Mesoscopic simulation of entanglements using dissipative particle dynamics: Application to polymer brushes

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We use a simple spring-spring repulsion to model entanglements between polymers in dissipative particle dynamics (DPD) simulations. The model is applied to a polymer brushes system to study lubrication. We demonstrate that this method leads to mechanical equilibrium in polymer brushes using the normal DPD time step. The number of bond crossings is calculated to provide a quantitative description of the entanglement. We demonstrate that it is possible to avoid 99% of the bond crossings with the values of spring-spring repulsion that can be used without significantly decreasing the time step. A shear force is applied to the system to study the effect of the decrease in the bond crossings on the structure and rheological properties of the brushes. In particular, we show how the friction coefficient increases with the decrease in the bond crossings of the polymers. © 2008 American Institute of Physics. [DOI: 10.1063/1.2954022]

I. INTRODUCTION

Polymers grafted onto solid surfaces have a wide range of technological and industrial applications, such as oil recovery, modification of surface,1 friction, lubrication, colloidal stabilization,2–6 and biocompatibility. Modeling lubrication requires a detailed understanding of the effects of polymer brushes on the rheology of a confined liquid. Polymer brushes have been studied in detail both theoretically7–11 and experimentally using the surface force apparatus (SFA).12–14 The system has been extensively studied using molecular dynamics15 and mesoscopic simulation techniques such as Brownian dynamics16–20 and dissipative particle dynamics (DPD).21–24

In general, when studying the dynamical and rheological properties of a polymer brush system we would avoid the molecular description of the polymer chains since it requires a time step of $10^{-15}$ s and a simulation of hundreds of millions of steps to explore the relevant timescales for the relaxation of the system. In a series of previous papers we have shown that it is possible to use DPD to study this system efficiently. The time step in these simulations is approximately $10^{-9}$ s because of the soft nature of the interactions between the polymer segments. However, this soft potential results in unphysical bond crossings in the DPD model; entanglements are precluded in the molecular model by steep repulsive interactions. Bond-crossings cannot be avoided in the normal DPD simulation and in studies of polymer melt using this method the chains exhibit Rouse dynamics. We believe that unphysical bond crossings may have a profound effect on the friction between the polymer brushes and we will explore the correlations in this paper.

We propose here to implement a simple spring-spring repulsion model introduced originally by Kumar and Larson.25 In this approach an additional point force acts along the line joining the closest approach between bond segments.

This paper is organized as follows: Section I describes the DPD model and the geometry of the pore system. The DPD forces are detailed, and the parameters for simulating a polymer brushes system are given. Section II describes the entanglement force and the method of evaluating the number of bond crossings and defining the entanglement efficiency. Section III contains our results including the discussions on the system under shear and the effects of the bond crossings on the friction coefficient and brush structure. Section IV contains our conclusions.

II. MODEL

A. Dissipative particle dynamics

DPD is a coarse-grained method in which individual particles do not represent a single atom but an entire fluid element or segments of polymers. It was introduced by Hoogerbrugge and Koelman27,28 as a mesoscopic simulation method that conserves hydrodynamics. Consequently, the conservative forces between DPD particles are softer than those used in molecular simulations. They also enable us to use a longer time step in these simulations.

Throughout the paper, we use reduced units for all variables, where the cutoff radius $r_c$ and the particle mass $m$ are taken to be unity. The interaction between particles is the sum of three pairwise additive contributions: a repulsive conservative force between particles, a dissipative force, and a stochastic or random force. The conservative force is
\[
\mathbf{f}^i_{ij} = \begin{cases} 
  a_{ij} \left(1 - \frac{r_{ij}}{r_c}\right) \hat{r}_{ij}, & (r_{ij} < r_c) \\
  0, & (r_{ij} \geq r_c),
\end{cases}
\]

(1)

where \(a_{ij}\) is the maximum repulsion parameter between particles \(i\) and \(j\), \(r_{ij}\) is the relative displacement of particles \(i\) and \(j\), and \(\hat{r}_{ij}\) is the corresponding unit vector. The dissipative force \(\mathbf{f}^D_{ij}\) and the random force \(\mathbf{f}^R_{ij}\) are given by

\[
\mathbf{f}^D_{ij} = -\gamma \omega^D (\hat{r}_{ij} \times \mathbf{v}_{ij}) \hat{r}_{ij},
\]

