Study of asphaltene adsorption at fluid-fluid interface

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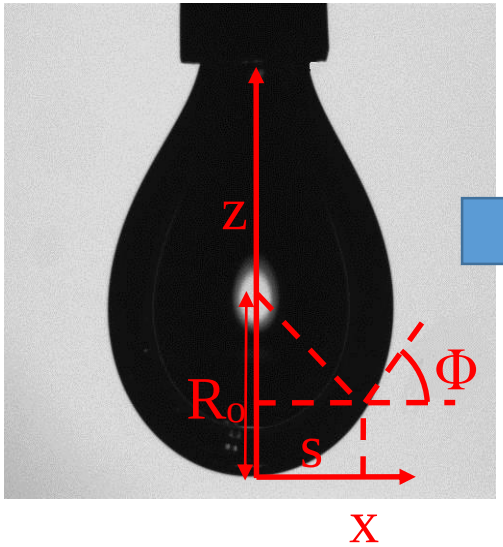
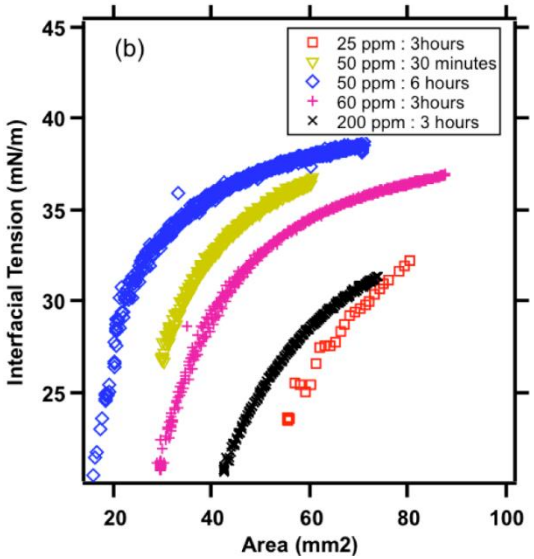
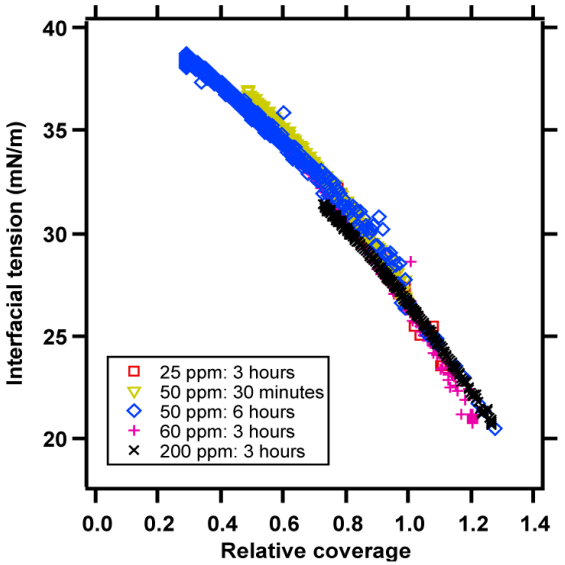
A 10 year journey in the asphaltenes field

- The story started (for me) in Trondheim in 2019 within the FACE project (IFE-SINTEF-NTNU).
- Collaboration was developed with CCNY, ENSIACET and IMFT to restart asphaltenes studies “from scratch”.
- The endeavor goes on within the PIRE project with somewhat the same partners.

