \sigma\). The initial size of the simulation box along the z direction was set to \(L_z = 205 \sigma\). The system was compressed to the final box size \(L_z\) by performing MD simulation runs with electrostatic interactions turned off. In all simulations the volume fraction of particles filling the space between the substrates in the final state was close to \(\rho \sigma^3 = 0.8\). The actual numbers of particles used in simulations are listed below in Table 1.

Systems were equilibrated for up to \(8 \times 10^6\) MD steps with the last \(1 \times 10^6\) MD steps used for the data analysis. The actual numbers of particles used in simulations are listed below in Table 1.

<table>
<thead>
<tr>
<th>(D [\sigma])</th>
<th>(L_z [\sigma])</th>
<th>(N_{tot})</th>
</tr>
</thead>
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<tr>
<td>30</td>
<td>35.05</td>
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</tr>
<tr>
<td>40</td>
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<td>277588</td>
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<tr>
<td>80</td>
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<td>100</td>
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<tr>
<td>120</td>
<td>125.4</td>
<td>510375</td>
</tr>
<tr>
<td>140</td>
<td>145.6</td>
<td>587971</td>
</tr>
</tbody>
</table>
3. SIMULATION RESULTS

3.1. Interaction between Brush Layers. We first study static properties of the bottle-brush layers. Figure 3 shows dependence of the average value of the $z$-component of the pressure tensor (longitudinal pressure) $P_{zz}$ on substrate separation in confined pure solvent and bottle-brush systems. Note that contributions from the substrate beads to the pressure tensor were excluded from calculations of the pressure $P_{zz}$. The data points for pure solvent systems are shown by crosses connected by a dotted line. Images on the right show snapshots of the pure solvent and charged brush simulations.

The system pressure $P = 6.80 \pm 0.01k_BT/\sigma^3$, obtained for our largest substrate gap, $D = 140 \sigma$, approaches that obtained from the equation of state for WCA liquid based on MD simulation data of the bulk systems, $6.61k_BT/\sigma^3$. This is also close to the pressure $6.59 \pm 0.03k_BT/\sigma^3$ obtained in our 3-D simulations of pure solvent system consisting of $2.5 \times 10^5$ particles. The value of the zero shear viscosity $\eta_0 = 1.77 \pm 0.01k_BT\tau_\ell/\sigma^2$ for $D = 100 \sigma$ is close to the value of the bulk viscosity $\eta_0 = 1.79k_BT\tau_\ell/\sigma^3$ of the WCA liquid obtained by linear interpolation of the viscosity data.

Using average values of the longitudinal $P_{zz}$, transversal $P_{xx}$ and $P_{yy}$ components of the pressure tensor we can calculate the free energy excess per unit area (surface energy) of the bottle-brush layers.

$$\gamma_x = \frac{D}{2} \left( P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right)$$

For the low brush grafting density, $\rho_g = 1.24 \times 10^{-3}$, the longitudinal pressure $P_{zz}$ in both charged and neutral bottle-brush systems increases with decreasing substrate separation. This corresponds to an effective repulsion between two brush coated surfaces. However, for the high brush grafting density, $\rho_g = 4.33 \times 10^{-3}$, the longitudinal pressure decreases with decreasing the brush separation which corresponds to an effective attraction between substrates.

Thus, in simulations of open systems allowing solvent exchange with reservoir one should expect a compression of the brush layer caused by expulsion of the solvent. In inset we show the longitudinal pressure difference (excess of the longitudinal pressure) $\Delta P_{zz} = P_{zz} - P_{zz}$ between pure solvent and brush systems. Note that the data sets corresponding to two different brush grafting densities are shifted one with respect to another and the longitudinal pressure difference is inversely proportional to the substrate separation, $\Delta P_{zz} \propto D^{-1}$. This indicates that we can plot our data in terms of the longitudinal pressure excess $\Delta P_{zz}$ as a function of the polymer density $c_p$ (see Figure 4). As expected the simulation data for two different brush grafting densities collapsed into universal line. The overlap between charged and neutral brush data sets shows that the linear dependence of the pressure difference is not due to counterions and is dominated by the excluded volume effects imposed by the bottle-brush macromolecules on the solvent. This decreases configurational entropy of the solvent and reduces system pressure. Therefore, simulations with explicit solvent are qualitatively different from implicit solvent simulations for which interactions between two brush layers are dominated by osmotic pressure localized between substrates counterions, by bending of the bottle-brush macromolecules and by monomer–monomer interactions.

