Studies of Asphaltene Deposition onto Hydrophilic Surfaces Using Quartz Crystal Microbalance with Dissipation

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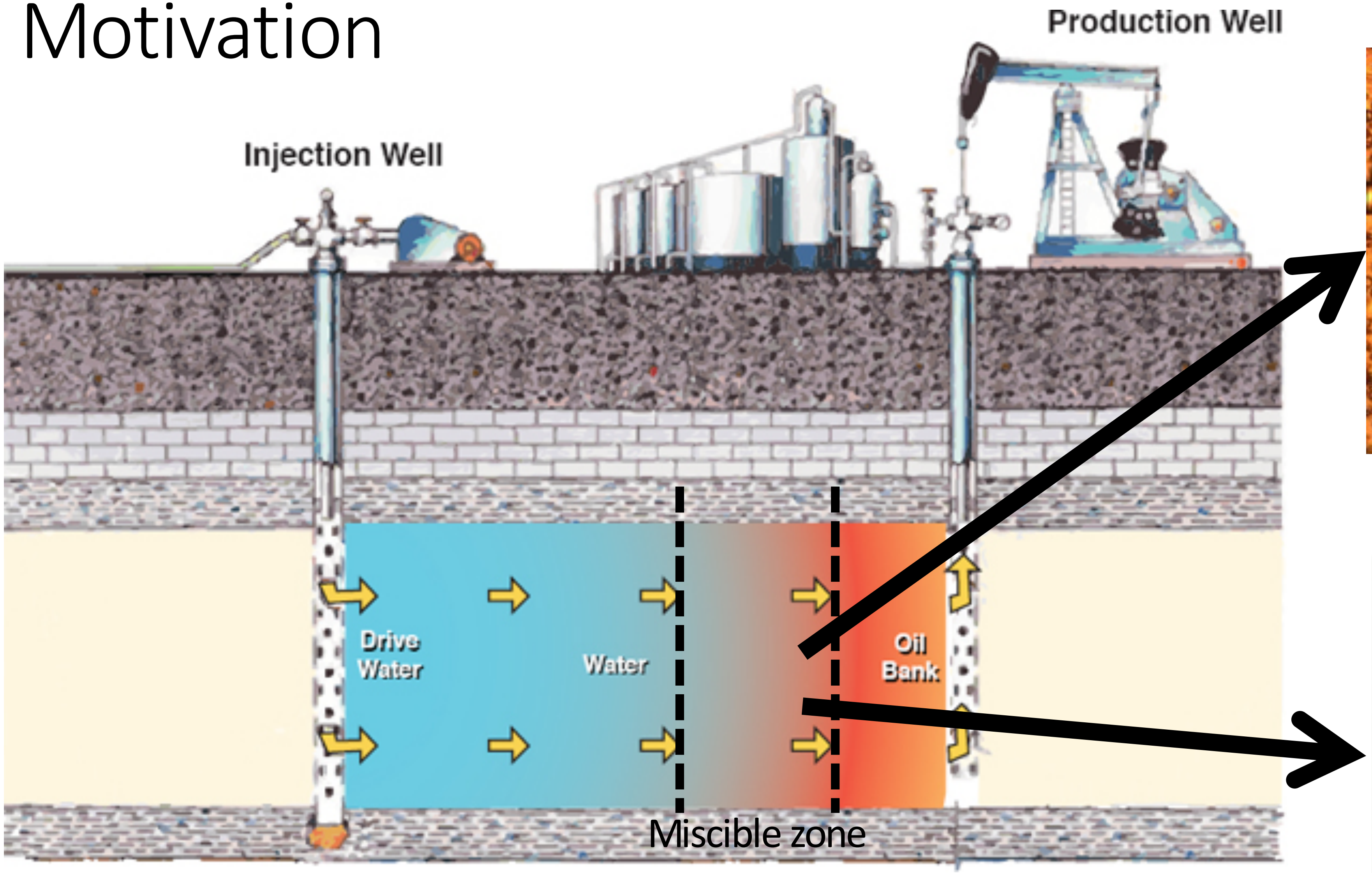
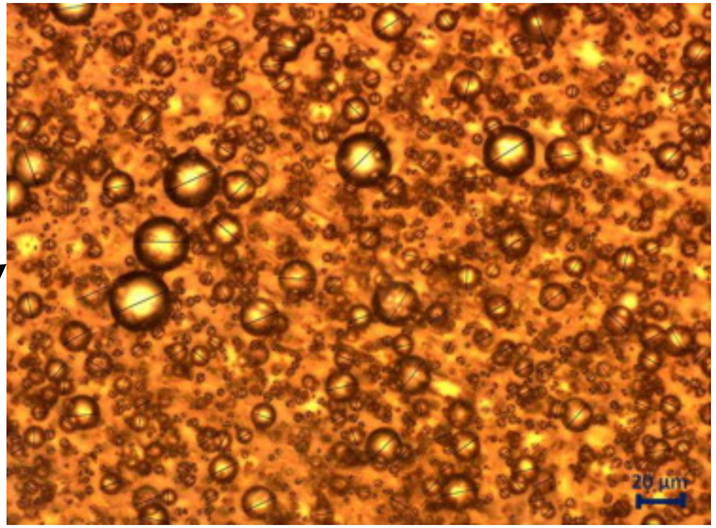
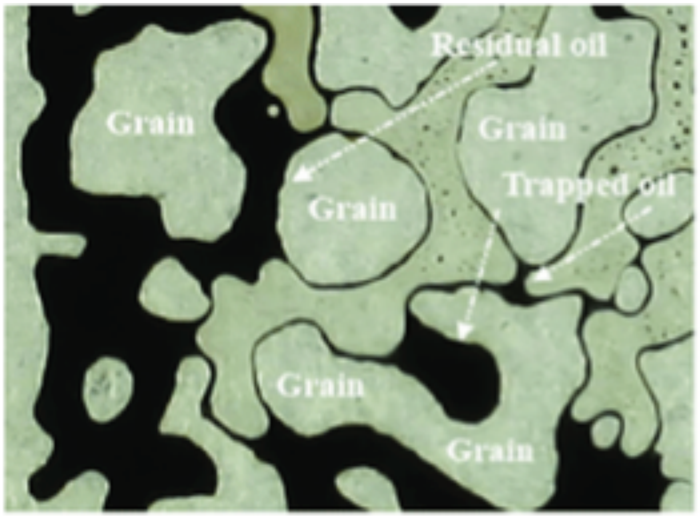
Motivation