Expansion of asphaltenes covered droplets







- Laplacian shapes
- After renormalization all curves collapse

→ no gelling but an Equation of State

Asphaltenes Equation of state

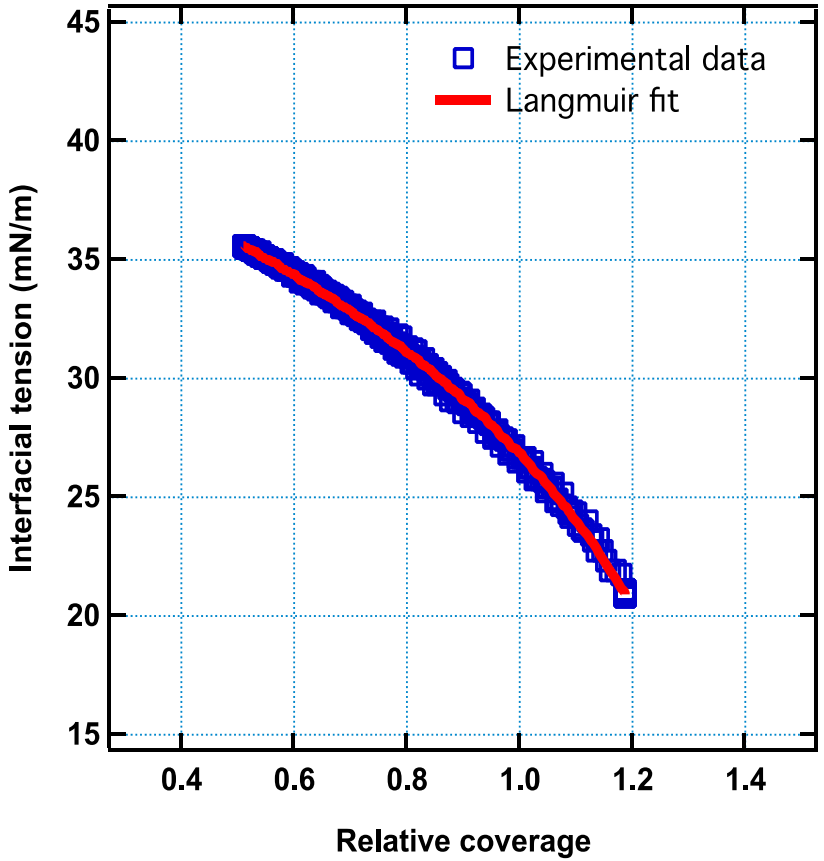
- Good fit with a Langmuir EOS

$$\gamma(\Gamma) = \gamma_0 + kT\Gamma_\infty \ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right)$$

- Surface excess coverage

  =1/molecular area

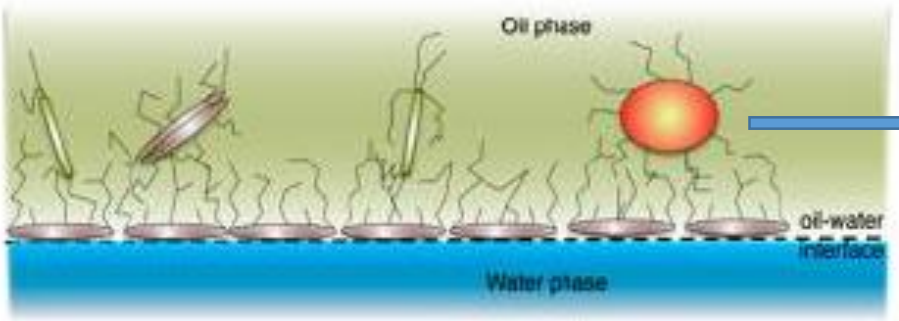
Γ_∞ =3.3 molecule/nm^2



Significance of surface excess coverage

Molec. area=0.3nm^2 ~carbon skeleton of 6 fused aromatic rings (~average asphaltenes)

→Flat on adsorption of polyaromatic core?



Deposition of clusters might explain SAXS measurements

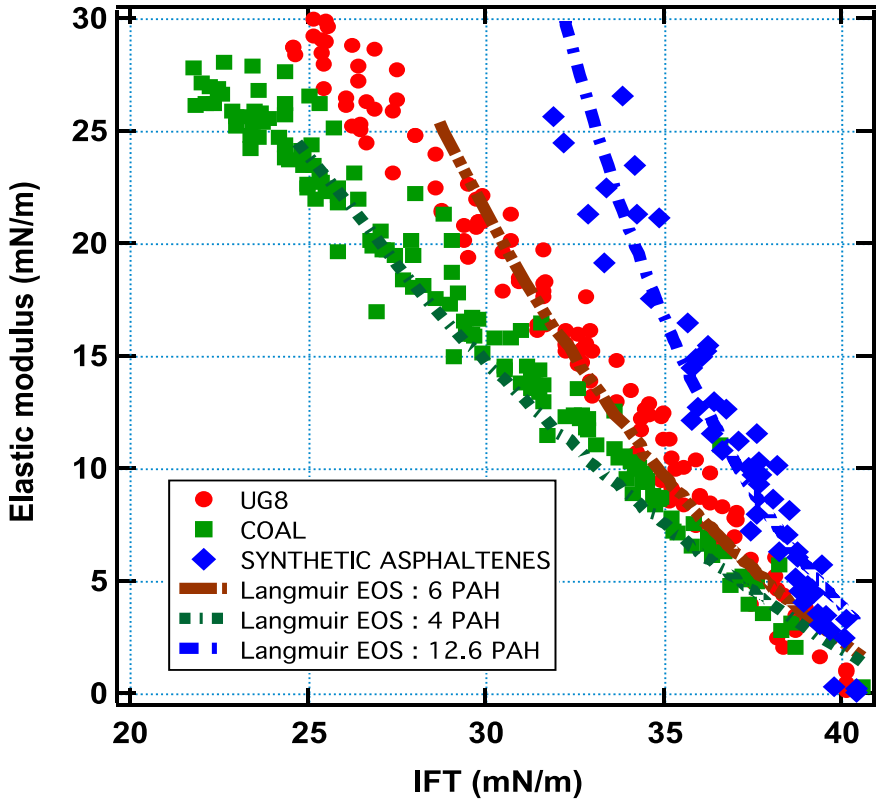
Coherent with SFG spectroscopy: asphaltenes with aromatic core flat on water and alkyl chains perpendicular