Using average values of the longitudinal $P_{zz}$, transversal $P_{xx}$ and $P_{yy}$ components of the pressure tensor we can calculate the free energy excess per unit area (surface energy) of the bottle-brush layers.

$$\gamma_x = \frac{D}{2} \left( P_{zz} - \frac{1}{2} (P_{xx} + P_{yy}) \right)$$
The factor $1/2$ in eq 7 accounts for two surfaces per simulation box. Figure 5 shows dependence of the surface energy on the brush separation. For the low brush grafting density, $\rho_g = 1.24 \times 10^{-3} \sigma^{-2}$, there is no significant difference between surface energy in the brush and pure solvent systems. In this case the main contribution to the surface energy is due to solvent layering at the substrate surface. For the large brush grafting density, $\rho_g = 4.33 \times 10^{-3} \sigma^{-2}$, we see a significant difference in surface energies of charged and neutral bottle brush systems at large substrate separations. This difference is due to redistribution of the solvent and counterions inside brush layers as seen in Figure 6 showing the density profiles in the gap between substrates. Close to substrate surface all density profiles are identical and are dominated by layering of a solvent induced by interaction with substrate. Further away from the surface the presence of the bottle-brush macromolecules changes the density profile. Note that due to strong electrostatic repulsion within charged brush layer the charged bottle-brush macromolecules are more extended thus filling the larger portion of the gap between substrates. However, neutral bottle-brushes show larger variations in density across the gap. The lower density in the middle of the gap between substrates observed in brush systems in comparison with that for pure solvent system is in agreement with the lower value of the longitudinal pressure seen in brush systems (see Figure 3). In the next section we will discuss how different layer structures influence friction between brush layers.

### 3.2. Effect of Shear on Layer Structure and Lubrication

Parts a and b of Figure 7 show dependence of the average velocity of the top substrate on the gap thickness $D$ between two brush bearing surfaces. The values of the shear stresses $\sigma_{xy}$ were obtained from the values of the shear forces $f_y$ acting on the beads of the last layer of the top substrate, $\sigma_{xy} = f_y/a$ (where $a = 0.866 \sigma$ is the area per substrate bead). The average substrate velocity, $v_x$, monotonically increases with increasing magnitude of the shear stress and monotonically decreases with decreasing the gap thickness $D$ for both charged and neutral systems. The values of the velocities are smaller for the charged brush layers in comparison with corresponding neutral systems at the same value of the shear stress. Thus, charged brush systems have a higher effective friction coefficient between brush bearing substrates than neutral systems. This is qualitatively different from what was observed in simulations of brush systems without explicit solvent. In these simulations substrates covered by charged brush layers move faster than neutral ones at the same magnitudes of the shear and normal stresses. The main reason for such behavior is the dominant role of the osmotic pressure of counterions which results in larger separation between charged brush layers and therefore results in lower overlap and lower friction at the same value of the normal stress. In simulations with explicit solvent, the majority of the normal stress is generated by the solvent such that for both charged and neutral systems the load-separation curves are almost identical with counterions and polymeric contributions accounting for less than 12% of the system longitudinal pressure (see Figure 3). Note that this
contribution increases with decreasing separation between substrates, $D$.

In Figure 7, one can identify two different regimes in the velocity dependence on the shear stress. At low shear stresses the velocity increases linearly with increasing the magnitude of the shear stress. Above a crossover value of the shear stress average velocity of the top substrate begins to increase faster than linear with the applied stress. This increase of the velocity with shear stress is due to changes in the bottle-brush conformations upon shear (see images A–L in Figure 8). As the magnitude of shear stress increases, the bottle-brush chains tilt and stretch. The charged bottle-brush macromolecules demonstrate slightly larger deformation due to additional contribution of the electrostatic interactions to the chain stretching which results in slightly stronger interactions between charged brush layers and lower average velocity. Tilting of the bottle-brushes opens a gap between brush layers decreasing the overlap between opposing brush macromolecules. In the case of the charged bottle-brushes this gap is filled with counterion. This is shown in Figure 9, where we plot charge distribution between two substrates at different shear stresses shown in Figure 8.

![Figure 7](image1.png)  

Figure 7. Dependence of the shear velocity $v_y$ on shear stress $\sigma_{yz}$ for charged (a) and neutral (b) bottle-brush layers with brush grafting density $\rho_g = 1.24 \times 10^{-3} \sigma^2$ as a function of the gap thickness: $D = 30 \sigma$ (charged, ●; neutral ○), $D = 40 \sigma$ (charged, red ▲; neutral, red □), $D = 60 \sigma$ (charged, blue ◆; neutral, blue ○), $D = 80 \sigma$ (charged, green ▲; neutral, green ●), $D = 100 \sigma$ (charged, brown ▼; neutral, brown △), $D = 120 \sigma$ (charged, gray hexagons); $D = 140 \sigma$ (charged, purple ●). Letters A–L correspond to snapshots of bottle-brush macromolecules and brush layers at different shear stresses shown in Figure 8.

