Research Thrust I. Asphaltene adsorption, aggregation, and Interfacial Effects

Shaghayegh Darjani, Joel Koplik, , Aude simon, Vincent Pauchard, Sanjoy Banerjee

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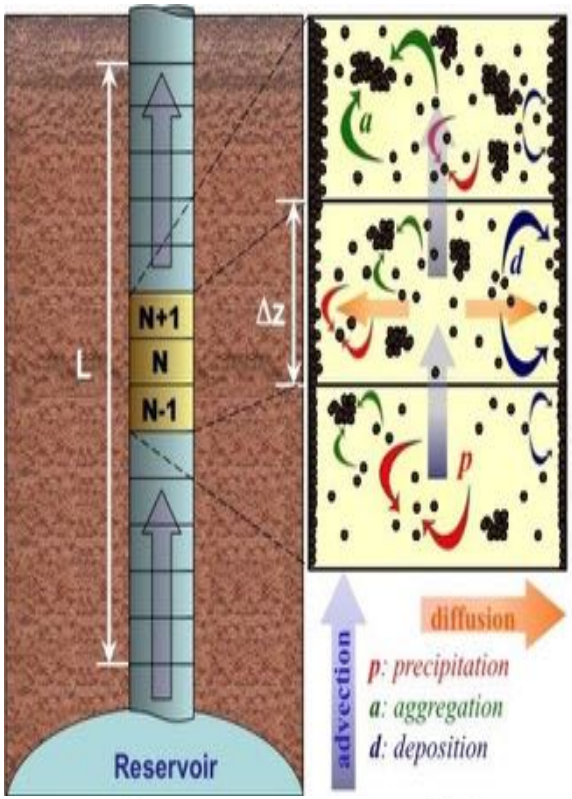
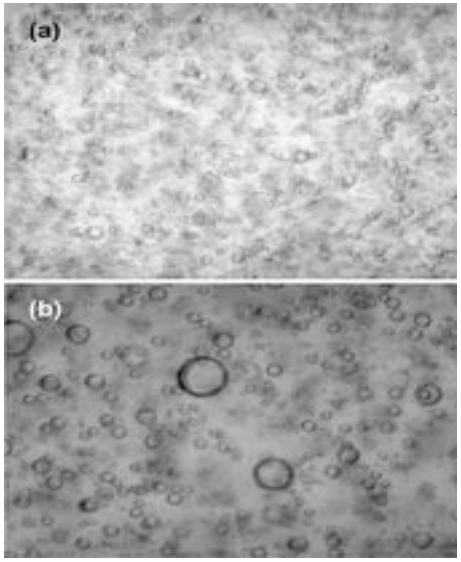
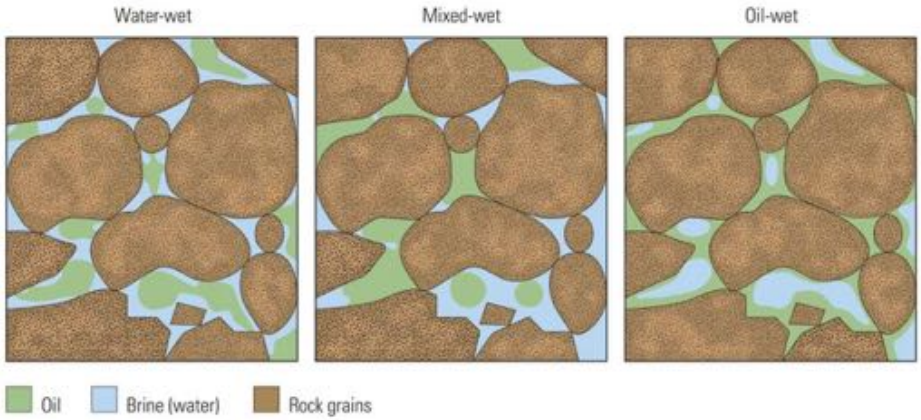
Motivation

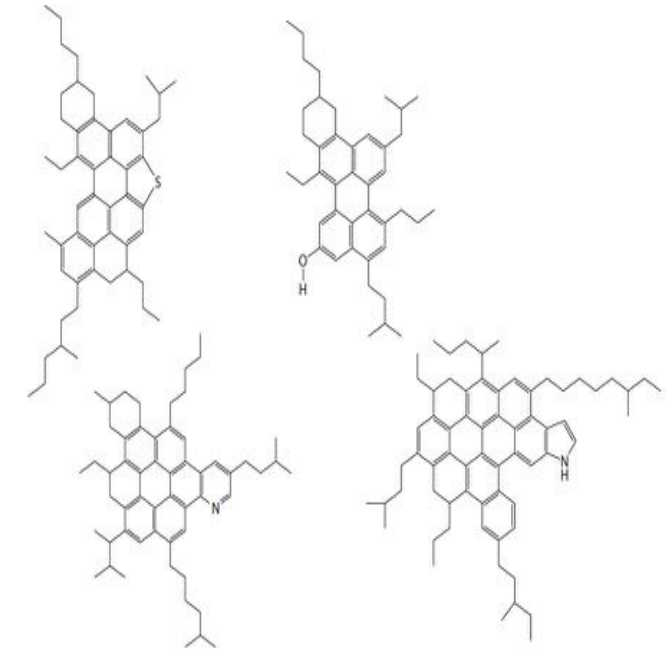
- *New reservoir with asphaltenic nature*
- *Precipitates*
- *Extreme viscosity*
- *Emulsion stability*







Asphaltene



Increased asphaltenes concentration

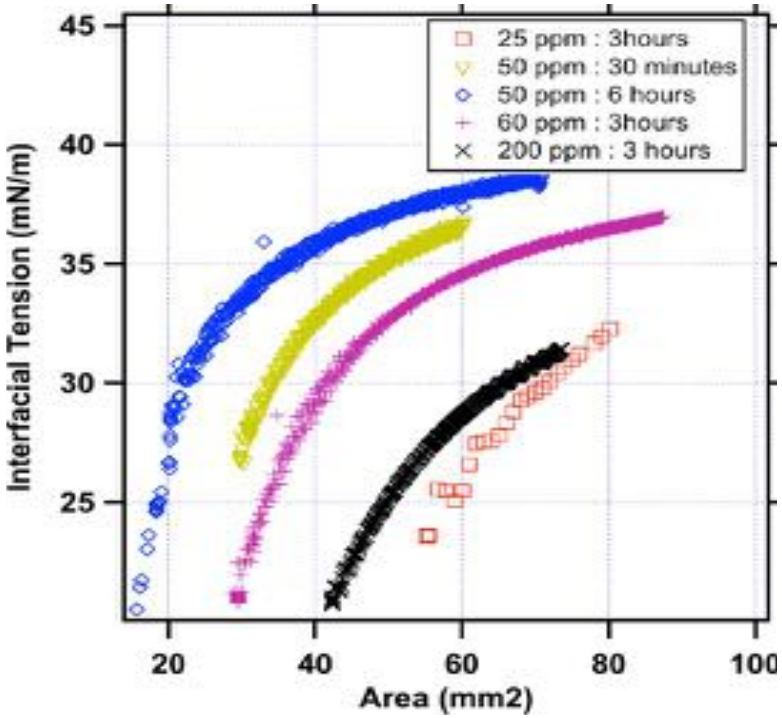
- Poly-disperse mixture: peripheral alkyl chains with different length, different heteroatoms with polar functionality in the PAH core
- Average molecular weight ~ 750 g/mol Range from 400 to 1500 g/mol
- Solubility class: insoluble in alkanes, soluble in aromatic solvent
- The most polarizable & surface active component of the crude oil

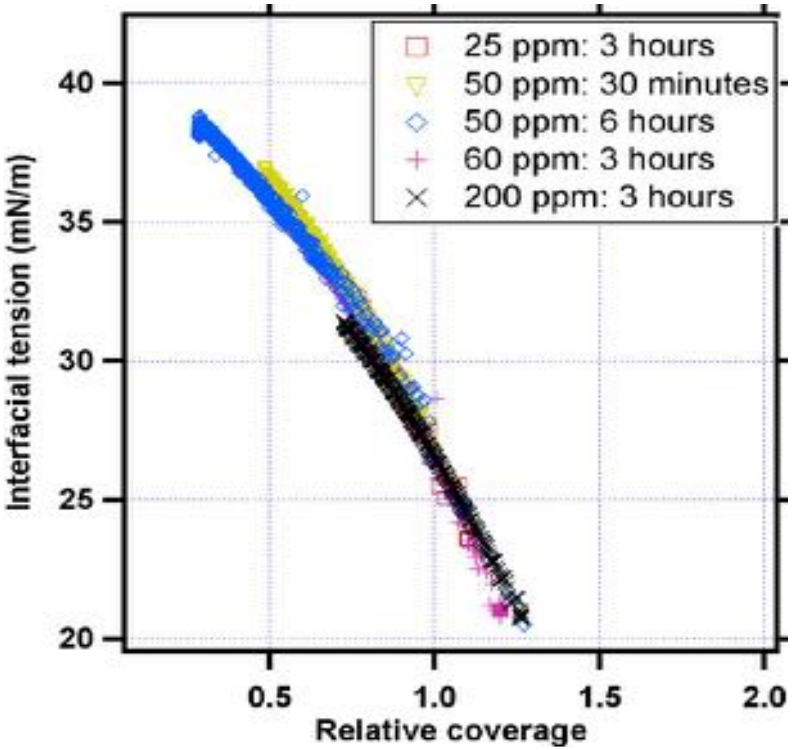
n-C_7 asphaltenes n-C_5 asphaltenes

Ramos et al. (2001); New Mexico Tech. Petroleum Recovery Research Center; Mullins. (2010)