Confirmation of equation of state

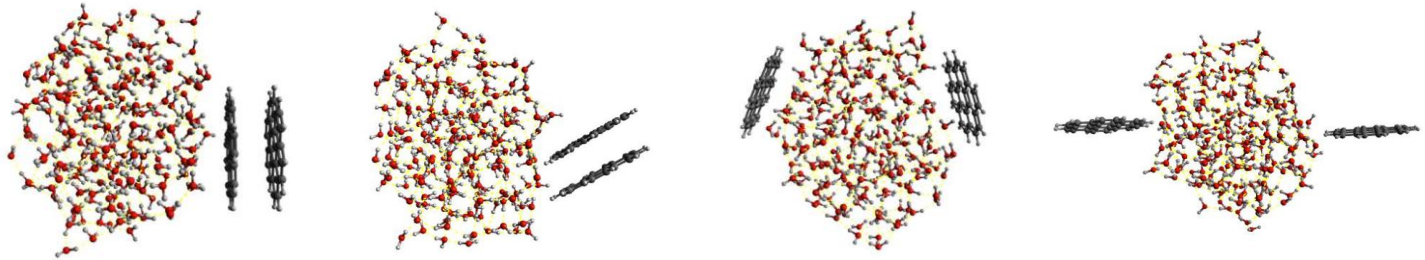
Dilatational rheology with a poor and viscous solvent at high frequency

$$E' \sim E_0 = \frac{-\partial\gamma}{\partial \ln \Gamma} = \frac{kT\Gamma}{\left(1-\Gamma/\Gamma_\infty\right)}$$

→ expected unique relationship between elastic modulus and surface pressure dependent upon core size



Quantum Based molecular dynamic simulations (DFTB) With Aude Simon U. of Toulouse (France)



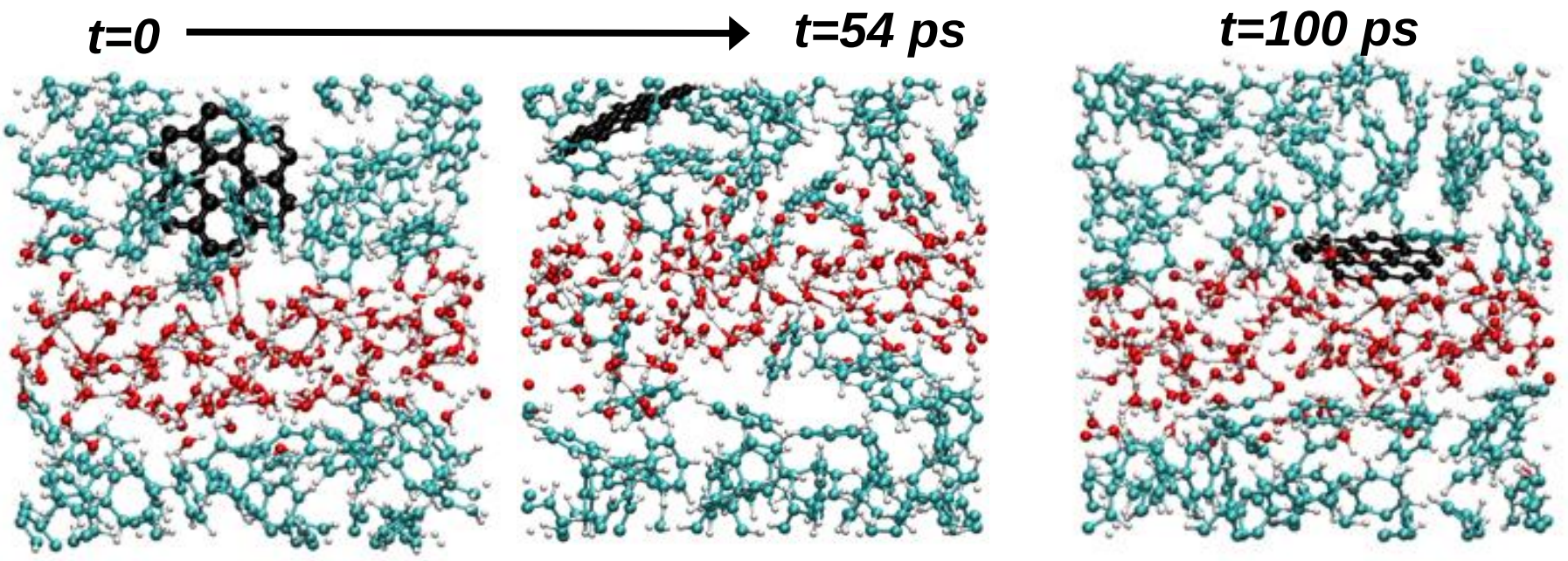
PAH - $(H_2O)_{200}$ interaction energy in eV

1.16 ***0.8*** ***2.05*** ***0.65***

PAH – PAH interaction energy in eV

0.74 ***0.76***

Extension of MD simulations to water benzene interface.



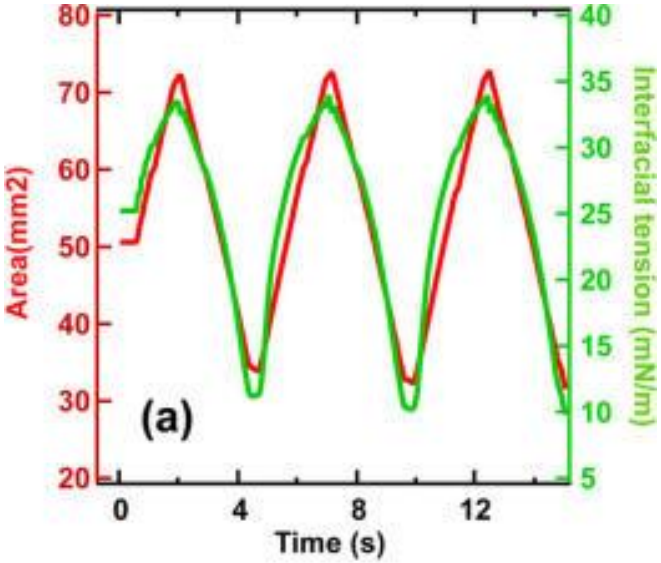
How to use the gained knowledge to explain?

