

Polymer brushes for friction control: Contributions of molecular simulations F

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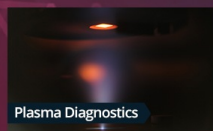
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ABSTRACT

When polymer chains are grafted to solid surfaces at sufficiently high density, they form brushes that can modify the surface properties. In particular, polymer brushes are increasingly being used to reduce friction in water-lubricated systems close to the very low levels found in natural systems, such as synovial joints. New types of polymer brush are continually being developed to improve with lower friction and adhesion, as well as higher load-bearing capacities. To complement experimental studies, molecular simulations are increasingly being used to help to understand how polymer brushes reduce friction. In this paper, we review how molecular simulations of polymer brush friction have progressed from very simple coarse-grained models toward more detailed models that can capture the effects of brush topology and chemistry as well as electrostatic interactions for polyelectrolyte brushes. We pay particular attention to studies that have attempted to match experimental friction data of polymer brush bilayers to results obtained using molecular simulations. We also critically look at the remaining challenges and key limitations to overcome and propose future modifications that could potentially improve agreement with experimental studies, thus enabling molecular simulations to be used predictively to modify the brush structure for optimal friction reduction.

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I. INTRODUCTION

Polymer chains that are end-grafted onto a substrate at sufficiently high density such that they extend perpendicularly away from the substrate due to steric excluded volume repulsion are known as polymer brushes (PBs).^{1,2} The critical grafting density, σ_g^* , above which neighboring chains repel and extend upward, is given by $\sigma_g^* \approx 1/\pi R_g^2$, where R_g is the radius of gyration of an isolated free chain suspended in the solvent. The mushroom-to-brush transition (MBT) corresponds to $(L \approx 2R_g)$, where L is the distance between the grafting points.^{3,4} The grafted chains could be neutral polymers, polyelectrolytes (PEs)^{5,6} or polyelectrolytes (PZs),^{7–11} which can be synthesized through both “grafting from”^{12–24} and “grafting to”^{25–30} approaches.

PBs have garnered a lot of attention for their ability to modify surface properties for the purposes of colloidal stabilization,³¹

protein adsorption prevention,^{26,32–35} lubrication,^{32,36,37} and adhesion.^{38,39} More recently, smart brushes that are thermoresponsive,⁴⁰ pH-responsive,^{41,42} or sugar-responsive⁴³ have been developed for use as switchable friction contacts or biomolecular sensors.⁴³

In nature, PBs can be found on cell walls, in mussels, and on the articular cartilage lining the synovial joints of mammals.⁴⁴ The lubricity of synovial joints such as hips and knees remains superior to any man-made alternatives as they are able to maintain friction coefficients as low as ($\mu \approx 0.001$) at pressures up to ($P_n \approx 10$ MPa).⁴⁵ Despite their robustness, cartilage degradation leading to osteoarthritis (OA) remains to be a common problem faced by many adults, and this has provided inspiration for a large number of studies on the design of biomimetic PBs to replace degraded cartilage.⁴⁶ The synovial joint also provides physiologically relevant conditions in which to study polymer brush performance.⁴⁷

A simplified model of the synovial joint can be thought of as two opposing PBs that are immersed in a good solvent and compressed as they articulate. This system is often called a polymer brush bilayer (PBB) and is the most common geometry for studying PB lubrication. For this reason, PBBs will be the main focus of this review. However, PBs grafted on alternate geometries, such as on curved surfaces,⁴⁸ on nano tubes,⁴⁹ on colloidal particles,^{50,51} in nano-channels, and even on human hair⁵² have also been explored.

The main lubrication mechanism for neutral PBBs immersed in a good solvent is thought to arise from the combined effect of osmotic repulsive forces between the surfaces and entropic restriction of brush interpenetration, leading to a highly fluid layer at their interface where the slip plane lies.^{53–56} This allows the PBB to maintain low friction coefficients while sustaining substantial normal loads. However, this mechanism alone was found to be insufficient to describe the extremely high lubricity observed in synovial joints and charged brushes.

For such charged brushes, i.e., those composed of biological or biomimetic macromolecules and PE or PZ brushes, which are immersed in aqueous media, an additional mechanism was proposed, known as hydration lubrication.^{57,58} When this mechanism is active, lubrication arises from the presence of highly hydrated shells that form around the charged components of the chains via hydrogen bonds with polar water molecules.⁴⁵ On the one hand, these shells allow the grafted layers to retain their hydration even when strongly compressed increasing their load-bearing capacity, and on the other hand, allow rapid exchange, on the scale of nanoseconds, of water molecules within the layers leading to improved frictional dissipation and lubrication. Furthermore, since liquid water is denser than its solid phase, it retains its fluidity even when strongly compressed and confined to films of less than a few nanometers.⁴⁵

PBs have been rigorously studied from three main paradigms: experimentally,^{6,8–11,33,36,37,55,59–90} theoretically,^{47,91–97} and computationally.^{87,92,94–115} There have also been many reviews concentrating on various aspects of PBs from their synthesis and promising applications,^{24,116} such as friction control^{32,56,61,117,118} and biopassivity,³³ to theory and computational modelling.^{47,48,94,119,120}

Experimentally, the tribological performance of PBs has been studied against various control parameters such as grafting density,^{37,68,71,74,78,84,86,89,90,121} the degree of polymerization,^{8,10,37,65,70,73} or architecture of the grafted chains^{11,33,56,87} as well as for different solvents,^{6,9,55,64,66,72,75–77,80–83} which for charged brushes could also include different counterions or salt concentrations.^{9,83,122–124} The measurement of the interaction forces between PBs was originally performed using the surface forces apparatus (SFA),^{59,64,67–69,125} which is a microscale technique. Sliding contact tests are usually performed using nanoscale atomic force microscopy (AFM),^{8,9,55,65,67,70–73,78–82,84,85,87–89} macroscale pin-on-disk (PoD) tribometers^{37,63,74,76,80} or, for mixed sliding-rolling contact, the mini-traction machine (MTM).^{37,63,68,74,76} The chemical composition of the grafted layer can be determined using x-ray photoelectron spectroscopy (XPS).^{9,22,26,73} The brush height (h) is a function of all of the above control parameters and is an important quantity for verifying theoretical descriptions as well as comparing with computational results. The dry film thickness can be determined using variable

angle spectroscopic ellipsometry (VASE).^{80,85,89} Using a combination of optical waveguide lightmode spectroscopy (OWLS) and a quartz crystal microbalance with dissipation (QCM-D), which measure the adsorbed dry and wet mass, respectively, the areal solvation (mass of solvent per unit area) can be calculated as their difference.^{55,71,90}

The first theoretical description of PBs was developed by Alexander³ and de Gennes,⁴ who assumed a step function for the monomer density profile $\phi(z)$ and that all of the chain ends are located at the equilibrium brush height h , which is then determined by taking each chain as an extended “cigar” correlation blobs of size $\xi \approx 1/\sqrt{\sigma_g}$, of the order of the distance between grafting points.¹²⁶ This was later improved upon by Milner *et al.* who used a self-consistent field theory (SCFT) in the strong stretching limit (SSL), allowing the chain ends to be freely distributed in the brush layer, to predict a parabolic monomer density profile that vanishes smoothly at h .¹²⁷ For PBBs, Witten *et al.* determined the free energy required for a chain to interpenetrate into the opposing brush.¹²⁸ This was used to determine scaling descriptions for the brush interpenetration length l .⁵⁴ The interpenetration length is a key quantity in determining the interaction forces between the PBBs during compression and shear.⁹⁶ The compression of a PBB can be measured by $d = D/2h$, where D is the distance between grafting planes and h is the equilibrium height of each uncompressed brush. Kreer *et al.* developed scaling descriptions for the strong ($d = D/2h < 0.5$) and intermediate ($0.2 < d < 0.6$) regimes,^{47,92,93} whereas Desai *et al.* investigated the weak ($0.5 < d < 1$) regime. A similar scaling approach was also used by Zhulina *et al.* and Desai *et al.* for the case of PE brushes.^{129,130}

Early computational efforts used molecular dynamics (MD)^{99,131–134} and Monte Carlo (MC)^{135,136} techniques to confirm the theoretical predictions for the parabolic density profile as well as the scaling of the brush height and the interpenetration length.¹³⁷ Most recent computational studies on the tribology of PBBs employ non-equilibrium MD (NEMD). All-atom shear simulations are rare^{113,138,217} due to the enormous computational load associated with performing such simulations on large polymer systems. Instead, studies often employ coarse-grained (CG) models to describe the grafted polymers and the surrounding solvent, which could either be taken into account implicitly, via the applied thermostat,^{64,95–97,99,101,103,105,106,108,109,111,139} through the inclusion of explicit solvent particles^{87,92–94,98,100,107,112,140–145} or by using a dissipative particle dynamics (DPD) approach.^{102,104,146–151} Note that it is quite common to apply a DPD-type thermostat to non-DPD, hard sphere models for the beads.^{92,107,112,142,143,145,152–154} A consequence of using CG models is that comparing to experimental data for real polymers becomes a major challenge, which will be discussed later; on the other hand, CG models provide the advantage of scalable results.¹⁰⁸

The various contributions of molecular simulations to improve understanding of PB lubrication have been the subject of several previous reviews. For example, Grest reviewed early molecular simulation studies studying PB friction in 1997¹⁰⁰ and 1999.¹¹⁹ Binder, Kreer and Milchev gave a more general overview of molecular simulations of the non-equilibrium response of PBs in 2011.⁹⁴ Most recently, Kreer provided a detailed overview of theoretical advances in PB lubrication, with emphasis on scaling theories developed by his group in 2016.⁴⁷

The purpose of this review is to provide a critical overview of the progress made by theoretical studies and simulations in the investigation of polymer brushes and their applicability in the context of friction control across different applications. A key feature of the review will be the comparison of results from models with experimental evidence and the identification of possible avenues to bridge the existing gap between them, so that MD simulations can be used more effectively to design solutions with better lubrication properties and with the potential to offer active control of friction in soft contacts.

II. COARSE-GRAINED MODELS OF POLYMER BRUSHES

Simulating large enough systems and times is crucial to avoid problems with finite-size effects and to provide enough statistical accuracy to the simulations, without which interpretation of their results becomes meaningless. In order to access the required length- and time-scales to study PB lubrication, coarse-graining becomes essential. Coarse-graining consists of representing the polymer as a chain of interacting beads, each of which represents a group of chemical monomers. This is justified when studying the mechanical

properties of such systems since the response is expected to be largely dependent on the collective macroscopic behavior of many neighbouring chains, rather than on local chemical structure. This section presents the most common coarse-grained models employed for studying polymer brushes under shear.

For all the models discussed, the components of the system are composed of spherical beads of mass m that interact with each other through a combination of various potentials (pair, bonded, angle, and Coulombic), which will be discussed in detail in this section. The main components of CG polymer models are the grafted chains, the substrate, and the solvent. The chains are either composed of $N + 1$ connected beads that are immobilized from one end on opposing faces of the simulation box, what we will refer to as the case of “smooth walls,” or they are of length N and are bound to explicit wall atoms arranged in a lattice. An advantage of having explicit wall atoms is the ability to thermostat the walls, thus maintaining a constant bulk substrate temperature. The solvent is either taken into account implicitly through the applied thermostat or simulated explicitly by adding single beads, dimers, or chains, also interacting via a different potential. Examples of such systems are shown in Fig. 1.

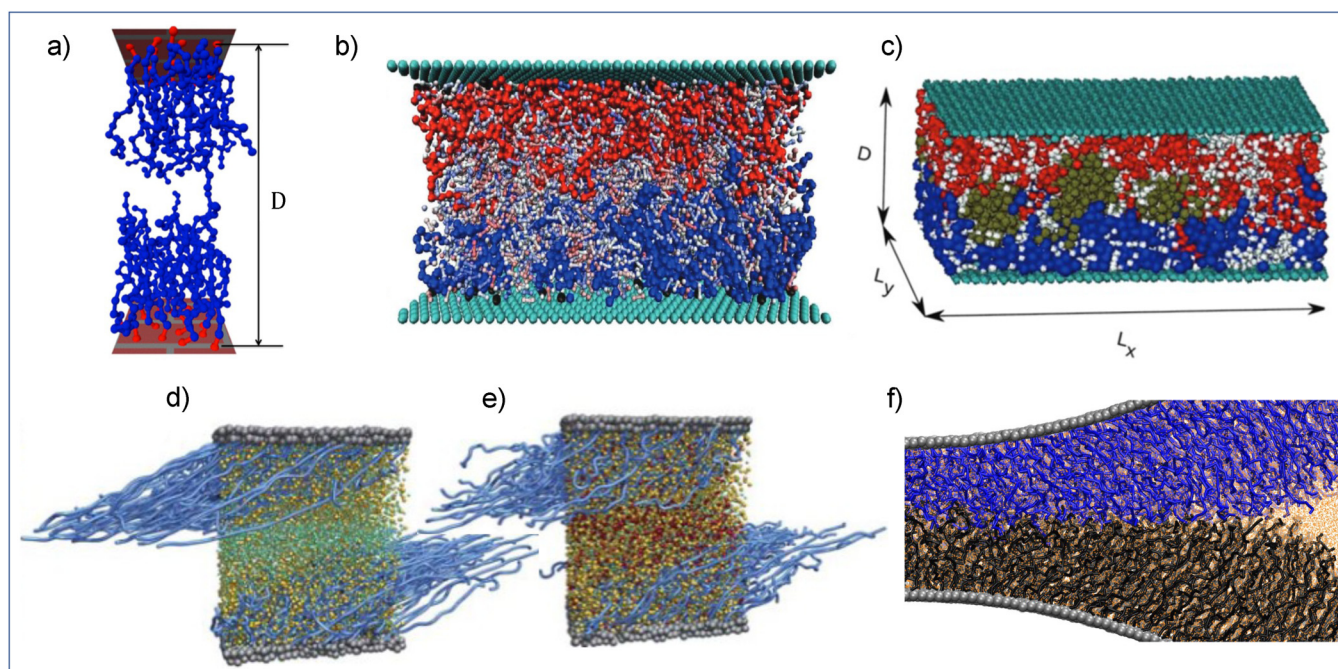


FIG. 1. Snapshots of simulated polymer brush bilayers of varying complexities compiled from the literature. (a) Uncompressed bilayer with an implicit solvent treatment at rest.¹⁰⁸ (b) Intermediately compressed bilayer with grafted chain beads (red/blue), explicit solvent dimers (white) and explicit wall beads (cyan).⁹² (c) Same as previous but with added macromolecular inclusion (green).¹⁹⁷ (d) Polyelectrolyte brush bilayers with negatively charged chains (blue), positively charged counterions (yellow), explicit solvent (green), and wall (gray) beads.¹⁴⁸ (e) Same as previous but with added negatively charged salt ions (red).¹⁴⁸ (f) Simulated bilayers composed of chains (blue/black) grafted onto curved wall atoms (gray) with explicit solvent particles (orange), giving the geometry of two opposing cylinders, used to study the dynamics of nonconformal contact.¹⁴³ Adapted with permissions from Singh *et al.*, *Langmuir* **31**, 4798 (2015). Copyright 2015, American Chemical Society (Ref. 108); Galuschko *et al.*, *Langmuir* **26**, 6418 (2010). Copyright 2010, American Chemical Society (Ref. 92); Spirin *et al.*, *Macromolecules* **44**, 9399 (2011). Copyright 2011, American Chemical Society (Ref. 197); Goujon *et al.*, *Soft Matter* **8**, 4635 (2012). Copyright 2012, Royal Society of Chemistry (Ref. 148); and de Beer and Muser, *Macromolecules* **47**, 7666 (2014). Copyright 2014, the authors (Ref. 143).

