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Dissolution of Surfactant lamellar phases

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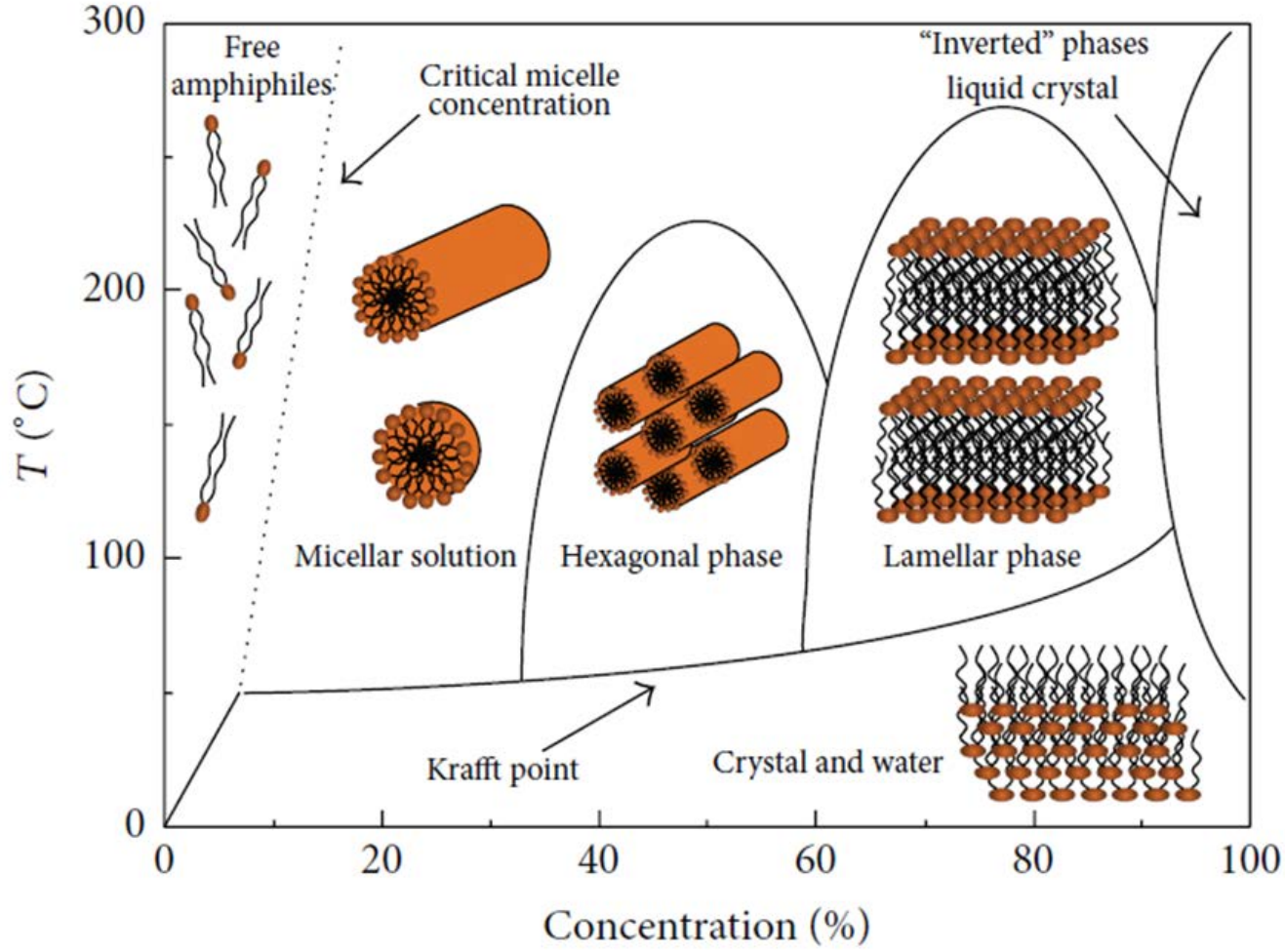
Introduction

- Consumer and pharmaceutical-based products play a major role in chemical industry
- These products seems different, but they all contain some of surfactants, oil, water, particle and air
- Surfactant dissolution is essential in formulated products preparation and use

Objectives

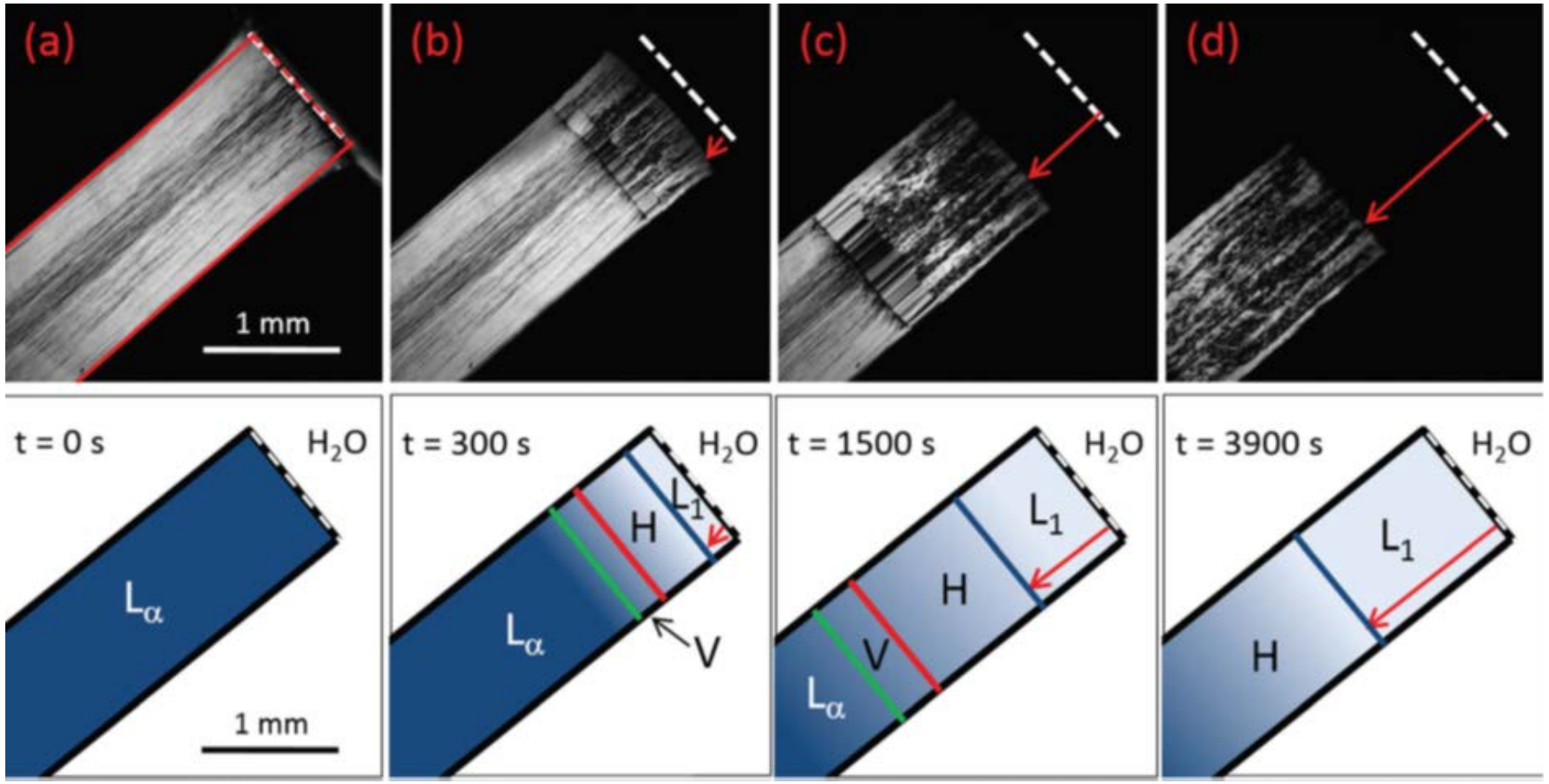
- Dissolution process of surfactants
- Dissipative particle dynamics (DPD) simulations
- Effect of changing the size and shape of surfactant
- Changing the end concentration
- Degree of surfactant hydrophobicity or hydrophilicity

Phase Diagrams



Typical lipotropic liquid crystalline (LLC) phase diagram of a normal surfactant dissolved in a selective solvent.