(2)

and

\[
\mathbf{f}^R_{ij} = \sigma \omega^R \theta_j \frac{1}{\sqrt{\delta t}} \hat{r}_{ij},
\]

(3)

where \(\gamma\) is a constant, \(\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j\) is the relative velocity, \(\sigma\) is the amplitude of the noise, \(\theta_j\) is a random Gaussian number with zero mean and unit variance, and \(\delta t\) is the time step expressed in the natural unit of time \((mr_c^2/k_BT)^{1/2}\), where \(k_B\) and \(T\) are the Boltzmann constant and temperature, respectively. The terms \(\omega^D(r_{ij})\) and \(\omega^R(r_{ij})\) are dimensionless weighting functions. Español and Warren\(^{29,30}\) have shown that the system will sample the canonical ensemble and obey the fluctuation-dissipation theorem if the following conditions are satisfied:

\[
\gamma = \frac{\sigma^2}{2k_BT} \quad \text{and} \quad \omega^D(r_{ij}) = (\omega^R(r_{ij}))^2.
\]

(4)

The weighting function \(\omega^R(r_{ij})\) is chosen to be

\[
\omega^R(r_{ij}) = \begin{cases} 
  (1 - r_{ij}/r_c) & (r_{ij} < r_c) \\
  0, & (r_{ij} \geq r_c)
\end{cases}
\]

(5)

The equations of motions are then integrated using a modified version of the velocity-Verlet algorithm and additional details of this simulation method can be found in our previous paper.\(^{21-24}\)

**B. The polymer brushes system**

In order to simulate polymer chains an harmonic spring force is used to connect some of the particles in linear chains.\(^{31,32}\)

\[
f^i_{ij} = k_c (r_{ij} - r_{eq}) \hat{r}_{ij},
\]

(6)

where \(k_c\) is the spring force constant and \(r_{eq}\) is the equilibrium bond length.

We have simulated a polymer brush system consisting of two planar solid surfaces composed of three layers of DPD particles tethered by spring to lattice points in a regular array. These two surfaces are positioned at the top and bottom of the simulation cell. The two surfaces are coated with polymer chains which are grafted by an harmonic force acting between the ends particles of the chains and the particles of the first layer of the wall.

The polymer chains are immersed in a solvent composed of free DPD particles. Our system is composed by 100 polymer chains of length of 20 particles grafted on each of the two walls (200 chains in the total). As each surface is composed by 324 wall particles, the grafting density is close to \(1/3\). The number of solvent particles is adjusted so that the overall reduced number density between the two nearest layers is set as \(\rho_o r_c^3 = 3.5\), which leads to a total of approximately 2500 solvent particles. This reduced density corresponds to a dense liquid following the work of Groot and Warren.\(^{30}\) The cell dimensions are \(L_x = 16.659\), \(L_y = 6.412\), and \(L_z = 18.016\) in reduced units. This corresponds to an inner separation \(h = 16.0\) between the two walls. The \(x\) dimension is chosen to be greater than the \(y\) dimension because this model system will be used later for simulations under shear along the \(x\) axis. A representation of the simulation geometry is shown in Fig. 1.

The repulsive force parameter \(a_{ij}\) is set at \(30k_BT/r_c\) for all interactions so that we model athermal solvent conditions, which corresponds to the \(\Theta\) solvent. The temperature is fixed to \(k_BT = 2.0\) (in reduced units) and the dissipative force was defined by \(\sigma_R = 100.0\), where \(\sigma_R = \sigma / (\delta t)^{1/2}\).

**C. Thermal and mechanical equilibrium**

The profile of the kinetic temperature tensor is evaluated along the \(z\) axis to ensure that the system is at thermal equilibrium,

\[
k_B T_{\alpha\beta}(z) = \frac{\langle \sum_{i=1}^{N} \mathbf{H}_n(z_i) m_i v_{i\alpha} v_{i\beta} \rangle}{\sum_{i=1}^{N} \mathbf{H}_n(z_i)},
\]

(7)

where \(\langle \ldots \rangle\) denotes a time average, \(m_i\) is the mass of particle \(i\) (the reduced mass is taken as unity), \(v_{i\alpha}\) is the \(\alpha\) component of the velocity of particle \(i\). \(\mathbf{H}_n(z_i)\) is a top-hat function
used to sort the profile into slabs, and defined in Eq. (8).

\[
H_s(z) = \begin{cases} 
1, & \text{if } z_n - \Delta z/2 < z < z_n + \Delta z/2 \\
0, & \text{otherwise}
\end{cases}
\]

The mechanical equilibrium can be checked by evaluating the pressor tensor profile along the z axis. We have used two definitions to evaluate the pressure tensor components: the Irving–Kirkwood (IK) definition and the method of planes (MoP).