w/o emulsion



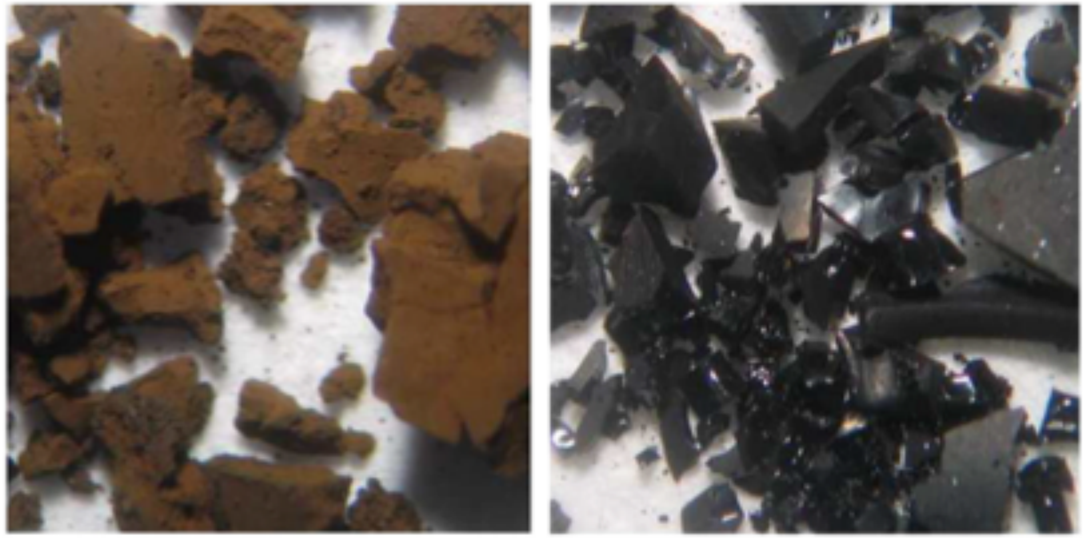
w/o/r interaction



NETL (2010); Ghahremani et al. (2017); Petropedia (2018)

Asphaltenes

- Most polar and surface-active fraction (1.8 – 18wt%) in crude oil
- Solubility class
  - Soluble in aromatic solvent (eg. toluene)
  - Insoluble in n-alkanes (eg. n-heptane)
- Adsorb at water-oil interface
  - Hinder water droplets coalescence
  - Stabilize water-in-oil emulsion
- Deposit on pipeline and reservoir rocks
  - Block the wellbore and prevent further flow
  - Change surface wettability upon adsorption

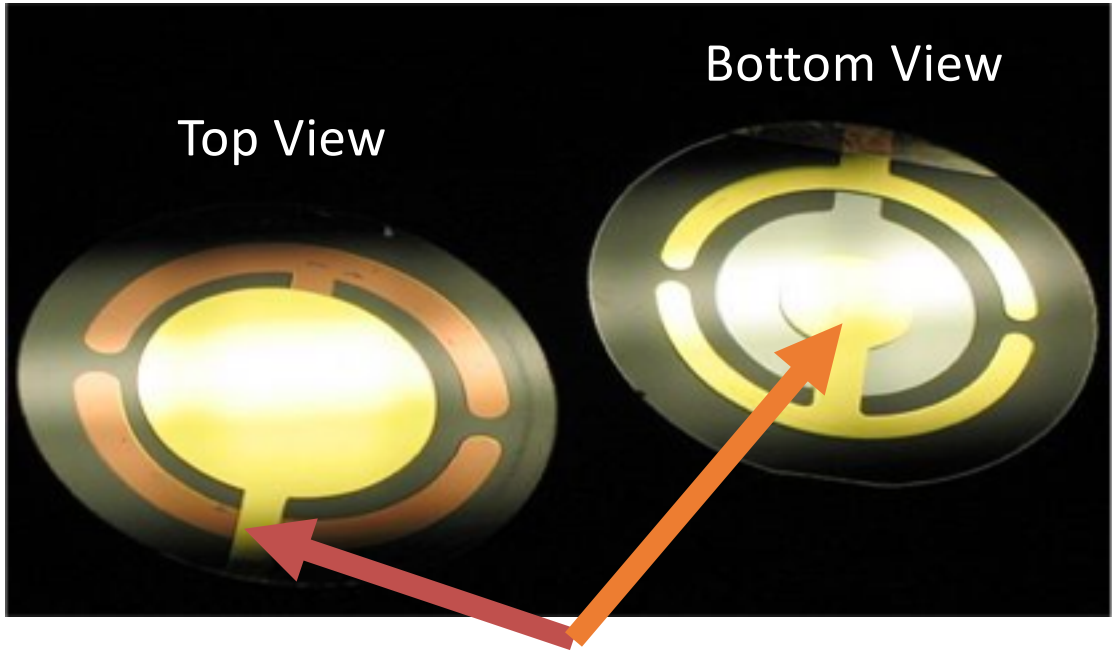


A) n-C_5 asphaltenes   B) n-C_7 asphaltenes

Ramos et al. (2001); New Mexico Tech. Petroleum Recovery Research Center; King (2016)