Linear Penetration Scan



Poulos, A.S., C.S. Jones, and J.T. Cabral, *Dissolution of anionic surfactant mesophases.* Soft matter, 2017. **13**(31): p. 5332-5340.

Dissolution of surfactants (Simulation)

- Computer simulations of surfactant dissolution are used to access the seconds and less time scales

- Number of mesoscale methods have been used including dissipative particle dynamics (DPD) simulations which is used in this study

Dissipative Particle Dynamics (DPD)

- DPD is a mesoscale particle method which bridges the gab between the microscopic and macroscopic simulations

- The method of DPD was introduced by Hoogerbrugge and Koelman to study the hydrodynamic behaviour in complex geometries like colloidal suspensions

- DPD study the hydrodynamic time and space scales beyond those accessible by MD

The DPD algorithm

- $$\frac{\mathrm{d}r_i}{\mathrm{d}t} = v_i \qquad\qquad \frac{\mathrm{d}v_i}{\mathrm{d}t} = \frac{f_i}{m_i}$$
- $$f_i = \sum_{i \neq j} \left(F_{ij}^{C} + F_{ij}^{D} + F_{ij}^{R} \right)$$

The DPD algorithm

- $F_{ij}^{C} = \begin{cases} a_{ij}\left(1 - r_{ij}\right) n_{ij} & r_{ij} < r_{\text{cut}} \\ 0 & r_{ij} \geq r_{\text{cut}} \end{cases}$
- a_{ij} is the maximum repulsion between particle i and particle j
- r_{ij} is the distance between the beads which equals to

$$r_{ij} = r_i - r_j, n_{ij} = \frac{r_{ij}}{\left|r_{ij}\right|}$$

The DPD algorithm

- $F_{ij}^{R} = \sigma \omega^{R}\left(r_{ij}\right) n_{ij} \frac{\xi_{ij}}{\sqrt{\Delta t}}$
- $F_{ij}^{D} = -\gamma \omega^{D}\left(r_{ij}\right)\left(v_{ij} \cdot n_{ij}\right) n_{ij}$
- Where v_{ij} is the relative speed among the beeds
- ξ_{ij} is a Gaussian random variable with 0 mean and unit variance equal to 1
- σ is the random force constant
- $\boldsymbol{\gamma}$ is the dissipative force constant
- $\boldsymbol{\omega^{R}}$ and $\boldsymbol{\omega^{D}}$ are dimensional functions for weight

The DPD algorithm

- $$\omega^D\left(r_{ij}\right) = \left[\omega^D\left(r_{ij}\right)\right]^2 = \begin{cases} \left(1 - r_{ij}\right)^2 & r_{ij} < r_{\text{cut}} \\ 0 & r_{ij} \geq r_{\text{cut}} \end{cases}$$

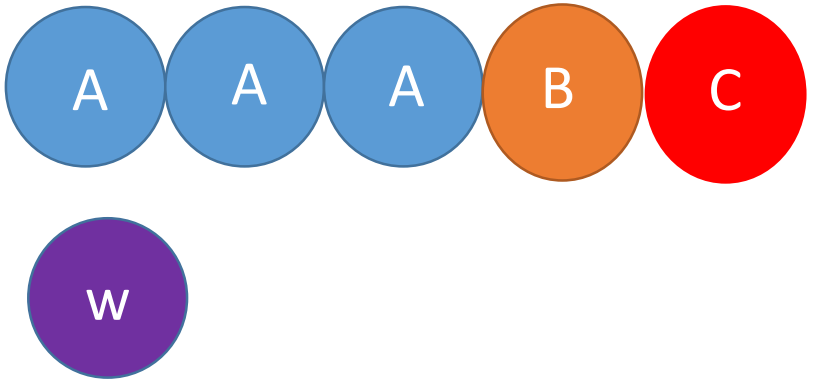
- $\sigma^2 = 2k_B T\gamma$

- $r_{cut} = 1$

Simulation of the lamellar phase

Parameter	Value
time step, Δt	0.02
Cut-off distance r_c	1
Reduced energy , $k_B T$	1
Repulsion parameters , a	Varied
density of the beads, ρ	3
friction coefficient, γ	4.5
Number of beads	24000
Box size	20 x 20 x 20 x σ^3
Beads per molecule	5
Bead diameter, σ	1