Following the IK definition, the normal component of the pressure tensor can be expressed as

\[
P_{zz}(z) = \rho_s(z) \frac{k_B}{L} 
\left( \sum_{i<j} \frac{z_i f_{ij}}{|z_i|} \theta \left( \frac{z-z_i}{z_j} \right) \theta \left( \frac{z_j-z}{z_i} \right) \right),
\]

where \( \rho_s(z) \) is the density profile along the z direction, \( \theta(x) \) is the unit step function which is equal to 1 when \( x > 0 \) and zero otherwise. The first term represents the kinetic part of the pressure tensor arising from the change in momentum due to particles crossing the boundaries of an elemental volume at \( z \) whereas the second term refers to the configurational part, related to the intermolecular interactions between the particles within the elemental volume and the rest of the particles. The pairwise force \( f_{ij} \) between \( i \) and \( j \) represents the sum of \( F_{ij}^R \) and \( F_{ij}^T \). As there is no unique way to evaluate the configurational part, we also used the MoP definition \([\text{Eqs. } (10) \text{ and } (11)]\) which makes use of planes instead of slabs to calculate the contribution of each force between two particles \( i \) and \( j \).

\[
P^\text{MoP,kin}_{zz}(z) = \frac{1}{L_x L_y} \sum_{i=1}^N \sum_{j>i} m_i v_{i,z} \cdot \text{sgn}(v_{i,z}) \frac{\partial f_{ij}}{\partial z}
\]

\[
P^\text{MoP,com}_{zz}(z) = \frac{1}{L_x L_y} \sum_{i=1}^N \sum_{j>i} f_{ij} \left[ \theta(z_i - z) \cdot \theta(z - z_j) - \theta(z_j - z) \cdot \theta(z - z_i) \right] .
\]

Although the method of planes is considered to be a more rigorous way of calculating the pressure tensor components, \( \text{IK} \) definition allows us to calculate all the components, in particular, \( P_{xx} \) and \( P_{yy} \), which are of great interest in accessing the interfacial properties: the two methods will then be implemented.

III. MODELING OF ENTANGLEMENTS

A. Spring-spring repulsion

Two models have been developed in the recent years to study entanglements. The Padding model detects entanglements at particular crossing points, after which the bonds are viewed as slippery elastic bonds. The elasticity slows down the relative speed of the bonds and prevents crossings. It is time consuming and may not be compatible with the simple bead spring force between two real particles due to the topological complexity of many entanglements along one bond. The method of Kumar and Larson is simpler because it considers only the repulsion between bonds, which are well defined in terms of distance and topology.

Consider two polymer bonds \( i \) and \( j \), represented by two segments \( R_i \) and \( R_j \) respectively (Fig. 2). The bond \( i \) is that joining particles \( i \) and \( i+1 \), and bond \( j \) is the one joining particles \( j \) and \( j+1 \). Thus, the general distance between the two segments is the modulus of the vector \( d_{ij} \).

\[
d_{ij} = P_i + t_i R_i - (P_j + t_j R_j),
\]

where \( P = (r_i + r_{i+1})/2 \) is the vector from origin to the center of spring \( i \), and \( R_i = r_{i+1} - r_i \). The \( t_i \) and \( t_j \) represent the position of vector \( d_{ij} \) on the segments. We can calculate the minimum of \( d_{ij} \) using the relationship

\[
\frac{\partial d_{ij}}{\partial t_i} = \frac{\partial d_{ij}}{\partial t_j} = 0,
\]

where \( d_{ij} = |d_{ij}| \) is the distance between the two bonds (there is no maximum). Solving these equations, we obtain the values for \( t_i \) and \( t_j \).

\[
t_i = \frac{(P_i - P_j) \cdot (R_i^2 R_j - R_j^2 R_i)}{R_{ij}^2 - R_i^2 R_j^2},
\]

\[
t_j = \frac{(P_j - P_i) \cdot (R_i^2 R_j - R_j^2 R_i)}{R_{ij}^2 - R_i^2 R_j^2}.
\]

where \( R_i = R_i R_j R_j \). As we require the minimum distance between the segments (not between the lines), the values of \( t_i \) and \( t_j \) must be set between \(-0.5\) and \( 0.5 \). If \( t \) is greater than 0.5 it is chosen to be equal to 0.5, if \( t \) is less than \(-0.5\) it is chosen to be equal to \(-0.5\).