![Figure 8](image2.png)  

Figure 8. Snapshots of the bottle-brush conformations at different shear velocities in charged (a) and neutral (b) brush layers.

![Figure 9](image3.png)  

Figure 9. Charge number density distribution in bottle-brush layers with brush grafting density $\rho_g = 1.24 \times 10^{-3} \sigma^2$, substrate separation $D = 60 \sigma$ and at different values of the shear stress, $\sigma_{yz} = 2.9 \times 10^{-3} k_BT/\sigma^3$ (blue filled rhombs), $\sigma_{yz} = 5.8 \times 10^{-3} k_BT/\sigma^3$ (brown half-filled rhombs), $\sigma_{yz} = 1.2 \times 10^{-2} k_BT/\sigma^3$ (blue open rhombs) and $\sigma_{yz} = 2.9 \times 10^{-2} k_BT/\sigma^3$ (red crossed rhombs).
counterions. The amount of the excess charge accumulated by counterions in the middle of the simulation box increases with increasing the shear stress. For our highest shear stress $\sigma_{yz} = 2.9 \times 10^{-2} k_BT/\sigma^3$ the counterion peak splits into two indicating appearance of two overlapping counterion double layers forming outside the brush. Inside the bottle-brush layer counterions compensate the brush charge. Note that a slight asymmetry in charge distribution observed in Figure 9 is a manifestation of the random distribution of the bottle-brush grafting points over the substrate surfaces.

Deformation of the bottle-brush macromolecules within brush layers under shear is described by the deformation ratio of the bottle-brush backbone

$$\alpha = \frac{\langle R_e^2(\dot{\gamma}) \rangle}{\langle R_e^2(0) \rangle}$$

(8)

where $\langle R_e^2(\dot{\gamma}) \rangle$ is the mean square value of the backbone end-to-end distance at the shear rate

$$\dot{\gamma} = \frac{v}{D}$$

(9)

and $\langle R_e^2(0) \rangle$ is its value at zero shear rate. The values of $\langle R_e^2(0) \rangle$ were obtained from simulations with zero shear stress. Figure 10 shows deformations of the backbone of the bottle-brush macromolecules charged and neutral brush layers. Bottle-brush macromolecules begin to deform when shear rate exceed a crossover value $\dot{\gamma}^*$. The charged bottle-brush macromolecules have a larger value of the backbone deformation ratio $\alpha$ at the same values of the shear rates. This is due to additional contribution of the electrostatic interactions to the backbone deformation.

We have fitted the bottle-brush deformation curves shown in Figures 10 a and b to the following crossover equation

$$\alpha = \frac{\langle R_e^2(\dot{\gamma}) \rangle}{\langle R_e^2(0) \rangle} = \left(1 + \frac{\dot{\gamma}}{\dot{\gamma}^*} \right)^\beta$$

(10)

considering $\dot{\gamma}^*$ and $\beta$ as fitting parameters. The results of the fitting procedure are shown in Figure 11 where we plotted our simulation data for the bottle-brush backbone deformation as a function of the Weissenberg number, $W = \dot{\gamma}/\dot{\gamma}^*$. The values of the exponents $\beta$ used for these plots are $\beta = 0.49 \pm 0.02$ for charged and $\beta = 0.51 \pm 0.01$ for neutral bottle-brush systems. The values of the crossover shear rates $\dot{\gamma}^*$ obtained from the
fitting procedure are summarized in Table 2. The deviation from universal behavior is observed at large deformations where backbone approaches a fully extended conformation and nonlinear backbone deformation effects become important. The collapse of the simulation data indicates existence of the single characteristic time and length scale controlling brush deformation. Similar behavior was observed in simulations of neutral brushes of linear chains for which exponent $\beta = 0.5$. Therefore, one can consider bottle-brush macromolecules as linear chains with effective persistence length. It also worth pointing out that qualitatively similar behavior was observed in simulations of charged brush layers without solvent. However, the values of the exponent $\beta = 0.32 \pm 0.01$ was smaller. Note that these simulations modeled a Rouse dynamics of the brush layers that correspond to a complete screening of the electrostatic interactions by counterions. The larger value of the exponent obtained in simulations of neutral brush of linear chains, $\beta = 0.43$, indicates that for strongly overlapped charged brushes, monomer–monomer contacts begin to play a dominant role in interaction between charged brush layers. It is similar to what is observed in polyelectrolyte solutions for which at high polymer concentrations the solution properties have the same scaling laws as solutions of neutral polymers. This is due to effective screening of the electrostatic interactions by counterions and charged monomers at high polymer concentrations. The universal plots for charged and neutral bottle-brushes are shown in Figure 13. The collapse of the simulation data provides further confirmation of the existence of the single characteristic length and time scale associated with the bottle-brush backbone deformation that is responsible for the energy dissipation within sliding brush layers. It is worth pointing out that the value of the exponent $\xi = 0.42 \pm 0.02$ for neutral bottle-brush systems is within error bars from the viscosity exponent obtained in simulations of neutral brush of linear chains, $\xi = 0.43$.