Quartz Crystal Microbalance with Dissipation (QCM-D) Technique

Quartz Crystal Microbalance with Dissipation (QCM-D)

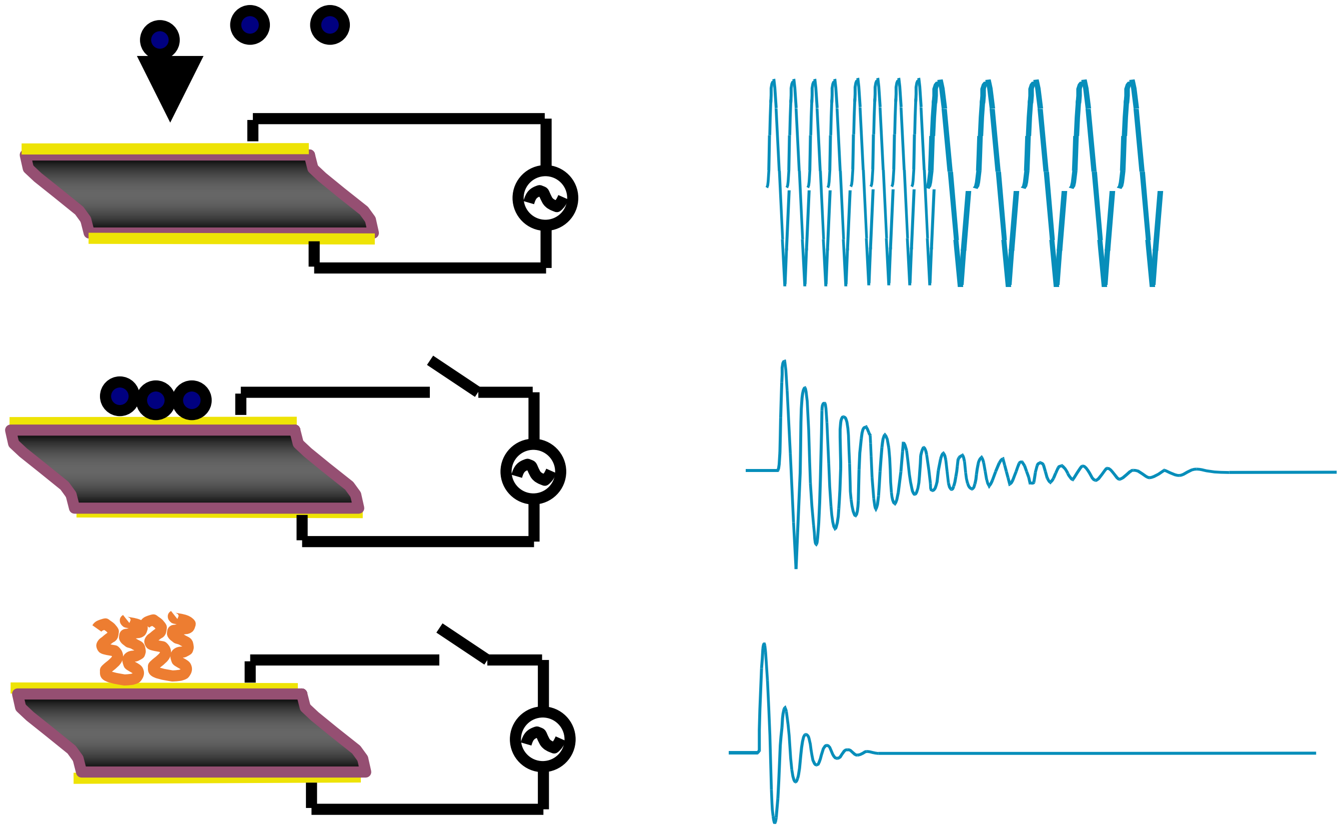


Electrodes

- Analyzes interactions/reactions occurring at surfaces
- Measures mass coupled with the surface or the thickness of the adsorbed film
- Quantifies viscoelasticity of the coupled layer (i.e. rigidity/softness changes)