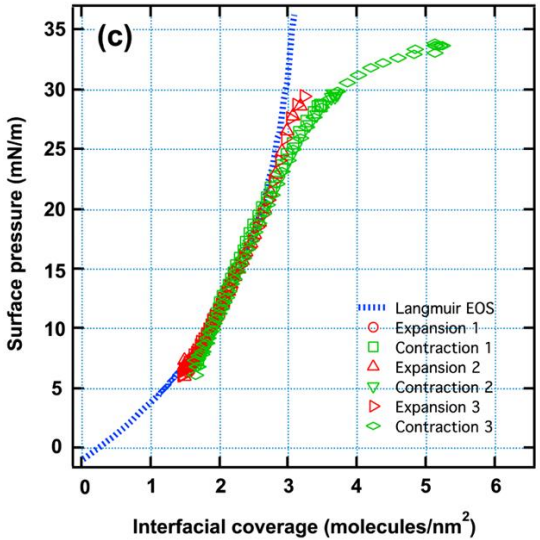
- ”Rigid skin”?
- Shear elasticity?
- Emulsion stability?
- Adsorption/relaxation kinetics?

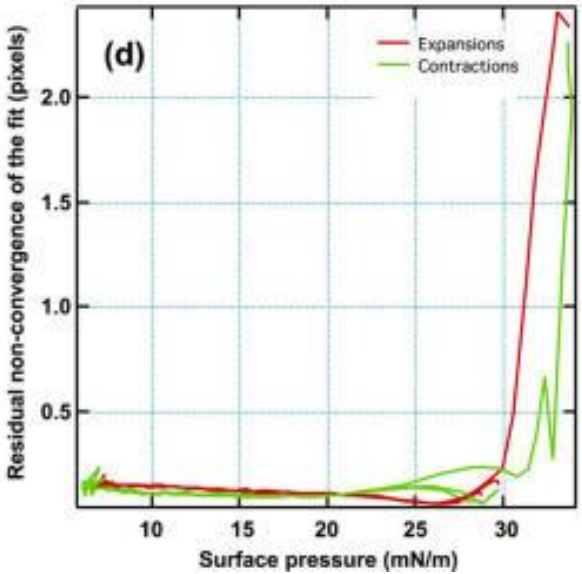
Phase transition due to packing

Mixture effects

Large amplitude area cycling around 20 mN/m surface pressure (~80% coverage)







Expansion: droplet remains Laplacian and IFT follows EOS

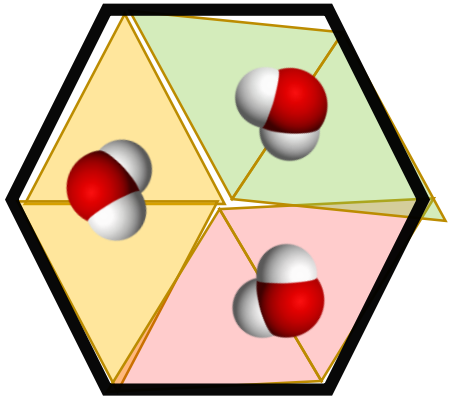
Contraction: droplet becomes non Laplacian and IFT flattens

Phase transition close to packing?