Experimental data on the friction between brush layers are usually presented as dependence of the kinetic friction coefficient as a function of the shear stress or shear rate. The

Table 2. Dependence of the Crossover Shear Rate on Substrate Separation

<table>
<thead>
<tr>
<th>$D$ [nm]</th>
<th>$\dot{\gamma}^*$ [s$^{-1}$] charged</th>
<th>$\dot{\gamma}^*$ [s$^{-1}$] neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>$(1.13 \pm 0.13) \times 10^{-3}$</td>
<td>$(1.25 \pm 0.07) \times 10^{-3}$</td>
</tr>
<tr>
<td>40</td>
<td>$(2.50 \pm 0.31) \times 10^{-3}$</td>
<td>$(2.84 \pm 0.14) \times 10^{-3}$</td>
</tr>
<tr>
<td>60</td>
<td>$(3.81 \pm 0.48) \times 10^{-3}$</td>
<td>$(8.03 \pm 0.39) \times 10^{-3}$</td>
</tr>
<tr>
<td>80</td>
<td>$(5.38 \pm 0.68) \times 10^{-3}$</td>
<td>$(1.91 \pm 0.08) \times 10^{-4}$</td>
</tr>
<tr>
<td>100</td>
<td>$(1.71 \pm 0.22) \times 10^{-4}$</td>
<td>$(2.14 \pm 0.11) \times 10^{-4}$</td>
</tr>
<tr>
<td>120</td>
<td>$(3.21 \pm 0.39) \times 10^{-4}$</td>
<td>–</td>
</tr>
<tr>
<td>140</td>
<td>$(6.56 \pm 0.73) \times 10^{-4}$</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 12. Dependence of shear viscosity, $\eta$, on shear rate, $\dot{\gamma}$, for charged (a) and neutral (b) bottle-brush layers with brush grafting density $\rho_g = 1.24 \times 10^{-3}$ $\sigma^{-2}$ at different gap thickness. Notations are the same as in Figure 7. The dashed lines correspond to bulk viscosity of the pure solvent system.
kinetic coefficient is defined as a ratio between shear and compression stresses

$$\mu(\dot{\gamma}) = \frac{\sigma_s(\dot{\gamma})}{\sigma_c(\dot{\gamma})}$$

(13)

In the simulations with constant substrate separation the value of the compression stress is $\sigma_c(\dot{\gamma}) = -P_{zz}(\dot{\gamma})$. Figure 14 shows dependence of the friction coefficient $\mu$ on the shear rate, $\dot{\gamma}$.

These plots provide a different representation of the data shown in Figure 12. The plateau regimes seen in Figure 12 correspond to the linear regime, $\mu \propto \dot{\gamma}$, while sublinear increase in the friction coefficient, $\mu \propto \dot{\gamma}^\delta$ with the exponent $\delta < 1$, corresponds to shear thinning regimes seen in Figure 12. The values of the friction coefficient for neutral systems are lower than the corresponding values of the friction coefficient for charged systems. For all systems the friction coefficient increases with decreasing substrate separation, $D$. Note that the range of variation in the friction coefficient is the same as in the simulations of friction between brushes of linear chains.33 It is also about two order in magnitude higher than the value of the friction coefficient obtained in simulations of the charged bottle-brush systems without explicit solvent.47