A. Early simulations of PBs under shear

In 1991, pioneering SFA experiments by Klein *et al.*⁵⁹ showed that PBBs could reduce the kinetic friction coefficient by several orders of magnitude compared to bare or oil-lubricated surfaces. The experiments also indicated an increase in normal pressure during the oscillatory shear motion of PBBs. Analytical solutions suggested that this could be caused by a swelling of brushes under shear.¹⁵⁵ These motivated a number of molecular simulation studies, as summarized below.

The first molecular-level simulations of PBs under shear were performed in 1993 by Lai and Binder.¹³⁵ They used a lattice bond fluctuation MC method, where the flow was modeled using an enhanced jump rate in the flow direction.¹³⁵ They solved the Brinkman equation¹⁵⁶ to determine the flow and density profile in the brush self-consistently. They found that the brush thickness decreased slightly for the largest shear rates. Lai and Lai¹⁵⁷ modified the algorithm of Lai and Binder to have the blob size input into the Brinkman equation that depend on shear force and not the volume fraction of monomers. They presented scalings for the stretch of the chain in the flow direction and reported that no significant change in the brush height was observed. A later MC simulation of PBs by Miao, Guo, and Zuckerman¹⁵⁸ used an off-lattice algorithm and a self-consistent calculation of the flow profile. They studied the tilting and stretching of the chains and found favorable agreement with the theory of Rabin and Alexander.⁵³ The brush thickness and bead density profile were unaffected by the shear flow over the range of shear rates they simulated.⁵³

Brownian dynamics (BD) simulations by Doyle *et al.*^{159,160} with hydrodynamics based on the Brinkman equation¹⁵⁶ suggested that PBs swell at certain frequencies of oscillatory shear. However, this result was criticized in a review article by Grest,¹¹⁹ who highlighted that the shear amplitude was comparable to the distance between the grafting sites, and thus the swelling may have originated from a monomeric resonance instead of being a characteristic property of polymer brushes.⁴⁷ Later MC simulations under oscillatory shear reproduced the abrupt increase in the normal stress at a critical value of the shear rate,¹⁶¹ in agreement with SFA experiments;⁵⁹ however, no brush swelling was observed.¹⁶¹

The first NEMD simulations of sheared PBBs were performed by Peters and Tildesley in 1995,¹⁴⁰ which included explicit solvent molecules. For context, the first NEMD simulations of atomic fluids were reported in 1975.¹⁶² Peters and Tildesley studied the uncompressed brush system consisting of chains of length $N = 20$ at a high surface coverage of 33%. The radius of gyration perpendicular to the walls decreased with the increasing shear rate while the component parallel to the walls increased. Peters and Tildesley¹⁶³ extended their study of the same system in which some chains were allowed to detach from the wall to study the shear of the tethered chain with free polymers. Shear stresses were largest at intermediate converges, which was attributed to entanglements between brushes and free chains.

In 1996, Grest performed further NEMD simulations of PBBs with an implicit solvent.⁹⁹ They found that, at high shear rates, the brushes stretched in the flow direction and disentangle; however, no brush swelling was observed. The normal and shear forces were in qualitative agreement with SFA experiments.³⁶

B. Kremer–Grest bead-spring model

The simplest CG model used to describe polymer chains is the Kremer–Grest bead-spring model (KG-BS).¹⁶⁴ The model consists of a purely repulsive Lennard-Jones (LJ)¹⁶⁵ interaction acting between all beads and a finitely extensible non-linear elastic (FENE) potential acting between all bonded beads. The purely repulsive LJ potential is achieved by truncating at the minimum of the potential well and shifting to ensure continuous forces, commonly referred to as the Weeks–Chandler–Andersen (WCA) potential,¹⁶⁶ which takes the form,

$$U_{WCA}(r) = \begin{cases} 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 + 1/4], & r \leq 2^{1/6}\sigma, \\ 0, & r > 2^{1/6}\sigma, \end{cases} \quad (1)$$

where ϵ controls the depth of the attractive well, since the attractive part of the well is truncated, epsilon sets the “hardness” of the beads, and sigma σ corresponds to the radius of the beads. MD simulations are often performed in dimensionless LJ units, meaning that the bead mass m , ϵ , and σ are used to set the mass, energy, and length scales of the simulation, respectively ($m = \epsilon = \sigma = 1$). In this case, the results can be reported in dimensionless LJ units or converted to real units to compare to experiments through careful choice of LJ parameters.

The FENE potential acts between bonded beads along the chain and at the grafting point for the case of explicit wall atoms,

$$U_{FENE}(r) = \begin{cases} -\frac{1}{2}kr_o^2 \ln[1 - (r/r_o)^2], & r \leq r_o, \\ \infty, & r > r_o, \end{cases} \quad (2)$$

where k is the bond stiffness and r_o is the maximum bond length. Typically, $k = 30\epsilon/\sigma^2$ and $r_o = 1.5\sigma$. In combination with purely repulsive interactions, this results in a finitely extensible fully flexible chain of beads with excluded volume interactions and an equilibrium bond length of $b_o \approx 0.97\sigma$. The KG-BS model can be used alongside a Langevin thermostat to model polymer chains in an athermal solvent.

C. Langevin thermostat

A Langevin thermostat¹⁶⁷ is used to couple the beads to a thermal heat bath at constant temperature T , typically ($T = 0.6 - 1.7 \epsilon/k_B$) as well as a means to implicitly model the solvent particles. This involves introducing two fictitious forces to the equations of motion for each bead i of mass m_i at position $\mathbf{r}_i$, a viscous damping term proportional to their velocity $\mathbf{v}_i(r) = \frac{d\mathbf{r}_i}{dt}$, and a random “white noise” $\mathbf{W}_i(t)$ force arising from collision with surrounding solvent particles,

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla U_i - m_i \gamma \frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i(t), \quad (3)$$

where $-\nabla_i U$ is the sum of all conservative forces acting on the bead i due to interactions with the surrounding beads, and these could be due to bonded, pairwise, Coulombic, or dihedral (angle) interactions. γ is the solvent-induced damping constant controlling the relaxation rate with typical values ($\gamma = 0.5 - 1 \tau^{-1} = \sqrt{\frac{\epsilon}{\sigma^2 m}}$). Care must be taken with higher values to avoid overdamping the

particles, thus influencing the dynamics. In the overdamped limit, no average acceleration takes place and Langevin dynamics reduces to Brownian dynamics (BD), where the inertia term is neglected in Eq. (3). The fluctuation-dissipation theorem provides a relationship between viscous damping and random collision terms,

$$\langle \mathbf{W}_i(t) \mathbf{W}_j(t') \rangle = 6m_i \gamma k_B T \delta_{ij} \delta(t - t'). \quad (4)$$

Applying a Langevin thermostat to simulated polymeric systems under shear incorrectly models the dynamics.¹⁶⁸ This is because it models a solvent that is at rest and uniformly distributed, which is not the case for sheared bilayers and would serve to overestimate the shear flow into the brush.⁹⁷ A common fix is to switch off the thermostat in the shear direction. However, Kreer *et al.* found that doing this altered the rheology of their simulated systems only slightly from those with the thermostat applied in all directions.⁹⁷

D. Explicit solvent models

Since opposing polymer brushes allow for a thin fluid film to develop, which significantly contributes to lubrication, it may be insufficient to take the solvent into account only implicitly. Furthermore, Langevin thermostats do not conserve momentum and, thus, cannot capture hydrodynamic effects. For this reason, more complex models have been developed to allow for more control when including explicit solvent particles. These solvent particles are usually composed of the same type of beads as the chains; however, it is more common to use dimers than single beads, in order to reduce the layering effect of solvent particles near the substrate.^{92,100,141} It is important to note that including the solvent explicitly is extremely computationally intensive, which often motivates the use of implicit solvents when hydrodynamic effects may not be the main focus.

Using the KG-BS model as a reference, a more versatile form often used for the pair interaction is the truncated and shifted LJ potential,

$$U_{LJ}(r) = \begin{cases} 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6 - (\sigma/r_c)^{12} + (\sigma/r_c)^6], & r \leq r_c, \\ 0, & r > r_c. \end{cases} \quad (5)$$

If $r_c = 2^{1/6}\sigma$, then $U_{LJ} = U_{WCA}$ and the potential is purely repulsive. An attractive well can be introduced by varying r_c . A common setup is to use $r_c = 2^{1/6}\sigma$ for simulating polymers in a good (athermal) solvent, where the polymer-polymer effective interaction is purely repulsive, and $r_c = 2.5\sigma$ for simulating polymers in a bad solvent, where they attract each other. Note in this regard that the form of the bead-bead interaction does not describe the direct, pair interaction between monomers but rather the indirect, effective one mediated by the solvent. In fact, it should be better considered as a free-energy, mediated over the solvent degrees of freedom. In any case, this more general form for the effective bead-bead interaction allows control over the solvent quality and has also been used to model polymer adsorption.⁹⁶

An alternative to the KG-BS scheme was introduced by Dimitrov *et al.* that uses the same FENE potential to connect the

chains but a cosine-modified LJ potential for bead interactions. The potential consists of the hard repulsive barrier of the WCA potential along with a tuneable attractive well,^{94,110,153}

$$U_{LJ,cos}(r) = \begin{cases} 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6 + 1/4] - \epsilon_{int}, & r \leq 2^{1/6}\sigma, \\ \frac{1}{2}\epsilon_{int} \{\cos[A(r/\sigma)^2 + B] - 1\}, & 2^{1/6}\sigma \leq r \leq 1.5\sigma, \\ 0, & r > 1.5\sigma, \end{cases} \quad (6)$$

where A and B are constants that are determined by solving $2^{1/3}A + B = \pi$ and $2.25A + B = 2\pi$ simultaneously yielding $A = 3.173\,072\,868$ and $B = -0.856\,228\,645\,4$. When combined with a FENE potential, the equilibrium bond length is $b_o = 0.97\sigma$, which is the same as the KG-BS model.

The interaction energy ϵ_{int} controls the pair interaction by introducing an attractive well that allows varying the interaction between purely repulsive ($\epsilon_{int} = 0$) and increasingly attractive ($\epsilon_{int} > 0$). Setting $\epsilon_{int} < 0$, merely adds a softer repulsion in the range $2^{1/6}\sigma \leq r \leq 1.5\sigma$ and is, thus, not very useful. Compared to the truncated LJ of Eq. (5), this latter form allows a complete decoupling of the repulsive and attractive parts, allowing for more flexibility.

For a system with explicit solvent beads (s) alongside the polymer beads (p), three separate pair interactions become governed by Eq. (6); as in ($\epsilon_{int} \rightarrow \epsilon_{pp}, \epsilon_{ss}, \epsilon_{ps}$), the solvent quality can be controlled by varying ϵ_{pp} and ϵ_{ps} . Usually, the solvent-solvent interaction is set to be purely repulsive ($\epsilon_{ss} = 0$), and this allows the varying of conditions from a good solvent ($\epsilon_{pp} = 0, \epsilon_{ps} > 0$) to a bad solvent ($\epsilon_{pp} > 0, \epsilon_{ps} = 0$). The interaction parameter $\chi = \epsilon_{ps} - (\epsilon_{pp} + \epsilon_{ss})/2$ is proportional to the Flory-Huggins parameter $\chi(T) = (\epsilon_{ps} - (\epsilon_{pp} + \epsilon_{ss})/2) \frac{z}{k_B T}$, where z is the coordination number and T is the temperature.

E. DPD thermostat

The DPD thermostat^{169–171} also introduces a dissipative viscous damping force and a random collision force; however, in contrast to the Langevin thermostat, the DPD thermostat conserves the total momentum of the system and, thus, accounts for hydrodynamic interactions. This is achieved by applying the dissipative $\mathbf{F}_i^D$ and random forces $\mathbf{F}_i^R$ in a pairwise manner, such that the total force acting on each pair is zero.¹⁵² Similar to Eq. (3), the DPD thermostat equation of motion becomes

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i U + \mathbf{F}_i^D + \mathbf{F}_i^R, \quad (7)$$

with

$$\mathbf{F}_i^D = -\Gamma \sum_{j(i \neq j)} \omega^D(r_{ij}) (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij}, \quad (8)$$

$$\mathbf{F}_i^R = \lambda \sum_{j(i \neq j)} \omega^R(r_{ij}) \theta_{ij} \hat{\mathbf{r}}_{ij}, \quad (9)$$

where $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$ and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. θ_{ij} is a random gaussian variable with zero mean and unit variance, Γ is the friction

coefficient, and λ is the noise strength that together obey the relation $\lambda^2 = 2k_B T \Gamma$. ω^D and ω^R are the dissipative and random weight functions respectively, which by the fluctuation-dissipation theorem must satisfy

$$[\omega^R]^2 = \omega^D. \quad (10)$$

There is a freedom in choosing the form of weight functions. The most common choice for ensuring continuous forces is

$$\omega^D = \begin{cases} (1 - r/r_c)^2, & r < r_c, \\ 0, & r \geq r_c. \end{cases} \quad (11)$$

The DPD thermostat is more computationally intensive than the Langevin thermostat, since the former requires the calculation of forces between pairs of particles rather than only once per particle in the latter.⁴⁷ In a detailed study, Pastorino *et al.* use NEMD simulations to compare the behavior of the two thermostats and find that the Langevin thermostat affects the dynamics more strongly than the DPD thermostat for similar values friction coefficients $\Gamma \approx \gamma$ from Eqs. (3)–(8). Additionally, the authors find that a Langevin thermostat that is switched off in the shear direction behaves similarly to a DPD thermostat for systems that are not strongly driven out of equilibrium.¹⁶⁸

That being said, switching the Langevin thermostat off in the shear direction to recover Galilean invariance is a questionable fix since it still assumes a certain symmetry in the thermostated directions.¹⁷² Furthermore, the basic Langevin thermostat does not account for the underlying streaming velocity that may be a feature of many non-equilibrium systems.¹⁷³ On the other hand, the DPD thermostat both conserves the momentum and preserves the Galilean invariance of the system by design without the need for an ad hoc fix and is found to outperform the “fixed” Langevin thermostat when Yong *et al.* compared them for the same time step.¹⁷² Hence, the DPD thermostat is a more suitable choice when simulating non-equilibrium systems. However, stability issues may limit the shear rates accessible using a DPD thermostat more so than they limit a Langevin thermostat.¹⁷³

F. Full DPD scheme

Although many studies use the DPD thermostat alongside a modified KG model, the full DPD scheme replaces the FENE potential with a simple harmonic spring, and the bonding force takes the following form:

$$\mathbf{F}_{ij}^B = k(|\mathbf{r}_{ij} - \mathbf{r}_o|)\hat{\mathbf{r}}_{ij}, \quad (12)$$

where k is the spring constant and $\mathbf{r}_o$ is the equilibrium spring length. Along with this, a soft-repulsive pair interaction $\mathbf{F}_{ij}^C$ replaces the usual hard bead LJ interactions of previous models,

$$\mathbf{F}_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij}/r_c)\hat{\mathbf{r}}, & r_{ij} < r_c, \\ 0, & r_{ij} \geq r_c, \end{cases} \quad (13)$$

where a_{ij} is the repulsive force parameter. Together with the DPD thermostat [Eq. (7)], the full DPD equation of motion is then given

by

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j(i \neq j)} (\mathbf{F}_{ij}^B + \mathbf{F}_{ij}^C) + \mathbf{F}_i^D + \mathbf{F}_i^R. \quad (14)$$

Similar to models using (harder) LJ potentials, the solvent quality can be controlled by varying the relative interactions between the polymer p and solvent s beads. It is quantified by the interaction parameter Δa_{ps} ,

$$\Delta a_{ps} = a_{ps} - 1/2(a_{ss} + a_{pp}). \quad (15)$$

Δa_{ps} is related to the dimensionless Flory–Huggins parameter through $\chi = z\Delta a_{ps}/k_B T$, where z represents the coordination number in the Flory–Huggins lattice model. Note that positive values of the interaction parameter correspond ($\Delta a_{ps} > 0$) to bad solvent and negative ($\Delta a_{ps} < 0$) to good solvent conditions, which is opposite to the behavior of the cosine modified LJ attractive interactions described above in Sec. II C.