From Schlumberger

Contraction & Expansion of solution of Norwegian asphaltenes in a poor solvent





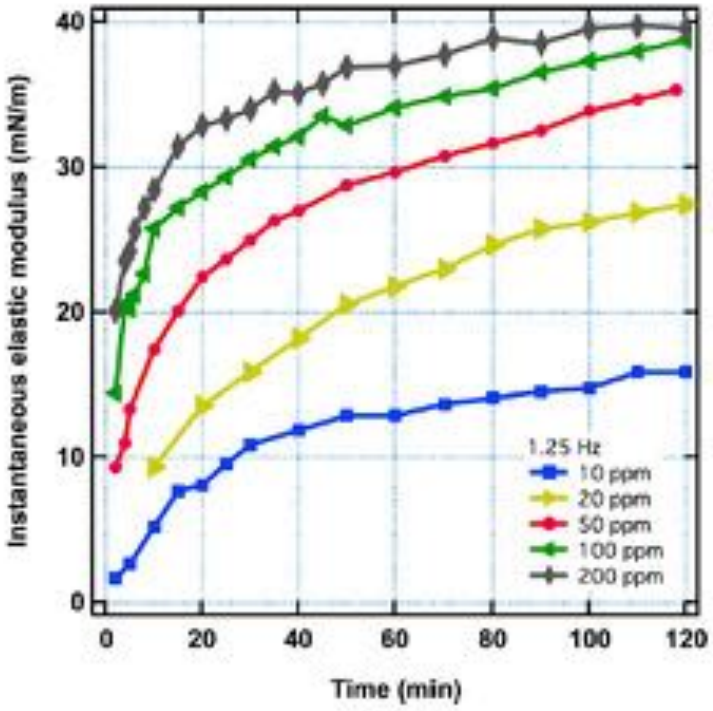
Langmuir EOS

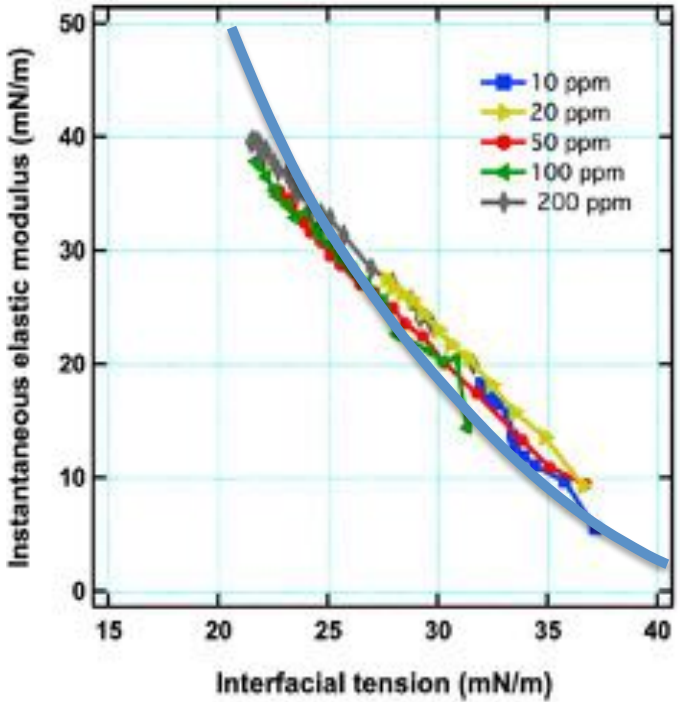
$$\Pi = -\frac{k_B T}{A_0}\ln(1-\Theta)$$

A_0= 0.3 nm^2/molecules

Rane et al, Langmuir 2013

Dilatational rheology of Norwegian asphaltenes in a poor solvent





$$E_0 = \Theta \frac{\partial \Pi}{\partial \Theta} = \frac{k_B T}{A_0} \frac{\Theta}{1-\Theta}$$

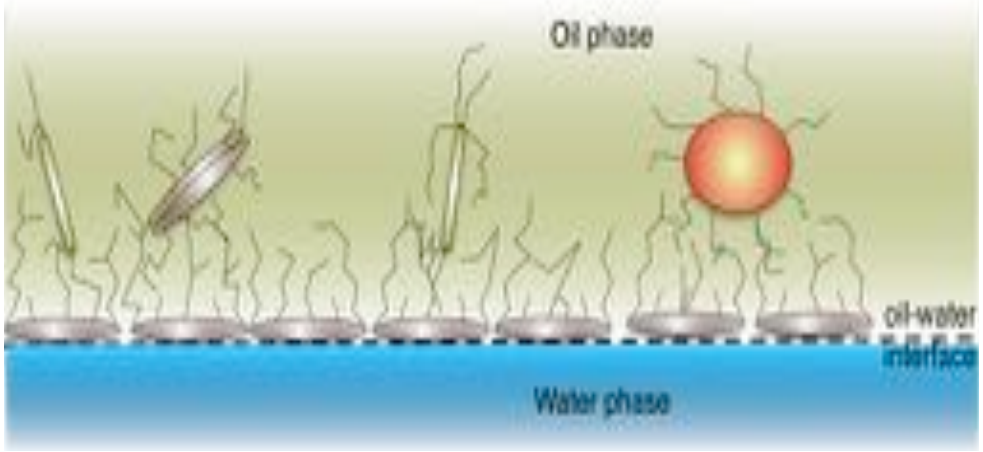
$$\Pi = -\frac{k_B T}{A_0} \ln(1-\Theta)$$

Langmuir EOS

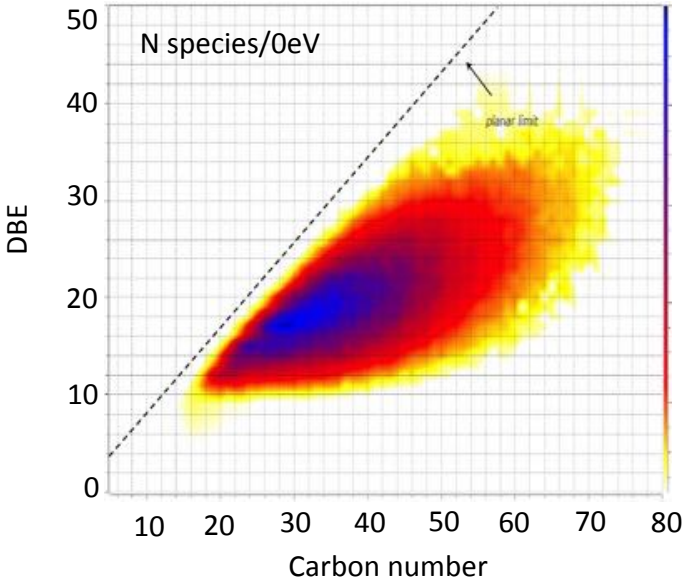
A_0= 0.3 nm^2/molecules

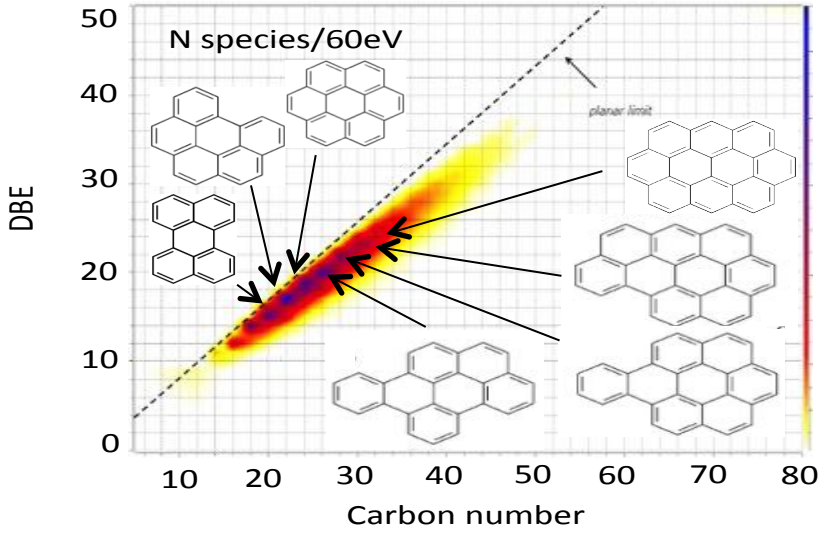
Rane, Pauchard, Couzis, & Banerjee (2013)