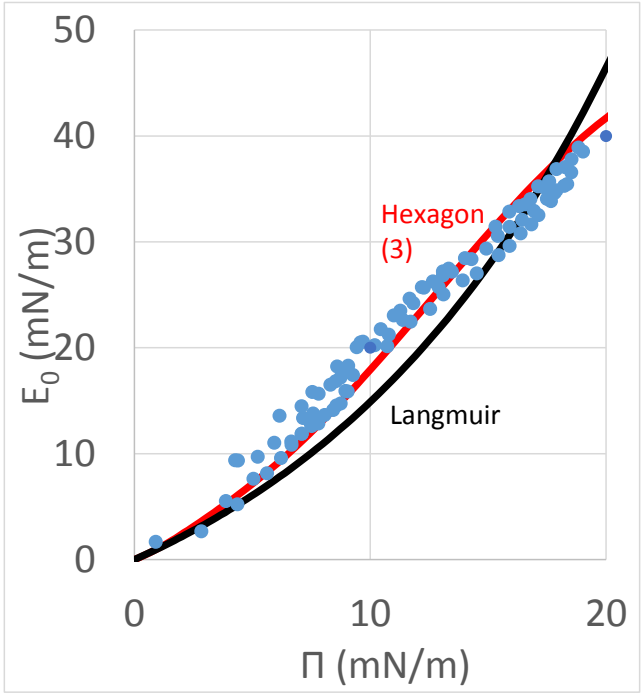
An alternate model

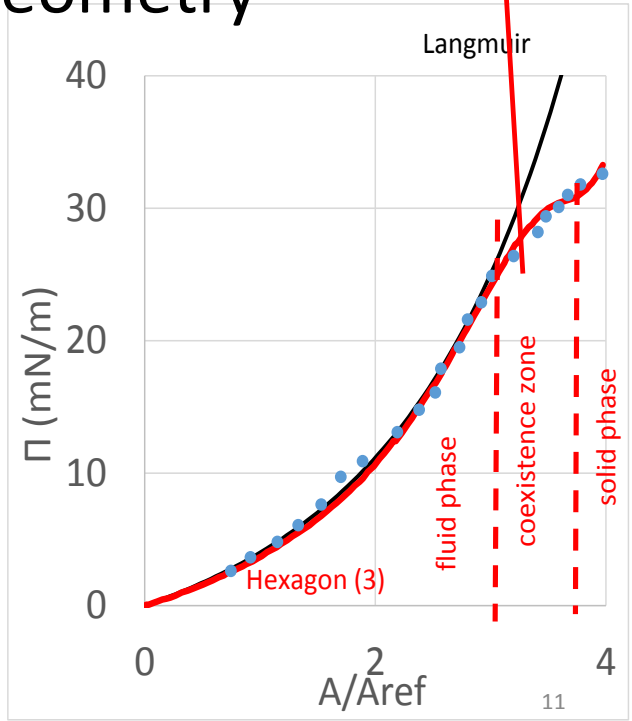
Dynamic frustration
→ shear elasticity

Γ_∞ =3.3 molecule/nm^2 → 3 to 4 water molecules per asphaltenes molecules with compact geometry



Hexagonal lattice gas

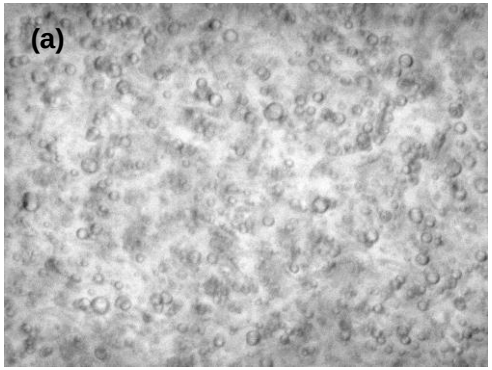


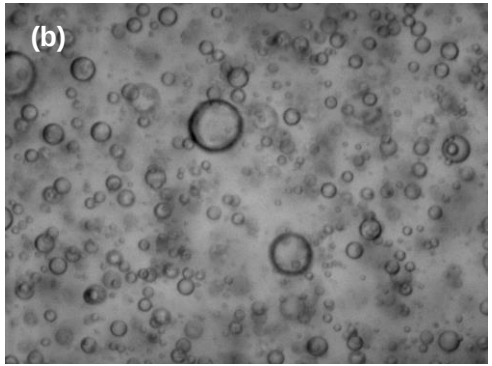


Stirred tanks experiments with aliphatic oil

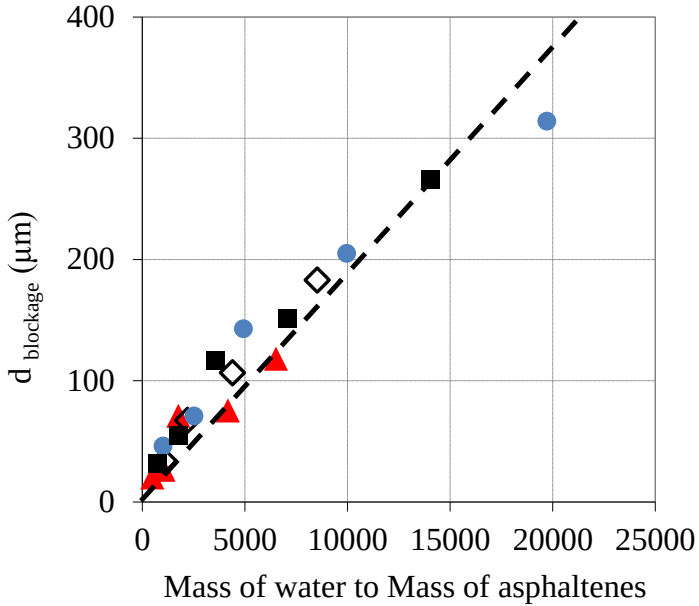
(a) Vigorous emulsification.
(b) Reduced agitation.
→Rapid increase in size
Followed by blockage for hours

? asphaltenes accumulation at interface
→ jamming → impossibility to open up asphaltenes free contact area?





Arrested coalescence principle



Irrespective to aging time

- Upon coalescence, area is reduced.
- Surface coverage increases up a critical value blocking further coalescence

$$d_{block} = \frac{6M_d / \rho_d}{M_p} \Gamma_{block}$$

→ Γ_{block}=3.3 mg/m²
(Similar estimate from Pr Yarranton)

M_w~750 g/mol → Γ_{block}~85% coverage

Hexagonal 3 LG model predicts a fully solid interface for 85% coverage

Stirred tanks experiments with good solvents

(a) Vigorous emulsification.
(b) Reduced agitation.
→Rapid increase in size
Slow drift
Free water overnight

Slow desorption by diffusion through the boundary layer?