Interactions –repulsion parameter

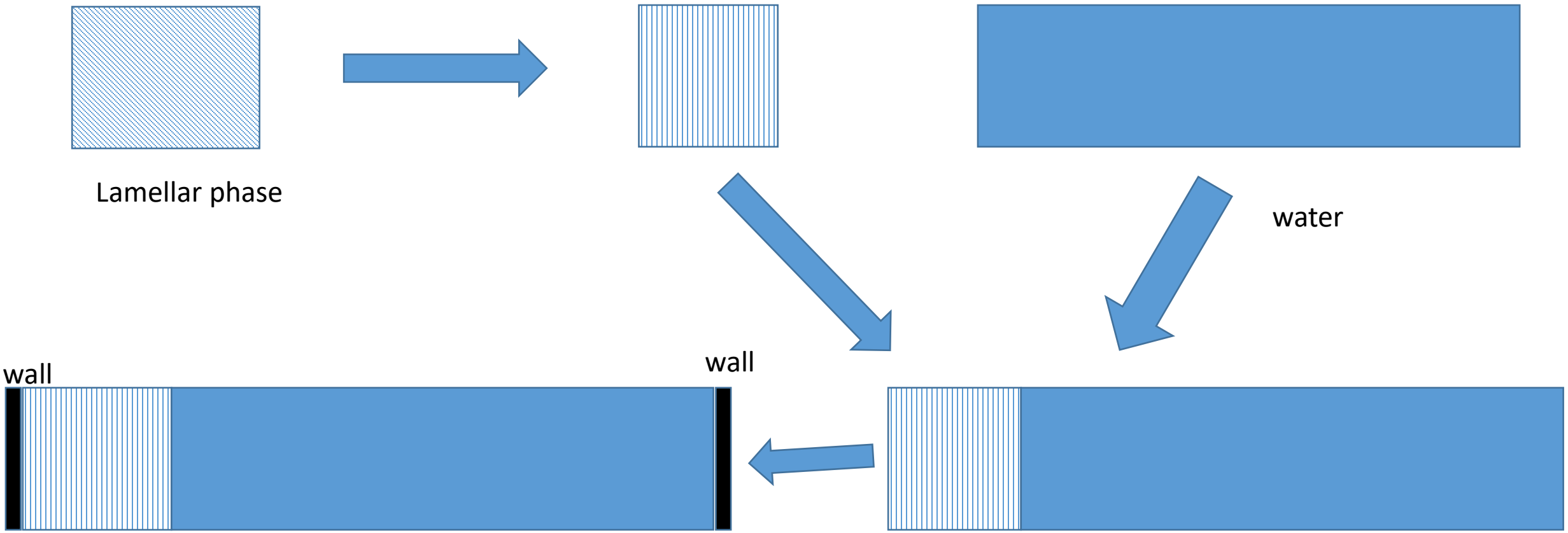


	A	B	C	W
A	106.5	113	127.7	a_{AW}
B	113	106.5	106.5	107.5
C	127.7	106.5	106.5	83
W	a_{AW}	107.5	83	106.5

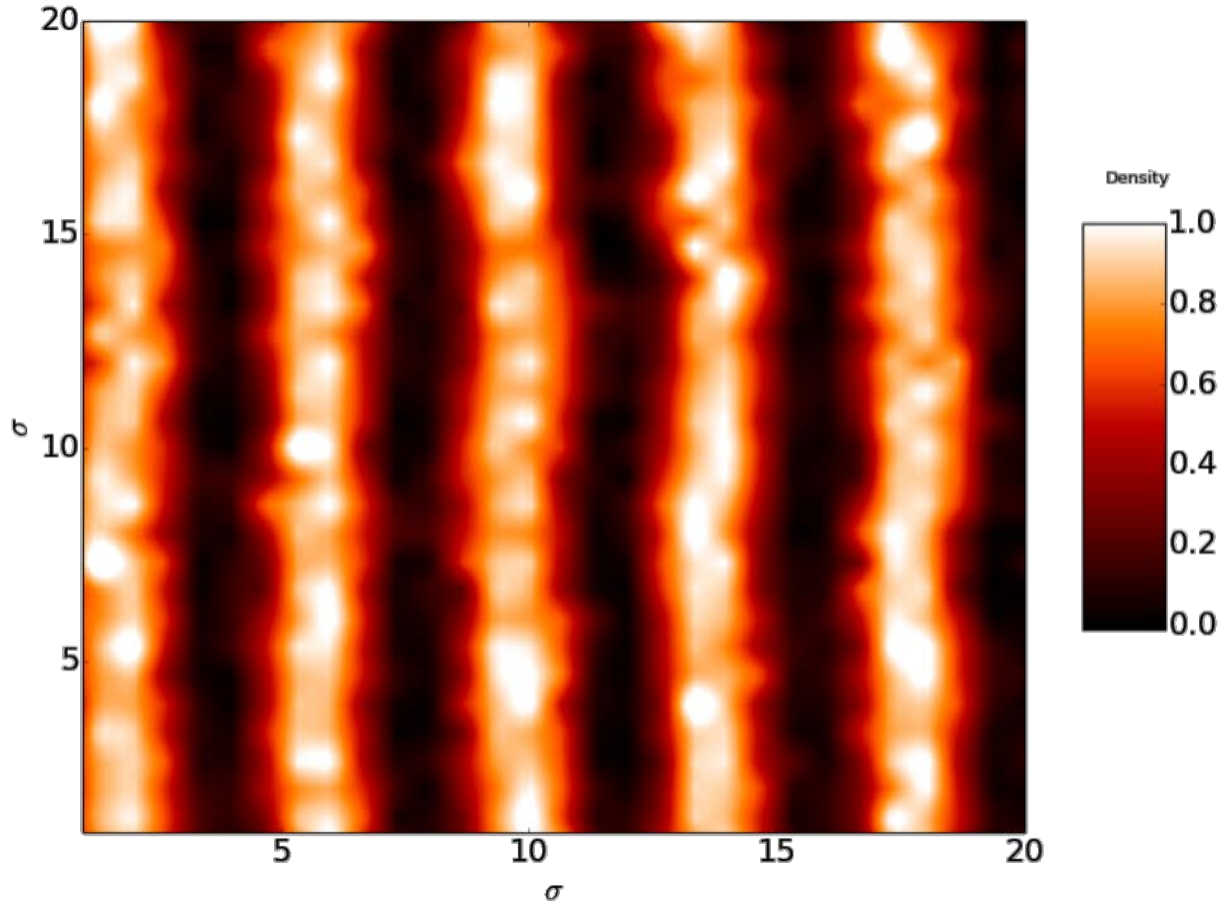
$$a_{AW} = a_{AA} + \Delta a_{AW}$$

Δa_{AW}		
19.5	24.5	34.5
44.5	54.5	

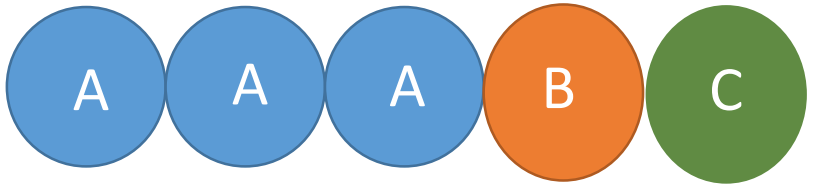
Dissolution – Setting up the system