- *0.3 nm^2/molecule correspond to carbon skeleton of 6 fused aromatic rings (NMR)*
- *Flat on* adsorption of asphaltenes core on water *(SFG)*
- ***Asphaltene molecule*** **approximately** ***covers 3 water molecule.***



FTICR MS with collision for de-alkylation

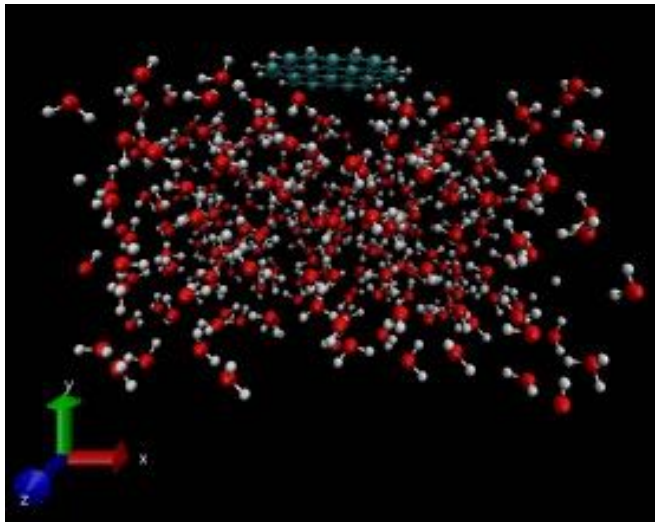




Similar behavior for most compound classes

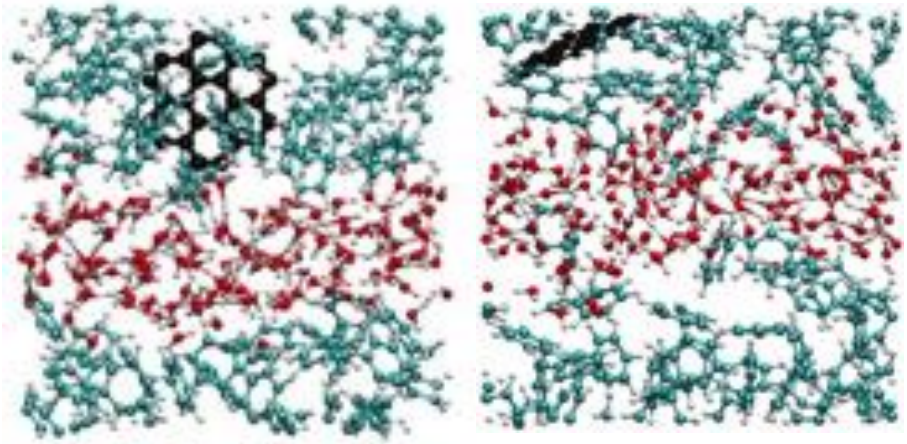
Pauchard et al, Petrophase 2013

DFTB simulations of Benzene and Coronene on water cluster.



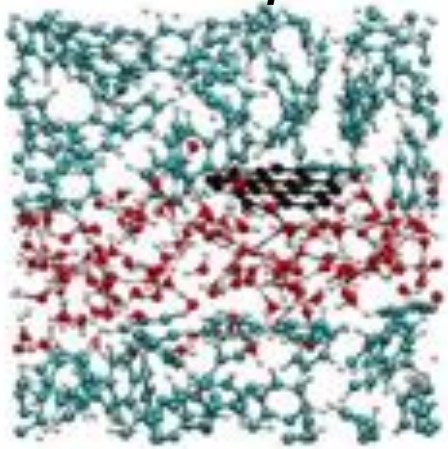
Coronene

t=0 ⟶ *t=54 ps*



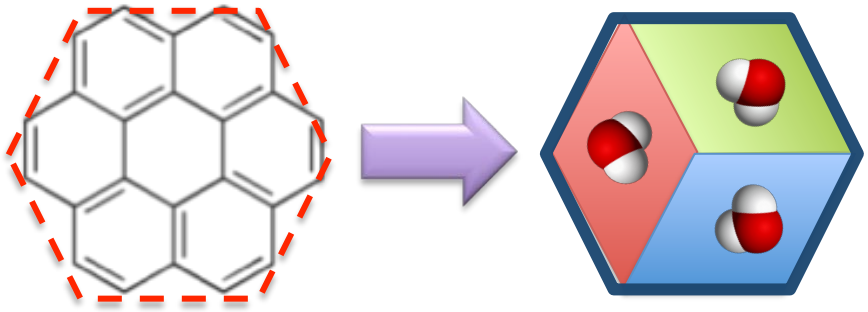
perpendicular -> desorption

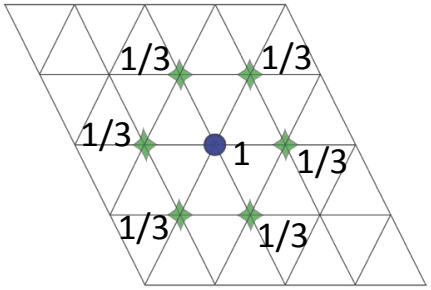
t=100 ps

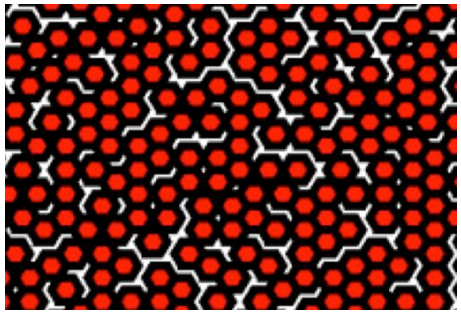


parallel -> stable

Lattice gas adsorption simulation





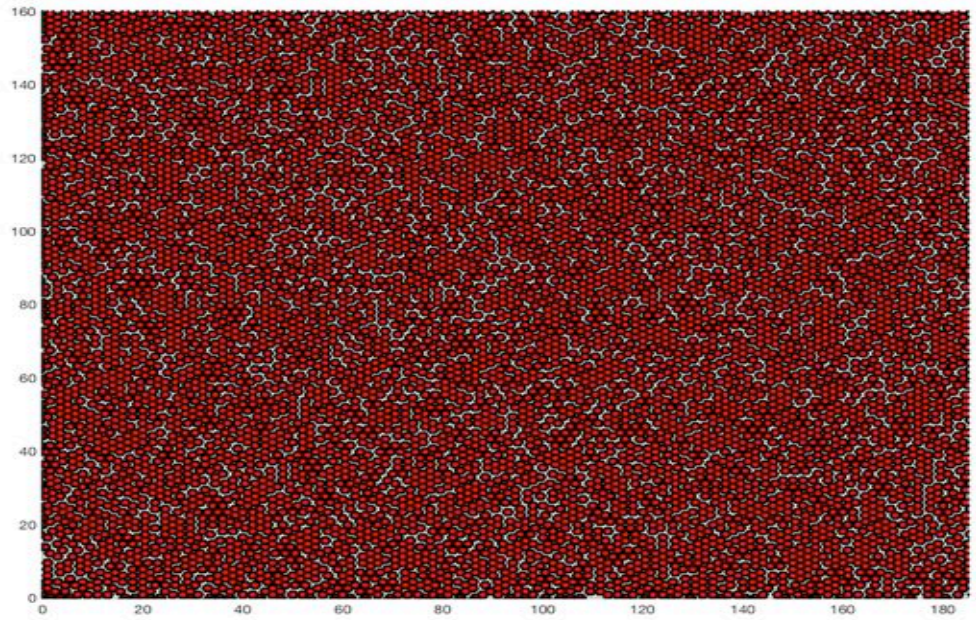


Monte Carlo simulation

- Adsorption Method(Empty to full lattice)
- Desorption Method(full to empty lattice

Assumption

- Infinite repulsive interaction between hard core molecule
- Infinite repulsive interaction between neighboring site



D=0 Θ→0.694

Kinetic Argument

→ At Equilibrium rate of Adsorption= Rate of Desorption

$$k_a C[1-\beta(\Theta)] = k_d \Theta$$

→ $\beta(\Theta)$ is blocking function, the fraction of the surface area which is excluded from further adsorption by already adsorbed molecules.