Biolin Scientific (2016); Wikipedia (2008)

Working Principle of QCM-D



Addition of Mass decreases frequency

Smaller dissipation indicates rigidly bound mass

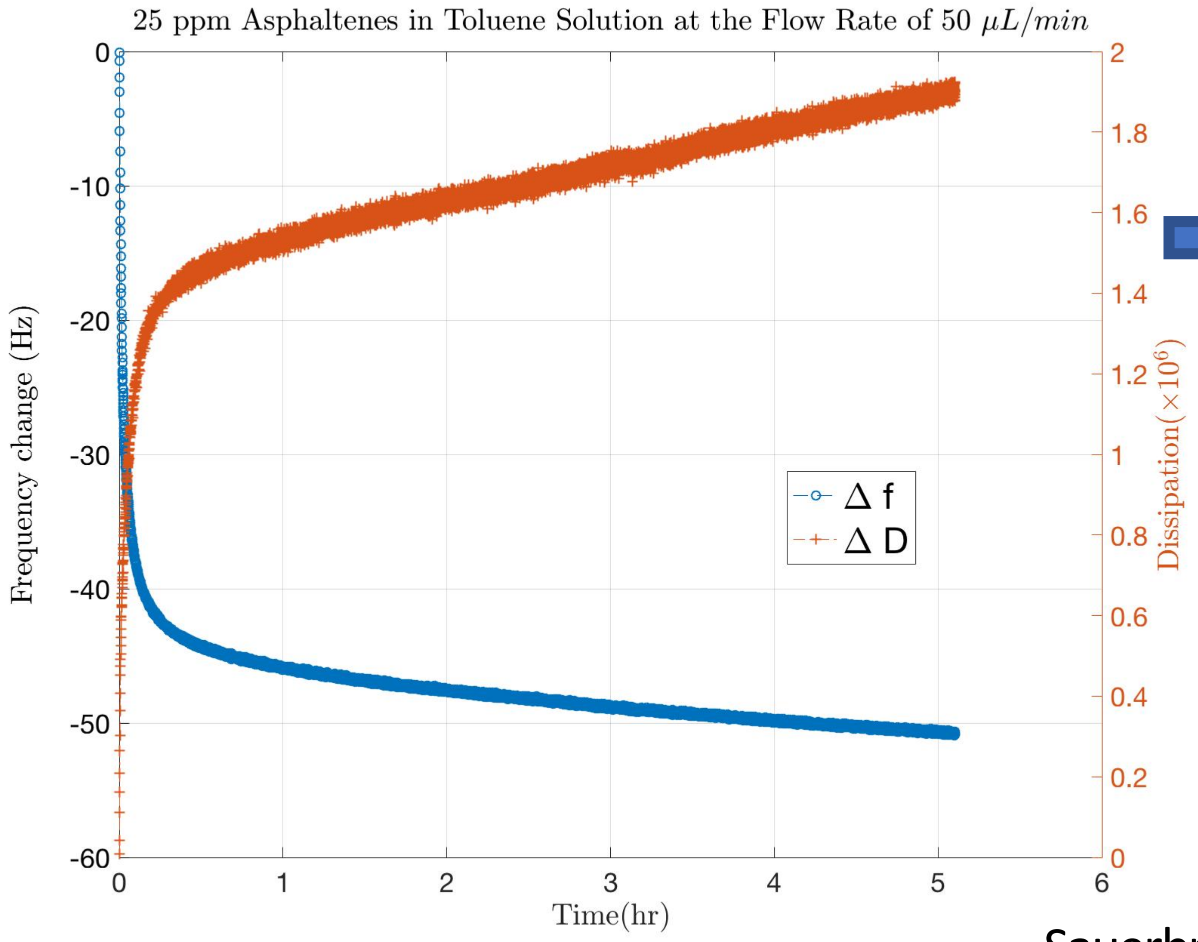