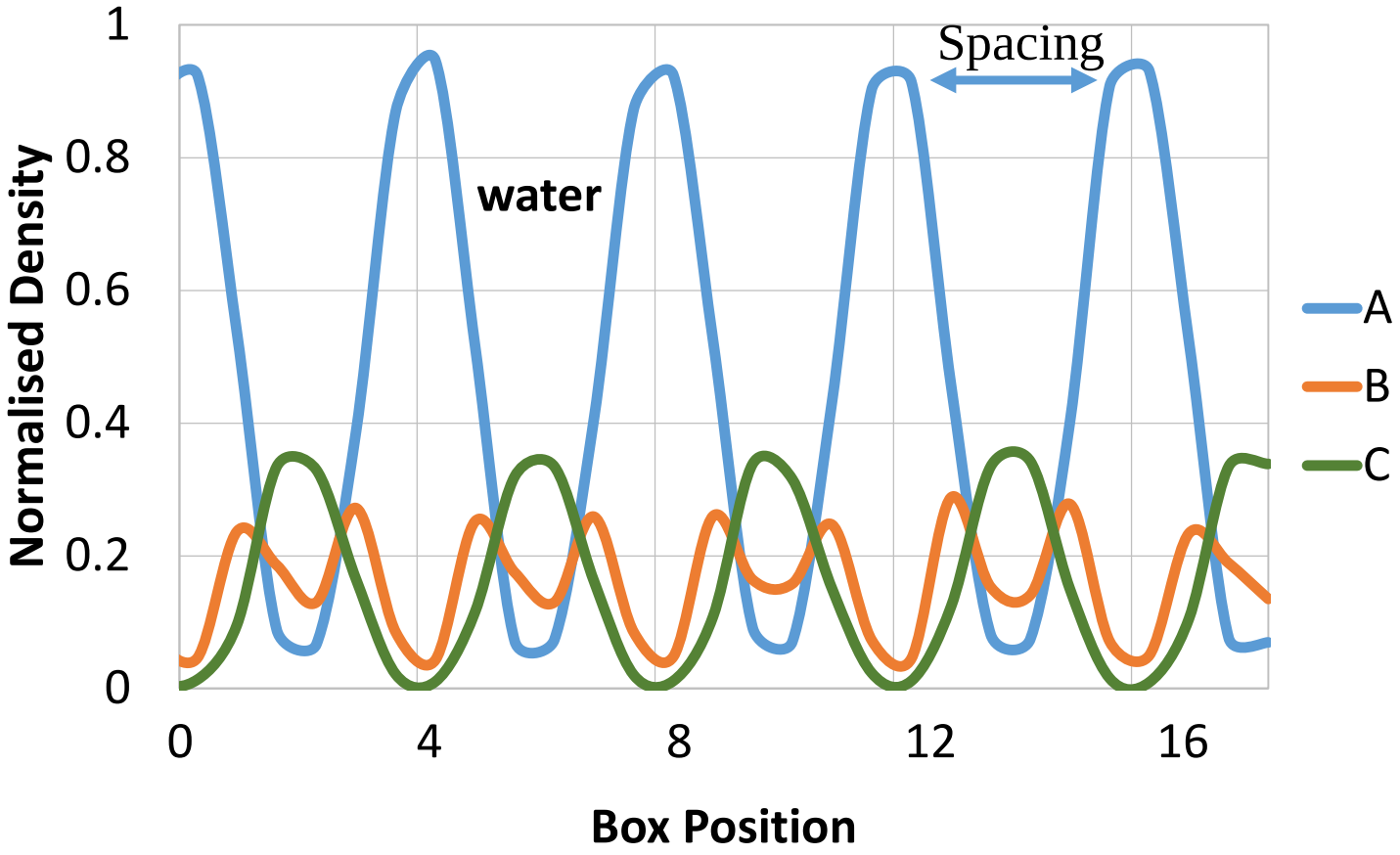


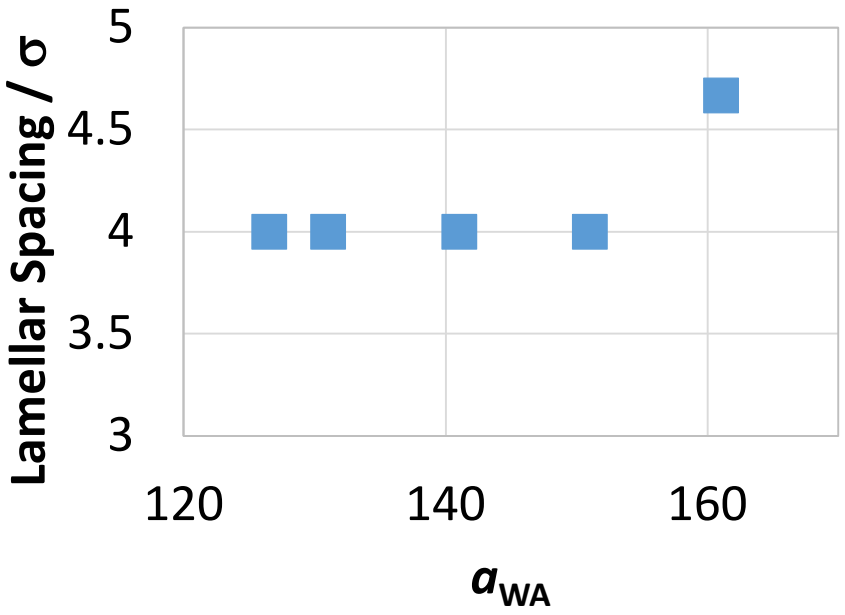
Equilibrium Structure



Lamellar Spacing

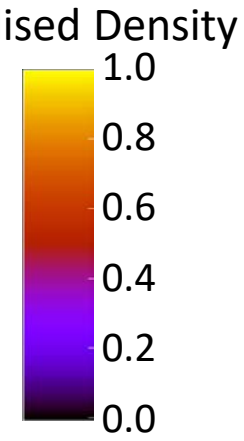






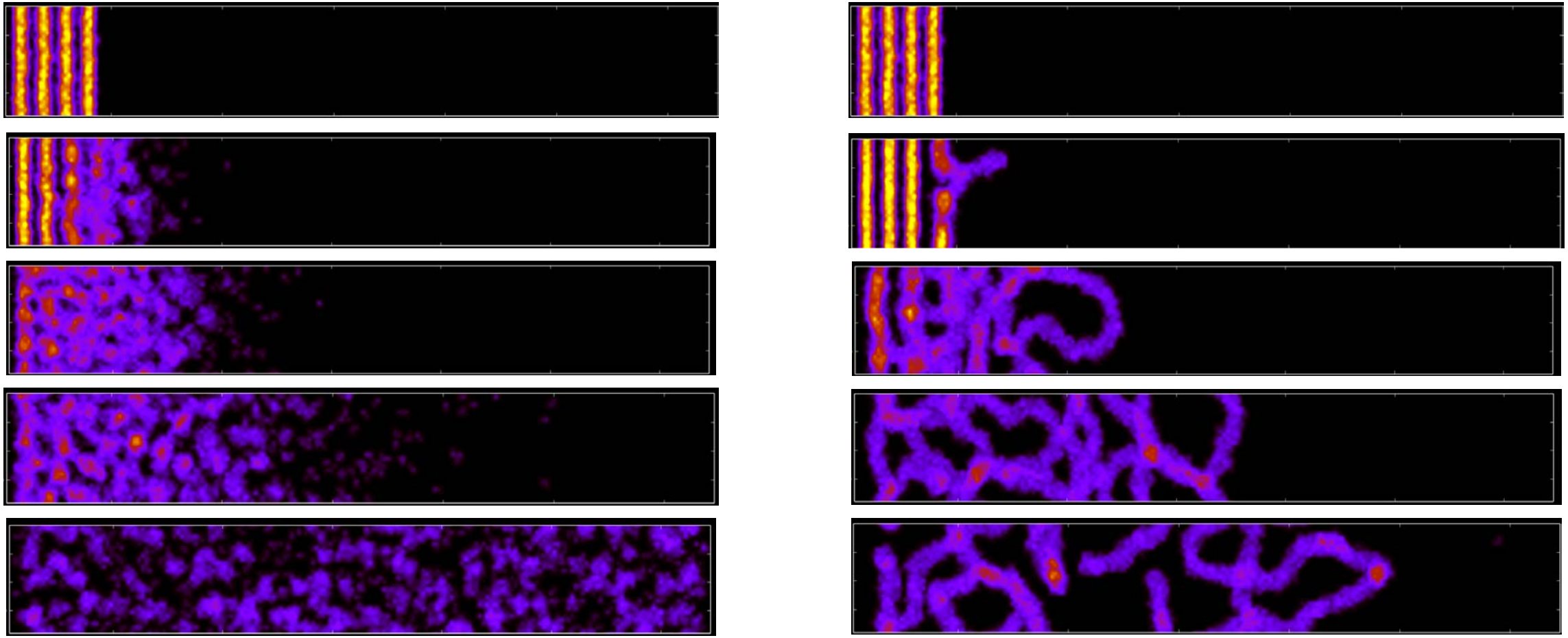
Dissolution

$$a_{AW} = a_{AA} + \Delta a_{AW}$$



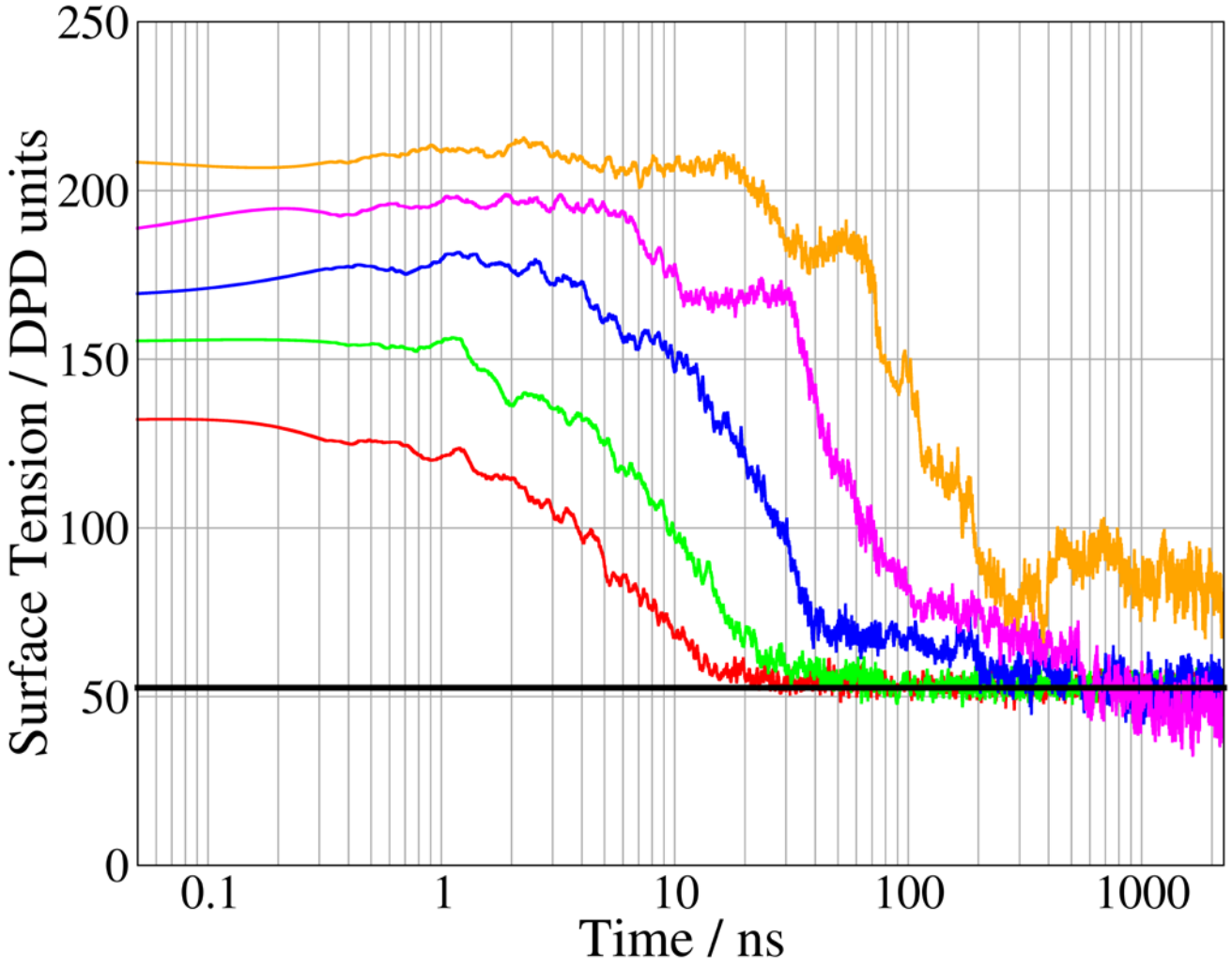
19.5

44.5



Surface Tension

$$\gamma = Lx\left[Px - \frac{(Py + Pz)}{2}\right]$$



