Supporting Information for:

DPD Simulations of Anionic Surfactant Micelles: A Critical Role for Polarisable Water Models

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1 A note on units

As discussed in the main article, when the degree of coarse-graining $N_{\mathrm{C}} = 4$ the Drude particle charge is chosen to be $q^{N_{\mathrm{C}}=4} = 0.6e$. In practice, charges are input into LAMMPS in reduced lennard-jones units. The reduced charge is calculated using $q^*= q/\sqrt{4\pi\epsilon_0 r_{\mathrm{C}} k_B T}$, where q is the charge in real units, ϵ_0 is the vacuum permittivity, r_{C} is the length scale conversion, k_B is the Boltzman constant, and T is the temperature.

In real units, the dipole moment $\mathbf{M}^2_{\mathrm{Real}} = [\sum q_{\mathrm{Real}}\mathbf{r}^{\mathrm{sep}}_{\mathrm{Real}}]^2 = 4\pi\epsilon_0 r^3_{\mathrm{C}} k_B T[\sum q^*\mathbf{r}^{\mathrm{sep}}_{\mathrm{DPD}}]^2 = 4\pi\epsilon_0 r^3_{\mathrm{C}} k_B T\mathbf{M}^2_{\mathrm{DPD}}$ (where $\mathbf{r}^{\mathrm{sep}}$ is the separation between the two Drude beads in a particle i.e. $\mathbf{r}^{\mathrm{sep}} = \mathbf{r}^+_k - \mathbf{r}^-_k$).

The dielectric constant of the solvent ϵ_r is calculated using the fluctuations of dipole moment $\mathbf{M}$

$$\frac{\epsilon_r}{\epsilon_s} = 1 + \frac{\langle \mathbf{M}^2\rangle - \langle \mathbf{M}\rangle^2}{3\epsilon_0\epsilon_s V k_B T} \tag{1}$$

where V is the volume of the simulation box and ϵ_s is the background relative permittivity. Substituting in the relation for the dipole moment and that $V_{\mathrm{Real}} = V_{\mathrm{DPD}} r^3_{\mathrm{C}}$, produces the relation in reduced units

$$\frac{\epsilon_r}{\epsilon_s} = 1 + \frac{4\pi}{3\epsilon_s V_{\mathrm{DPD}}}[\langle \mathbf{M}^2_{\mathrm{DPD}}\rangle - \langle \mathbf{M}_{\mathrm{DPD}}\rangle^2]. \tag{2}$$

This implies that keeping the reduced charge the same when changing the coarse graining from $N_{\mathrm{C}} = 4$ to $N_{\mathrm{C}} = 2$, will result in the same dielectric constant. Since the reduced charge is dependant on the conversation factor r_{C}, this implies a change in the charge in real units. Hence the reduced charge used in all simulations (for both coarse-graining $N_{\mathrm{C}} = 2$ and $N_{\mathrm{C}} = 4$), is $q^* = 5.33$, which corresponds charge in real units $q = 0.6e$ ($N_{\mathrm{C}} = 4$) and $q = 0.534e$ ($N_{\mathrm{C}} = 2$).

2 Number of beads/molecules per simulation box.

Concentration (wt. %)	Number of Surfactants	Number of Water Beads
2.5	150	23250
5	299	22505
7.5	448	21760
10	596	21020

(a) Mao *et al*[1] parameterisation

Concentration (wt. %)	Number of Surfactants	Number of Water Beads
2.5	75	23400
5	151	22792
7.5	227	22184
10	304	21568

(b) Anderson *et al*[2] parameterisation

Table S.1: The number of surfactant molecules and water beads for each simulation case.

References

[1] R. Mao, M.-T. Lee, A. Vishnyakov and A. V. Neimark, *J. Phys. Chem. B*, 2015, **119**, 11673–11683.

[2] R. L. Anderson, D. J. Bray, A. Del Regno, M. A. Seaton, A. S. Ferrante and P. B. Warren, *J. Chem. Theory Comput.*, 2018, **14**, 2633–2643.

3 Eccentricity example

Fig. 8 in the main article provides the micelle eccentricity as a function of aggregate size, while Fig. 9 provides an illustration of the fluctuation in shape of larger micelles ($N = 90$). Here we provide Fig. S1, to show the instantaneous eccentricity calculated over the simulation time. We observe a significant fluctuation, highlighted by the error bars provided on Fig. 8 in the main article.

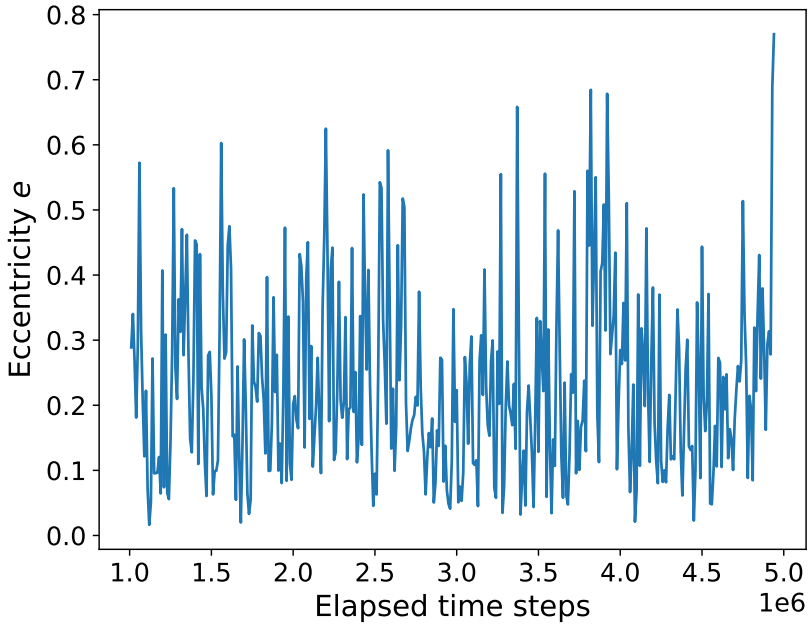

Fig. S1: Eccentricity as a function of time step for $N = 90$ micelles in the case of the polarisable water model.

