

# 1 Simulations details

## 1.1 Description

VWF was modeled as chain of spherical beads. The polymer was simulated with a Brownian dynamics simulations where the bead positions were updated based on numerical integration of the following discretized Langevin equation [1][2][3][4]

$$r_i(t + \Delta t) = r_i(t) + \left( \dot{\gamma} z_i \mu_0^{-1} \mu_{ii} \cdot \hat{x} + k_B T \frac{d\mu_{ii}^{zz}}{dz} \hat{z} - \sum_{j=1}^N \mu_{ij} \cdot (\nabla_{r_{ij}} U_m(t) + \nabla_i U_w(t)) + \xi_i(t) \right) \Delta t \quad (1)$$

Here,  $r_i(t)$  represents the position of bead  $i$  at time  $t$  and  $r_i(t + \Delta t)$  is the position of bead  $i$  at the next time step. The simulation is given a time step  $\Delta t = 2 * 10^{-4} \tau$ , with  $\tau$  being the characteristic bead diffusion time  $\tau = \frac{6\pi\eta a^3}{k_B T}$  ( $\eta$  is the viscosity,  $a$  is the bead radius,  $k_B$  is the Boltzmann Constant and  $T$  is temperature).

The first term,  $\dot{\gamma} z_i \mu_0^{-1} \mu_{ii} \cdot \hat{x}$ , accounts for the velocity due to the shear flow and is dependent on the specified shear rate  $\dot{\gamma}$ , the bead height above the surface  $z_i$ , the inverse of the Stokes mobility of a sphere  $\mu_0$ , and the corresponding component of the hydrodynamic mobility tensor  $\mu_{ii}$ . The velocity is in the direction of flow ( $\hat{x}$ ). The stokes mobility of a sphere is defined as  $\mu_0 = \frac{1}{6\pi\eta a}$ .

The last term,  $\xi_i(t)$ , represents the random velocities from the Brownian motion, which satisfies the fluctuation dissipation theorem

$$\langle \xi_i(t) \xi_j(t') \rangle = 2k_B T \mu_{ij} \delta(t - t') \quad (2)$$

The mobility matrix  $\mu_{ij}$  accounts for the hydrodynamic interactions between the  $i^{th}$  and  $j^{th}$  bead. For all surface tethered molecules, the hydrodynamic interaction is approximated as the Rotne-Prager-Blake tensor which accurately describes both the hydrodynamic interactions between beads and the surface [5][6]. The explicit terms of the mobility tensor can be found in Von Hansen et al.[7]. For the non-tethered cases, the Rotne-Prager-Yamakawa tensor was used for the mobility matrix which can be found explicitly written in Wajnryb et al. [8]. The hydrodynamic tensor was updated every 100 time steps.

$k_B T \frac{d\mu_{ii}^{zz}}{dz}$  is a correction for the divergence of the diffusion tensor resulting from the no-slip condition at the surface and is defined as [7]

$$k_B T \frac{d\mu_{ii}^{zz}}{dz} = \mu_0 \left( \frac{9a}{8z_i^2} - \frac{3a^3}{2z_i^4} \right) \quad (3)$$

Here,  $z_i$  is defined as the height of the  $i^{th}$  bead above the surface,  $a$  is the radius of a bead, and  $\mu_0$  is

the mobility of a sphere. This term is not included in the case where the surface is absent.

The potential energy of each bead is based on two terms,  $U_w(z_i(t))$  and  $U_m(t)$ . The first term,  $U_w$ , is the hard core repulsion due to the wall based on the height from the surface  $z$  of the  $i^{th}$  bead at time  $t$ . This potential is not included in the case where the surface is absent. At a given time, this is specified as [4]

$$U_w(z_i) = \begin{cases} 2\pi k_B T 1.5a(4/(5z_i))^{10} - (3/(2z_i)^4 + (3/5)) & \text{if } z_i < 1.5a \\ 0 & \text{if } z_i > 1.5a \end{cases} \quad (4)$$

The potential energy term  $U_m(t)$  is interactions between monomers and includes a Lenard Jones interaction, FENE potential connecting adjacent beads, and the additional self-associating interaction.

