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]

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

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 τ being the characteristic bead diffusion time $\tau = \frac{6\pi \eta a^3}{k_B T}$ (η 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 μ_0, and the corresponding component of the hydrodynamic mobility tensor μ_{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

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

The mobility matrix μ_{ij} accounts for the hydrodynamic interactions between the ith 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]

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

Here, z_i is defined as the height of the ith bead above the surface, a is the radius of a bead, and μ_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 ith 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]

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

The potential energy term $U_m(t)$ defines the interaction potential between monomers. The potential is based on non-specific a Lennard-Jones interaction between all beads and a FENE potential connecting adjacent beads.

$$U_m = U_{LJ} + U_{fene} \tag{5}$$

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

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

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 $u_{LJ} = 2.08k_BT$, with a radius of a = 80 nm. For the revised model, the interaction strength was also set to $u_{LJ} = 2.08k_BT$ 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 Θ-point $u_{LJ} = 0.314k_BT$, 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 $H_{FENE} = 800\ k_BT/a^2$ and a maximum bond length of $Q_{max} = 1.5 * 2 * a\frac{1}{2^6}$ [9]

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

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

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