G. Other thermostating strategies

Although the vast majority of NEMD studies presented in this review use either a Langevin thermostat that is switched off in the shear direction or a DPD thermostat as detailed above, the debate over their use as well as the development of alternative thermostating schemes continues.^{172,173} Notably, Leimkuhler and Shang have proposed a pairwise adaptive Langevin (PADL) thermostat,¹⁷⁴ which automatically corrects for thermodynamic averages using a negative feedback loop while mimicking the dynamical properties of a DPD thermostat. Like the DPD thermostat, the PADL thermostat conserves both momentum and Galilean invariance making them both profile-unbiased thermostats (PUT); on top of this, the PADL is found to outperform the DPD thermostat for a wide range of parameters while maintaining the low susceptibility to stability issues of the Langevin thermostat, making it a prime candidate for future NEMD studies.¹⁷³

All three (PADL, Langevin, DPD) thermostats sample the canonical (NVT) ensemble by dissipating energy on the localized scale, particles that are too hot are cooled down and vice versa, and hence, they are classified as local thermostats. A major advantage of using such local thermostats when simulating confined nano-fluids via CG models is the ability to tune the fluid viscosity, which may be useful for reproducing the dynamics of the desired system. This explains the popularity of local thermostats when compared to global thermostats, such as the Nosé–Hoover^{175,176} thermostat and velocity rescaling schemes, which are more commonly used for full-atom simulations.¹⁷² A PUT velocity-rescaling scheme commonly used to achieve Galilean invariance in NEMD simulations involves subtracting an averaged stream velocity from the velocity of each bead to obtain the bead’s thermal velocity, which is then rescaled to the required temperature before adding back the stream velocity.^{177,178} However, simple velocity rescaling algorithms sample noncanonical distributions of kinetic energies¹⁷⁹ and have been shown to violate the equipartition theorem leading in extreme cases to the flying ice cube effect, where all of the kinetic energy is transformed into translational and rotational degrees of freedom of

the centre of mass of the system.¹⁸⁰ Braun *et al.* have shown that such effects can be avoided if the thermal velocities are instead rescaled to a canonical distribution, for example, using a CSVR thermostat,¹⁸¹ which is the recommended approach moving forward for velocity-rescaling algorithms.¹⁷⁹

Despite being common practice in NEMD simulations, seeking to maintain the entire mass of the fluid at a constant temperature using any of the abovementioned thermostats is rather questionable, especially at high shear rates where viscous heating effects are expected. Khare *et al.* argue that imposing such isothermal conditions would imply that the confined fluid has infinite thermal conductivity and will, thus, exhibit unphysical dynamics; instead, they suggest that applying the thermostat only on the wall beads, allowing a heat flux across the fluid, is preferred as it would more closely resemble experimental conditions under shear where usually only the confining walls are maintained at a constant temperature.¹⁸⁰ Yong *et al.* have investigated the effect of applying different (Langevin/DPD/NHC) thermostats only on the walls compared to applying them only on the fluid or applying them on both the fluid and walls, as is most commonly adopted in the simulations presented in this review. The behavior of the fluid is found to be very similar at low shear rates regardless of which components are thermostated, while at higher shear rates, the viscous heating is indeed significantly reduced for systems where the thermostat is applied on both the fluid and wall beads.¹⁷² NEMD simulations of polymer brushes with only the wall atoms thermostated in the direction perpendicular to sliding and compression have been performed by de Beer *et al.*^{143–145,182}

H. Semiflexible chains

In the models presented so far, the chains are flexible, only considering excluded volume interactions. The persistence length L_p of a flexible chain is of the order of half the Kuhn monomer size b (i.e., $L_p = b/2$). When the length of the polymer simulated is smaller or comparable to the persistence length, it is necessary to add some form of bending stiffness to account for correlations between monomers along the chain with distances $d < L_p$. The introduction of this additional interaction allows to better match a coarse-grained model to stiff polymers and to address the effect of chain stiffness on the behavior of the polymer brush. Adding stiffness can be achieved by introducing some form of bending potential as a function of the angle formed by two consecutive bonds θ . The three most common and simplest forms, in order of decreasing stiffness (for the same bending stiffness constant), are the harmonic angle potential U_H , the cosine angle potential U_C , and the cosine squared angle potential U_{CS} . With respective forms,

$$U_H(\theta) = K(\theta - \theta_o)^2, \quad (16)$$

$$U_C(\theta) = K[1 - \cos(\theta - \theta_o)], \quad (17)$$

$$U_{CS}(\theta) = K[\cos(\theta) - \cos(\theta_o)]^2, \quad (18)$$

where θ_o is the equilibrium bond angle and K is the bending stiffness constant.

I. Charged brushes

Many of the polymer brushes studied experimentally consist of chains that are charged as opposed to neutral. In general, they could consist of polyelectrolyte or polyzwitterionic chains. This is modelled in a coarse-grained way by introducing charge valences z_i to selected beads, which could represent charged monomers, counterions, or salt ions.

Beads with charge valences z_i and z_j that are separated by $r_{ij} = |r_j - r_i|$ then interact with each other via a long-range coulomb potential of the form,

$$U_{Coul}(r_{ij}) = k_B T \frac{l_B z_i z_j}{r_{ij}}, \quad (19)$$

where $l_B = e^2 / \epsilon_d k_B T$ is the Bjerrum length, which is defined as the length scale at which the Coulombic interaction between two elementary charges e in a medium with a dielectric constant ϵ_d is of the order of thermal energy $k_B T$. If the Bjerrum length is larger than the separation of charged beads along the chain, it is argued that counterion condensation may occur.^{47,142} The persistence length of charged chains depends on the surrounding counterion concentration due to the effect of electrostatic screening.¹⁴¹

Coulombic interactions decay at longer distances compared to LJ interactions, so truncating them with a finite is not recommended, even for CG models.^{183,184} This means that calculating the long-range charge-charge or dipole-dipole interactions in an MD simulation is a more complex and computationally expensive process than for the pairwise, bonded, or angle interactions. This is mostly because typical cost-saving tricks, such as the use of neighbors lists, cannot be used. In fact, calculating electrostatic interactions requires, in principle, taking into account an infinitely large number of neighbors.

Techniques like Ewald summation and its extension the particle-particle particle-mesh (PPPM) solver are able to solve this problem by assuming periodic boundary conditions in all three Cartesian directions and then considering separately the interactions of each charged bead with all other charged beads within the simulation box and all charged beads in the more distant periodic images.¹⁷⁸ The PPPM technique, for example, divides the potential into a short-range part, to be solved in real space, and a long-range part, to be solved in k-space. This is achieved by mapping the charged beads to a 3d mesh and then employing fast Fourier transforms (FFTs) to solve for the electric field at the mesh points, which are then interpolated back to the beads. As a result of this, the PPPM method is significantly less computationally costly ($\sim N \log N$) than the Ewald sum solver ($\sim N^3/2$).¹⁸⁵

Polymer brush systems are not periodic in $3d$ but only in x - and y -directions (substrate plane) so applying any long-range solver will require some modification. This is most commonly solved by adding an empty volume around the bilayer in the z -direction (non-periodic direction), such that the total volume is tripled,^{141,178} and then treating the system as if it were periodic in all directions while excluding dipole interactions across the boundaries, effectively removing all long-range interactions between the images along the z -direction. Alternatively, a correction term can

be added to the standard Ewald summation formula,¹⁸⁶ which has also been extended to non-neutral systems.¹⁸⁷

J. Transferable CG models

Transferable CG models, such as the MARTINI model, are becoming increasingly popular in the simulation of biomolecules¹⁸⁸ and materials.¹⁸⁹ The MARTINI model is based on a four-to-one mapping, i.e., on average four heavy atoms plus associated hydrogens are represented by a single bead. This mapping was chosen as a compromise between computational efficiency on the one hand and chemical representability on the other.¹⁸⁸ It can be used to represent a wide range of polymer types and topologies.¹⁸⁹ The MARTINI model has been used to model the structure of single poly(ethylene oxide) brushes in water¹⁹⁰ and polystyrene brushes in benzene.¹⁹¹ It has also been used to study the compression of poly(ethylene oxide) brush bilayers in water.¹⁹² The MARTINI model has recently been applied to study the friction between poly(ethylene oxide) bottle-brush bilayers in water.¹⁹³

III. NONEQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS OF POLYMER BRUSHES

In this section, we will first briefly describe a few general aspects in setting up and performing the nonequilibrium simulations of polymer brushes necessary to look at their lubrication properties. Later, we will proceed to give a broad overview of the key results of such simulations focusing on polymer brush friction. A recent review of NEMD simulations of a wide range of tribological systems can be found in Ref. 194.

A. Simulation setup

Friction crucially depends on the applied force normal to the shearing direction, in particular, because depending on the magnitude of a such compressive force the brush can be found in qualitatively different physical states. In other words, the presence of different regimes means that when observed over a large range, a non-linear relation between the applied compressive and shear forces can be expected. In order to map out such a relation, the bilayer must be studied under different compressions. There are generally two setups that have been explored. One is to apply a constant normal pressure on the wall atoms in which case the bilayer at equilibrium is in the NPT ensemble and the wall separation D will fluctuate upon shearing or, more commonly, fix the wall separation D in which case the bilayer is in the NVT ensemble at equilibrium and the normal pressure will fluctuate upon shearing.

The bilayer shearing is usually achieved by setting the relative shear velocity between the top and bottom wall atoms to a steady value in a Couette flow configuration, respectively, with v_x being the relative shear velocity of the bilayer being sheared in the x -direction.⁹² Alternatively, one could fix a shear force on the substrates in equal and opposite directions. In either case, it is essential to monitor the conjugate variables to ensure that the bilayer has reached steady-state shear before extracting any thermodynamic or force data. For a PB bilayer at constant wall separation D and

relative velocity v_x , the shear rate $\dot{\gamma}$ is simply

$$\dot{\gamma} = \frac{v_x}{D}. \quad (20)$$

Normal P_n and shear stress P_s can be obtained from the components of the virial stress tensor P_{zz} and P_{xz} , calculated at steady-state shear from molecular variables and bead interactions via the Irving–Kirkwood method.^{146,195} The stress tensor is usually calculated for the entire simulation box. However, in order for the calculated normal pressure to correspond to the average pressure of the confined fluid, it is recommended to exclude the explicit wall atoms when calculating the P_{zz} component.¹⁴¹

Alternatively, in the case of explicit wall atoms, the shear P_s and normal stresses P_n can be obtained directly from the sum of the time-averaged forces acting between a layer of atoms, of either wall, and all other particles divided by the area of the simulation box A , assuming symmetric brushes and periodic boundary conditions in x and y .¹⁰⁵ These should match those obtained from the pressure tensor calculation within statistical accuracy.^{92,104}

For a fixed wall separation D at steady-state relative shear velocity v_x , we can define the effective viscosity η of the bilayer via

$$\eta \equiv \frac{P_s}{\dot{\gamma}} = \frac{P_s D}{v_x} \quad (21)$$

and its effective friction coefficient μ via

$$\mu \equiv -\frac{P_s}{P_n}, \quad (22)$$

where P_s and P_n are the shear and normal stresses obtained via either method detailed about of the virial stress tensor. The friction coefficient μ can also be estimated from the slope of the shear P_s vs normal forces P_n at different separations and at the same velocity. These two methods do not always give the same results.¹¹⁰

The number density profiles of different components making up the system are easily extracted from simulations, which can give insight into their internal ordering as well as allow evaluation of the degree of interpenetration between the brushes during shear. The conformations of the chains can be monitored by calculating the average chain inclination $\langle \cos\theta \rangle$, the order parameter P_1 , or by using the brush-averaged radius of gyration of the chains R_g^2 along with its components in the shear $R_{g,x}^2$, transverse $R_{g,y}^2$, and normal $R_{g,z}^2$ directions given by

$$R_g^2 = \frac{1}{N} \left\langle \sum_i (\mathbf{r}_i - \mathbf{r}_{cm})^2 \right\rangle, \quad (23)$$

$$R_{g,\alpha}^2 = \frac{1}{N} \left\langle \sum_i (r_{i,\alpha} - r_{cm,\alpha})^2 \right\rangle, \quad (24)$$

where r_{cm} is the center of mass of the chain and $\alpha = x, y, z$.

B. Shear response of compressed bilayers

Pioneering MD simulations by Grest,⁹⁹ employing a purely repulsive WCA potential and an implicit Langevin solvent to model a bilayer immersed in a good solvent under shear, identified two shear rate-dependant regimes at moderate compression. At low shear rates, the grafted chains are largely unperturbed even when the bilayer is strongly compressed. This Newtonian-like regime is characterized by a linear dependence of the shear stress on the strain rate ($P_s \sim \dot{\gamma}$). At higher shear rates, shear thinning is observed. The chains respond and tilt along the shear direction, thereby reducing the brush thickness as well as the amount of interpenetration and entanglement between the opposing brushes, resulting in a sublinear increase in shear stress with the shear rate.^{99,119} Furthermore, the normal stress was found to increase more rapidly than the shear stress with decreasing wall separation, leading to a decrease in the effective friction coefficient with increased compression. The normal stress was found to be independent of the shear rate for the range of velocities considered (up to $v_x = 0.2 \sigma/\tau$), whereas the shear stress increased first linearly and then sublinearly with the shear rate.^{99,119}

Grest performed another set of simulations,⁹⁸ this time including explicit solvent dimers, to study the response of a single brush exposed to the shear flow as well as for a bilayer under shear. In the former, the solvent velocity profiles in the shear direction were found to decay rapidly close to the brush while increasing linearly far away from the brush. For the sheared bilayer, the brush heights were found to shrink slightly, thus expelling more of the solvent into the interfacial region. They observed that while many chains stretch in the shear direction, many chain ends are buried deep into the brush and are less exposed to the shear field at low shear rates.⁹⁸ This is somewhat in contrast to earlier explicit solvent simulations by Peters and Tildesley for shorter chains and less dense system, where they observed a much sharper decrease in brush height at low shear rates.¹⁴⁰ Grest compared the shear forces for the two solvent treatments and found that they were in good qualitative agreement with both bilayers exhibiting a Newtonian and a shear thinning regime. However, the explicit inclusion of solvent particles was found to increase the shear forces observed in the bilayer compared to equivalent simulations using an implicit solvent.^{98,119}

Neelov *et al.*¹⁰¹ used the mean squared end-to-end distance $\langle R^2 \rangle$ and its components as well as the average chain inclination $\langle \cos\theta \rangle$ to study the conformations of grafted chains under shear in a polymer brush bilayer immersed in an implicit Langevin solvent. The results, reproduced in Fig. 2, show that increasing the shear rate leads to swelling of the chains in the shear direction ($\langle R_x^2 \rangle$) accompanied by shrinking in the transverse direction ($\langle R_y^2 \rangle$), whereas the brush height h , quantified by the normal component ($\langle R_z^2 \rangle$), was largely unchanged. It is only at even higher shear rates, when the finite extensibility of the chains comes into play, that the brush height decreases.¹⁰¹

Kreer *et al.*⁹⁶ employed a KG-BS model with an implicit Langevin solvent to show that the shear stress P_s is directly proportional to the degree of interpenetration, quantified by the bead density overlap-integral between the top and bottom brushes for various combinations of model parameters (Fig. 3). This result suggests that the degree of interpenetration dictates both the

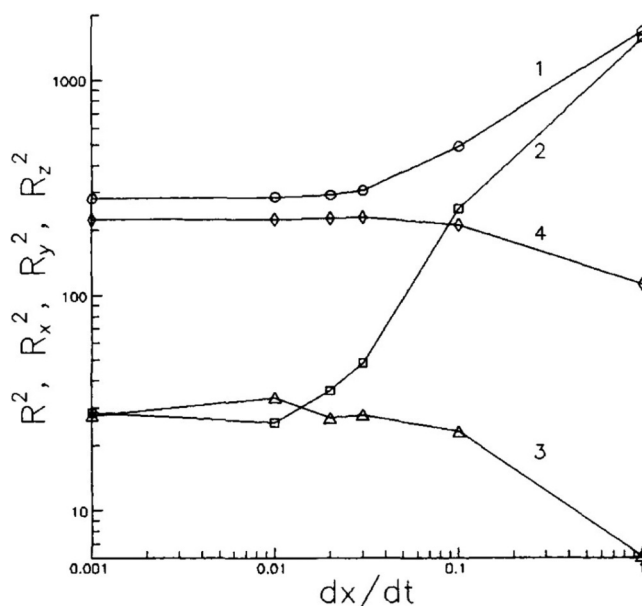


FIG. 2. Mean squared end-to-end distance (1) and its x (2), y (3), and z (4) components vs shear rate dx/dt for chains in a single brush under shear with $N = 51$ and $\sigma_g = 0.05/\sigma^2$ (LJ units). Reproduced with permission from Neelov *et al.*, *Macromol. Theory Simulations* 7, 141 (1998). Copyright 1998, John Wiley and Sons (Ref. 101).