3.3. Effect of the Added Salt. Addition of salt leads to screening of the electrostatic interactions between charges weakening electrostatic repulsion between charged monomers and electrostatic attraction between charged monomers and counterions. Depending on salt concentration there are two different salt concentration regimes.62,63 At low salt concentrations when local counterion concentration is higher than salt concentration the system behavior is similar to the salt-free
case. However, when the salt concentration exceeds local counterion concentration electrostatic interactions are exponentially screened on the length scales larger than the corresponding Debye screening length and can be considered as short-range interactions.62,63 In this high salt concentration regime the behavior of the charged brush system is qualitatively similar to that of the neutral brush. To illustrate this point in Figure 15, we show dependence of the chain deformation ratio and system shear viscosity on the shear rate at different salt concentrations. We do not see significant effect of the salt on bottle-brush deformation since bottle-brush backbone is already strongly stretched in the case of the neutral bottle-brush (see Figure 15 a). However, the shear viscosity data clearly show a screening of the electrostatic coupling between motion of bottle-brushes and counterions that results in reduction of the energy dissipation in a system and decrease in viscosity. Note that we do not expect viscosity of the neutral bottle-brush system to be the same as that for charged bottle-brush systems at very high salt concentrations because of the additional contribution from the screened electrostatic interactions.

4. CONCLUSIONS

Using molecular dynamics simulations, we studied friction between brush layers of charged and neutral bottle-brush macromolecules. In particular, we demonstrated what effect shear stress and substrate separation has on deformation of the bottle-brush macromolecules, shear viscosity, and friction coefficient between brush covered surfaces. Simulations were performed with explicit solvent which allowed us to account for the effect of the hydrodynamic interactions on brush lubrication.

Our simulations show that the main contribution to the longitudinal pressure between brush layers comes from the loss of the configurational entropy of the solvent with monomer–monomer and electrostatic interactions contributing less than 15% to the longitudinal pressure $P_{xx}$. Because of the dominant effect of the solvent both charged and neutral systems demonstrate similar dependence of the longitudinal pressure, $P_{xx}$, and longitudinal pressure difference, $\Delta P_{xx}$, on substrate separation, $D$ (see Figure 4). In the wide interval of brush separations the longitudinal pressure difference scales linearly with polymer concentration, $\Delta P_{xx} \propto c_p$. This is qualitatively different result from those obtained in simulations without explicit solvent.51 In these simulations osmotic pressure of counterions and monomer–monomer interactions play a dominant role in determining equilibrium spacing between brush covered substrates as a function of the disjoining pressure. This results in much stronger overlap between neutral brush layers in comparison with that for the charged brush layers.51

For both charged and neutral bottle-brush systems we have observed that under shear deformation of the bottle-brush backbone is the main deformation mode. The backbone deformation ratio $\alpha$ is a universal function of the Weissenberg number, $W$, (see Figure 11). In the interval of large Weissenberg numbers, $W \gg 1$, the size of the bottle-brush backbone increases with increasing shear rate as $R^2 \propto \dot{\gamma}^\alpha$. Also in addition to the backbone elongation with increasing the shear rate, bottle-brush macromolecules align along the substrate and orient along the shear direction (see Figure 8). In the opposite limit of the small Weissenberg numbers, $W \ll 1$, the shear forces are weaker than the tension induced by short-range and electrostatic interactions within brush layers and are too weak to force bottle-brush deformation. The crossover value of the shear rate $\dot{\gamma}_0$, defining crossover between two brush deformation regimes, monotonically increases with increasing separation between substrates, $D$, for both systems. It has smaller values for charged bottle-brush systems in comparison with those obtained for neutral bottle-brush layers. Thus, electrostatic interactions between charged side chains and counterions provide an additional contribution to the backbone stretching shifting a crossover to brush deformation regime to the smaller values of the applied shear rates (stresses).

The existence of the main deformation mode of the bottle-brush macromolecules is in agreement with dependence of the shear viscosity on the shear rate (see Figure 12). In the limit of the small shear rates, $\dot{\gamma} < \dot{\gamma}_0^*$, the shear viscosity is a constant $\eta \approx \eta_0$. This is followed by the shear thinning regime with $\eta \propto \dot{\gamma}^{-\delta}$ for both charged and neutral systems. Therefore, reduced shear viscosity $\eta/\eta_0$ of the bottle-brush layers is a universal function of the Weissenberg number $W$ (see Figure 13). It is important to point out that the zero shear rate viscosity $\eta_0$ is higher for charged bottle-brush layers in comparison with that for neutral ones at the same substrate separation, $D$. The
additional energy dissipation which occurs in charged bottlebrushes is associated with counterion motion. Because of electrostatic coupling sliding charged bottle-brush layers move their counterions with them. The counterions role in the additional system friction is further supported by decrease of the zero shear rate viscosity with increasing salt concentration (see Figure 15b). Addition of salt results in exponential screening of the electrostatic attraction between counterions and charged monomers reducing the solvent volume which is affected by the counterion motion.

**AUTHOR INFORMATION**

Notes

The authors declare no competing financial interest.

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