Supporting Information

Stretch and Breakage of Wormlike Micelles Under Uniaxial Strain: A Simulation Study and Comparison With Experimental Results

Taraknath Mandal and Ronald G. Larson*

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI-48109, USA.

Calculation of micelle radius: We employed the *Umbrella Sampling* method to calculate the micelle radius under *no external stress*. Note that the box length along the micelle axis may not be equal to the effective micelle length when there is *no external stress,* since in that case the micelle may adapt a curved configuration. Thus, in the absence of an external force, we used an umbrella sampling method to calculate the number of surfactants per unit length. This method calculates the free energy as a function of number of surfactants in a prechosen small region (small enough to be nearly straight) which adapts a cylindrical configuration during equilibration (**figure S1(a)** below). The details of the method can be found in our recent paper (**Phys. Rev. Lett. 2018, 121, 038001**). From the minima of the free energy (**figure S1(b)** below) we got the number of surfactant beads (which is proportional to the number of surfactant molecules) in this cylindrical region at equilibrium. Thus, the number of surfactants N_d in the cylindrical region is related to the length of this region d by $N_d = \rho\pi r^2 d$, where ρ is the number of surfactant molecules per unit micellar volume, and r is the micelle radius. We calculated ρ using the micelle radius $r \sim 2.5$ nm at $R = 0$ since this radius is relatively easier to measure from the trajectory as the micelle surface is very much uniform and the surface boundary is well defined in the absence of any hydrotrope. We used visual molecular dynamics (VMD) software to measure the distance between two beads located on opposite sides of the micelle along the radial direction, which is around ~4.5 nm when averaged over a trajectory. The MARTINI bead diameter is 0.47 nm. Thus, the micelle effective diameter is ~4.97 nm at $R = 0$. Hence the micelle radius at $R = 0$ is approximated as 2.5 nm. With increasing R, the micelle becomes longer and thinner. We assume that that the volumetric density of the surfactants in the micelle (number of surfactants per unit volume of micelle) does not change with R (although there might be slight change in the headgroup density in the surface region because of

some change in hydrotrope adsorption with increased micelle length). We calculated N_d/d for different values of R using the umbrella sampling method. Using these values and ρ estimated at R = 0 as mentioned above, we calculated radius of the micelle for different hydrotrope concentrations under no external stress.

However, even at the *lowest imposed stress* (~9 bar) in our simulations, the micelle adapts a straighter cylindrical configuration, and the length of the micelle is then just the length of the simulation box along the Z direction after it has adjusted to the imposed stress (**figure S1(c)** below). Thus, with imposed stress, the number of surfactants in the micelle N is related to its length L by $N = \rho\pi r^2 L$, where ρ is the number of surfactant molecules per unit micellar volume, and r is the micelle radius. So, from the known N, L and ρ we calculated the micelle radius r under different values of the *external stress*. In **figure S1(d)** below, we compare the micelle length obtained from the box length along Z direction and that obtained from the WHAM calculations for different values of R in the presence of lowest imposed external stress of ~9 bar. As can be seen from the figure, micelle length obtained from the two method are very similar.