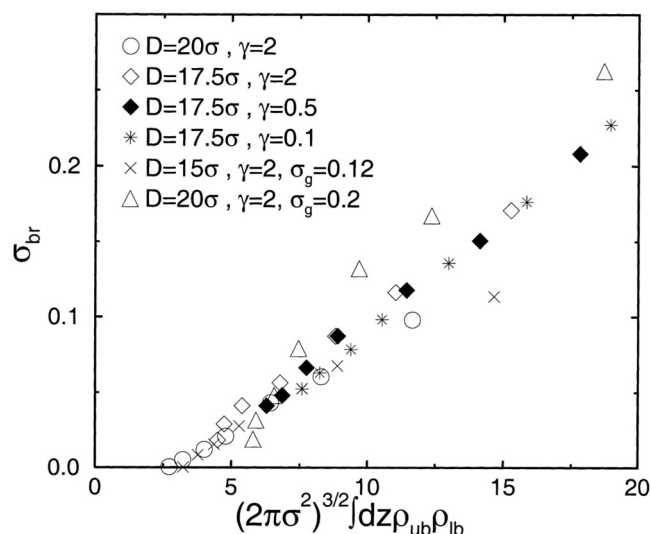


FIG. 3. Shear stress σ_{br} vs degree of interpenetration quantified by the density overlap integral for bilayers of $N = 30$ and $\sigma_g = 0.16/b^2$ (default) for different wall separations D , grafting densities σ_g , and Langevin damping constants γ . Reproduced with permission from Kreer *et al.*, *Langmuir* 17, 7804 (2001). Copyright 2001, American Chemical Society (Ref. 96).

normal and shear stress experienced in the bilayer during simulations. These authors also demonstrated that the degree of interpenetration is closely related to the number of binary interactions N_{int} between beads of the top and bottom brushes in the overlap zone.⁹⁶

In the same study, Kreer *et al.* investigated the behavior of bilayers immersed in an implicit bad solvent, and this was achieved using a TS-LJ potential with a cutoff ($r_c = 2.5\sigma$), such that there is an effective attraction between the chain beads. Beyond the expected collapse of the brush in a bad solvent, they observed an attraction between the brushes at the onset of compression, which translated into large shear stress in the bilayer when sheared.⁹⁶

Irfachsyad *et al.* used a full-DPD model with explicit solvent particles to study the effect of solvent quality on the bilayers under shear.¹⁴⁶ This was done by varying the interaction parameter as described by Eq. (15). For good solvent conditions, the chains extend and the brush height increases with increasing solvent quality, up to the athermal state, maintaining a parabolic density profile even when sheared. The chains contracted with worsening solvent quality and tilted less under shear. For bad solvent conditions, as the brushes collapse, the bilayer separates into a dense polymer phase close to the walls and a pure solvent phase in the center.¹⁴⁶ This leads to reduced friction for bilayers in a bad solvent, in contrast to the aforementioned result by Kreer for an implicit bad solvent.

By varying the solvent quality for the sheared bilayers, Irfachsyad *et al.* were able to control the amount of interpenetration and thus the friction. Their results reproduced in Fig. 4 show an excellent correlation between the computed effective friction coefficient and the amount of interpenetration observed, corroborating Kreer's arguments.

The authors then removed the solvent particles in order to study the behavior of what they termed "dry brushes,"¹⁴⁶ consisting of grafted chains exposed to an implicit solvent via the DPD thermostat. Importantly, they find that the dry brushes extend further

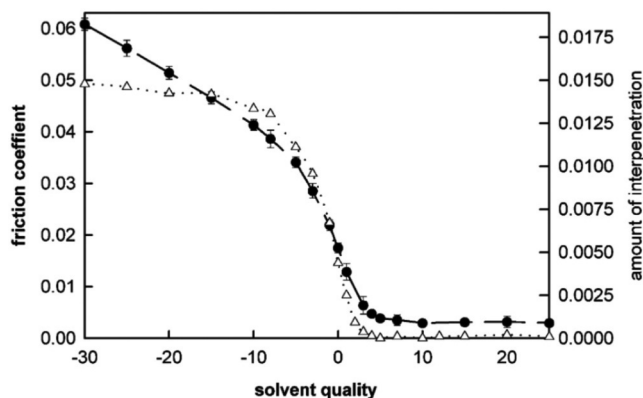


FIG. 4. Friction coefficient μ and amount of interpenetration l as a function of solvent quality quantified by the DPD interaction parameter $\Delta\epsilon_{ps}$ of Eq. (15). For bilayers of $N = 20$ and $\sigma_g \approx 1.96$ at $D \approx 17$ and $\dot{\gamma} = 0.1$ (DPD units). Reproduced with permission from Irfachsyad *et al.*, Phys. Chem. Chem. Phys. **4**, 3008 (2002). Copyright 2002, Royal Society of Chemistry (Ref. 146).

and exhibit a more steplike profile than corresponding "wet brushes" due to entropic effects and the empty volume left by the solvent. During shear, the dry brushes also exhibit stronger tilting, orientational ordering, and interpenetration than corresponding wet brushes, suggesting that the explicit solvent particles inhibit the ability of the chains to respond to the shear field.¹⁴⁶ This is in agreement with the earlier finding of Grest.⁹⁸

The existence of explicit solvent particles increases the normal⁹² and shear stresses⁹⁸ in the bilayer. However, since the normal force increases more rapidly than the shear force for a more dense system in confinement, the friction coefficient is about an order of magnitude larger for bilayers with implicit solvent treatments when compared to same bilayers with explicit solvent particles.^{92,146}

Pastorino *et al.*^{152,196} investigated the effect of grafting density on the static and dynamic properties of the interface between polymer brushes and a melt of identical chains at different shear rates. The grafted chains have their first bead randomly immobilized on two opposing smooth flat walls, and a DPD thermostat is applied to account for hydrodynamic interactions. A KG-BS model for chains in a bad solvent is used for the chains, incorporating an attractive LJ interaction between all chain beads allowing liquid-vapor coexistence below the Θ temperature. The wall separation is such that the opposing brushes come into contact only with the intervening melt but not each other. Between the two studies, the range of grafting densities considered is extremely wide ($\sigma_g/\sigma_g^* = 0.80 - 43.8$), allowing the authors to define three regimes for the dynamic response of the brush-melt interface based on the grafting density of the brush. At low grafting densities, the brush thickness is small and the interface is not well defined and is strongly affected by shear, the melt chains penetrate deeply into the brush reaching the walls and giving rise to a finite slip boundary condition due to incomplete entrapment of the melt by the brushes. The brush-melt interface develops and decreases in roughness with increasing grafting density as the free chains are expelled from the brush into the melt. For intermediate grafting densities, the interface is broad and the melt is entrained by the brushes, attaining the imposed wall velocities, giving rise to a stick boundary condition along with an increase in the shear viscosity in the vicinity of the interface. At very high grafting densities, the interface becomes narrow and the behavior of the brush approaches that of an impenetrable elastic solid inducing a slip boundary condition for the interface. Additionally, the bond orientations and chain conformations are investigated for both the grafted and free chains. Close to the grafting surface, the bonds of the grafted chains align with each other and this alignment is more perpendicular for denser brushes, whereas at the top of the brush, the orientation parameter decayed to zero.^{152,196}

In a major study by Galuschko *et al.*,⁹² extensive NEMD simulations of PBBs with different grafting densities, chain lengths, and at different wall separations have been performed using a KG-BS model and a DPD thermostat, a snapshot of the system has been reproduced in Fig. 1(b), the authors compare the behavior of bilayers with explicit solvent particles to those with an implicit DPD solvent. Similar to previous studies, they observe that, along with tilting of the chains, the explicit solvent particles are squeezed out of the brushes into the interfacial region under strong shear. This leads to reduced interpenetration, quantified by N_{int} , compared to their

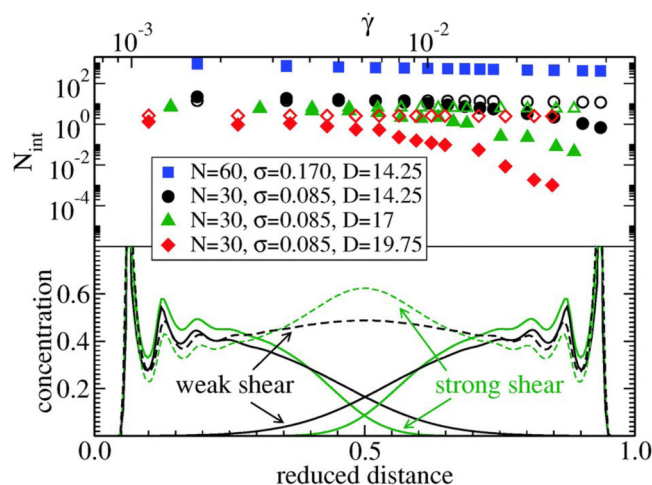


FIG. 5. Upper panel: Log-log plot of the number of binary interactions between beads from opposing brushes as a function of shear rate $\dot{\gamma}$ for bilayers of different chain lengths N , grafting densities $\sigma_g = \sigma$, wall separations D as well as implicit (open symbols) and explicit (closed symbols) solvent treatments. Lower panel: Concentration profiles vs reduced distance for grafted chain beads (solid lines) and explicit solvent beads (dashed lines) under both weak (black) and strong (green) shear conditions. Reproduced with permission from T. Kreer, *Soft Matter* **12**, 3479 (2016). Copyright 2016, Royal Society of Chemistry (Ref. 47). The data stem from Galuschko *et al.*, *Langmuir* **26**, 6418 (2010). Copyright 2010, American Chemical Society (Ref. 92).

implicit solvent counterparts; this effect is more pronounced for weaker interpenetrations as shown in Fig. 5.⁴⁷ Also, this work confirms that explicit solvent particles lead to increased shear stress and, more so, normal stress in the bilayer leading to reduced friction and indeed a qualitatively different shear response compared to using an implicit solvent.⁹² The simulation results in Galuschko *et al.* also show that bilayers with explicit solvent particles, larger chain lengths, or higher grafting densities exhibit a lower critical shear rate $\dot{\gamma}^*$ for transition into the shear thinning regime when compared to bilayers with shorter chains, less dense brushes, or with an implicit solvent. More importantly, it was also demonstrated that macroscopic quantities for both explicit and implicit solvent treatments exhibit the same shear thinning power law behavior when normalized by their values at $\dot{\gamma}^*$.⁹² This universal behavior was deduced by characterizing the shear response of the various bilayers by the dimensionless Weissenberg number W , defined as

$$W = \frac{\dot{\gamma}}{\dot{\gamma}^*} = \dot{\gamma}\tau, \quad (25)$$

where τ is the relaxation time of the bilayer that is given by the inverse of the critical shear rate $\dot{\gamma}^*$ as shown in Eq. (25). When $W \ll 1$, the response is Newtonian, and when $W \gg 1$, the bilayer exhibits shear thinning. Introducing scaling ratios for macroscopic quantities of interest allows the authors to characterize their shear thinning behavior. For the squared-radius of gyration

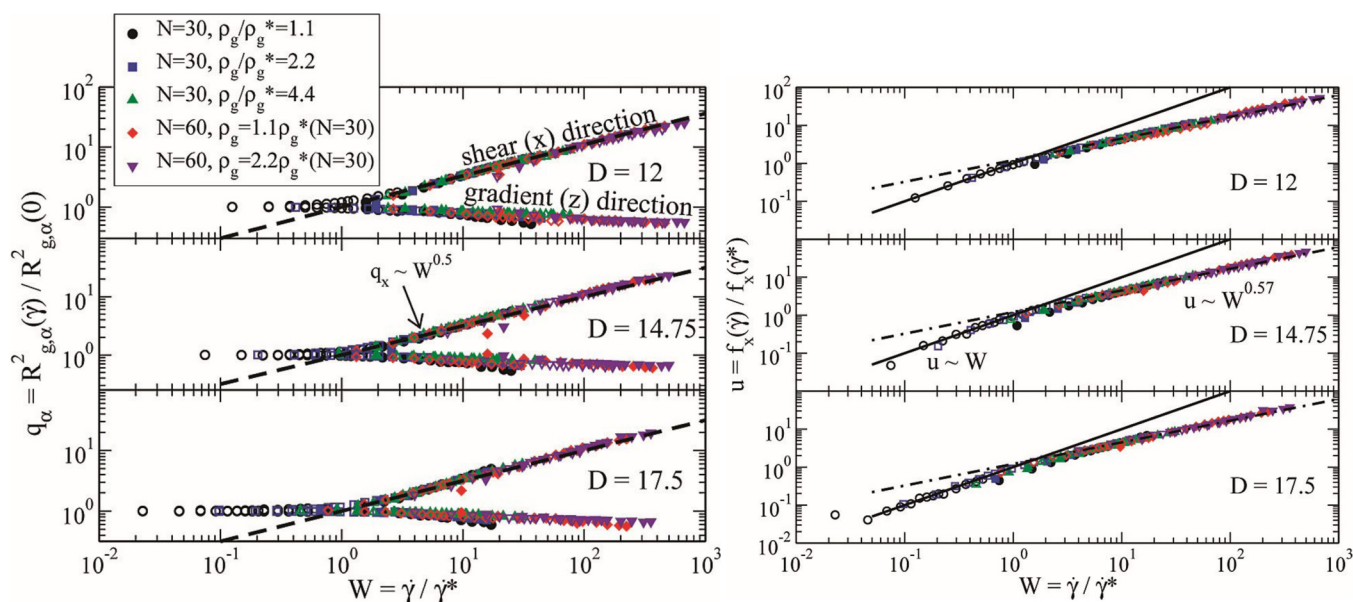


FIG. 6. Logarithmic scaling plots for chain extensions in the shear (q_x) and gradient (q_z) directions (left) and shear force u (right) as a function of the Weissenberg number W , for bilayers of chain lengths N , grafting densities σ_g , wall separations D , as well as implicit (open symbols) and explicit (closed symbols) solvent treatments. Adapted with permission from Galuschko *et al.*, *Langmuir* **26**, 6418 (2010). Copyright 2010, American Chemical Society (Ref. 92).