Larger dissipation indicates soft mass

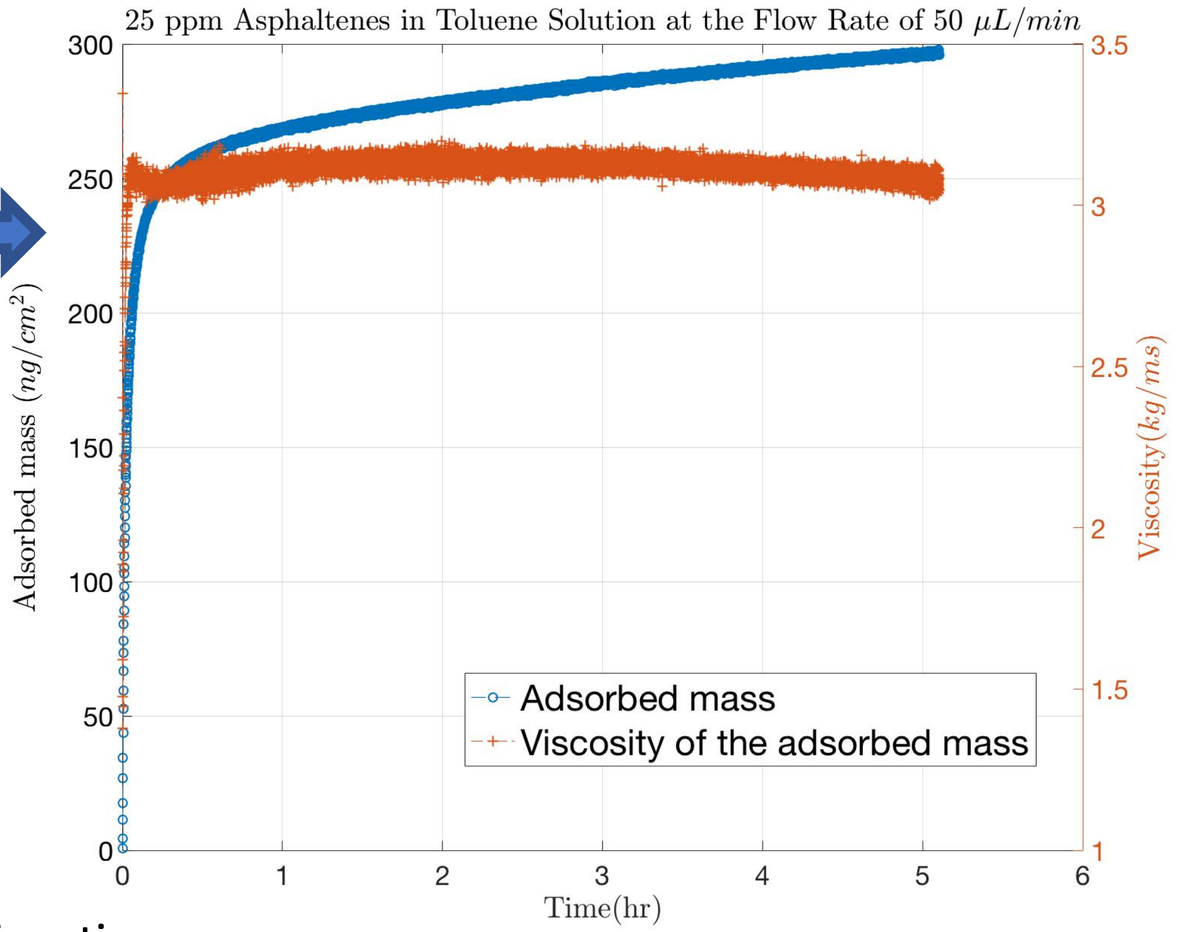
$\Delta f \ \alpha$ coupled mass

$\Delta D \ \alpha$ Viscoelastic properties

Biolin Scientific (2016)