$a_{AW} = a_{AA} + \Delta a_{AW}$

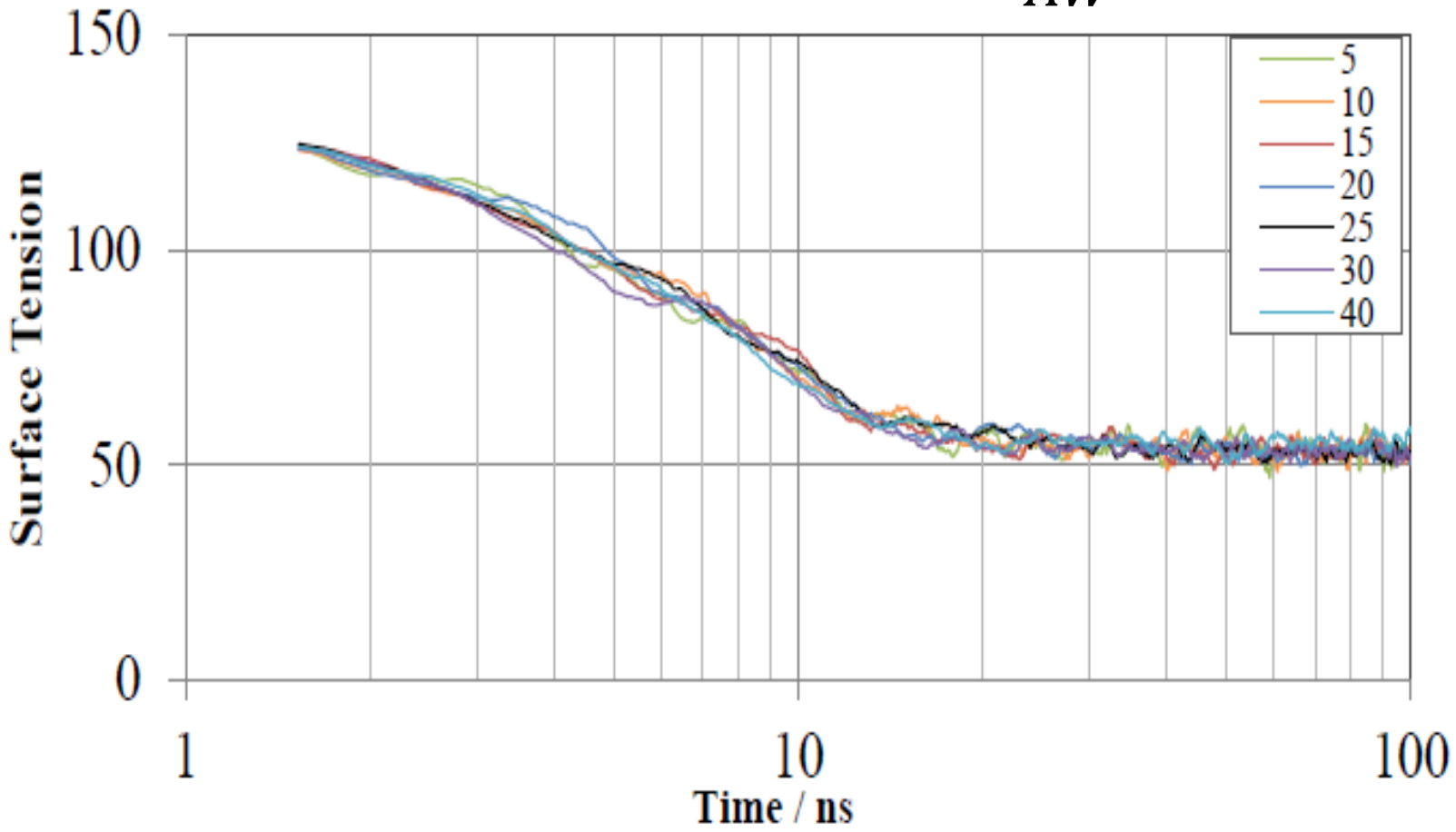
Δa_{AW}		
19.5	24.5	34.5
44.5	54.5	

Surface Tension

- As the lamellar phase breaks up the surface tension decreases.
- When the lamellar phase no longer exists the surface tension reaches just the value between the solution and the wall.
- The more hydrophobic the surfactant tail the more worm-like the resulting micelles are.