$$\frac{\partial N}{\partial n} = 1-\beta(\Theta)_{dynamic}$$

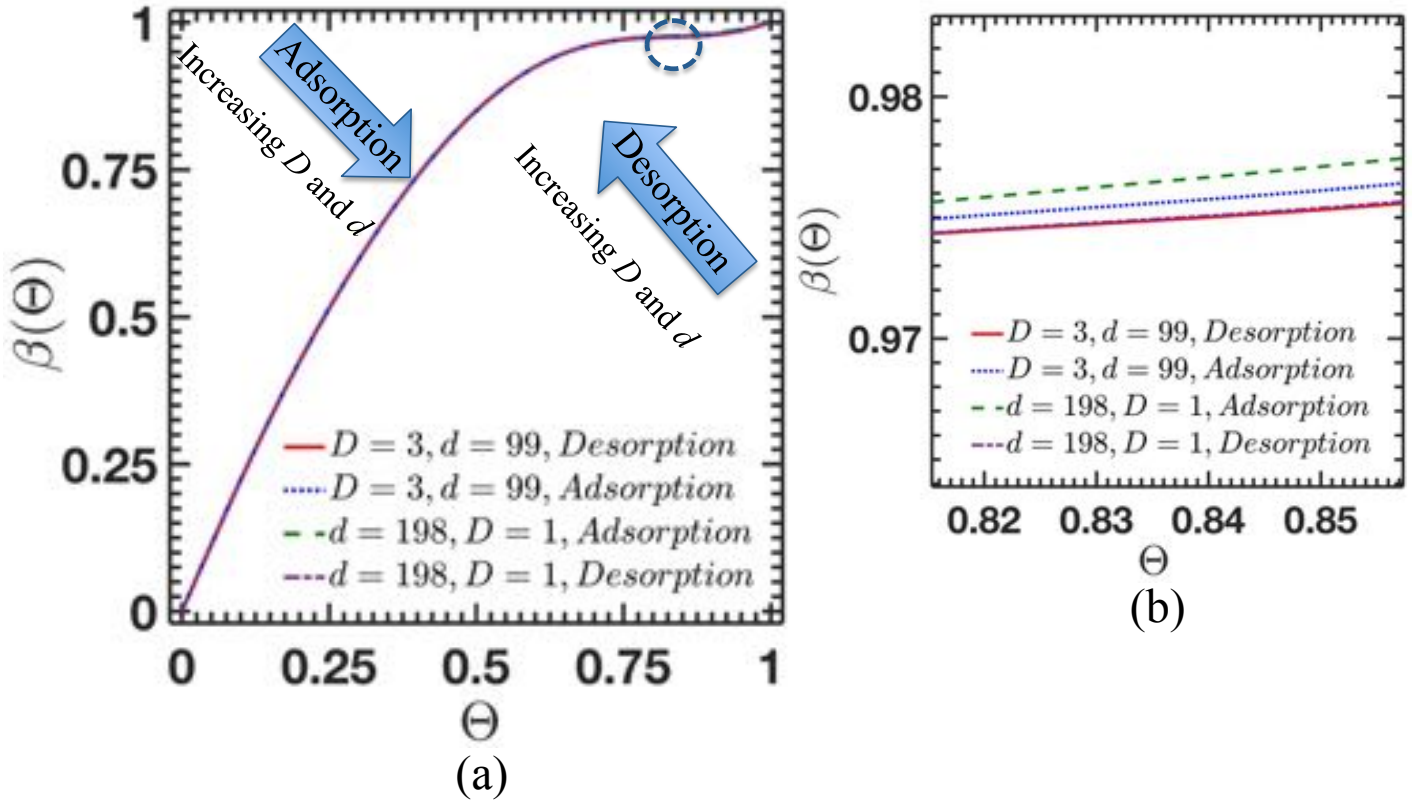
→ Gibbs adsorption isotherm from equality of chemical potential in the system

$$d\Pi = kT\frac{\Theta}{A_a}d\ln C$$

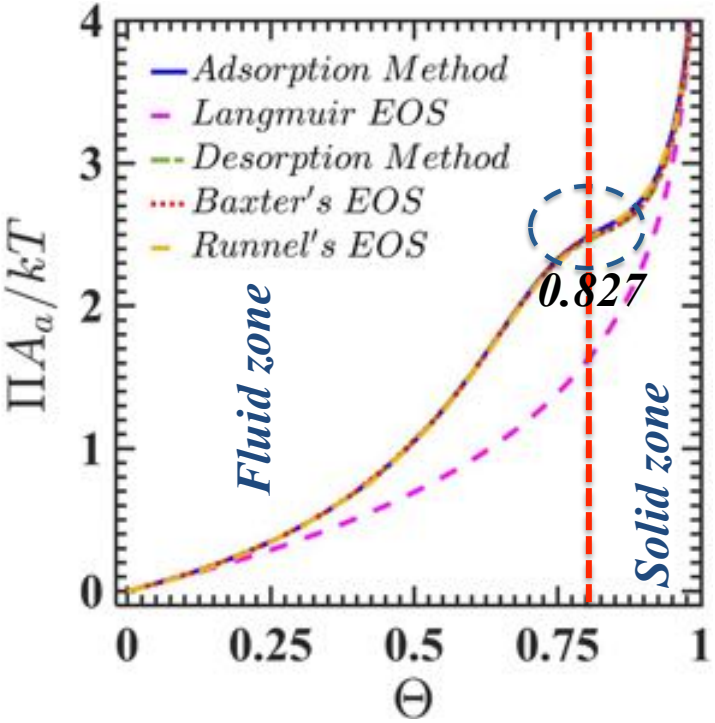
→ Finding the Equation of state from Gibbs Adsorption isotherm

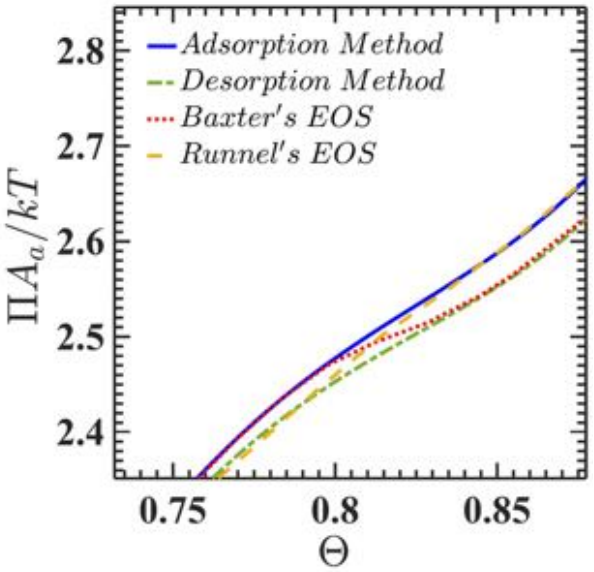
$$\int_0^{\Theta}(1-\beta(\Theta))\frac{\partial}{\partial\Theta}\left[\frac{\Theta}{1-\beta(\Theta)}\right]d\Theta = \frac{A_a}{kT}\Pi$$

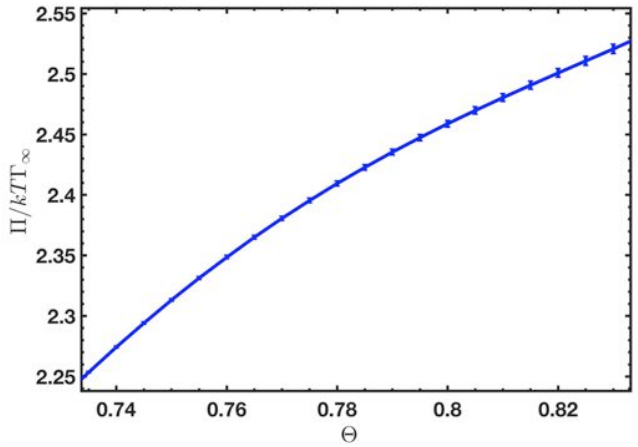
Same Blocking function obtained at equilibrium