Once the minimum distance \( d_{ij} \) is known, the entanglement force can then be calculated. We have chosen an expression

\[
f_{ij} = \begin{cases} 
1 - \frac{d_{ij}}{r_c^f}, & (d_{ij} < r_c^f) \\
0, & (d_{ij} \geq r_c^f)
\end{cases}
\]

where \( d_{ij} = d_{ij}/d_{ij} \) is the corresponding unit vector and \( r_c^f \) is the maximum force value and \( r_c^f \) represents the cutoff value.
for the entanglement interactions. We have chosen an expression which is close to that of the conservative force used in DPD. This is different from the classical repulsive part of a Lennard-Jones (LJ) expression in Brownian dynamics simulation.25 Although the steep repulsive LJ force prevents any bond crossings, it is not compatible with the time step used in DPD method. The disadvantage of the Eq. (16) is that we will still experience some bond crossings and we will discuss the consequences of these topology violations in the next section.

B. Topology violations

The use of a soft entanglement force allows the bonds to overlap so bond crossings are still possible. In addition, when a bond is crossed, it is repelled away in the forward direction, which is clearly unphysical. However, this problem cannot be avoided in DPD simulations. We need to obtain quantitative informations about the number of crossings which will help us to determine the degree of entanglement.

Kumar and Larson25 suggested a way of detecting the topology violations in polymer chains, i.e., the bond crossings. We create two triangles for the four points which define segment 1 at time t and time t + δt. We check if the second segment intersects either one of the two triangles. This method is more clearly explained in a recent paper by Holleran and Larson.26 The test for crossing is well explained in the angle method. Fortunately, we see that there is only a few undetermined cases, and classifying them as crossing or no crossing is unimportant. Figure 3(e) shows zooms in α ranging from 160° to 180°; these angle values correspond to almost all the bond crossings. Our method shows excellent agreement with the extended HL method, removing many false positive cases. The total number of each outcome for the [simulation of Fig. 3(d) is listed in Table I] simulation with no shear. An example of the same simulation with a shear rate applied to the system (see next section) has been added.

It appears that the angle method is a powerful and simple technique for the detection of bond crossing. As the vector d is already calculated to obtain the distance between the bonds, no additional computational time is needed. This method is then a good alternative to the extended HL method, which is much more time consuming, and can remove many of the undetermined cases.

IV. RESULTS AND DISCUSSIONS

A. Energy stability

We have calculated the total energy of the system as a function of time in order to check the energy stability of entangled system. These simulations are run in the canonical ensemble so we do not expect the energy to be precisely conserved. However, a divergence in the energy is the sign of an instability of the simulation. We have compared the behavior of two systems (one with and the other without entanglements) as a function of the time step, δt. Figure 4 shows the energy evolution for the following time steps: δt =0.005, 0.010, 0.015, 0.020, 0.025, 0.030, and 0.050. Each simulation was run for a total time of t=50.0. Figure 4 shows the behaviors of the system from the beginning of the simulation until t=5. The energy diverges for both systems at
Δt=0.05 but it is approximately constant for all the other time steps. However, a smaller time step of 0.01 is better for simulations with entanglements and this will be discussed in the next section. Interestingly, the random dissipative force is necessary to provide stability in the simulation with entanglement force. Without random force, the entanglement force pumps energy into the polymer bonds which causes instability.

B. DPD parameters

Now that we accurately account the topology violations and we can check the stability of the thermodynamic equilibrium in our systems, we can choose an appropriate set of parameters.

FIG. 3. (Color) Schematic examples of different cases for the bond crossing tests: (a) crossing: bond i goes through bond j; (b) no crossing: bond i pushes bond j; (c) undetermined: the crossing does not depend on the test but on the relative positions of the bonds. (d) Distribution of the α angle (°) between two bonds at time t and t+Δt for each type of events. The inset zooms on the number of events between 0 and 100. (e) Distribution of the α angle between 160° and 180°. We add for comparison the values of α (diamond) calculated from Eq. (17).