components $R_{g,\alpha}^2(\dot{\gamma})$, for example, a scaling ratio q_α is defined as

$$q_\alpha = \frac{R_{g,\alpha}(\dot{\gamma})}{R_{g,\alpha}(\dot{\gamma}^*)} \quad (26)$$

The critical shear rates $\dot{\gamma}^*$ are obtained for different bilayers by shifting the MD results such that for each bilayer the shear-induced lateral chain extension $q_x(W=1)=1$.⁹² Their results for q_x and q_z vs W shown in Fig. 6, reveals a remarkable data collapse allowing the authors extract a universal power law behaviour for shear deformation,

$$q_x = \frac{R_{g,x}(\dot{\gamma})}{R_{g,x}(\dot{\gamma}^*)} \sim W^\phi \sim W^{0.5}, \quad (27)$$

where $\phi \approx 0.5$ is the shear-thinning exponent for the lateral chain extension.⁹² Another scaling ratio u is defined for the shear force $f_x(\dot{\gamma})$, and the data collapse when they are scaled such that $u(W=1)=1$, revealing another universal power law for shear force [Fig. 6(b)],

$$u = \frac{f_x(\dot{\gamma})}{f_x(\dot{\gamma}^*)} \sim W^\kappa \sim W^{0.57}, \quad (28)$$

where $\kappa \approx 0.57$ is the shear-thinning exponent for shear stress.⁹²

C. Theoretical scaling descriptions

In order to interpret the results of simulations, Galuschko *et al.* develop a scaling approach to describe both linear and shear thinning regimes for strongly compressed semidilute bilayers with Zimm dynamics. The developed theoretical approach is able to predict scaling laws for the lateral chain extension and the shear force as a function of shear rate as well as molecular parameters, with scaling exponents ($\phi \approx 0.5$ and $\kappa \approx 0.57$) that match their simulation results (Fig. 6). Using the same framework, scaling exponents are also obtained for “dry brushes” (i.e., without hydrodynamic interactions), in both melt ($\phi \approx 0.46$ and $\kappa \approx 0.69$) and semidilute regimes (SD) ($\phi \approx 0.65$ and $\kappa \approx 0.73$).⁹²

Two assumptions are made by the authors when deriving the scaling laws, the first is that the shear force in the linear regime is directly proportional to the length of the overlap region, consistent with the simulation results presented in Sec. III B.^{92,96} The second is a brush averaged chain deformation under shear, which would mean that all of the chains sustain the shear stress equally. The second assumption is used to obtain the relaxation time for the bilayer and hence the critical shear rate, but, as the authors themselves noted, it is not fully justified because due to thermal fluctuations, the chains' ends would cyclically exchange between two states, being exposed to the shear field vs being buried deeper in the brush.¹⁹⁸ For this reason, more chains sustain the load than those in the overlap region at any instant, and as such, the chain deformation would not be even. The shear thinning response is obtained based on the assumption that chains are strongly stretched in the shear direction such that both the lateral chain extension and the shear force are directly proportional to the length of the chain ($\sim N$). The authors include a more detailed

analysis of the relaxation time of the bilayer in the linear response regime in the Appendix in Ref. 92, arriving at a key result. Namely, that the largest relaxation time of the bilayer, dictating the critical shear rate, corresponds to the Rouse/Zimm relaxation time of a single chain within the brush in the melt/SD regimes.⁹²

This result is taken into consideration and the theory is recast in later studies,^{93,197} where slightly altered scaling exponents ($\phi \approx 0.53$ and $\kappa \approx 0.54$) are obtained for strongly compressed semidilute brushes, which remain in excellent agreement with simulation results^{92,104} as well as experimental SFA results by Schorr.⁶⁴ In the recent review by Kreer,⁹⁶ these scaling descriptions are presented in far more detail but also scaling predictions for the dependence of macroscopic quantities on the molecular parameters of the brushes of the bilayer, as will be discussed in Sec. IV B.

Goicochea *et al.* have performed simulations of sheared bilayers in a theta solvent employing a DPD model with explicit solvent beads representing three water molecules each. Theta solvent conditions are ensured by setting equal DPD pair interaction parameters a_{ij} between all beads in the system. They extract a shear-thinning exponent ($\kappa \approx 0.69$) in exact agreement with scaling prediction for “dry brushes” as discussed above.¹⁵⁰

The interesting prospect of solvent-induced immiscibility between brushes was studied by de Beer and Muser. They used both MD simulations^{143,182} using a KG-BS model with a LJ truncated-shifted interaction with two different explicit solvents as well as colloidal probe AFM experiments of a solvated hydrophilic brush in contact with the solvated hydrophobic brush.¹⁴⁴ This simply means that the chains of the top and bottom brushes have their own preferred solvent and the two solvents themselves could be immiscible. This is achieved by controlling the cutoff-radius for the LJ interaction, in order to introduce an attractive interaction for beads that are miscible, while leaving immiscible beads to interact purely repulsively. The MD shear results reveal a major decrease in the friction coefficient at all explored velocities for immiscible brushes when compared to miscible brushes. This is accompanied by an increased shear-thinning exponent (up to $\kappa \approx 1$) compared to that expected for SD brushes ($\kappa \approx 0.54$) under shear. Suggesting that immiscible brushes exhibit Newtonian behavior over a much wider range of shear rates. Likely because for immiscible bilayers, the interpenetration can become almost nonexistent.

Notably, in their simulations, de Beer *et al.* opt to use substrates in the form of curved cylinders^{145,182,199} [Fig. 1(f)] as opposed to idealized flat substrates and chose to apply a thermostat only to the curved wall beads in the direction perpendicular to shear motion to avoid influencing the dynamics of the fluid. This setup allows them to study the shear behavior of more experimentally relevant cases such as asperity collision,¹⁴⁵ which may be found between rough surfaces under compression and shear, or quasi-flat (ideally conformal) steady-state shear by choosing to move the plates in either orthogonal shear direction. For the latter case, they identify the interpenetration as the main dissipation mechanism, as is the case for flat surfaces. However, due to shear-induced spreading of the contact area, they initially observed a shear thinning exponent ($\kappa \approx 0.67$). After accounting for the effect of such spreading, the same exponent ($\kappa \approx 0.57$) found earlier for SD brushes was recovered. For the case of asperity collision,¹⁴⁵ perhaps expected velocity-dependent peak in the shear force is

observed. Additional dissipation mechanisms were also identified, e.g., transient interpenetration or capillary and shape hysteresis. These additional mechanisms could become as important as steady-state interpenetration in determining the shear response of the colliding brushes.¹⁸²

Spirin *et al.*¹⁹⁷ extend the scaling analysis of Galuschko *et al.*⁹² to the case of quasi-instantaneous shear inversion, with accompanying MD simulations, during which an overshoot in N_{int} is observed shortly after inversion, consistent with earlier simulation results by Kreer *et al.*, who also reported an overshoot in the shear stress as a function of time.⁹⁷ They relate the overshoot to a minimum in the lateral chain extension, when the brush reswells and the chains are more or less perpendicular to the surface as they are tilting to the opposite shear direction and hence are able to develop a scaling law for the characteristic time of the inversion process and which predicts that it is linearly dependant on the chain length N and weakly dependent on the grafting density σ_g .¹⁹⁷ Along with the overshoot in the shear stress, a dip is observed in the normal stress, which seems to disagree with the increase in normal forces observed in oscillatory shear experiments. Importantly, both the overshoot of the shear and dip of the normal stresses were not observed for systems without explicit solvent particles. These results further support the view that implicit solvent treatments are not suitable for studying bilayers in non-stationary processes.¹⁹⁷

The simulations of Spirin and co-workers further demonstrated the existence of nanoinclusions alongside the explicit solvent particles in the bilayer [Fig. 1(c)], while detrimentally affecting the measured friction coefficient in steady state shear, which could serve to suppress the overshoot observed during shear inversion and, importantly, did not affect the shear thinning exponents observed.¹⁹⁷ This is in keeping with earlier results by Milchev *et al.*¹⁵⁴ who performed simulations of low density single brushes with rather large nanoparticles under shear flow and observed that the solvent and nanoparticle density profiles were largely unaffected by the shear rate, while the grafted chains responded and tilted strongly in the shear direction.^{94,154} Spirin *et al.* were able to show that the nanoinclusions undergo rotational motion during steady-state shear, while occupying much of the space between the brushes, thus attenuating the degree of interpenetration.^{197,200} This finding has inspired a recent DPD study by Nguyen *et al.* who suggest the use of grafted nanoparticles as nanobearings to improve the mechanical stability of brush interfaces while only losing about 20% of the lubricity.¹¹² In general, these later studies where nanoscale inclusions are added to a polymer brush bilayer provide a more realistic picture of the tribology of complex biological systems of interest (e.g., synovial joint lubrication), which undoubtedly experiences nonstationary loading conditions and contain macromolecular inclusions.⁴⁷

The Appendix of the earlier study by Galuschko *et al.*⁹² additionally includes a detailed discussion of the limits of the strong compression regime as well as an early theoretical treatment for the regime of weak compression. They are able to obtain scaling relations that depend on the molecular parameters of the brush for the interpenetration depth δ at both the upper ($D \approx h$) and the lower ($D \approx \delta$) limits of the strong compression regime. The authors argue that upon compression past the lower limit, the chains would

cease to stretch and be reflected by the surfaces, and thus, the assumption of strongly stretched chains is no longer valid. Through scaling arguments, the authors relate the number of monomers per chain in the interpenetration layer at the upper limit to the case of brushes just coming into contact, meaning that the number may be a constant throughout the weak interpenetration regime. This allows them to predict scaling relations for the correlation length ξ_d , penetration depth δ , and lateral chain extension in this regime, which is found to be dependent on the ratio (δ/ξ_d) .⁹²

More recently, Desai *et al.*⁹⁵ have reported NEMD simulations of bilayers in the weak compression regime accompanied by a scaling description using much the same framework as Spirin, Galuschko, and Kreer *et al.*^{47,92,93,197} Employing a KG-BS model with an implicit Langevin solvent, they perform shear of bilayers at separations ($d = D/2h = 0.6 - 1$) and observe a sublinear increase in the shear stress with the shear rate even at low shear rates where a Newtonian response is to be expected. They obtain a value for the scaling exponent ($b \approx 0.81 \pm 0.015$) from a best fit of the simulation data across different compressions. The authors proceed to develop a scaling theory, first for compression²⁰¹ and then for shear⁹⁵ behaviors, based around the assumption that for weakly compressed bilayers, each chain can be divided into an interpenetrated and noninterpenetrated segment and that the stretching behavior is then some linear combination of the two behaviors. Using the extracted value for the scaling exponent b , the scaling description is able to predict shear-thinning exponents ($\phi \approx 0.18$ and $\kappa \approx 0.62$), in excellent agreement with the simulation results.⁹⁵

D. Polyelectrolyte brush bilayers

In an early effort to simulate the shear response of PE bilayers, Sirchabesan and Giasson¹⁰² used a DPD model along with explicit solvent particles to model a bilayer composed of a diblock copolymer immersed in water. To study the effect of electrostatic interactions, the charge fraction q of the chains is controlled to produce bilayers varying from neutral ($q = 0$) to highly charged ($q = 1$). Notably, they did not include explicit counterions, but rather, each counterion is treated as a localized continuous charge density field as dictated by the solution to the Poisson-Boltzmann equation using the charged beads on the chain as the background fixed charges. The effect of electrostatic screening is studied through the addition of monovalent pairs of salt ions as oppositely charged beads. With this model, they observed significant electrostatic repulsion between the charged chains when no salt ions were added, which lead to heterogeneous density profiles, high normal pressures, and greatly reduced interpenetrations between the bilayers when compared to neutral ones ($q = 0$). The lack of interpenetration leads to a very low friction coefficient for charged bilayers; furthermore, their results show an almost linear increase in interpenetration and friction coefficient with increasing salt concentration due to the effect of electrostatic screening.¹⁰²

While the previous study included explicit solvent beads and implicit localized counterions, later studies by Carillo *et al.*¹³⁹ for bottle-brush PE bilayers and Ou *et al.*¹⁰⁵ for linear bilayers considered the alternate case of explicit counterions and an implicit

solvent, in which case a greatly reduced μ for charged bilayers compared to neutral ones is also observed.¹⁰² These results, although in qualitative agreement with experimental observations of the superior lubricity of PE bilayers^{5,122,202} are, however, rather misleading since the comparisons are between charged PE bilayers that are neutralized with explicit counterion beads, and neutral bilayers with only an implicit Langevin solvent, and thus, the two systems represent bilayers at vastly different number densities.⁴⁷ The explicit counterions act as solvent beads and, as such, would lead to reduced friction coefficient with respect to an implicit solvent treatment as described in Sec. III C, without the need to invoke any electrostatic effects, expressing the need for a fully explicit model in order to achieve a fair comparison.