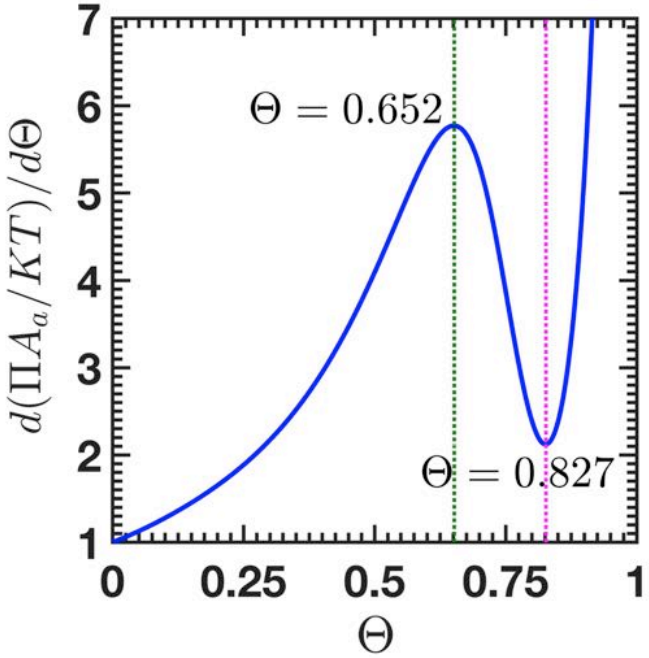


Comparison of Equation of State With Literature



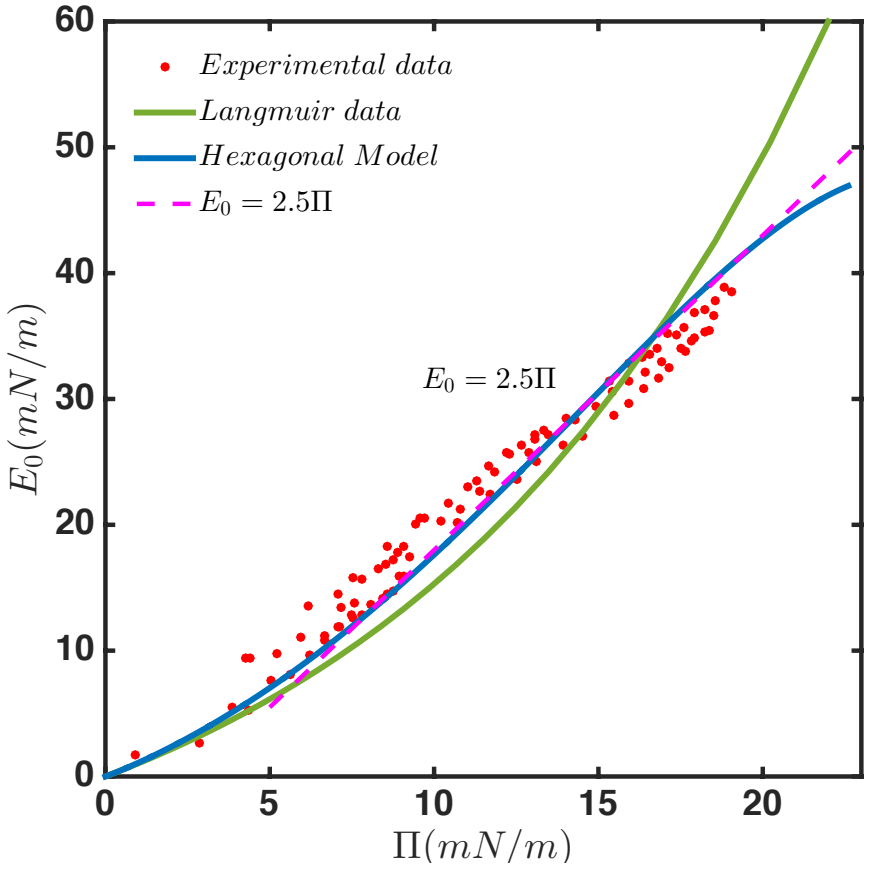


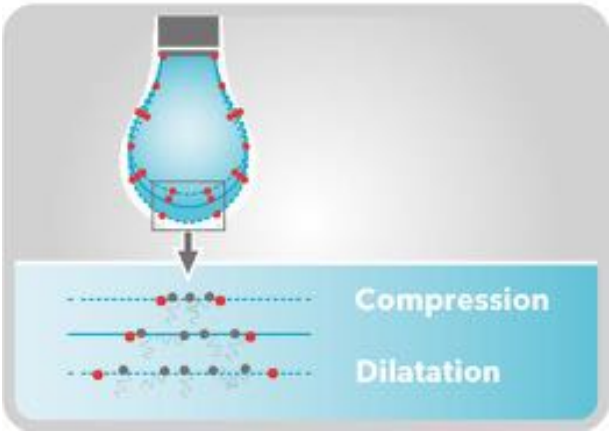


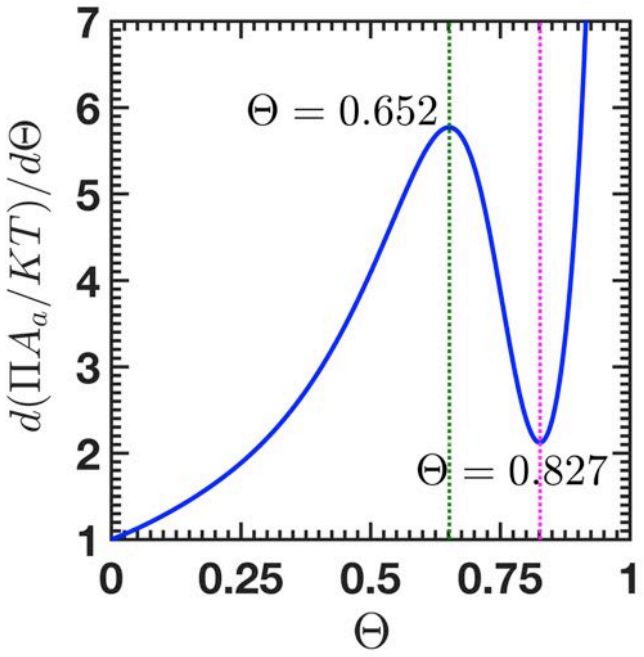


Darjani, Koplik, Pauchard, PRE, 2017

Dilatational Rheology Experiment





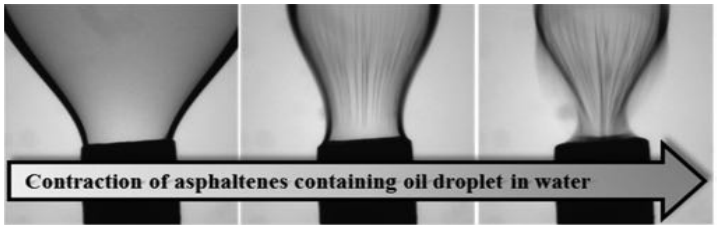


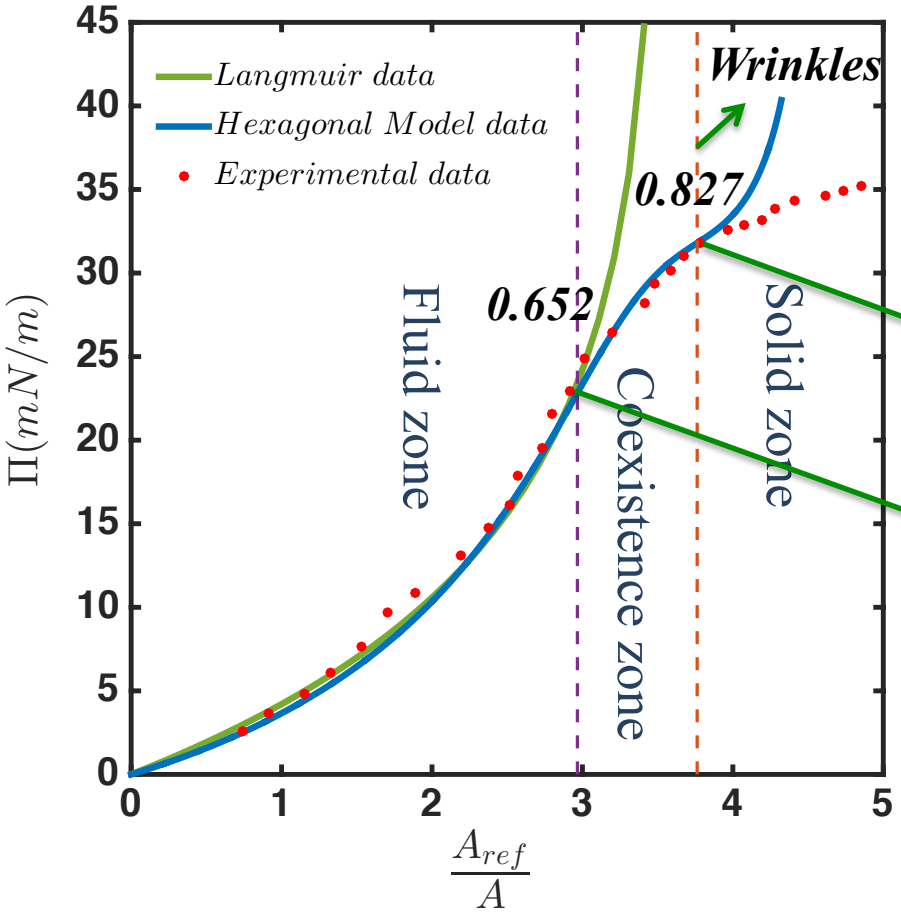
Expansion-Contraction Experiment

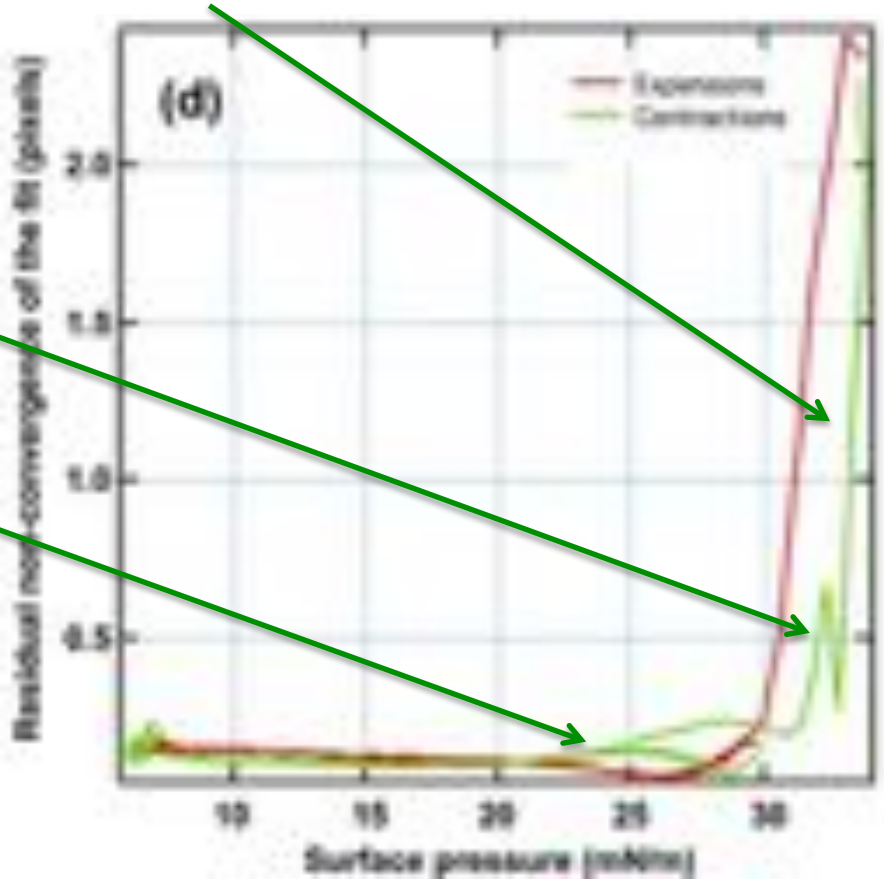
Hysteresis between Expansion and Contraction