FIG. 4. (Color) Total energy as a function of time for two systems: without entanglements (lower series) and with entanglements (upper series, translated of 10.0 along the energy axis for clarity). The different time steps Δt used in simulation are given in the legend.

TABLE I. Number of the different events obtained from crossing tests during a total reduced simulation time of t=5000.0 using the extended HL method developed in this work. The last column corresponds to the number of crossings determined from the angle α calculated with Eq. (17).

<table>
<thead>
<tr>
<th>Simulation</th>
<th>No crossing</th>
<th>Crossing</th>
<th>Undetermined</th>
<th>Crossing (α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No shear</td>
<td>8.37 × 10⁶</td>
<td>59 777</td>
<td>3056</td>
<td>62 728</td>
</tr>
<tr>
<td>Shear</td>
<td>7.96 × 10⁶</td>
<td>88 402</td>
<td>5130</td>
<td>93 253</td>
</tr>
</tbody>
</table>
parameters \((a_{ij}^{ent} \text{ and } r_E)\) to inhibit bond crossings. We aim to come to a compromise between reducing the number of topology violations and keeping the entanglement contribution as small as possible. We have performed four sets of simulations using four values for entanglement cutoff radius \(r_E\): 0.20, 0.40, 0.60, and 0.80 with the cutoff radius used for the conservative force set to unity. Each of these sets contains 17 simulations using different values for maximum interaction parameter \(a_{ij}^{ent}\) ranging from 0.0 to 80.0.

Each simulation consists in an equilibration period of 100 000 steps, followed by an acquisition period of 300 000 steps, during which the number of topology violations \(V_T\) is calculated. Using a reference system without entanglement \((a_{ij}^{ent}=0)\), we have plotted in Figure 5 the evolution of the proportion of topology violation \(V_T/V_T^0\) normalized by \(V_T^0\) the number of topology violations in the reference system. As predicted, the bond crossings decrease as the entanglement cutoff value increases. The same observation applies when 

\[
\text{crossing reduction of more than 95% if using a value of } a_{ij}^{ent}=20.0 \text{ is necessary for the higher cutoff value; this reduction falls to more than 99.5% if using a value of } a_{ij}^{ent}=40.0. \text{ Nevertheless, we can usefully reduce the number of topology variations up to 0.5 % with a time step of 0.01.}
\]

\section*{C. Thermodynamics}

To demonstrate the mechanical equilibrium of this system, we have calculated the pressure and temperature profiles across the brushes. The pressure can be calculated using the Irving–Kirkwood approach. The configurational contribution of the entanglement interactions to the pressure can be calculated from the pairwise entanglement forces acting at the two points of minimum bond separation. We can also partition the entanglement forces onto the two closest particles using the lever rule and calculate the configurational pressure using the primitive form of the method of planes (MopPr),

\[
p_{\text{MopPr,conf}} = \frac{1}{2} \sum_{i=1}^{N} f_{\alpha i}^{\text{tot}} \text{sgn}(z_i - z),
\]

where \(f_{\alpha i}^{\text{tot}}\) is the \(\alpha\) component of the total force acting on particle \(i\) defined as

\[
f_{\alpha i}^{\text{tot}} = f_{\alpha i}^{\text{ent}} + \sum_{j \neq i} (f_{ij})_{\alpha},
\]

and \(f_{\alpha i}^{\text{ent}}\) is the force due to the bond repulsion contributions of the neighboring bonds on \(i\) and \(f_{ij}\) is the force defined in Eqs. (9) and (11). This relation does not require a pairwise decomposition of the force. As a result, the \(f_{\alpha i}^{\text{ent}}\) contribution can be straightforwardly used in Eq. (18). The kinetic part of the pressure tensor is calculated in the normal way from the velocities of the particles. The entanglement interaction makes no kinetic contribution since the mass at its point of application is zero.