Nonetheless, Cao *et al.* used a similar model (with an implicit solvent) to compare the lubricity of PE bilayers with explicit monovalent or trivalent counterions included. In this case, the comparison is more justified as it is between systems at the same overall number density. At high shear rates, similar to explicit solvents in neutral bilayers, the counterions are squeezed into the overlap zone as the brushes collapse. The interpenetration and friction coefficient are found to be greater while the shear and normal stresses generally smaller for bilayers with included trivalent compared to monovalent counterions. The diminished lubricity is attributed to the bridging effect of trivalent counterions.²⁰³

In a later study by Carrillo *et al.*,¹⁴¹ another comparison between neutral and charged bilayers composed of bottle-brush chains is conducted; however, this time, both counterions and the solvent are included explicitly. Meaning that for bilayers of a given charge fraction, counterion beads are added to ensure charge neutrality and solvent beads are added to ensure a constant number density ($\rho = 0.8$) at a given wall separation. Thus, when comparing bilayers of increasing charge fractions, the solvent beads are replaced by counterions and vice versa. The simulation results suggest that for partially charged bilayers, the dominant contribution to the normal stress arises from the excluded volume interactions of the mobile beads (solvent or counterions) and not the electrostatic interactions confirming that the earlier studies, for PE bilayers with only an implicit solvent, were unjustified and incapable of providing a fair comparison. In fact, when compared at the same number density charged bilayers were found to have a higher friction coefficient than neutral bilayers and not a lower one as had been previously predicted.¹⁴¹

An alternative approach, which serves to isolate the effect of electrostatic interactions on the behavior, was adopted by Spirin *et al.*¹⁴² The value of the Bjerrum length is controlled directly by varying the dielectric constant which allows them to vary the strength of the electrostatic relative to excluded volume interactions in order to study bilayers varying from neutral ($\lambda_b = 0$) to highly charged ($\lambda_b = 3$).¹⁴² The shear simulation results, for strongly compressed charged bilayers with explicit counterions and solvent dimers at a constant number density ($\rho = 0.9$), are reproduced in Fig. 7. For neutral bilayers ($\lambda_b = 0$), the counterions are found to accumulate in the overlap region and the shear force exhibits the expected Newtonian regime, with a linear increase with the shear rate and the shear-thinning regime with a sublinear exponent ($\kappa \approx 0.57$). The shear thinning exponent for $\lambda_b = 0$ then, as expected, matches the theoretical prediction for

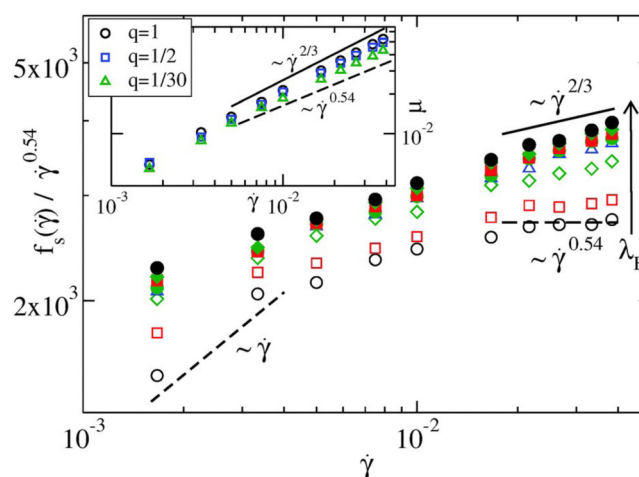


FIG. 7. Double-logarithmic scaling plot for shear stress normalized by the predicted dependence on shear rate for neutral SD bilayers ($\kappa = 0.54$) as a function of shear rate $\dot{\gamma}$ for a range of values of the Bjerrum length from $\lambda_b = 0$ (empty circles) to $\lambda_b = 3$ (filled circles) controlled through direct variation of the dielectric constant. The inset figure shows a double-logarithmic scaling plot of the friction coefficient μ as a function of shear rate $\dot{\gamma}$ for a single bilayer at $\lambda_b = 1$ but with different charge fractions q on the chains. Reproduced with permission from T. Kreer, *Soft Matter* **12**, 3479 (2016). Copyright 2016, Royal Society of Chemistry (Ref. 47). The data stem from L. Spirin and T. Kreer, *ACS Macro Lett.* **2**, 63 (2012). Copyright 2012, American Chemical Society (Ref. 142).

semidilute brushes as presented in Sec. III C. Increasing λ_b leads to more homogenous charge density profiles as the counterions penetrate into the brushes from the overlap region along with an increase in the shear force and a disappearance of the Newtonian regime. For strong electrostatic interactions ($\lambda_b = 3$), counterion immobilization (CI) occurs around the charged chain beads, effectively neutralizing them, as can be seen from pair correlation functions shown in Fig. 2 of Ref. 142. CI leads to an almost uniform charge density profile; furthermore, the shear thinning exponent becomes $\kappa \approx 2/3$.^{47,142} As counterions make up most of the mobile solvent particles, it is argued by the authors that CI results in both a screening of the hydrodynamic interactions as well as a quasineutral behavior of the bilayer, with effectively bulkier beads, which then explains the observed shear thinning exponent which is in line with the theoretical predictions for neutral bilayers at melt concentration where hydrodynamic interactions are indeed screened.^{47,92} This also explains the absence of an overshoot in the shear force during shear inversion simulations for strongly charged bilayers ($\lambda_b = 3$), since this is what was observed to occur for neutral bilayers in an implicit Langevin solvent where hydrodynamics are not captured as presented earlier in Sec. III C on the response of a neutral bilayer to shear inversion.

Perhaps the most insightful and comprehensive comparison between neutral and charged brushes is provided in the pair of studies by Goujon *et al.*, where they employ a DPD model

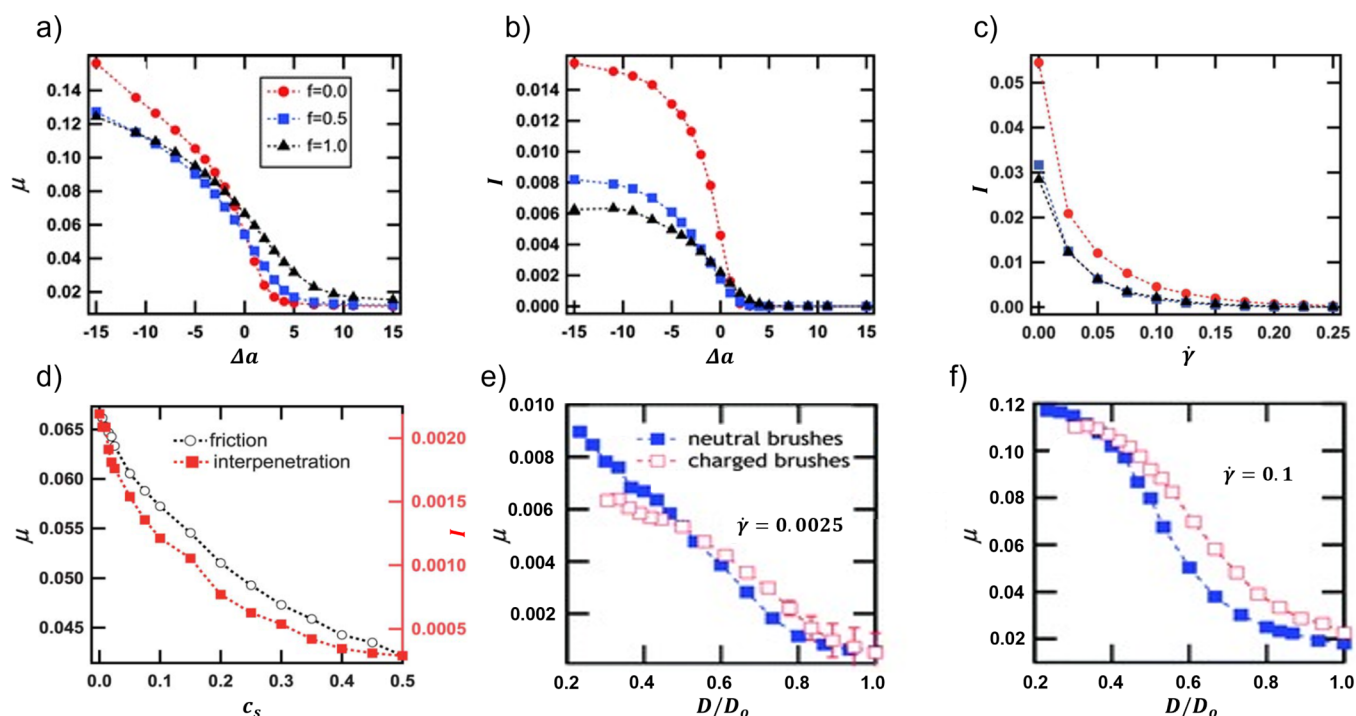


FIG. 8. DPD simulation results for PE bilayers composed of chains of length $N = 20$ at a grafting density $\sigma_g = 0.5$ (DPD units) from Goujon *et al.* (a)–(d)¹⁴⁸ (e) and (f).¹⁴⁹ (a) and (b) friction coefficient μ and interpenetration I vs solvent quality (via interaction parameter Δa) for bilayers composed of chains of different charge fractions f at wall separation $d = D/D_o = 0.5$. (c) I vs shear rate $\dot{\gamma}$ for bilayers at different f , (d) μ (empty circles) and I (red squares) vs salt concentration c_s for a bilayer with $f = 1$ at $d = 0.5$ and $\dot{\gamma} = 0.1$. (e) and (f) Friction coefficient $\mu \equiv \varepsilon$ vs wall separation d for neutral (filled squares) and charged (empty squares) at different (e) and high (f) shear rate. Adapted with permissions from Goujon *et al.*, *Soft Matter* **8**, 4635 (2012). Copyright 2012, Royal Society of Chemistry (Ref. 148) and Goujon *et al.*, *Soft Matter* **9**, 2966 (2013). Copyright 2013, Royal Society of Chemistry (Ref. 149).

including explicit solvent, positively charged counterion beads to ensure bilayer neutrality [Fig. 1(d)], as well as the possible addition of negatively charged salt ions [Fig. 1(e)].^{148,149} An additional Kumar and Larson spring repulsion model²⁰⁴ is added, which acts between distant beads along the chain to prevent bond crossings and account for entanglements, which would otherwise be ignored due to the soft nature of DPD interactions.¹⁴⁸

In the first study,¹⁴⁸ they investigate the effect of charge fraction f , solvent quality [via Δa of Eq. (15)], shear rate $\dot{\gamma}$, and salt concentration c_s on the interpenetration and friction coefficients (μ) for two values of compression ($d = 0.5, 0.8$). The results for the case of strongly compressed PE bilayers ($d = 0.5$) are summarized in Figs. 8(a)–8(d), beyond confirming earlier results for the effect of solvent quality on interpenetration and friction for neutral bilayers,¹⁴⁶ the results reveal that the friction coefficient for neutral bilayers is more strongly affected by variations in solvent quality than charged bilayers. In fact, as shown in Fig. 8(a), neutral bilayers ($f = 0$) exhibit a higher μ for good solvent conditions ($\Delta a = 0$) but a lower μ for bad solvent conditions when compared to the partially ($f = 0.5$) or fully ($f = 1$) charged bilayers. Figure 8(b) confirms that variations in solvent quality have a more drastic effect on the conformations and interpenetration of neutral bilayers when compared to

charged bilayers at a constant number density, where some of the solvent beads are replaced by counterions. Additionally, they observe that the bead density profiles of the individual brushes are more steplike for charged brushes compared to the well-known parabolic shape for neutral brushes. Furthermore, at strong compressions, inhomogeneities appear in the density profiles of charged brushes. These inhomogeneities disappear with the addition of salt ions due to electrostatic screening, which also leads to a decrease in interpenetration as well as friction as shown in Fig. 8(d).¹⁴⁸

In the second study,¹⁴⁹ Goujon *et al.* use the same model to investigate the effect of compression over a much wider range ($d = 0.2 - 1$). This time the simulations are not performed in the usual NVT-ensemble but rather the μ VT-ensemble, i.e., keeping the chemical potential μ constant instead of the total number of particles N , and this is achieved by occasionally performing particle creation/deletion moves within a MC scheme in a way that minimizes the effect on the dynamics. Using a μ VT-ensemble allows one to study conditions closer to what are kept during experiments on shearing of PBBs and is thus better suited for direct comparison between simulations and these experimental results. They find that the friction forces for charged and neutral bilayers are actually of the same order of magnitude, contrary to the earlier studies of this

section, but that, quite interestingly, charged bilayers gave a higher friction coefficient at weak compressions and a lower one at high compression compared to neutral bilayers when sheared at moderate to low shear rates [Fig. 8(e)]. This behavior disappeared at higher shear rates where the charged bilayers exhibited a higher friction coefficient than that of neutral bilayers at all compressions as demonstrated in Fig. 8(f).¹⁴⁹

IV. CURRENT CHALLENGES AND OUTSTANDING QUESTIONS

A. Efforts to bridge the gap between experiments and models

In Sec. III, the most important results from NEMD simulations of PB tribology have been presented, along with accompanying scaling theories that seem to describe the friction behavior of the simulated bilayers quite well. However, it becomes crucial to ask, how well do these computational and theoretical approaches capture what is observed experimentally? Answering this question is rather complex for multiple reasons, mostly arising from computational resource limitations, which make it a challenge to simulate sheared bilayers that correspond exactly to those studied experimentally. In this section, we will discuss the sources of discrepancy as well as methods and efforts to bridge the gap between simulation results and experimental data.

1. Challenges arising from coarse-graining

As explained earlier, there is a need to use some form of the CG model for the chains as well as the solvents, if taken into account explicitly, in order to be able to simulate the dynamics of large enough bilayers at the required timescales using NEMD. Coarse-graining involves reducing the degrees of freedom of the polymer chain in order to increase its fundamental time scale,²⁰⁵ accomplished by grouping segments of the polymer chains into beads that interact with one another through interactions such as those presented in Sec. II. Regardless of the CG model employed, there is an associated loss of information as the dynamics of real polymers depend on a wide range of time and length scales. Thus, an efficient but still effective coarse-graining procedure should aim to retain the smallest length scales needed to correctly represent the dynamics of the system but no smaller.²⁰⁵

A consequence of using CG models is that the simulations are performed, and the results are presented, in dimensionless units, whether they be LJ or DPD units. While this provides scalability to the results, as the CG polymer chains lose their specific atomic structure, it adds a further barrier to comparison with experiments, namely, what is the best choice for the various parameters to map a DPD or LJ system to a specific polymer and its chemistry, such that a meaningful comparison to experimental data can be made? Choosing the optimal value for the interaction parameters can itself be a rather involved task depending on the approach adopted, ranging from simply trusting values found in the existing literature to, performing a separate set of simulations and tuning the parameters to match to experimentally available data or full-atom simulations. This can be accomplished, for example, by simulating a melt of CG chains and matching to experimentally available densities or

by simulating a free CG chain in solution and matching to data for the radius of gyration of the chains for a known degree of polymerization.¹⁰⁸ Incorporating a bond angle potential into the CG model can allow for matching to the persistence length for a semiflexible or stiff polymer. The aforementioned structural matching is used to obtain the chain lengths and bead sizes for the CG model. The mass of the CG bead will depend on the particular polymer chain being modelled and the degree of coarse-graining. We notice in this regard that while the choice of mass is completely irrelevant when one is interested in equilibrium quantities (at least in situations where classical physics applies), this is not the case when intrinsically non-equilibrium (dynamic) properties like friction coefficients are involved. The energy scale, on the other hand, can be set, for instance, by matching the normal stress under compression with experimental data.¹⁰⁸ The recent reviews by Dhamankar *et al.*,²⁰⁶ Grest *et al.*,²⁰⁵ and the earlier review by Merchant *et al.*²⁰⁷ delve into the process of coarse-graining polymers and its limitations in far greater detail than we do here and are highly recommended.