Experiment ⟶ ***Dynamic Frustration***

$$\Gamma(t)A(t) = \Gamma(A_{ref})A_{ref}$$



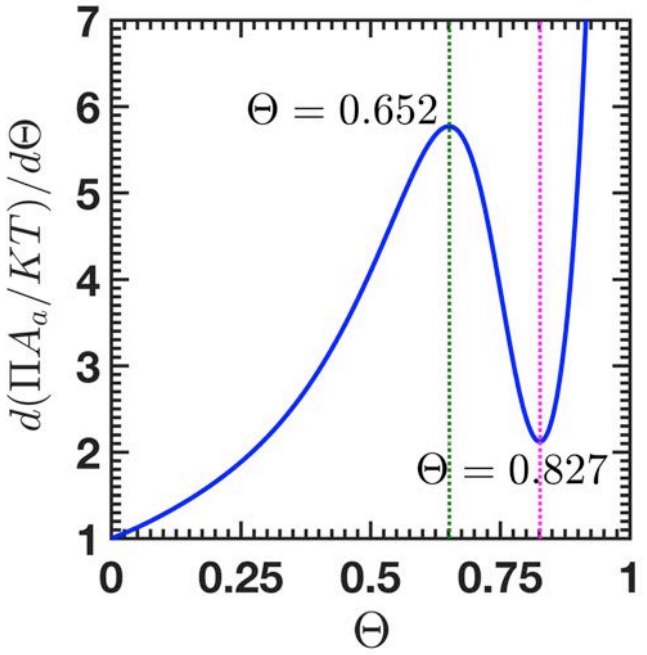


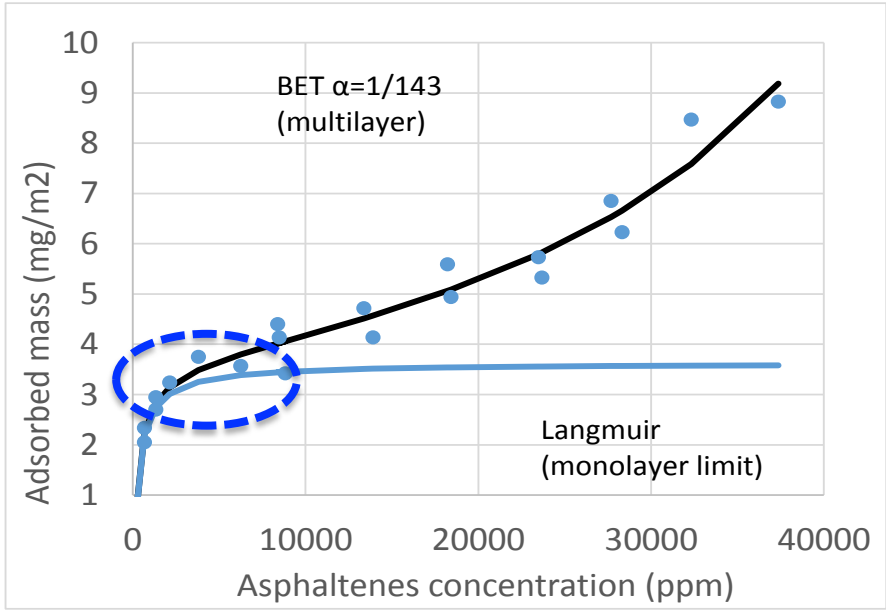


Pauchard et al., *Langmuir (2014)*

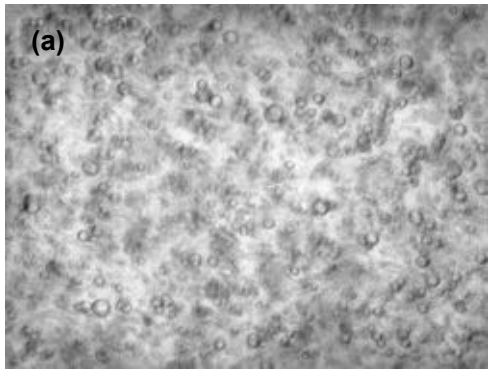
Emulsion stability & Transition to multi-layer

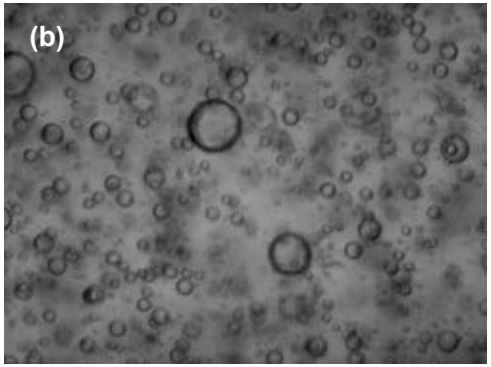
By considering M_w~750 g/mol:
Θ=0.827 → 3.86 mg/m²





This value reported as a critical value for emulsion stability in the literature where blockage of coalescence occurs.