Model for short times

- Assumptions:
  - droplets have coalesced.
  - critical surface coverage has been reached.
  - no desorption has occurred yet.
- Mass conservation during coalescence:

$$\frac{\Gamma_i}{d_i} = \frac{\Gamma_{block}}{d_{block}}$$

With d_i the diameter and Γ_i the coverage of droplets during emulsification.

With d_{block} the diameter and Γ_{block} the coverage of droplets at blockage of coalescence.

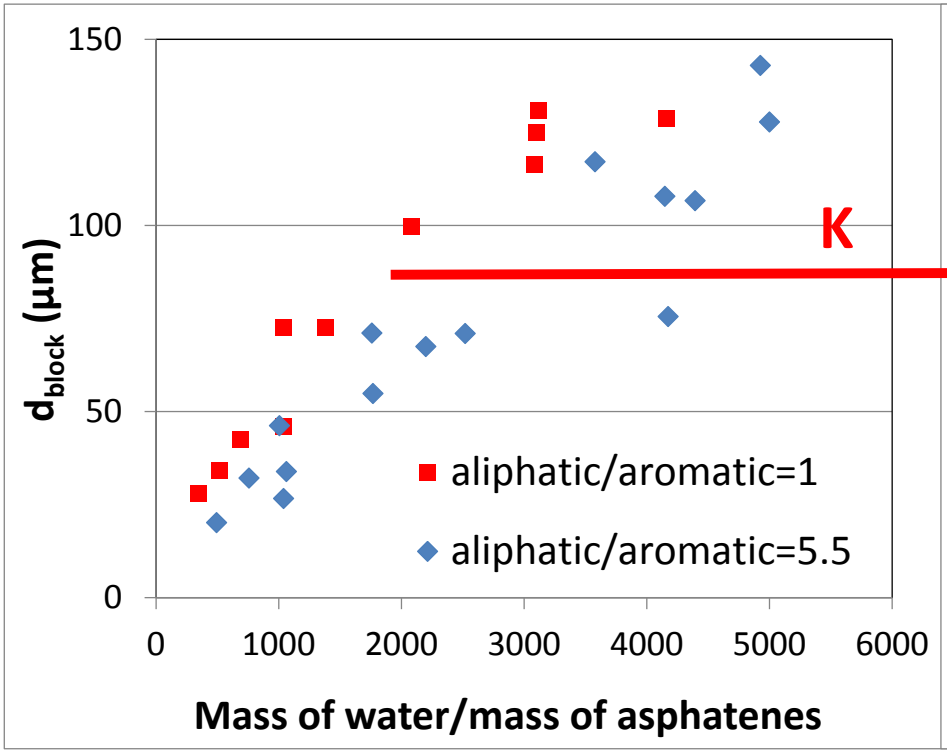
- Γ_i is defined by adsorption equilibrium during emulsification:

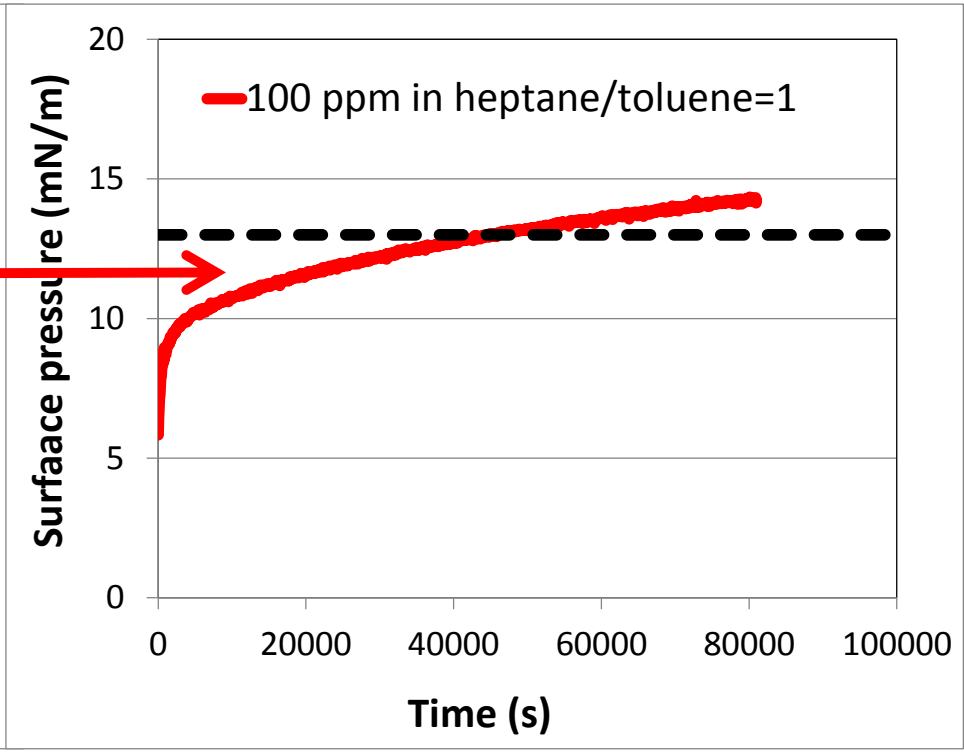
$$\Gamma_i = d_i \frac{(c_0 - c_i)(1-\alpha_w)}{\alpha_w}$$