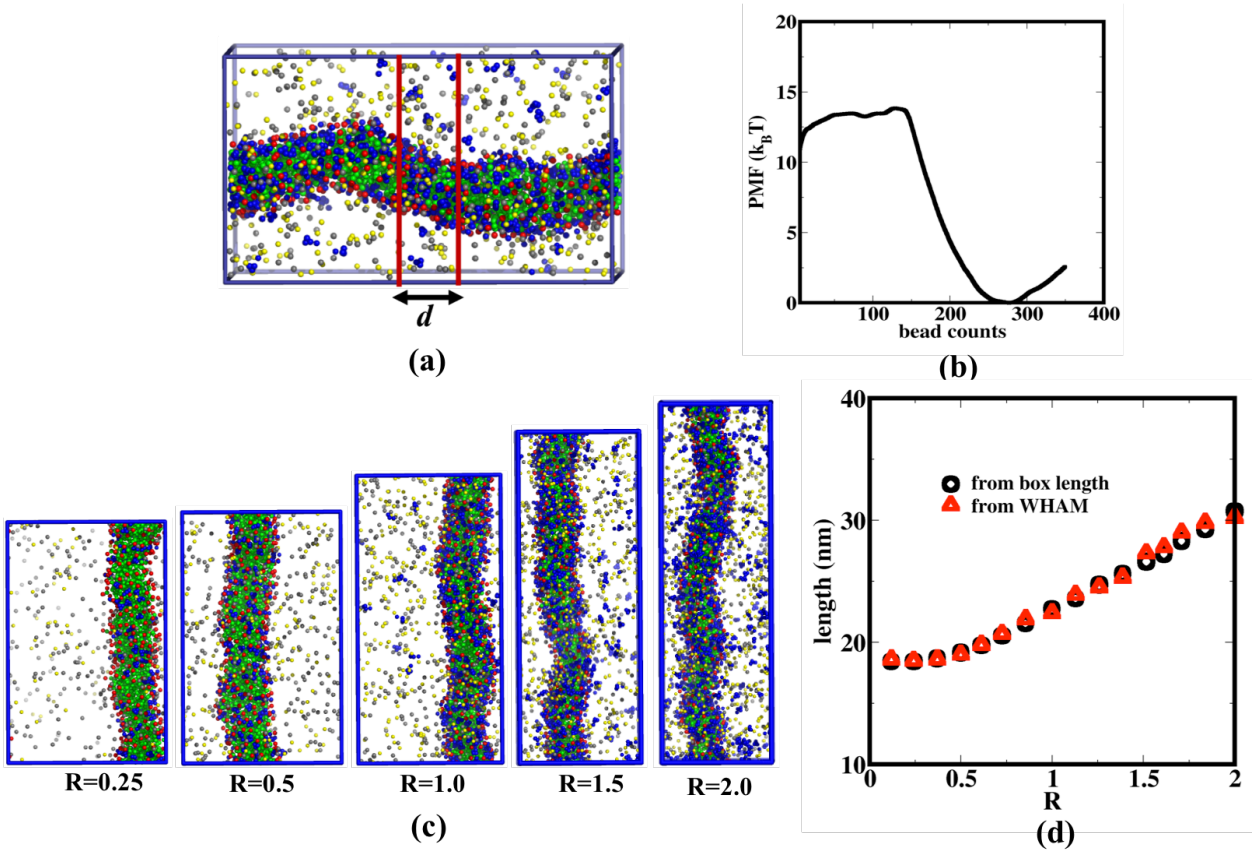

Figure S1: (a) Snapshot of a micelle under a bias potential that controls the number of surfactants in small prechosen region of width d. (b) The PMF as a function of number of surfactant beads in the region of width d. (c) Five representative snapshots of the micelle in the presence of lowest imposed stress (~9 bar) for different values of R. (d) comparison of the micelle length obtained from WHAM calculations and obtained from the box length along Z direction at lowest imposed stress (~9 bar).

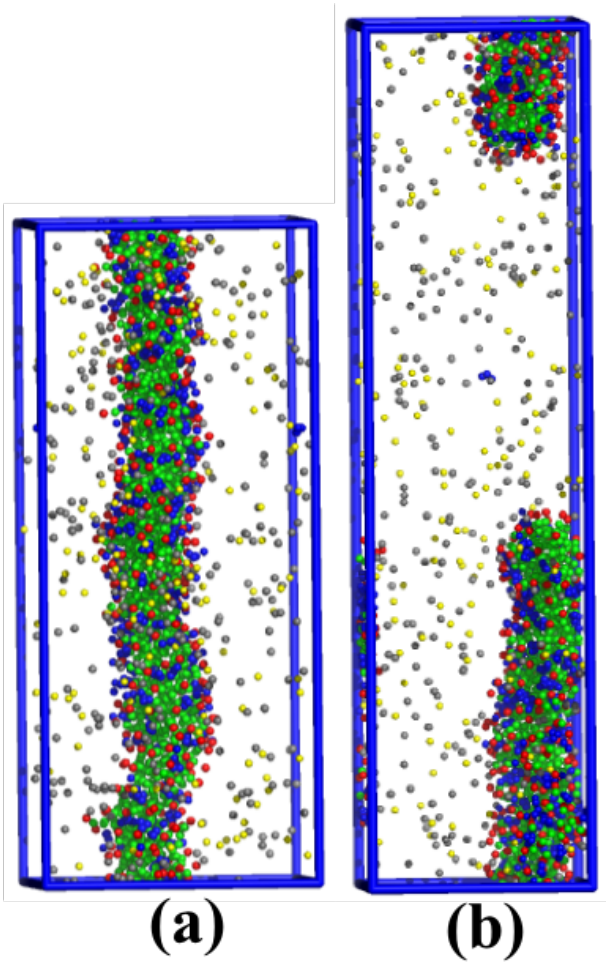

Figure S2: Typical snapshots of the micelle at R=0.5 (a) before breaking and (b) just after breaking.

Typical GROMACS input file (.mdp file) for simulation of a micelle under external strain

```
integrator              = md
dt                      = 0.02
nsteps                  = 50000000
nstcomm                 = 100

nstxout                 = 000
nstvout                 = 000
nstfout                 = 000
nstlog                  = 50000
nstenergy               = 50000
nstxtcout               = 50000
xtc_precision           = 100

nstlist                 = 10
ns_type                 = grid
pbc                     = xyz
rlist                   = 1.4

coulombtype             = Shift
rcoulomb_switch         = 0.0
rcoulomb                = 1.2
epsilon_r               = 15

vdw_type                = Shift
rvdw_switch             = 0.9
rvdw                    = 1.2

tcoupl                  = v-rescale
tc-grps                 = system
tau_t                   = 1.0
ref_t                   = 298


Pcoupl                  = berendsen
Pcoupltype              = semiisotropic
tau_p                   = 3.0
compressibility         = 3e-4 3e-4
ref_p                   = 1.0 -5.58

gen-vel                 = yes
gen-temp                = 298
gen-seed                = 400

constraints             = none
constraint_algorithm    = Lincs
continuation            = no
lincs_order             = 4
lincs_warnangle         = 30
```