2. Challenges comparing to experiments

Even after coarse-graining, the time and length scales accessible through simulations remain limited, which makes it difficult to compare to experimental conditions. To illustrate this, let us consider a Kremer–Grest bead-spring CG model for a polymer brush composed of hydrocarbon chains. Typically used LJ bead parameters, where a bead would represent about three chemical (CH_2) monomers, are $\sigma = 0.5 \text{ nm}$ and $m = 38.6 \text{ Da} \approx 6.41 \times 10^{-26} \text{ kg}$,¹⁶⁴ assuming room temperature $T = 300 \text{ K}$ allows one to estimate a rough energy scale through $\epsilon = k_B T = 4.14 \times 10^{-21} \text{ J}$, which then would together determine the time $\tau = \sqrt{\frac{\sigma^2 m}{\epsilon}} \approx 2 \text{ ps}$ and velocity $\sigma/\tau \approx 254 \text{ m/s}$ units for the simulation. A common MD timestep for such a model is $\Delta t = 0.005\tau \approx 9.84 \text{ fs}$ and the bilayers are usually sheared for time periods of the order ($10^7 \Delta t \approx 100 \text{ ns}$). It is already clear then that simulations could at most capture time scales in the range of microseconds or milliseconds at most with typical computing facilities. This fact severely limits the chain lengths accessible, since longer chains have larger relaxation times. Indeed, chain lengths in most PB experiments are about an order of magnitude larger than those in simulations. Furthermore, this makes simulating bilayers at experimentally observed shear rates incredibly computationally demanding. In simulations, the bilayers are typically sheared at relative wall velocities in the range $v = [0.0002 - 1]\sigma/t \approx 0.05 - 254 \text{ m/s}$, keeping in mind that lower velocities will need to be sheared for a longer period. This is because for statistical accuracy and to reduce finite size effects during the simulation time the system needs to sample a large number of conformations, which requires a total displacement in the shear directions by the length of the simulation box multiple times. Velocities in experiments vary depending on the technique employed. Traditional SFA/SFB experiments typically only manage velocities up to 0.450 nm/s while AFM velocities can go up to about 5 mm/s and a PoD tribometer a bit higher still at about 19 mm/s , all of which are various orders of magnitude below the range accessible in simulations. On the other hand, MTM

experiments cover velocities in the range of 0.025–2.5 m/s which is in fact comparable with the lower range velocities accessible only through long simulations. Note that the values presented above are only rough estimates based on the assumed parameters above as well as experimental data available in the literature. While the MTM is capable of performing mixed sliding/rolling at high speeds reaching into the hydrodynamic lubrication regime, the slower pure-sliding PoD offers more control and may be preferred for investigating the boundary and mixed lubrication regimes.³⁷

It is important to highlight that by removing some degrees of freedom, the effect on dynamic quantities due to coarse graining is difficult to gauge. For example, it has been shown by Zwanzig that the smoothing of the underlying energy scale might lead to faster dynamics than what would be expected in the full-atom systems.^{208,209} In practice, this means that the correct timescale to simulate in a CG system might be shorter than the one calculated by the simple arguments presented above, at least partially closing the gap between experiments and simulations. However, it is difficult to estimate exactly how much faster the dynamics become due to coarse-graining. In other words, even if one had the necessary computational resources to simulate much slower rates, the idea to match experimental and simulation timescales might be flawed in

the first place by lack of correspondence between real and simulated time in a CG system. In this regard, a somewhat better approach, and one more in line with the general spirit of coarse graining, would be to try to look at trends as a function of shear rate rather than comparing at an arbitrary value. However, most experimental studies of PBBs under shear are limited to a single or a few sliding velocities,¹⁹⁴ whereas only a few look at the effect of shear velocity explicitly. This is even more important considering that the measured friction coefficient depends strongly on the shear rate. Spencer *et al.* have performed shear MTM experiments covering almost four orders of magnitude for poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) and PLL-g-dex bilayers in various HEPES/glycerol mixtures, the friction coefficient was found to decrease with increasing shear velocity up to a minimum at a velocity of the order $v \approx 1 \text{ m/s}$, after which μ begins to increase with increasing shear velocity.^{74,76} This finding is in good agreement with the simulation results, where an increase in μ is observed with increasing shear velocity [Fig. 9(a)], assuming the velocity ranges accessed in simulations would generally lie above $v > 1 \text{ m/s}$, regardless of CG effects.

A further complication arises from the fact that the various above-mentioned techniques exhibit different curved geometries¹¹⁷

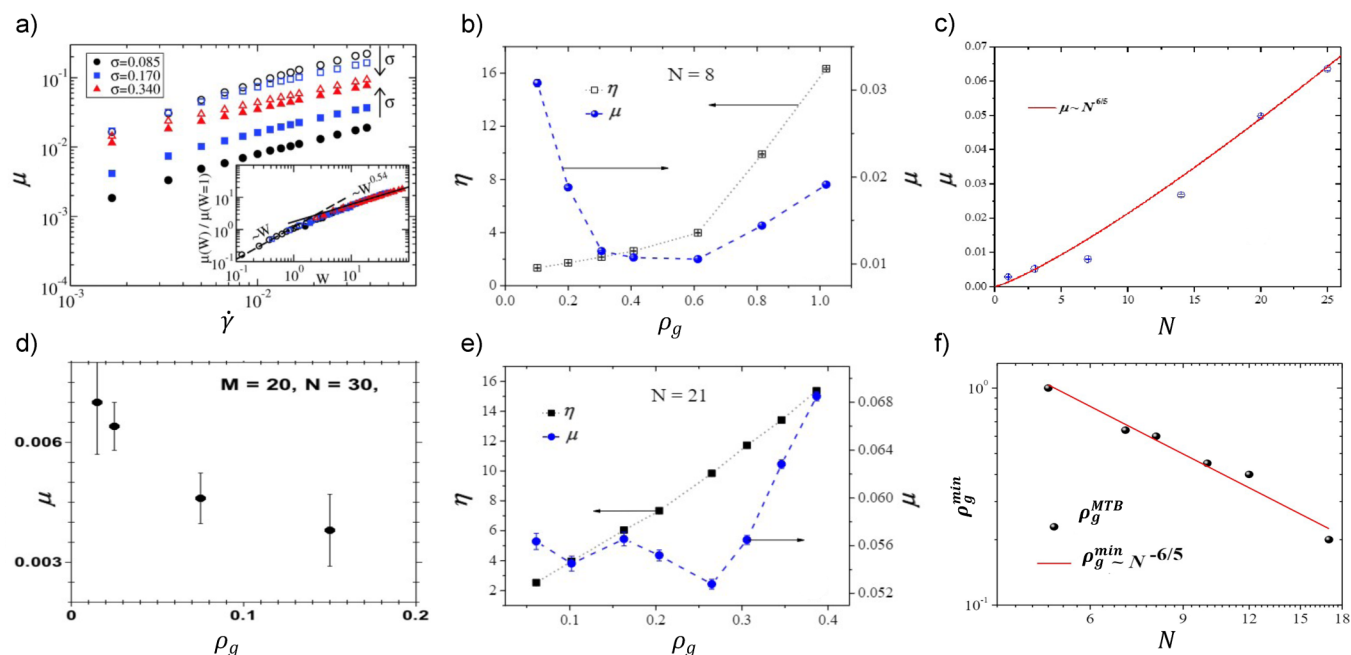


FIG. 9. (a) Friction coefficient μ vs shear rate $\dot{\gamma}$ for strongly compressed neutral bilayers at different grafting densities σ_g for both implicit (empty symbols) and explicit (filled symbols) solvent treatments from MD simulations.⁸² (b) Friction coefficient μ vs grafting density σ_g obtained from the slopes of the normal vs shear stress curves at a constant shear velocity $v = 0.001$ (LJ units) as described in Ref. 110. Figures (c)–(f) show DPD simulation results¹⁵¹ for sheared bilayers at a constant wall separation $D = 7$ and shear rate $\dot{\gamma} = 0.028$ (DPD units). (c) and (d) viscosity η (black squares) and friction coefficient μ (blue circles) vs grafting density $\sigma_g \equiv \Gamma$ for chains of length $N = 8$ (c) and $N = 21$ (d). (e) DPD results for friction coefficient μ (blue crossed-circles) vs chain length N with proposed scaling law (solid red line). (f) Double logarithmic scaling plot grafting density at minimum of friction for different chain lengths (black circles) along with the expected scaling for the mushroom-to-brush transition (MBT) (solid red line). Adapted with permissions from T. Kreer, *Soft Matter* **12**, 3479 (2016). Copyright 2016, Royal Society of Chemistry (Ref. 47); Singh *et al.*, *Polymers* **8**, 254 (2016). Copyright 2015, American Chemical Society (Ref. 110); and Mayoral *et al.*, *Phys. Rev. E* **95**, 012505 (2017). Copyright 2017, American Physical Society (Ref. 151).

that may deviate quite strongly from the idealized flat substrates used in most PBB simulations. Although the SFA/SFB interacting surfaces that are in a crossed-cylinder configuration with radii of curvature on the order of centimeters may be somewhat comparable to flat substrates at the simulation scale,^{59,210} AFM incorporates a spherical tip that is about 5 μm in diameter mounted on a cantilever, which scans the sample at a resolution of nanometers.^{73,79} Both the PoD tribometer and MTM consist of a ball, that is, millimeters in diameter, which comes into contact with a rotating disk.^{74,76} Indeed, these experimental techniques are intended to probe fundamentally different length scales, and it may be difficult to mimic their geometries in simulations.

Moreover, the longer chains explored in experiments could lead to increased entanglements in the bilayer within a single brush as well as between chains on opposing brushes, entanglements that are neglected completely for simple DPD models and otherwise not commonly observed for the relatively short grafted chains ($N < 200$) used in simulations of sheared bilayers.⁴⁷ These entanglements as well as possible microcontacts due to the roughness of physical substrates could lead to damage and chain detachment that is also not typically accounted for in simulations, where the chains are irreversibly bound to the substrate. In experiments, the synthesis technique will determine the chain grafting mechanism, while brushes synthesised through grafting-from approaches may indeed be covalently bound to the substrates, those synthesized through grafting-to approaches may be loosely adsorbed to the surface and more prone to detachment. For brushes where chain adsorption is electrostatic in origin, shearing leading to chain detachment can be followed by subsequent reattachment from a polymer-rich solution arising due to the detached chains, this is often referred to as the “self-healing” capacity of the polyelectrolyte-anchoring approach.¹¹⁸ DPD simulations of sheared bilayers in the μVT ensemble where chain detachments were introduced in a controlled manner show that the detached chains are expelled from the brush into the overlap zone under shear inhibiting mutual brush interpenetration and hence reducing the measured friction.^{104,152}

Another discrepancy arises because simulations are usually carried out at a constant number density and substrate separation which would correspond to the thermodynamic NVT ensemble at equilibrium, whereas in experiments, bilayers are sheared at a fixed normal load and the overall density may in fact change with increased load.⁹⁸ Goujon *et al.* attempt to take this discrepancy into consideration by performing the bilayer shearing simulations at a constant chemical potential (μVT ensemble) as described in Sec. III D.^{149,211} Furthermore, as pointed in Sec. II F, in experiments, isothermal conditions are not necessarily ensured across the sheared bilayer due to viscous heating effects in the overlap region, but rather, expected only for the substrates, this may promote the use of thermostating schemes that apply a thermostat only on the explicit wall beads but not the brush or solvent beads for comparison to experimental data.^{172,180}

Due to all the aforementioned challenges, many computational studies aim for a qualitative rather than exact agreement with experimental results.

It is important to note, however, that even qualitatively, there are stark differences between some simulation predictions as presented in Sec. III and experimental outcomes. For instance, it is

well established from many experiments of sheared PBBs immersed in solvents of varying quality that the higher the solvent quality the lower the observed friction coefficient.^{8,55,72,73,76,77,82} For example, Müller *et al.* performed shear experiments of PLL-g-PEG bilayers immersed in solvents of decreasing quality (water, methanol, ethanol, and 2-propanol) where the exact degree of areal solvation was determined from the difference between the wet and dry adsorbed masses obtained from QCM-D and OWLS measurements, respectively. The obtained friction coefficient was found to decrease with increasing degree of solvation of the brushes.⁵⁵ All these experiments are in contrast to simulation results (e.g., Fig. 4), which show the opposite trend, attributed to reduced interpenetration between the brushes as described in Sec. III B.

Furthermore, experimentally, a much lower friction is usually observed for charged brushes when compared to neutral ones at similar grafting densities,¹¹⁸ in contrast to simulation results which suggest that the friction is of the same order of magnitude for both cases, with the charged brushes generally exhibiting a higher friction under most conditions. It is difficult to isolate the effects of electrostatic interactions experimentally and any comparison will likely involve a change of polymer species.

In practice, these clear qualitative discrepancies point to the fact that the current simulation approaches are missing some key ingredient controlling the physics of PB friction and finding the solution to this conundrum a particularly interesting problem.

B. Effect of brush thickness and chain architecture on friction

We now turn to another important area in which further developments are needed to enable simulations to be bridged with experiments, therefore providing a route to adopt molecular simulations as a design tool for the next generation of solutions for friction control based on polymer brushes. In simulations, we have precise, and individual, control of chain lengths N , grafting densities σ_g , chain architectures, charge fraction, or stiffness of the chains composing the brushes; however, experimentally, achieving such strict control is not as straightforward and may involve a change of synthesis technique, polymer species, or even characterization methods. For instance, “grafting-to” approaches allow significant control over the adsorbed chain architectures and thus allow easier characterization of the molecular parameters of the brush, but due to increased steric repulsion, it becomes difficult to prepare dense brushes composed of long chains when compared to “grafting-from” approaches, which themselves would then suffer from weaker control over the polydispersity and chain architecture. Furthermore, it is not possible to obtain the grafting density directly through measurements, but rather it is usually estimated through characterization of the dry brush thickness (via VASE) or adsorbed mass (via OWLS) of the chains along with prior knowledge of the grafted polymer species.^{73,78,90}

Shear experiments of PBBs where the molecular parameters of the brushes are varied over a wide range for the same grafted polymer species are quite rare. That being said, significant efforts have been made to isolate the effect molecular parameters on friction using both “grafting-to”^{71,74} and “grafting-from”^{8,78}

approaches. The experimental data suggest that there is a decrease in the friction coefficient μ with increasing brush thickness at moderate loads.⁸ What is less clear is the particular dependence on degree of polymerization N or grafting density σ_g as an increase in either should lead to an increase in brush thickness. To this end, Perry *et al.* have performed shear experiments on PLL-g-PEG brushes with different grafting ratios as well as lengths of PEG side chains, which suggest a decrease in friction with an increase in either N or σ_g , within the regime ($0.5 < L/2R_g < 1$) approaching the mushroom-to-brush transition ($L \approx R_g$).⁷¹ On the other hand, Klein *et al.* found that the brush thickness had little effect on μ when comparing highly dense poly((2-(methacryloyloxy)ethyl)phosphorylcoline) (pMPC) brushes synthesized through surface-initiated atom transfer radical polymerization (SI-ATRP).¹⁰ More recently, Benetti *et al.* have conducted experiments comparing PEOXA brushes composed of linear and cyclic chain architectures at different grafting densities in the range of 0.05–0.37 chains/nm². They confirm the finding of decreased friction for thicker brushes that are due to a higher grafting density but also find greatly reduced friction for cyclic compared to linear bilayers over a wide range of applied loads as can be seen from the AFM measurements in Fig. 10(a), where we see that with increasing contact pressure, linear bilayers showed a monotonic increase in μ , whereas cyclic bilayers in fact showed a slight decrease. The authors attribute this enhanced lubricity of cyclic brushes to their greater steric repulsion leading to reduced bilayer interpenetration under compression [Figs. 10(b) and 10(c)] as well as an increased measured hydration than that of linear brushes.¹²¹

The most complete theoretical description of sheared bilayers is laid out in the instructive review by Kreer,⁴⁷ which has served as a major inspiration for the present review. Kreer combines the scaling approaches^{92,197} of Sec. III C for the shear force with their own scaling theory for compressed bilayers²¹² to obtain scaling

relations as a function of molecular parameters (N, σ_g) of the brushes for lateral chain extension, viscosity, and friction coefficient μ for both melt and semidilute bilayers under strong compression. For everyone's convenience, Kreer has calculated all of the exponents and compiled the predictions for both the Newtonian and shear-thinning regimes in Table 1 of Ref. 47. The result for the friction coefficient of a SD bilayer $\mu^{(sd)}$ is as follows:⁴⁷

$$\mu^{(sd)} \sim \begin{cases} N^{-0.77} \sigma_g^{-0.77} D^{2.77} \dot{\gamma} & (W \ll 1), \\ N^{-1.82} \sigma_g^{-0.91} D^{2.40} \dot{\gamma}^{0.54} & (W \gg 1), \end{cases} \quad (29)$$

As can be observed from exponents, the theory agrees with experiments on the fact that friction decreases with increasing brush thickness through increases in either the chain length N or grafting density σ_g or with decreasing wall separation (increasing pressure) for a fixed system, which is in line with the simulation results of Sec. III B.