Mass conservation during emulsification

$$\Gamma_i = \frac{Kc_i\Gamma_\infty}{1+Kc_i}$$

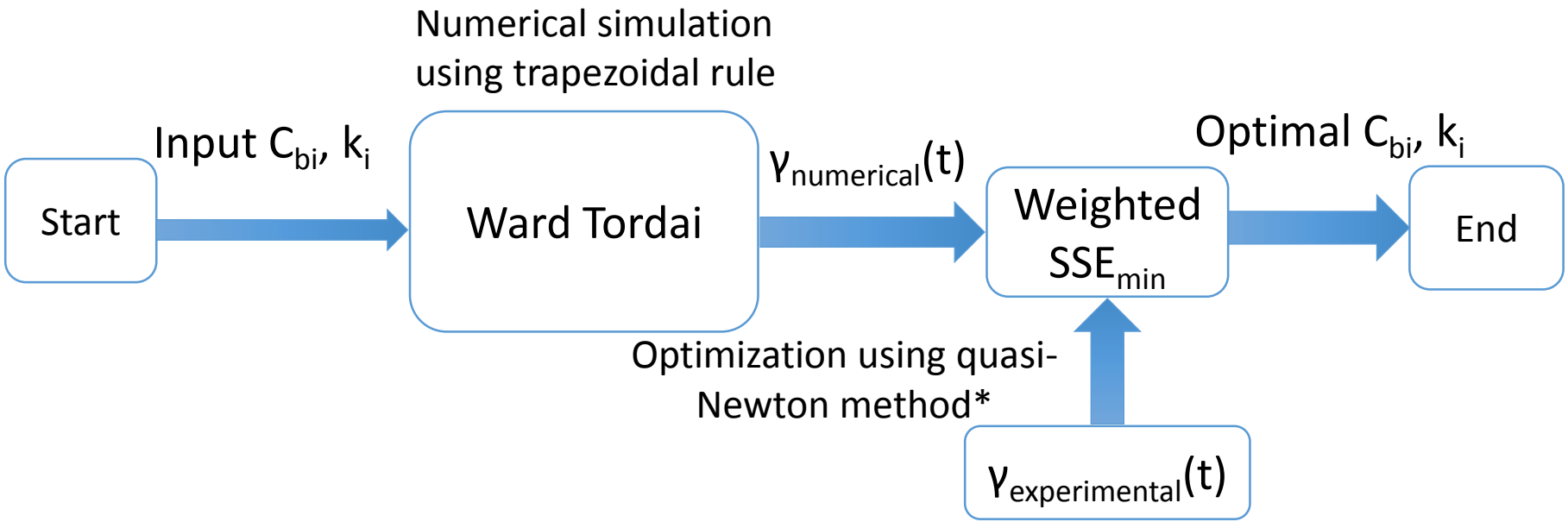
Langmuir adsorption isotherm





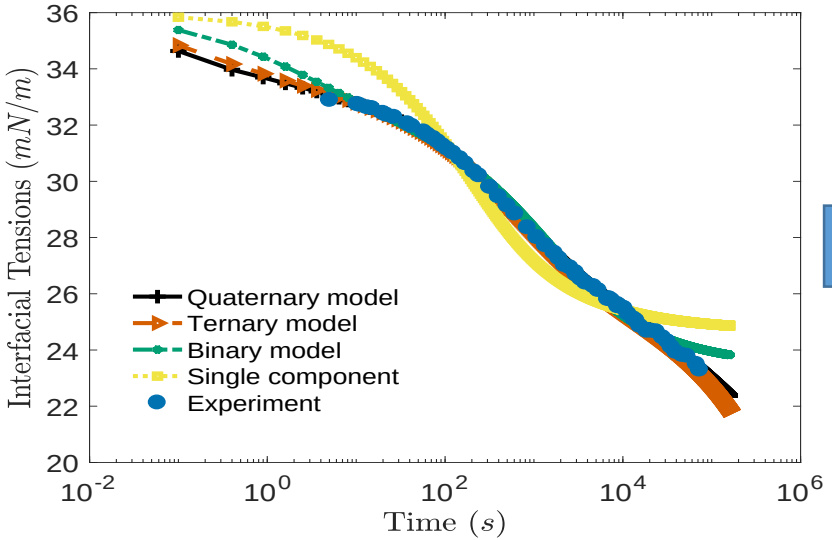
Long term IFT decay due to mixture effects?
(adsorption of minority components)