We have compared these two methods in Fig. 6(a). In addition, we have shown the profile without consideration of the entanglement interactions. The entanglement parameters used in this simulation \((a_{ij}^{ent}=40.0 \text{ and } r_E=0.80)\) prevent bond crossings. First, we observe that the MopPr method and the 1K method give identical results for the configurational part of the pressure and that the entanglement contribution is

\begin{table}

<table>
<thead>
<tr>
<th>(NVE) ensemble</th>
<th>(\delta t)</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>39 394</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>39 532</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(NVT) ensemble</th>
<th>(\delta t)</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>37 969</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>45 354</td>
</tr>
</tbody>
</table>

The sets of simulations using higher values for \(r_E\) shown in Fig. 5 exhibit a very strong dependence with the number of topology violations depending on \(a_{ij}^{ent}\). In order to have a crossing reduction of more than 95%, a value of \(a_{ij}^{ent}=20.0\) is necessary for the higher cutoff value; this reduction falls to more than 99.5% if using a value of \(a_{ij}^{ent}=40.0.\) Nevertheless, we can usefully reduce the number of topology variations up to 0.5 % with a time step of 0.01.
significant and varies across the box. The kinetic contribution to this profile is also constant with \( z \) and the system is at a mechanical equilibrium.

Figure 6 shows the temperature calculated from the same simulation. The calculated temperature matches with the imposed temperature perfectly when \( R = 100.0 \).

**D. Effect of the entanglements on the layer thickness**

In this section we focus on the structure of the entangled polymer brushes. Figure 7(a) shows the density profiles for the solvent particles and for top and bottom brushes. We can see that the entangled brushes are stretched along the normal \( z \) direction, compared to the nonentangled system. This causes a larger crossing zone between the brushes in the middle of the simulation box. This can be quantified by the interpenetration parameter \( I \) between the brushes defined as

\[
I = \left. \frac{1}{L_z^2} \right| \int_{-L_z/2}^{L_z/2} \rho_1(z)dz \int_{-L_z/2}^{L_z/2} \rho_1(z)dz, \tag{20}
\]

where \( \rho_1(z) \) is the density profile of the bottom brush (the same relation can be written for the top brush, using obvious different integration limits). For the same system as studied in the previous section, we find the following values for interpenetration coefficient: \( I = 0.0162 \) for non-entangled brushes and \( I = 0.0218 \) for entangled brushes. The swelling of the brushes causes the solvent density to increase inside the brushes to avoid some chain-chain interactions: entangled brushes adopt a structure which is similar to brushes in a better solvent quality.

The brush height can also be calculated from these density profiles by

\[
h = \frac{\int_{-L_z/2}^{L_z/2} \rho_1(z)dz}{\int_{-L_z/2}^{L_z/2} \rho(z)dz}, \tag{21}
\]

which corresponds to the height of bottom brush like the previous relation. Values for this system are \( h = 3.87 \) and \( h = 3.96 \) for the nonentangled and the entangled system, respectively. In order to check the consistency of the entangled polymer brushes system, we compare the brush height as a function of the polymer grafting density with the theoretical prediction.41


\[ h \sim N \rho^{1/3}, \]

(22)

where \( N \) is the number of beads in the chain and \( \rho \) is the grafting density. This behavior has been checked by many authors, providing that the grafting density is greater than the critical value. We have simulated a larger system along the \( z \) axis to prevent any interpenetration between the brushes. For a wall separation \( h=22.0 \), the grafting density varies from 0.03 to 0.57 by grafting onto each wall 5–180 polymer chains. The number of solvent particles is then changed from 7610 to 960, respectively. The total density in the simulation cell is kept constant. Figure 7(b) shows the rescaled brush height as a function of \( \rho \) for entangled and nonentangled brushes. For both systems the theoretical scaling law is respected for increasing grafting density (dashed lines). Thus, the entanglement forces cause the brush thickness to increase but do not modify the scaling behavior of the polymer brushes.

### E. Effect of the entanglements on the friction

It is possible to study friction between the two brushes by shearing the fluid in the \( x \) direction. To apply the shear, we move the surface particles of the top wall in a direction and the bottom wall in the opposite direction. The imposed displacement of the wall particles is given by

\[ \delta x = \pm \frac{\gamma \Delta L}{2} \delta t, \]

(23)

where \( \gamma \) is the applied shear rate and is expressed in units of \((k_B T/m \rho)^{1/2}\). Two systems have been simulated using different values for the separation between the walls: \( h=16.0 \) and \( h=14.0 \). The number of solvent particles is adjusted to 2500 and 1700 respectively, in order to keep the total density constant \((\rho \sigma_r^3=3.5)\).