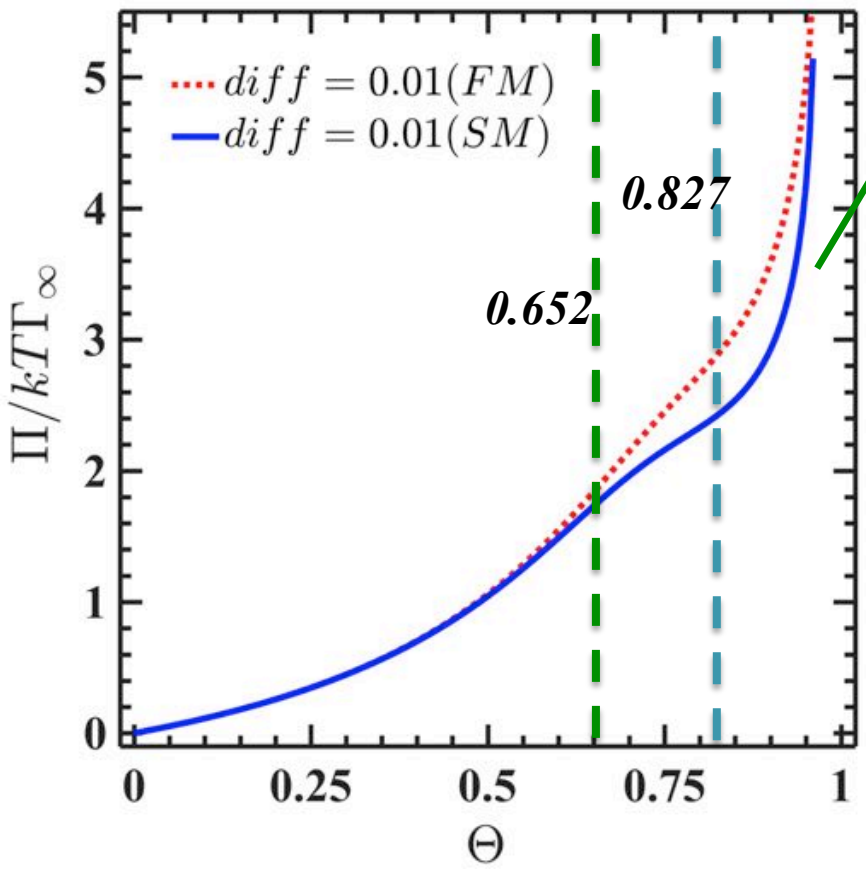


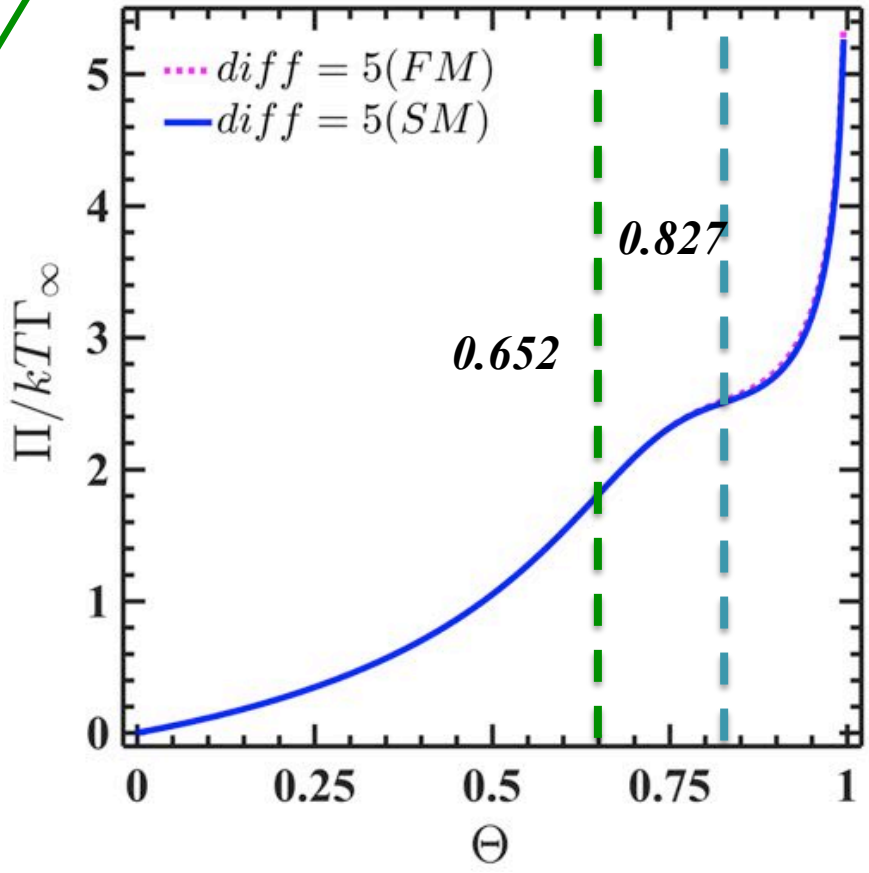


Data from Sztukowski et Journal of colloid and interface science 2003
Pauchard and Roy Colloids and Surfaces A 2014

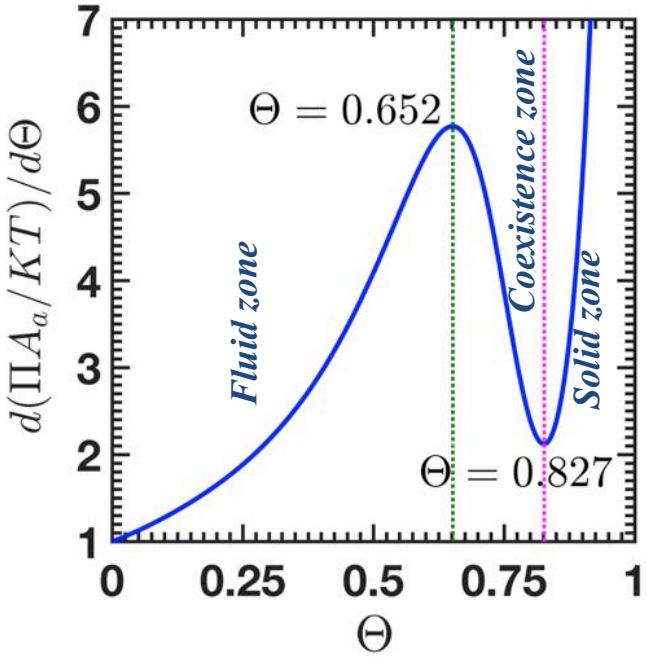
Kinetic Frustration around Phase Transition Zone

Caging effect relaxed by thermal motion or stress (diffusion here)
Soft Glass Rheology model could be a good option





Ordering

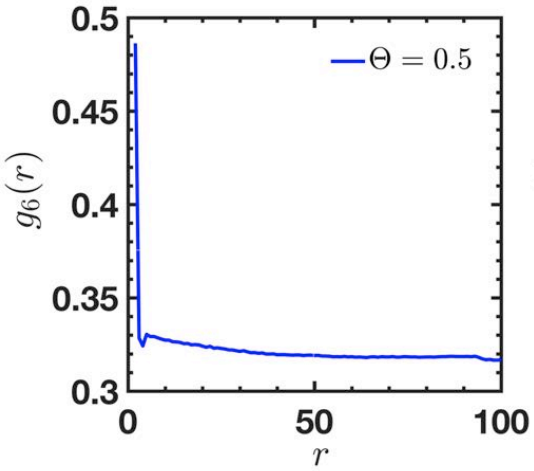


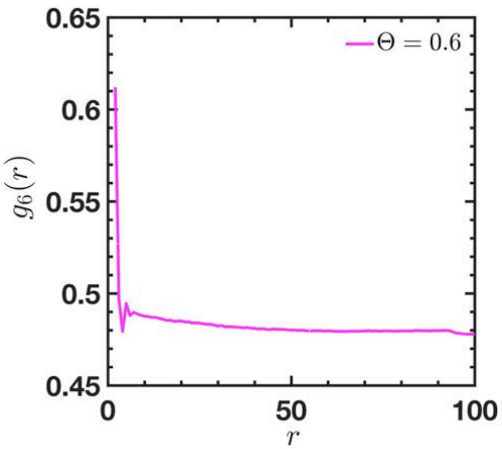
Local Bond orientation order:

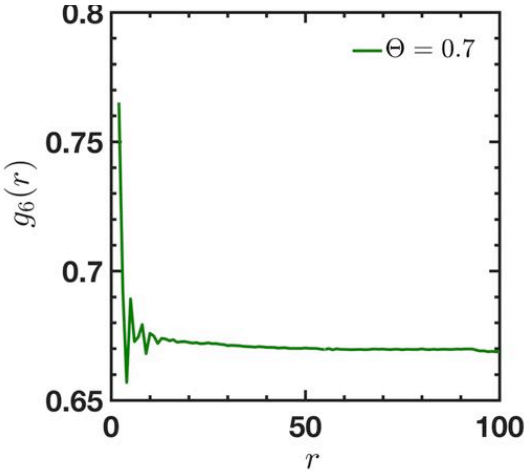
$$\Psi(r_j) = \frac{1}{N_k}\sum_{k=1}^{N_k} e^{i6\theta_{jk}}$$

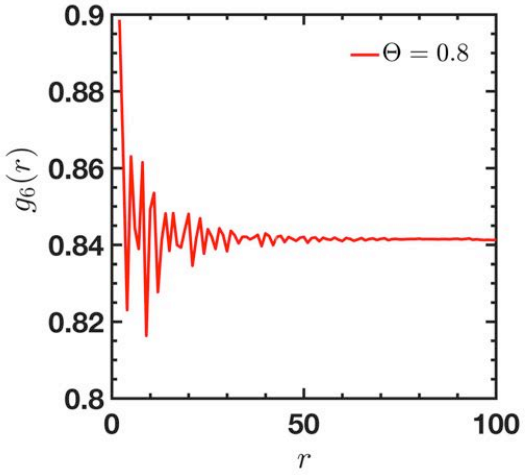
Bond orientational correlation function:

