# Development of a Coarse-Grained Polyoxyethylene Glycol Non-ionic Surfactant Model Using the SAFT-$\gamma$ Mie Force-field for Molecular Dynamics Simulations

Imperial College London

Centre for Process Systems Engineering

MOLECULAR SYSTEMS ENGINEERING

Emma C. L. Richards, Erich A Müller, George Jackson

## 1

Surfactant = 'Surface-active agent':
- Adsorb onto interfaces
- Reduce surface tension

### POE Surfactants:

- Nonionic
- Low toxicity
- Biodegradable
- High performance at low temperature

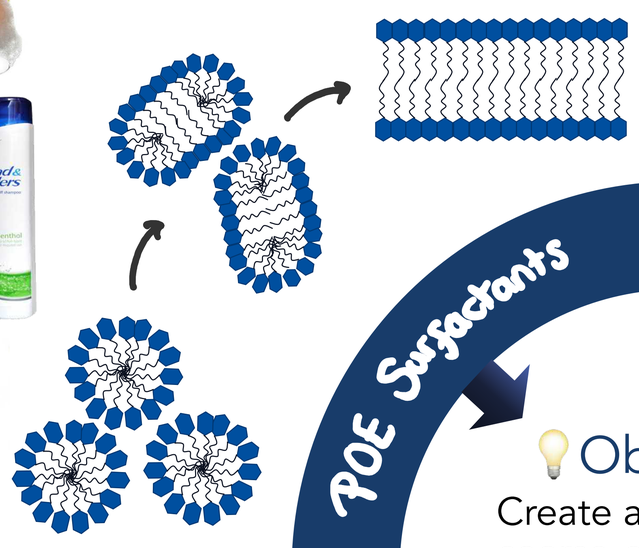
### Uses:

- Detergents
- Personal Care e.g. Shampoo
- Paint formulations
- Petrochemicals
- Biomedical applications e.g. drug delivery



Understanding the nature of surfactants allows you to 'design' specific systems for the application required

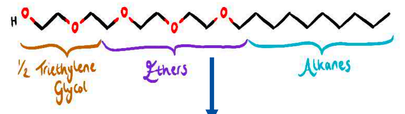
### Complex Structures
- Micelles (Spherical, rodlike…)
- Cylindrical
- Mesophases i.e. Lamellar, bilayers



## Methodology

1. Determine surfactants you wish to be able to build
   - e.g. POE's: $C_{10}E_4$, $C_{13}E_6$


2. Breakdown the surfactants into functional groups

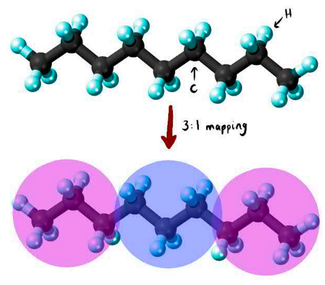



3. Find which groups are available and what needs to be developed


4. Parameterise groups that aren't made - gSAFT
5. Parameterise the unlike interactions - gSAFT or MD

## 2

### Coarse-Graining:

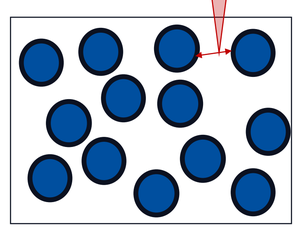



### SAFT:
- EoS based on molecular theory[2]

$$\frac{A}{Nk_BT} = \frac{A^{ideal}}{Nk_BT} + \frac{A^{mono.}}{Nk_BT} + \frac{A^{chain}}{Nk_BT}$$

- Interactions between beads – Mie potential

$$u^{Mie} = C\varepsilon\left[\left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a}\right]$$



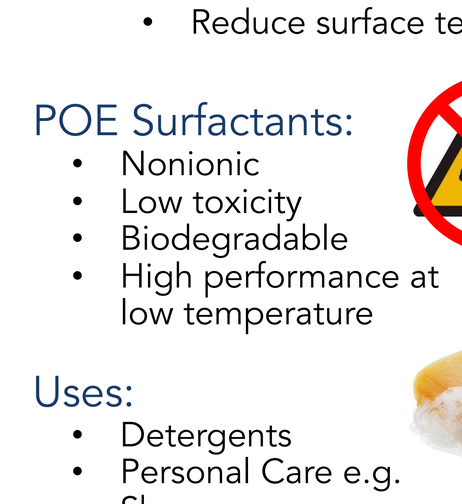
Experimental Data i.e. VLE data – $P_v$, $\rho_l$


Models

## Objective

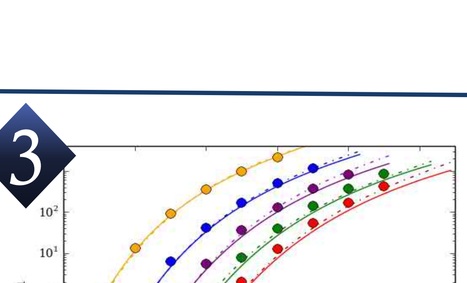
Create a buildable coarse-grained (CG) POE surfactant model using SAFT theory to use in MD simulations