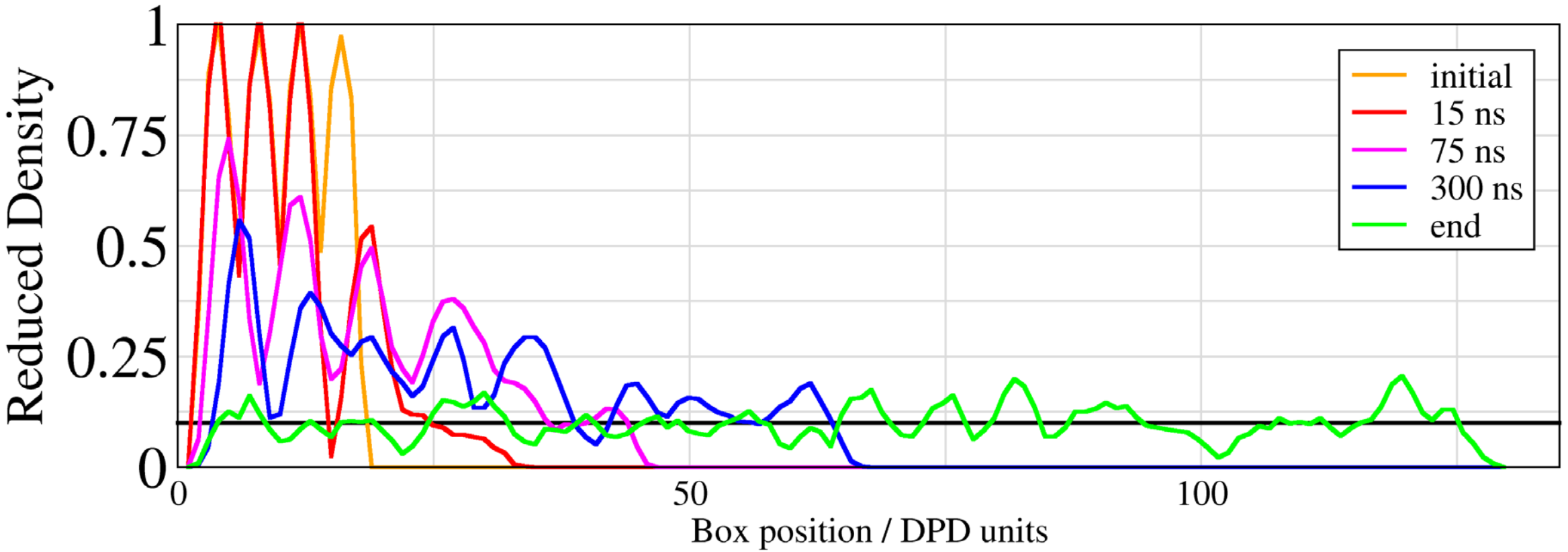
Surface Tension

$a_{AW} = 19.5$

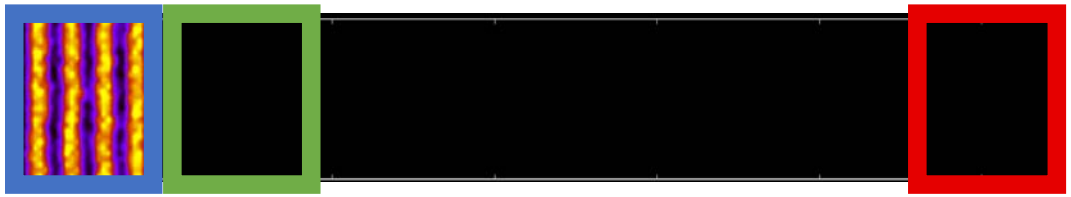


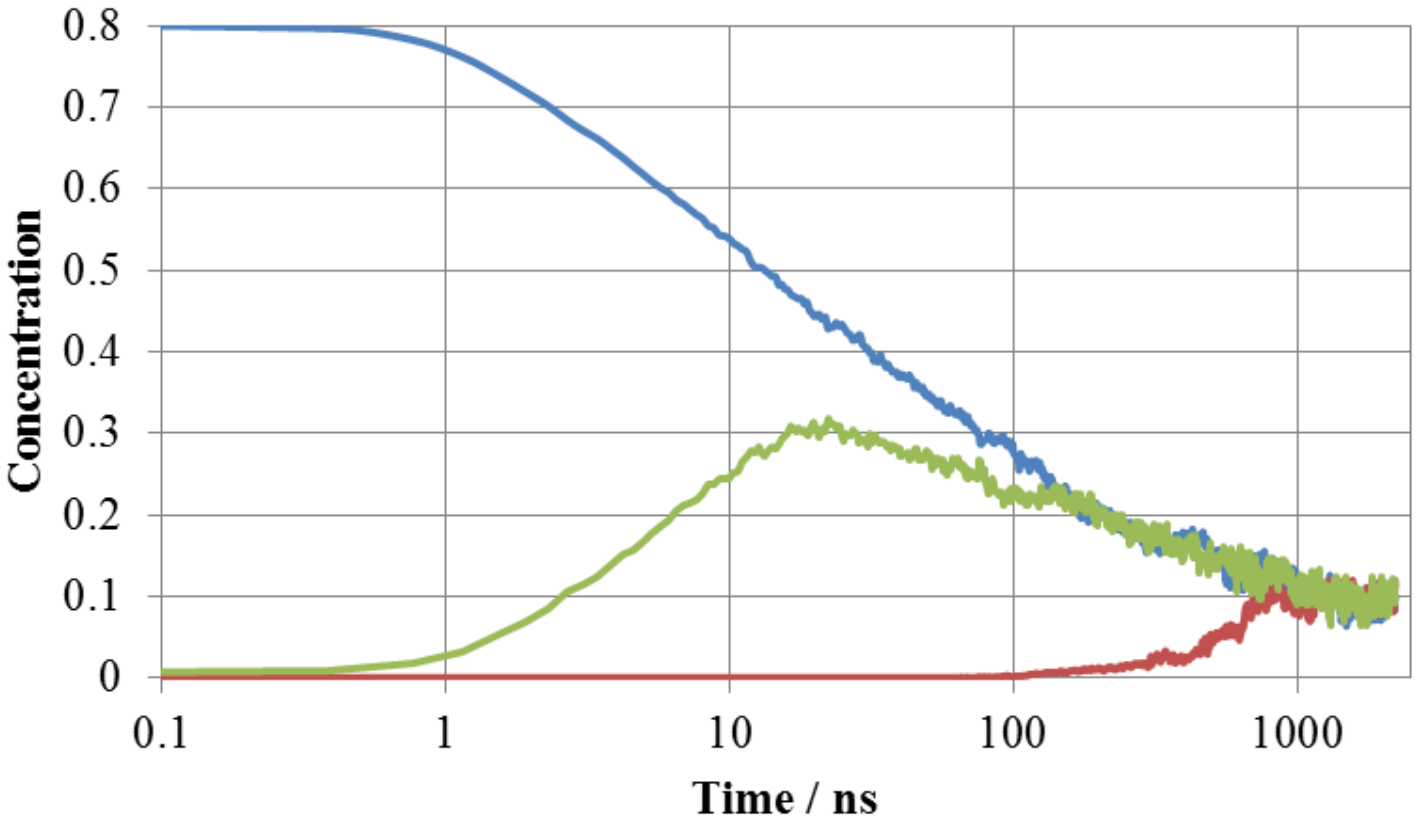
Density

$$a_{AW} = 19.5$$



Density



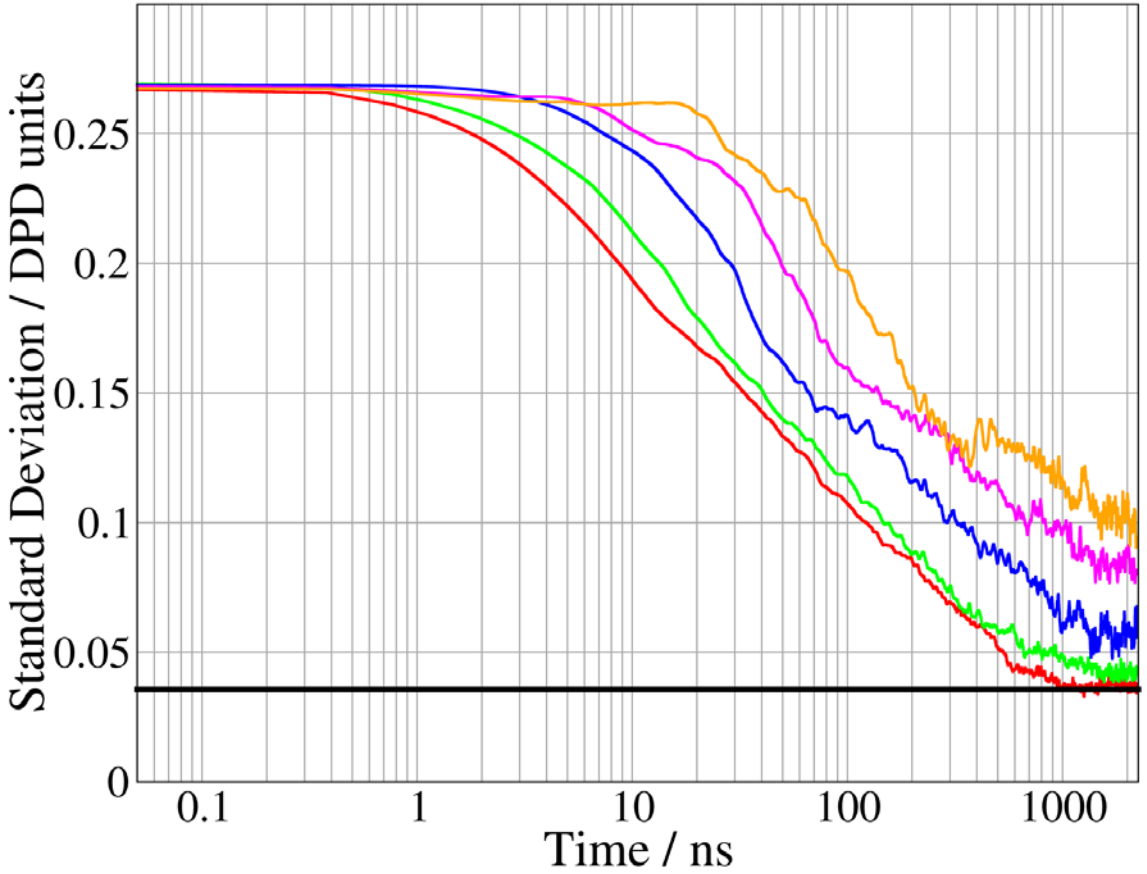


$a_{AW} = 19.5$

Density Difference

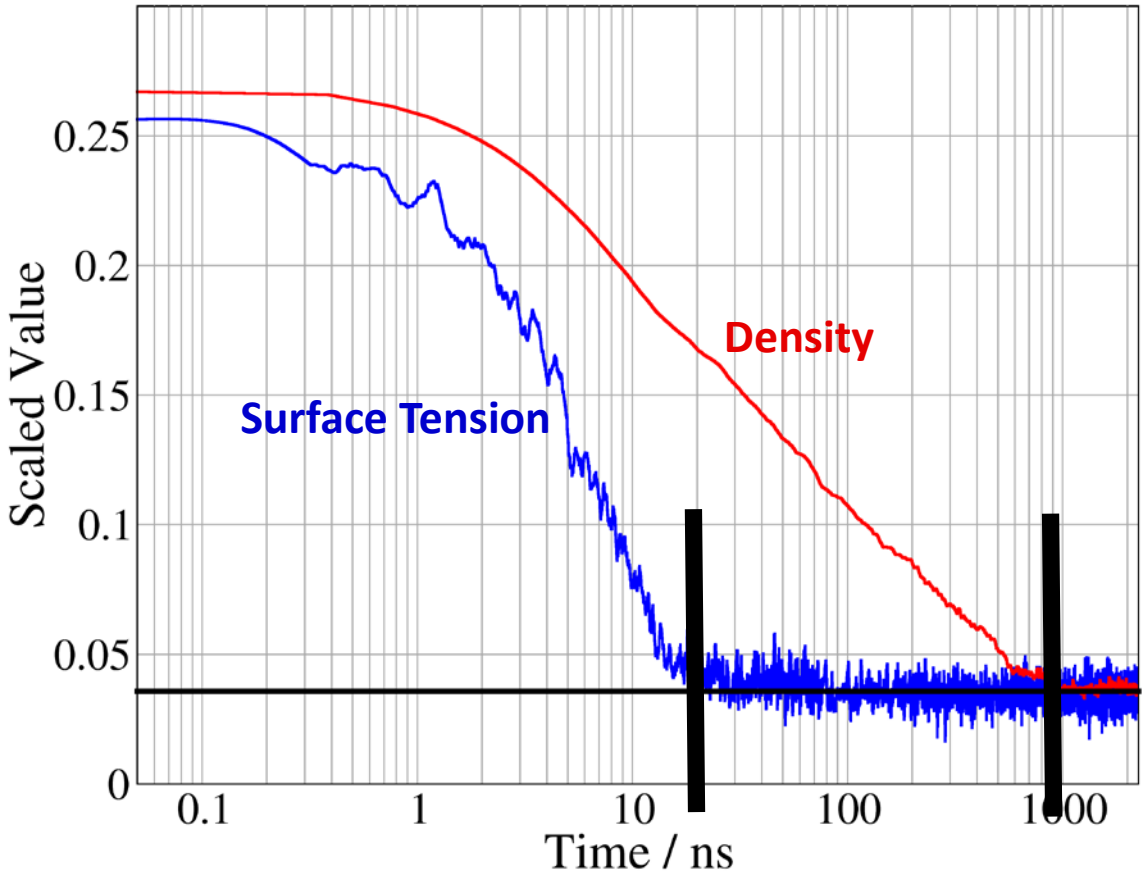
$a_{AW} = a_{AA} + \Delta a_{AW}$

Δa_{AW}		
19.5	24.5	34.5
44.5	54.5	

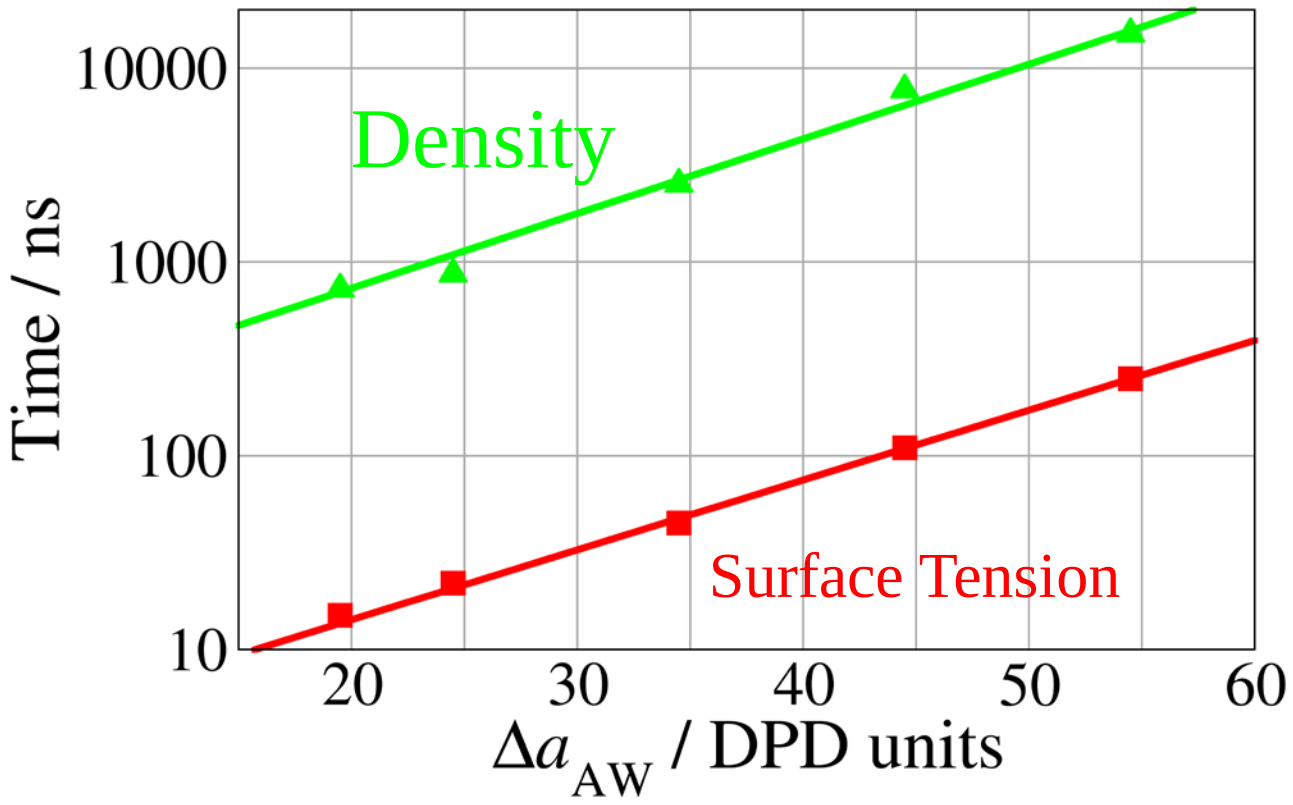