In the MD study by Galuschko *et al.* presented earlier in Sec. III B, it was observed that bilayers with an implicit DPD solvent exhibited high μ that indeed decreased with increasing σ_g , whereas the opposite trend (low μ that increases with σ_g) was observed for bilayers with explicit solvent dimers. This result is not as surprising as it may seem. Because for the explicit solvent treatment, the total number density is kept constant across different brushes by removing mobile solvent particles in order to increase the number of grafted (immobile) chains. Both cases (implicit and explicit) are identical only at the highest σ_g when there are no more solvent particles and all of the beads belong to grafted chains, as illustrated in Fig. 9(a). However, the difference in number density for all other points means the two solvent treatments are not strictly comparable. Again, we see a nontrivial effect of choosing certain coarse-graining.

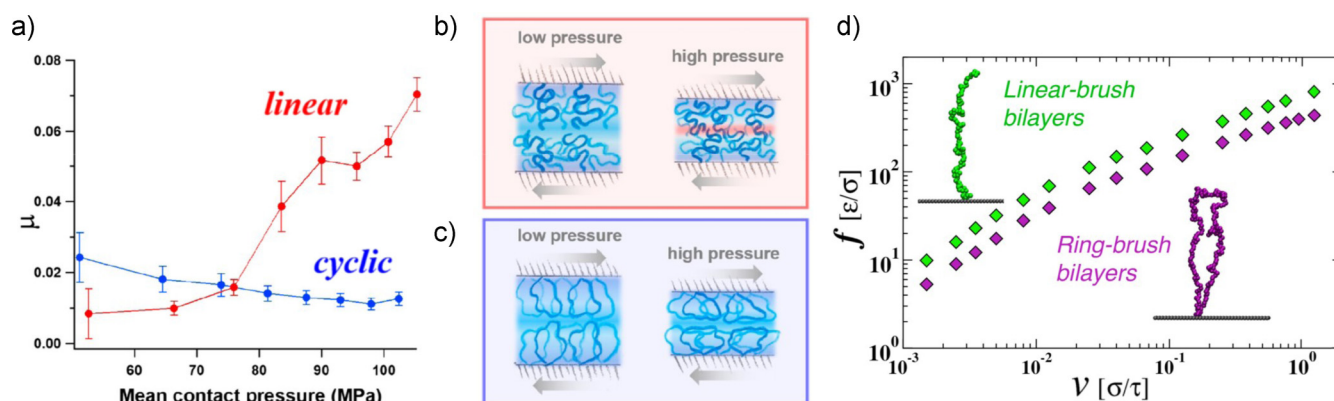


FIG. 10. (a) Experimental AFM results for the friction coefficient μ as a function of mean contact pressure for linear (red line) and cyclic (blue line) PEOXA brush bilayers grafted.¹²¹ (b) Schematic of linear PEOXA bilayers at low and high contact pressures. (c) Schematic of cyclic PEOXA bilayers at low and high contact pressures. (d) NEMD simulation results for friction force f as a function of shear velocity v for linear (green) and ring (cyclic) (purple) brush bilayers along with snapshots of single grafted chain conformations for both architectures.¹⁰⁹ Adapted with permissions from Divandari *et al.*, ACS Macro Lett. 7, 1455 (2018). Copyright 2018, American Chemical Society (Ref. 121); and A. Erbas and J. Paturej, Soft Matter 11, 3139 (2015). Copyright 2015, Royal Society of Chemistry (Ref. 109).

In the previous study, the simulated bilayers were all above the mushroom-to-brush transition (MBT) ($\sigma_g > 1.1\sigma_g^*$).⁹² On the other hand, Goicochea *et al.* used a DPD model with explicit solvent particles at a constant number density to study the effect of both chain length and grafting density on the friction coefficient of sheared bilayers that are around the MBT. The bilayers are composed of rather short chains ($N = 7 - 21$) and the number of grafted chains is varied over a wide range, covering the MBT for different chain lengths considered. The simulations are performed at a single shear rate ($\dot{\gamma} = 0.028$) and wall separation ($D = 7$) (DPD units). The results, reproduced in Figs. 9(c)–9(f), show a nonmonotonic behavior of μ with increasing σ_g , in particular, for bilayers of shorter chains, first a drastic decrease leading up to a clear minimum $\sigma_{g,min}$ followed by a shallow increase with greater σ_g . By varying N at constant σ_g [Fig. 9(f)], the authors observed an increase in μ for increasing chain length N to which they fit a scaling law $\sigma_g \sim N^{6/5}$, an outcome in disagreement with the predicted exponents of Eq. (29). Furthermore, the authors report a decrease in $\sigma_{g,min}$ with increasing chain length, which follows $\sigma_{g,min} \sim N^{-6/5}$ and matches theoretically predicted scaling for the critical grafting density σ_g^* ,⁴ suggesting to them that the minimum in friction observed occurs at the MBT ($\sigma_{g,min} = \sigma_g^*$).¹⁵¹

Similarly, Singh *et al.* have performed MD simulations employing the modified LJ pair interaction [Eq. (6)] with explicit solvent beads using interaction parameters that model PBBs in good solvent conditions.¹¹⁰ The temperature is maintained constant through a profile unbiased thermostating (PUT) velocity-rescaling scheme. In these simulations, the bilayers are composed of chains of length $N = 30$ and a range of grafting densities ($\sigma_g \approx 0.6 - 6\sigma_g^*$) with $\sigma_g^* \approx 0.025$ (LJ units). When comparing two brushes ($\sigma_g = 0.075, 0.015$) over a range of shear velocities but a constant wall separation ($D = 30$), the authors found that the higher density brush exhibited a higher friction coefficient μ . However, when μ was extracted for bilayers of different σ_g from the slopes of the shear vs normal stress curves obtained for a single velocity ($v_s = 0.001$) at different wall separations ($0.5 < d = D/2h < 1$), μ is found to decrease with increasing grafting density, within the range of σ_g explored [see Fig. 9(b)]. Additionally, the model used in this study incorporates a cosine angle potential (17) to study the effect of chain-stiffness, which was used to show that, for the range bending stiffnesses explored ($K = 0, 1, 2, 3$), the friction coefficient μ decreases with increasing persistence length L_p .¹¹⁰

More recently, Goicochea *et al.* have performed an extensive DPD study of the effect of grafting density and solvent quality on the tribology of bilayers composed of mixtures of two CG polymers immersed in solvent particles and free chains at a constant number density. The results are reported in physical units assuming a CG degree of three for a wide range of grafting densities ($\sigma_g \approx 0.1 - 1.2$ chains/nm²) covering the upper range of experimentally observed values. In agreement with the previous results, the friction coefficient is found to decrease with increasing grafting density as well as with increasing number of free chains in the solution for a given grafting density, in line with the predictions due to chain detachment of Sec. IV A 2. Interestingly, the authors find that the friction coefficient follows a scaling law that depends only on the solvent quality but not the brush composition or the

number of free chains and that mixed brushes may result in reduced friction compared to monochain brushes.²¹³

There have been only a few computational studies looking at bilayers composed of chains of an architecture other than linear. Notably, Yin *et al.* used a WCA potential and harmonic bonds with an implicit Langevin solvent to study loop (doubly-bound) bilayers at three grafting densities ($\sigma_g = 0.004, 0.014, 0.06\sigma^{-2}$).¹⁰³ As well as, Erbas and Paturej, who used a KG-BS model, also with an implicit Langevin solvent, to study cyclic (ring) bilayers at two, relatively high, grafting densities ($\sigma_g = 0.11, 0.25\sigma^{-2}$).¹⁰⁹ In both cases, the performance of loop/cyclic brushes is compared to linear ones with half the chain length and double the number of grafted chains to achieve a fair comparison at the same number density. Both studies found a markedly reduced interpenetration for cyclic or loop bilayers when compared to their linear counterparts, in line with the observations of Benetti *et al.* [Figs. 10(b) and 10(c)]. The difference in interpenetration is more pronounced for moderate grafting densities and for the lower range of shear velocities simulated, which may be close to those imposed in experiments, and almost disappears at higher shear velocities $v > 0.01\sigma/\tau$ when the chains are fully stretched regardless of their architecture.¹⁰⁹

Both studies opt to obtain the shear and normal stresses directly from the forces on the explicit wall atoms divided by the sheared wall area and not from the virial stress tensor. Unusually, Yin *et al.* observed that both the normal and shear stresses between loop bilayers and linear bilayers were of the same order,¹⁰³ whereas Erbas and Paturej found the normal and shear stresses [Fig. 10(d)] for linear bilayers to be a factor of two greater than the corresponding cyclic bilayers for all shear velocities considered and that only the forces per chain were equivalent for the two chain architectures.¹⁰⁹ As a result, both studies reported friction coefficients, μ , that were largely independent of the grafted chain architecture.

Interestingly, Erbas and Paturej found the number of beads in the overlap zone to be greater and the number of binary collisions to be smaller for cyclic compared to linear bilayers, leading the authors to conclude that the stretched cyclic chains adopt double stranded conformations, partially shielding the collisions while maintaining their presence in the overlap zone.¹⁰⁹

It should be mentioned that Yin *et al.* did manage to find a slight reduction in the friction coefficient when comparing loop and linear strongly compressed bilayers ($0.21 < D/2h < 0.53$) at the highest grafting density $\sigma_g = 0.06\sigma^{-2}$ and lowest velocity $v = 0.002\sigma/\tau$ considered, where the normal stresses remained equal, but the shear stress is slightly reduced for loop bilayers.¹⁰³ Additionally, this study explores more grafting densities at a wider range of relative wall separations $D/2h = 0.1 - 0.9$ than the study concerned with cyclic (ring) brushes,¹⁰⁹ which looks at only a single wall separation for each bilayer but a wide range of velocities. The simulation results reveal a strong dependence of friction coefficient μ on grafting density σ_g as well as wall separation D regardless of the grafted chain architecture, with μ decreasing with increasing σ_g or decreasing wall separation D in good agreement with Eq. (29), except for the highest grafting density considered ($\sigma_g = 0.06$) (LJ units) where an increase in friction was observed due to a glassy transition at very strong compressions ($d < 0.2$), where the scaling theory would not apply.

Canchaya *et al.* investigated the rheology of single brushes composed of chains of linear and Y-shaped architectures in contact

with a melt of free chains using a semirealistic DPD model that is parameterized through the recently developed technique of statistical trajectory matching (STM),²¹⁴ which uses Bayesian optimization to determine the DPD parameters to maximize the likelihood that the CG model will reproduce trajectory of an atomistic simulation. The Y brushes exhibited more steplike density profiles due to them having double the number of polymer arms and higher friction than their linear counterparts for simulated shear velocities of ($v = 5 - 20$ m/s).²¹⁵

Although the previous studies concentrated on grafted but otherwise free chains, Singh *et al.*¹¹¹ also performed simulations using the same model as Ref. 110, but this time including explicit cross-linking chains that are inserted randomly into a preformed brush. The cross-linking chains are composed of beads that are connected with each other and to the cross-linked grafted chains at each end using a harmonic bond potential [Eq. (12)], allowing them to vary both the degree of cross-linking (number of cross-linkers) as well as the length of cross-linkers in the brushes independently. The simulations are performed for a single cross-linked brush ($N = 50$, $\sigma_g = 0.075 \approx 5\sigma_g^*$) sheared against an explicit wall. The results show that the friction coefficient μ increases with the degree of cross-linking and decreases with increasing length of cross-linkers, meaning that the more gel-like the brush becomes the higher the observed friction. The authors later confirm that these predictions are in good agreement with experiments using PGMA brushes and hydrogels.⁸⁷ The findings of these studies can be linked to the recently developed technique by Simić *et al.* for controlling the friction of hydrogels through oxygen inhibition of cross-linking during the synthesis. By carefully controlling the amount of oxygen available, they are able to control the degree of cross-linking close to the surface of the hydrogel and thus produce highly tunable, lubricious, and dense brushy surfaces.²¹⁶

In summary, while current CG models can give insight into particular aspects of polymer brush tribology as well as aide in the development of theoretical descriptions, they are still insufficient for the purpose of being used as a design tool for lubricious surfaces. However, with growing computational power, simulations will be able to access denser brushes composed of longer chains, sheared at slower rates and using CG models that incorporate more of the local chemistry of the polymers. This should eventually close the gap between experimental systems and those accessible through simulations, opening the door for collaborative efforts and combined computational and experimental studies.

V. CONCLUSION

Molecular simulations of the tribology of polymer brushes have demonstrably provided access to experimentally unmeasurable quantities and have played a key role in the development of theoretical descriptions and scaling laws for the shear response.

In order to simulate large enough systems at the required timescales, coarse-graining is usually needed. In this review, the most common coarse-grained models and thermostating strategies employed for NEMD simulations polymer brushes have been presented along with their various strengths and limitations.

Recently developed and underutilized but potentially promising models and thermostating strategies have been highlighted for

future use as well as better comparison to experiments along with examples of efforts to bridge the gap between simulated and experimental systems.

The key results of CG NEMD simulations looking at the effects of compression, shear velocity, solvent quality, electrostatic interactions, chain length, grafting density, and chain architecture on the tribology of PBBs have been surveyed, along with the conformations and shear response of the individual components of the system that are the grafted chain, solvent, counterion, salt, and/or free chain beads.

Since, despite, and partly because of, coarse-graining, it is challenging to perform shear simulations of bilayers in conditions that correspond exactly to those of experiments of sheared bilayers. In experiments, substrates are often curved and not flat as in simulations; furthermore, experimental bilayers are usually composed of chains of a higher degree of polymerization, grafted at a lower surface density and sheared at slower rates than those generally accessible in simulations. Nonetheless, shear rates in simulations have begun to coincide with the upper range of experimental values achievable only for long simulations of strongly compressed bilayers.

Beyond the issues of scale, some of the well-established predictions of current CG models of polymer brush bilayers seem to qualitatively disagree with experimental observations, in particular, pertaining to the effect of solvent quality and charged chains on the friction coefficient. The former sees the opposite behavior from that observed experimentally, while the latter is unresolved as real charged bilayers may involve additional mechanisms such as hydration lubrication which are not yet accounted for in simulations. Unfortunately, simulating a more detailed solvent is associated with a huge computational effort.

This brings into question the currently utilized solvent models and accompanying thermostats and whether they are suitable to capture the correct hydrodynamics of the confined fluid. In fact, applying a thermostat on the fluid, as is most commonly adopted in simulations, may suppress viscous heating by imposing isothermal conditions during shear. Instead, when simulating the slow shear rates comparable to experiments, it may be useful to apply a thermostat only to the confining walls and not on the fluid itself accounting for viscous heating effects and allowing a heat flux through the walls as would be the case experimentally.

Further computational studies are required to resolve the discrepancies identified between computational and experimental observations and hence should aim to simulate experimentally imposed velocities and obtainable grafting densities; additionally, more data are necessary to test the theoretical scaling descriptions, and thus, future studies should also look to simulate bilayers with a systematic variation of the molecular parameters, wall separations, and shear velocities spanning several orders of magnitude; both of which are quite computationally demanding objectives. However, the increasing availability of computational resources should allow them as well as more representative CG models for PBs to be explored and further developed.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Ethics Approval

Ethics approval is not required.

Author Contributions

Mohamed A. Abdelbar: Conceptualization (equal); Data curation (equal); Methodology (equal); Writing – original draft (equal). **James P. Ewen:** Supervision (equal); Writing – review & editing (equal). **Daniele Dini:** Supervision (equal); Writing – review & editing (equal). **Stefano Angioletti-Uberti:** Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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