4 Example LAMMPS scripts

4.1 Example for 10% SDS in polarisable water

```
variable T    equal 1.0
variable rc   equal 1.24

units        lj
boundary     p p p
atom_style   full
bond_style harmonic
angle_style harmonic
dimension    3
newton       on
comm_modify  vel yes
neigh_modify delay 0 every 1 check no
kspace_style pppm 1.0e-4

variable     L equal 20.0
region       simBox block 0 ${L} 0 ${L} 0 ${L}
create_box   7 simBox bond/types 4 angle/types 2
extra/bond/per/atom 2  extra/special/per/atom 2 extra/angle/per/atom 1
molecule sur Surfactant.data
molecule wat Water.data
create_atoms 0 random 304 12456 simBox mol sur 2348
create_atoms 0 random 21568 12456 simBox mol wat 2348

mass 1 0.6666
mass 2 1.0000
mass 3 1.0000
mass 4 1.0000
mass 5 1.0000
mass 6 0.1666
mass 7 0.1666
bond_coeff 4 256.0 0.35
angle_coeff 2 0.5 0.0
bond_coeff 1 75.0 0.59
bond_coeff 2 75.0 0.39
bond_coeff 3 75.0 0.29
angle_coeff 1 2.5 180.0

pair_style   hybrid/overlay    dpd ${T} ${rc} 3854262 coul/slater/long 1.076 3.0

pair_coeff   1 1 dpd 25.0 4.5 1.0000
pair_coeff   2 2 dpd 24.0 4.5 0.9550
pair_coeff   1 2 dpd 45.0 4.5 0.9775
pair_coeff   3 3 dpd 22.0 4.5 1.0740
pair_coeff   4 4 dpd 13.3 4.5 1.2340
pair_coeff   4 2 dpd 28.5 4.5 1.0945
pair_coeff   3 2 dpd 23.0 4.5 1.0145
pair_coeff   4 1 dpd 17.9 4.5 1.1170
pair_coeff   4 3 dpd 28.5 4.5 1.1540
pair_coeff   1 3 dpd 45.0 4.5 1.0370
pair_coeff   5 5 dpd 25.0 4.5 1.0000
pair_coeff   5 4 dpd 17.9 4.5 1.1170
pair_coeff   5 3 dpd 45.0 4.5 1.0370
```

```
pair_coeff   5 2 dpd 45.0 4.5 0.9775
pair_coeff   5 1 dpd 25.0 4.5 1.0000
pair_coeff   6 6 dpd 0.0 4.5 1.0000
pair_coeff   5 6 dpd 0.0 4.5 1.0000
pair_coeff   4 6 dpd 0.0 4.5 1.0000
pair_coeff   3 6 dpd 0.0 4.5 1.0000
pair_coeff   2 6 dpd 0.0 4.5 1.0000
pair_coeff   1 6 dpd 0.0 4.5 1.0000
pair_coeff   7 7 dpd 0.0 4.5 1.0000
pair_coeff   6 7 dpd 0.0 4.5 1.0000
pair_coeff   5 7 dpd 0.0 4.5 1.0000
pair_coeff   4 7 dpd 0.0 4.5 1.0000
pair_coeff   3 7 dpd 0.0 4.5 1.0000
pair_coeff   2 7 dpd 0.0 4.5 1.0000
pair_coeff   1 7 dpd 0.0 4.5 1.0000

pair_coeff * * coul/slater/long

timestep     0.01
run_style    verlet
velocity all create ${T} 68768932
thermo_style custom step time temp press
thermo       100
fix 1 all    nve
neigh_modify one 10000
restart 10000 restart.*
dump 2 all atom 10000 dump.lammpstrj
dielectric 2.0
run          50000000
```

The following two files define the surfactant and water molecules. Note the definition of the special bonds in the surfactant file to force interactions between bonded surfactant beads.

4.2 Surfactant.data

```
8 atoms
6 bonds
5 angles

Coords

1 0.0 0.0 0
2 0.29 0.0 0
3 0.68 0.0 0
4 1.07 0.0 0
5 1.46 0.0 0
6 1.85 0.0 0
7 2.44 0.0 0
8 4.0 0.0 0

Types

1 2
2 3
3 3
```

```
4 3
5 3
6 3
7 4
8 5

Charges

1 0.0
2 0.0
3 0.0
4 0.0
5 0.0
6 0.0
7 -9.9665
8 9.9665

Bonds

1 3 1 2
2 2 2 3
3 2 3 4
4 2 4 5
5 2 5 6
6 1 6 7

Angles

1 1 1 2 3
2 1 2 3 4
3 1 3 4 5
4 1 4 5 6
5 1 5 6 7

Special Bond Counts

1 0 0 0
2 0 0 0
3 0 0 0
4 0 0 0
5 0 0 0
6 0 0 0
7 0 0 0
8 0 0 0

Special Bonds

1
2
3
4
5
6
7
8
```

4.3 Water.data

```
3 atoms
2 bonds
1 angles

Coords

1 0.0 0.0 0
2 0.35 0.0 0
3 0.7 0.0 0

Types

1 7
2 1
3 6

Charges

1 5.33069
2 0.0
3 -5.33069

Bonds

1 4 1 2
2 4 2 3

Angles

1 2 1 2 3
```