- the variation of the standard deviation of the density across the length of the box during the dissolution process.
- takes longer after the initial lamellar break-up for it is dissolve across the box to an even concentration.

Surface Tension vs Density

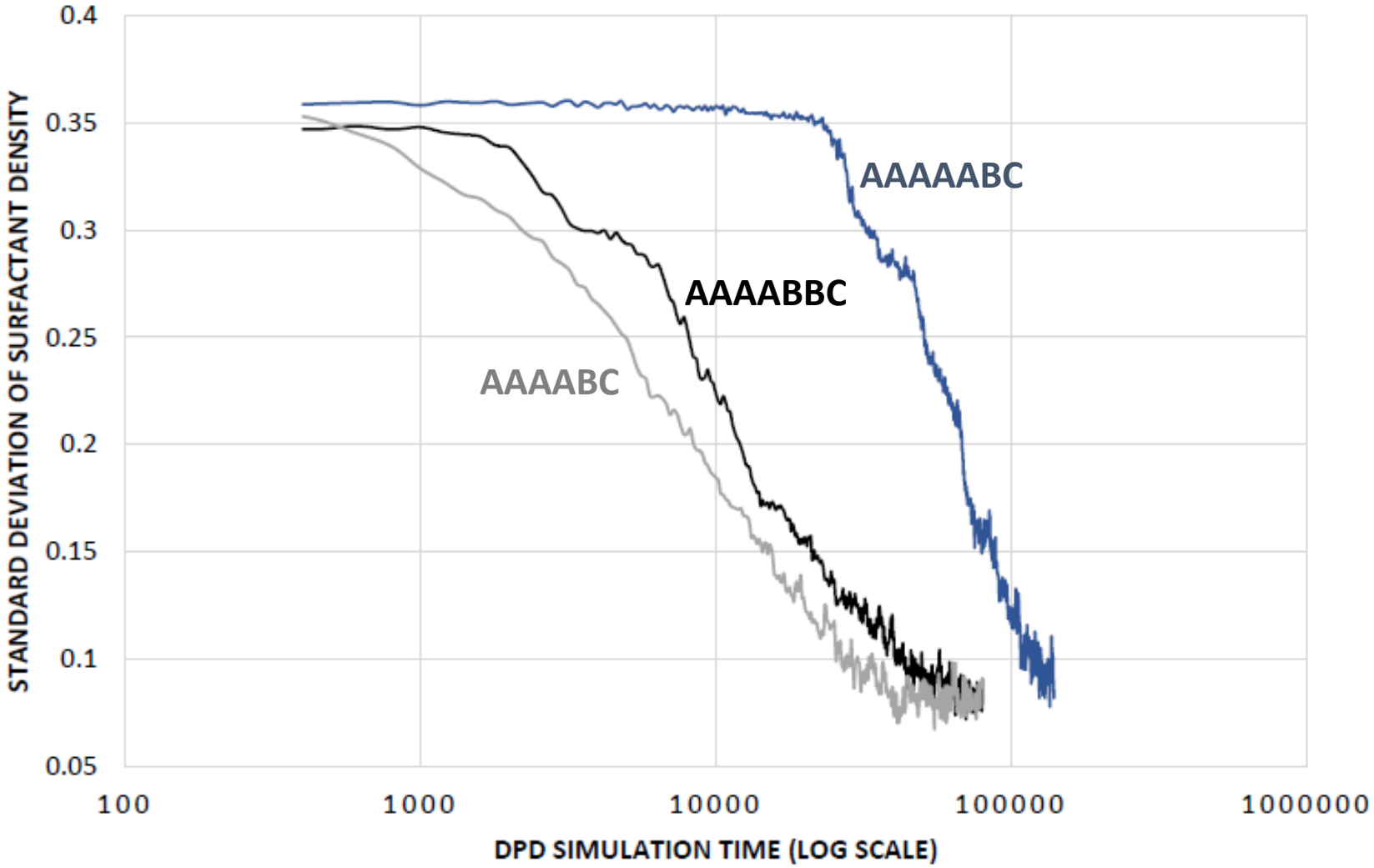


Surface Tension vs Density



- the variation of the dissolution time with the hydrophobicity of the surfactant tail
- the more hydrophobia the slower the dissolution.

Effect of Chain Length



Conclusions

- The lamellar phase breaks-up at a faster rate than the full dissolution process

- Dissolution of the surfactant with higher hydrophobicity produces micelles which are more elongated and worm-like in nature

- Surfactants with more hydrophobic tails take longer for the lamellar phase to break down and to dissolve fully into the box