We have calculated the friction coefficient profile from the IK pressure tensor components following the macroscopic definition which considers the ratio of the tangential and normal pressures

\[ \epsilon(z) = -\frac{P_{x z}(z)}{P_{x x}(z)}. \]

(24)

For both of the wall separations, we have simulated polymer brushes under a shear rate of \( \dot{\gamma}_0 = 0.10 \) in reduced units. Different simulations were performed using increasing values of the entanglement repulsion parameter \( a_{ij}^{em} \) from 0.0 to 80.0 (same values as in Sec. III B). Figure 8(a) shows the friction coefficient as a function of the number of topology violations, \( V_T \). This plot shows two regimes: at high values of \( V_T \) corresponding to low values of \( a_{ij}^{em} \), the friction coefficient increases steadily as the number of bond crossings decreases; at low \( V_T \) the friction continues to increase sharply even when bond crossing are almost totally excluded.

As already discussed, the swelling of the brushes due to the repulsive interactions between the chains causes an increase in the brush height which, in turn, increases the interpenetration coefficient. This additional overlap or interpenetration is a significant factor in the steady increase of the friction, i.e., as \( V_T/10^3 \) decreases from 1400 to approximately 50. However, this is not the only factor which influences the increase of the friction: we have compared the friction coefficient values for a simulation without entanglement forces but with a better solvent quality \((a_{pol-sol}=57)\) so that the brush height is the same in the two simulations. The spring repulsion parameter is set to \( a_{ij}^{em}=40.0 \), which was retained as a good value from previous discussions. We observe in both systems an increase in the friction coefficient due to the spring repulsion contribution: the increase in \( \epsilon \) is 15% for a wall separation \( h=16 \), and more than 20% for \( h=14 \). Because the relative fluctuation of the friction coefficient \( \epsilon \) does not exceed 2%, the increase in the friction coefficient is mainly caused by the entanglement forces.

As we continue to increase \( a_{ij}^{em} \) in the low crossing region, the additional repulsive force does not change the structure of the layer or decrease the number of topological violations. The friction coefficient continues to rise abruptly due to the increasing repulsion between the moving bonds.

To demonstrate this we have plotted the correlation between the friction and the interpenetration coefficient \( I \) in Fig. 8(b). The two sets of simulations show \( I \) levels off at high entanglement forces, (added dashed lines) and the height of the layer stops changing. For both wall separations considered this change in behavior corresponds to a value of
mesoscopic simulation of entanglements} of ≈40. This results confirms that the entanglement parameters suggested and used in this paper are appropriate for removing bond crossings and cause changes in the friction due to changes in the brush structure.

V. CONCLUSIONS

We have implemented the Kumar and Larson model for entanglement in a polymer brushes system modeled by means of dissipative particle dynamics. After choosing an expression for the entanglement force similar to the soft DPD conservative force, we have developed a way to get a quantitative information about the efficiency of this model by detecting and counting the bond crossings considering the topology violation between each pair of polymer segment. Using the method of planes for the pressure tensor calculation in its primitive form, we have shown that the entangled polymer brushes under shear shows that the entanglement force induces a swelling of the polymer layer, leading to a larger interpenetration zone in the brush. The entanglement force can be found to reduce the number of polymer segment contacts, which means that the entanglement force reduces the number of elasticity violation between each pair of polymer segment. This results confirms that the entanglement parameters are appropriate for checking the efficiency of the entanglement model. It appears that the entanglement force must be not be too short-range force since the random force used in dissipative particle dynamics could then overcome the bond repulsion. We have then shown that an appropriate set of parameters defining the entanglement force can be found to reduce the number of bond crossings by more than 99%. These parameters have been successfully applied to polymer brushes. The density profile for each brush shows that the entanglement forces induce a swelling of the brushes, leading to a larger interpenetration zone in the middle of the simulation box. The height of entangled polymer brushes follows the theoretical scaling law. The study of polymer brushes under shear shows that the entanglement parameters prevent more than 97% of the topology violation even for more compressed systems. It appears that the increase of the entanglement force, beyond $a_{ij}^{ent} = 40$ does not significantly change the layer thickness or the number of topological violations but may cause the friction coefficient to not increase physically.

We plan to apply this model to simulate the compression of brushes of grafted and adsorbed polymers, as a function of the entanglement of the polymer chains.

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