## 3

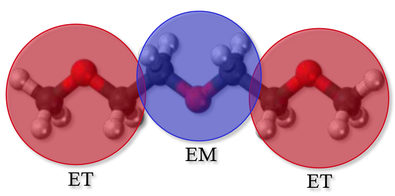








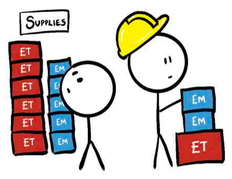

Parameterised to three different glymes:
- Diglyme
- Triglyme
- Tetraglyme




ET & EM distinguish between chemistry of terminal and middle sections

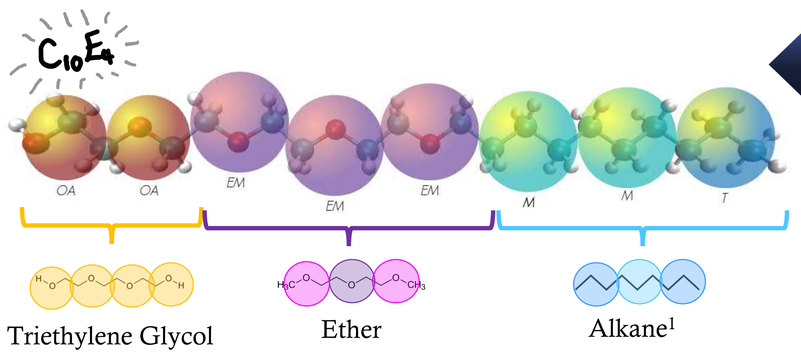
### Benefits of a heteronuclear model

1. Buildable:
   - No parameterisation for every compound
2. Predicitve:
   - A good model can predict other properties/lengths

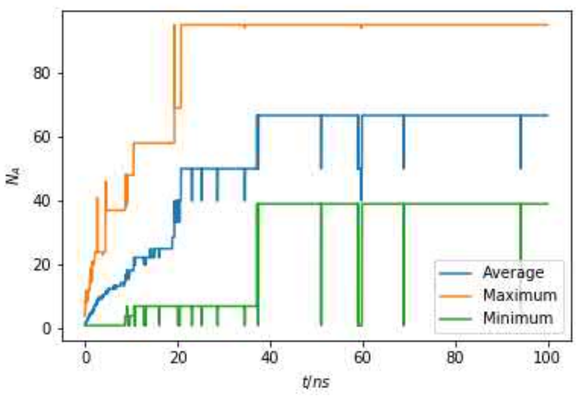



Vapour pressure $P_v$ and saturated liquid density $\rho_l$: Very close agreement to experimental data, Monoglyme and Hexaoxaoctadecane purely predictive. Dashed lines – NIST data[3], solid line – SAFT EoS, circles – MD simulation
Surface tension $\gamma$: purely predictive, solid lines and shaded area shows error associated with NIST data[3], circles – MD simulation

## 4

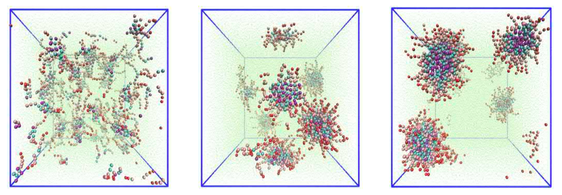



### Preliminary Studies:
- System equilibration time
- Low concentration aggregation number




### Model:
- Any length $C_iE_j$ surfactant with:
  - $i = 3n+1$ i.e. $C_3$, $C_7$, $C_{10}$, $C_{13}$ …
  - $j = n$ i.e. $E_1$, $E_2$,…,$E_{10}$,$E_{11}$,…

Weight fraction $w_{Surf}$ = 3.64 %



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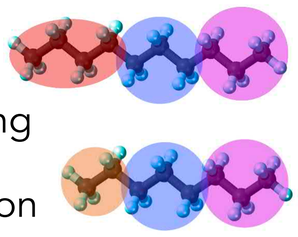
## 5

## Conclusions + Future Work

### Summary:
- ✓ Successful Ether model that accurately describes VLE data through MD simulation and SAFT theory
- ✓ Ether model also capable of calculating purely predictive properties such as surface tension, not utilized within parameterisation
- ✓ Fully formed POE surfactant model for alkane lengths $C_i$ in multiples of 3 carbon atoms and any ethoxylated length $E_j$

### Future applications:
- ❑ Thorough morphology investigation, including high concentration systems corresponding to mesophases
- ❑ Rheology studies, including comparison between varying methods and calculation of CMC[4]
- ❑ Extensions of alkane model to include 2:1 and 4:1 carbon mapping to extend model to intermediate lengths



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