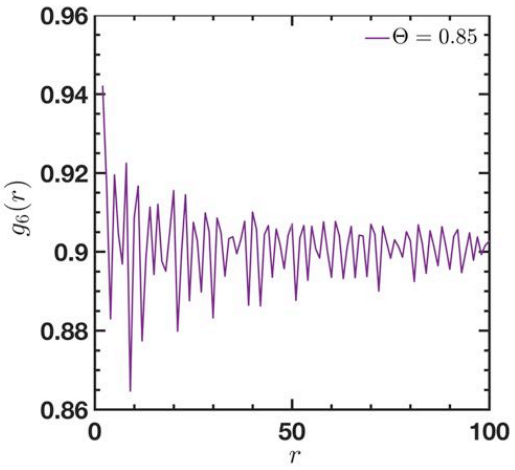
$$g_6(r) = \frac{\left\langle \sum_{k\neq j}^{N} \Psi(r_j)^* \Psi(r_k)\delta(r - |r_j - r_k|) \right\rangle}{\left\langle \sum_{k\neq j}^{N} \delta(r - |r_j - r_k|) \right\rangle}$$

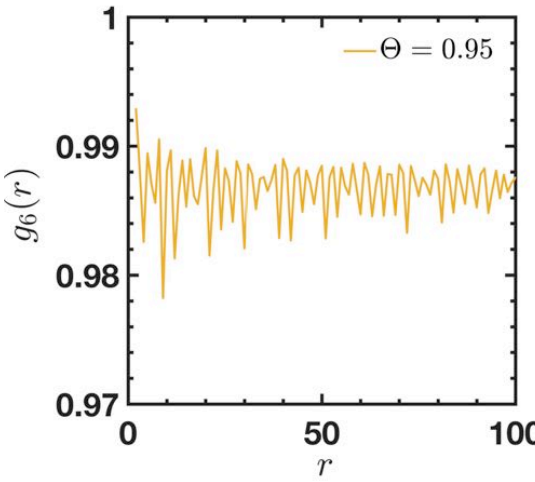












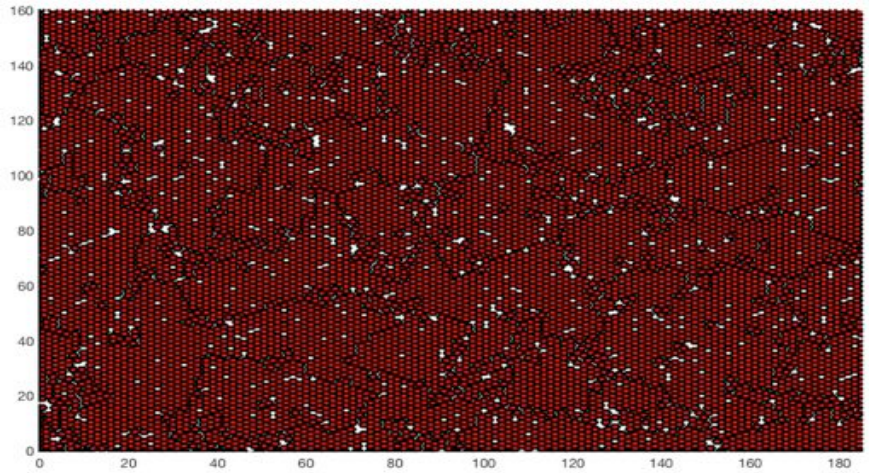
Relaxation dynamics of glassy states

2 step simulations:

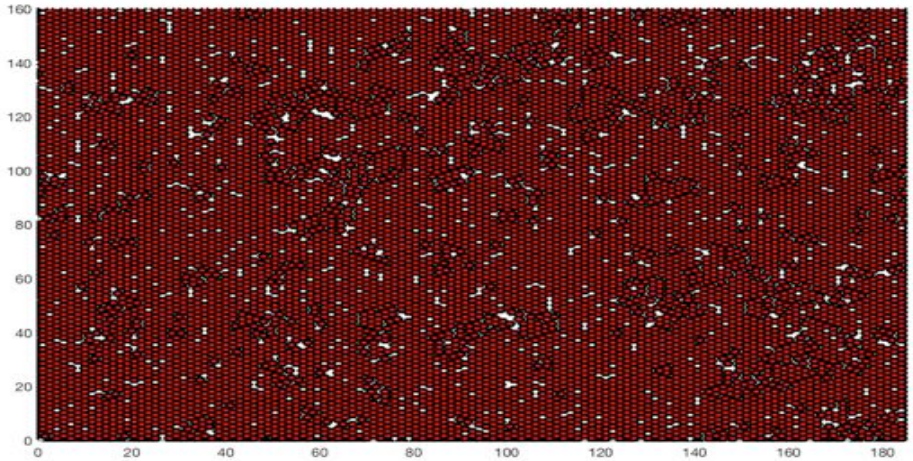
1. RSA with diffusion

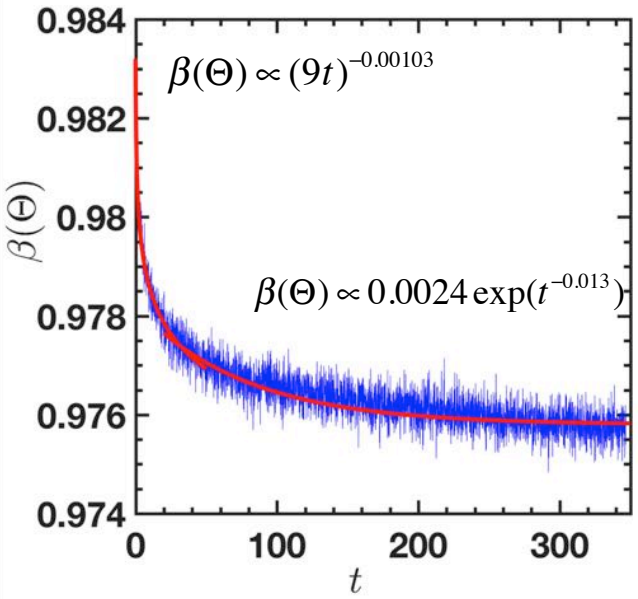
2. Diffusion only to see the evolution of β with time

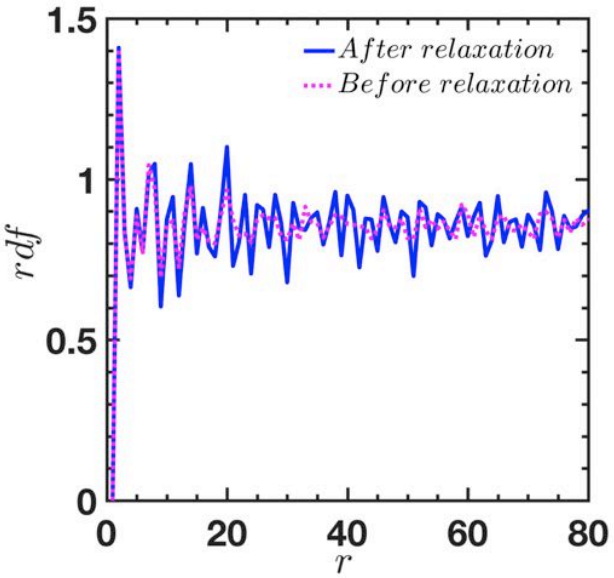
t=0

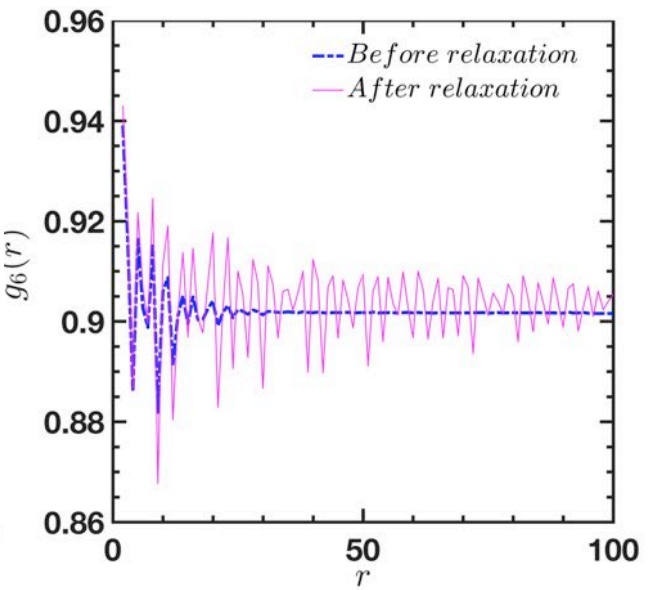


t=350









Birefringence is Observed on Contracted droplet

Varadaraj et al., *Energy & Fuel (2012)*

Conclusion

1. *Adsorption of asphaltene on the oil/water interface follow an EOS which can be found from Lattice gas model*
2. *Asphaltene adsorbed as a monolayer up to 3.86 mg/m^2 and after that multilayer is built.*
3. *Transferring to solidification zone stopped the coalescence and cause wrinkle appears on the droplet.*
4. *Diffusion and desorption in the system leads the system toward equilibrium. But if there are not sufficient enough, relaxation took a longer time.*
5. *Equilibrium system shows a strong ordereringwhich is in agreement with birefringence observation by Varadaraj et al.*

Thanks For Your Attention!