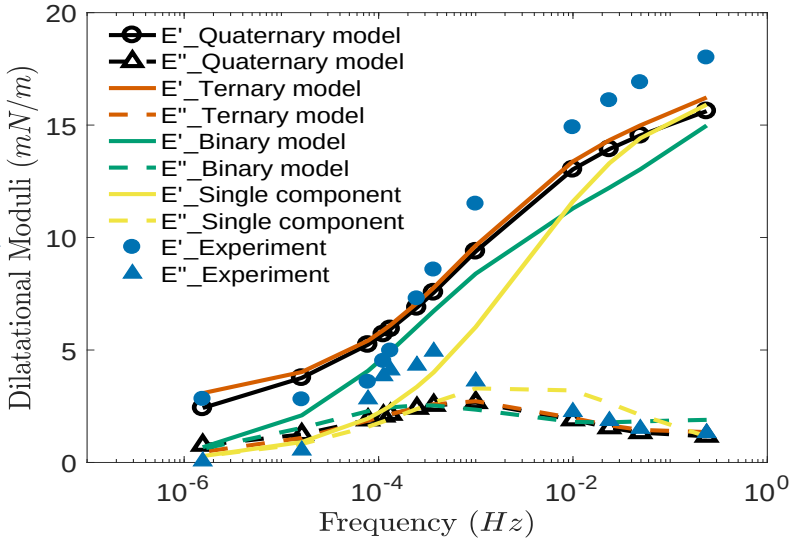
Extraction of pseudo component properties from IFT measurements



* L-BFGS (Limited memory Broyden-Fletcher-Goldfarb-Shanno) algorithm

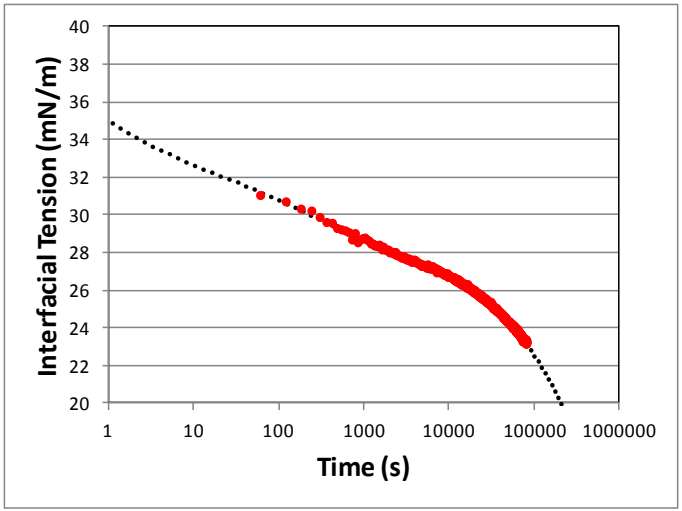
Validation against Freer and Radke's data (J. of Adhesion 80 (6), 481-496, 2004)

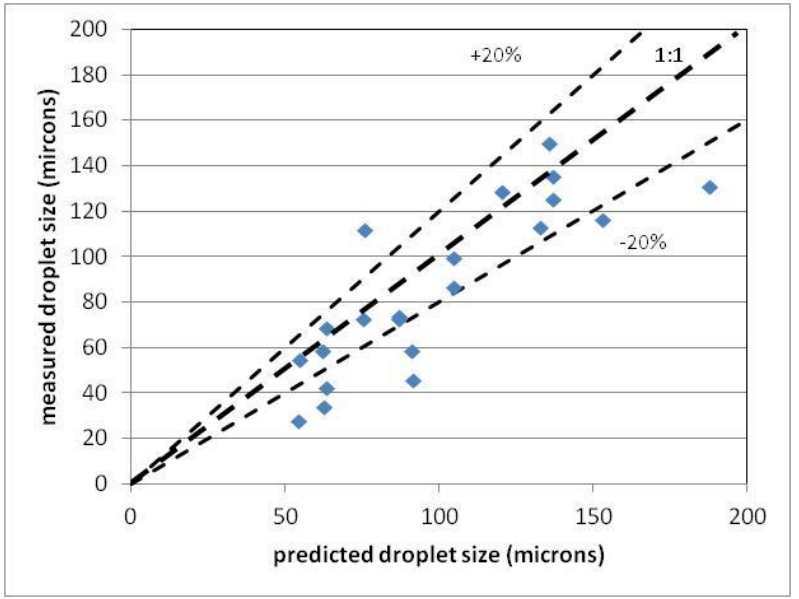




Extracting pseudocomponents properties from dynamic IFT enables prediction of dilatational rheology (seems to work for crude oil as well)

Application to the stirred tank experiments with good solvents





Most predicted droplet sizes fall within 20% of experiments

Publication forecast for the asphaltenes thrust

- CCNY on the extraction of pseudo-components from IFT and its use to predict rheology.
- CCNY on the use of Lattice gas model for asphaltenes.
- Joint SINTEF/CCNY on the prediction of droplet size in stirred tank experiments.
- Joint CCNY/SINTEF/Toulouse on the the analysis of IFT and rheology with crude oil?
- Joint CCNY/U. Toulouse on DFTB?

Contributors

S. Banerjee, F. Liu, S. Darjani, J. Rane (CCNY), A. Simon, J. Cuny (U. Toulouse), C. Sneegen, T. Didriksen, U. Farooq (SINTEF) T. Roy (NTNU)…….