$$U_m(t) = U_{LJ} + U_{fene} + U_{SA} \quad (5)$$

The first potential  $U_{LJ}$  is the Lennard-Jones term which applies a non specific potential between all beads defined as

$$U_{LJ}(r_{ij}) = u_{LJ} \left[ \left( \frac{2a}{r_{ij}} \right)^{12} - 2 \left( \frac{2a}{r_{ij}} \right)^6 \right] \quad (6)$$

Here,  $r_{ij}$  is the distance between bead  $i$  and  $j$ ,  $a$  is the bead radius, and  $u_{LJ}$  is the interaction strength. The potential is set to zero for any beads farther than  $24a$  apart. For the Lennard-Jones model, the interaction parameter is set to  $u_{LJ} = 2.08k_B T$ , with a radius of  $a = 80$  nm. For the revised model, the interaction strength was also set to  $u_{LJ} = 2.08k_B T$  based on matching experimental data for the shear stress required for half extension given a bead radius of  $a = 14$  nm. For the uncollapsed polymer, this is set to the  $\Theta$ -point  $u_{LJ} = 0.314k_B T$ , where the beads neither repel nor attract each other with the bead radius set to  $a = 3.7$  nm.

To keep successive monomers together, a finitely extensible nonlinear elastic model or FENE potential  $U_{FENE}$  was used. Due to the high flow used, the FENE spring constant is set at  $H_{FENE} = 800 k_B T/a^2$  and a maximum bond length of  $Q_{max} = 1.5 * 2 * a^{1/6}$  [9]

$$U_{FENE} = \frac{-1}{2} H_{FENE} Q_{max}^2 \sum_i^{N-1} \text{Log} \left[ 1 - \left( \frac{r_{i,i+1} - 2a}{Q_{max}} \right)^2 \right] \quad (7)$$

The first bead is tethered to the surface by a bond with its center point  $2a$  above the surface.

The next term is the self associating term which allows bonding between non-successive beads [10] and applied for the self-associating model. A FENE potential is used with a spring constant of  $H_{rxn} = 300k_B T/a^2$  and defined as

$$U_{rxn} = \frac{-1}{2} H_{rxn} Q_{max}^2 \sum_{i,j}^N \Omega(i,j) \text{Log} [Q_{max}^2 - (r_{i,j} - 2a)^2] \quad (8)$$

$$\Omega(i,j,t) = \begin{cases} \begin{cases} 1 & \Xi < P_{on} \\ 0 & \Xi > P_{on} \end{cases} & \text{if } \Omega(i,j,t - \Delta t) = 0 \\ \begin{cases} 1 & \Xi < P_{off} \\ 0 & \Xi > P_{off} \end{cases} & \text{if } \Omega(i,j,t - \Delta t) = 1 \end{cases} \quad (9)$$

This potential is dependent on bead bonding which occurs through a monte carlo simulation updated based on  $\Omega(i,j,t)$  with  $\Xi$  being a random number uniformly distributed between zero and one. Each bead was allowed to form up to 2 bonds with other beads and could not self-associate with nearest neighbors. The order in which the potential bonds were formed and broken was randomized for every time the binding was updated, which occurred every 10 time steps. The probability of bond formation is defined by [11]

$$P_{on}(\Delta t) = 1 - \exp(-k_{on} V_{overlap} \Delta t / V_{norm}^2) \quad (10)$$

Here,  $k_{on}$  is a free parameter and  $V_{overlap}$  is the average volume overlap between two probability spheres centered around the two beads of interest with radius = 1.1a over the 10 time step period.  $V_{norm}$  is the possible binding volume of the probability spheres defined as

$$V_{norm} = \frac{4}{3} \pi (1.1a)^3 - \frac{4}{3} \pi (0.94a)^3 \quad (11)$$

Bounds of 1.1a was chosen as the farthest distance two beads could form a bond based on previous self association models[12]. An inner sphere of 0.94a was empirically found as the minimum distance for overlap based on the hard core repulsion in the Lennard-Jones potential.

The off rate is based on a bell-evans model and modeled as a basic unbinding with no probability to rebind within the time step.

$$P_{off}(\Delta t) = \exp\left(-\int_0^{\Delta t} k_{off}(t) dt\right) \quad (12)$$

$$k_{off}(t) = k_{off}^0 \exp(f(t)/f_b)$$

The free parameters include off rate is based on a bell-evans model with  $k_{off}^0$  being the intrinsic off rate that is a ,  $f_b$  is the force scale, and  $f(t)$  is the force applied across the SA bond at a given time step.

## References

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