Analysis of Experimental Data



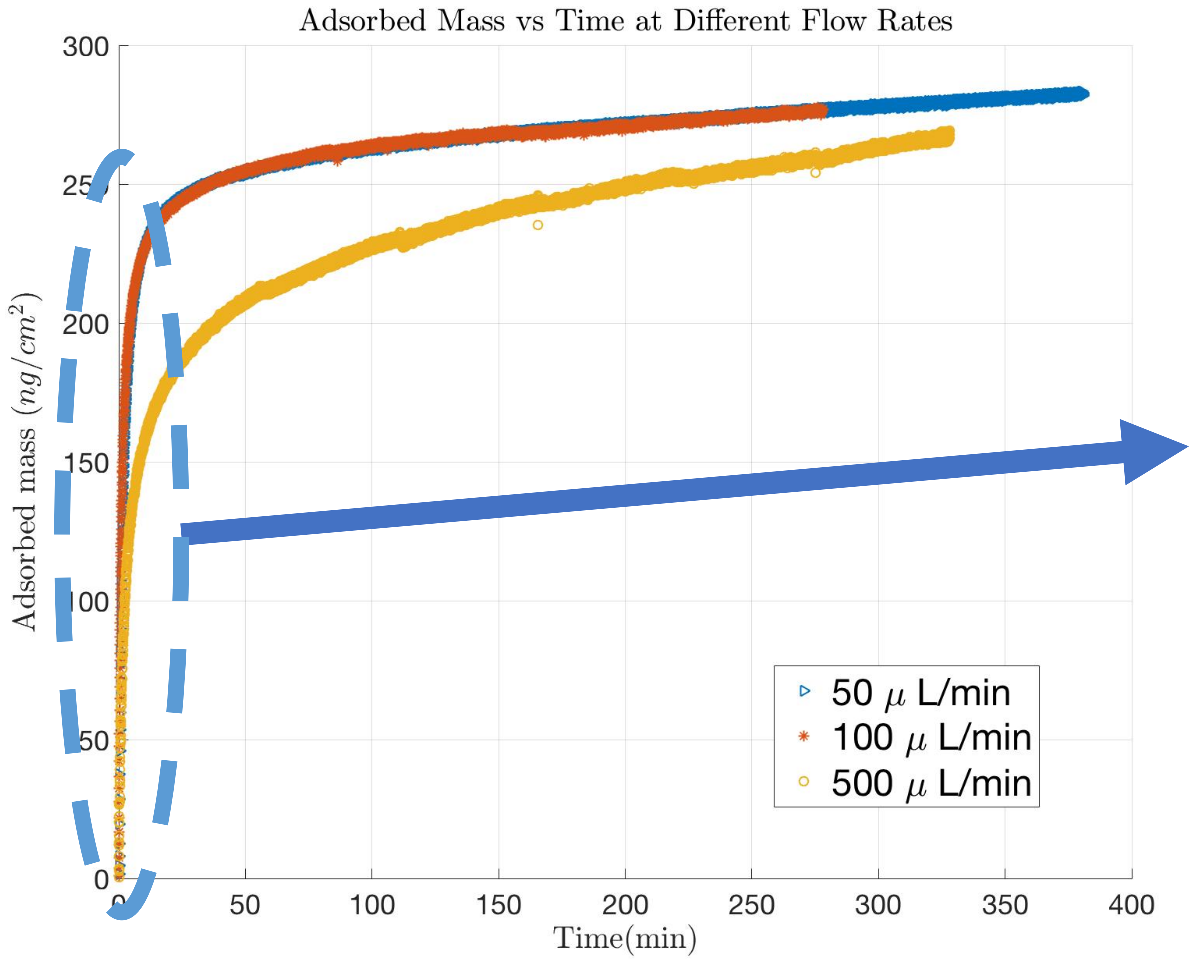


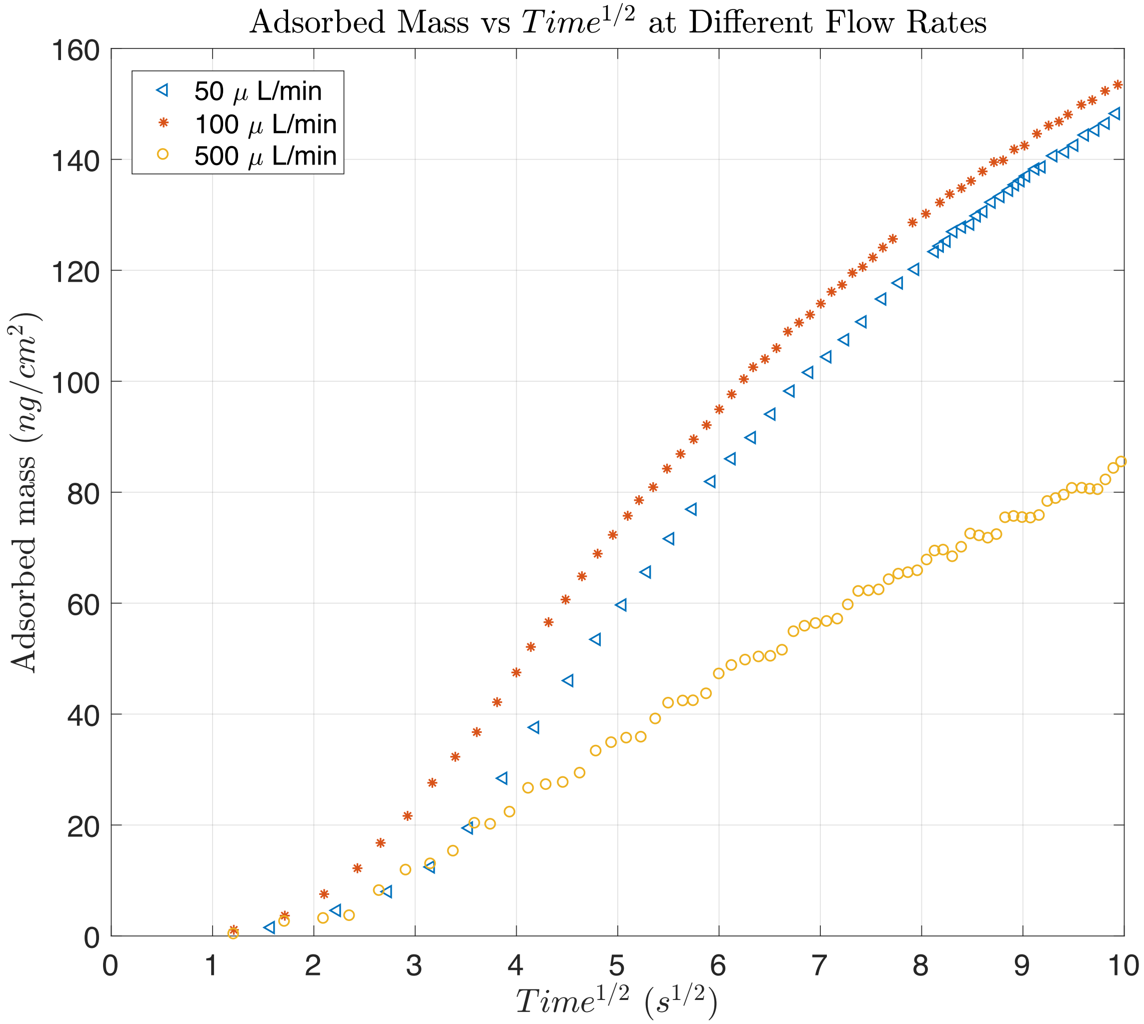
For rigid film: Input: Δf — Sauerbrey Equation → Output: mass

For soft film: Input: Δf, ΔD — Viscoelastic modeling → Output: mass, viscosity, elasticity

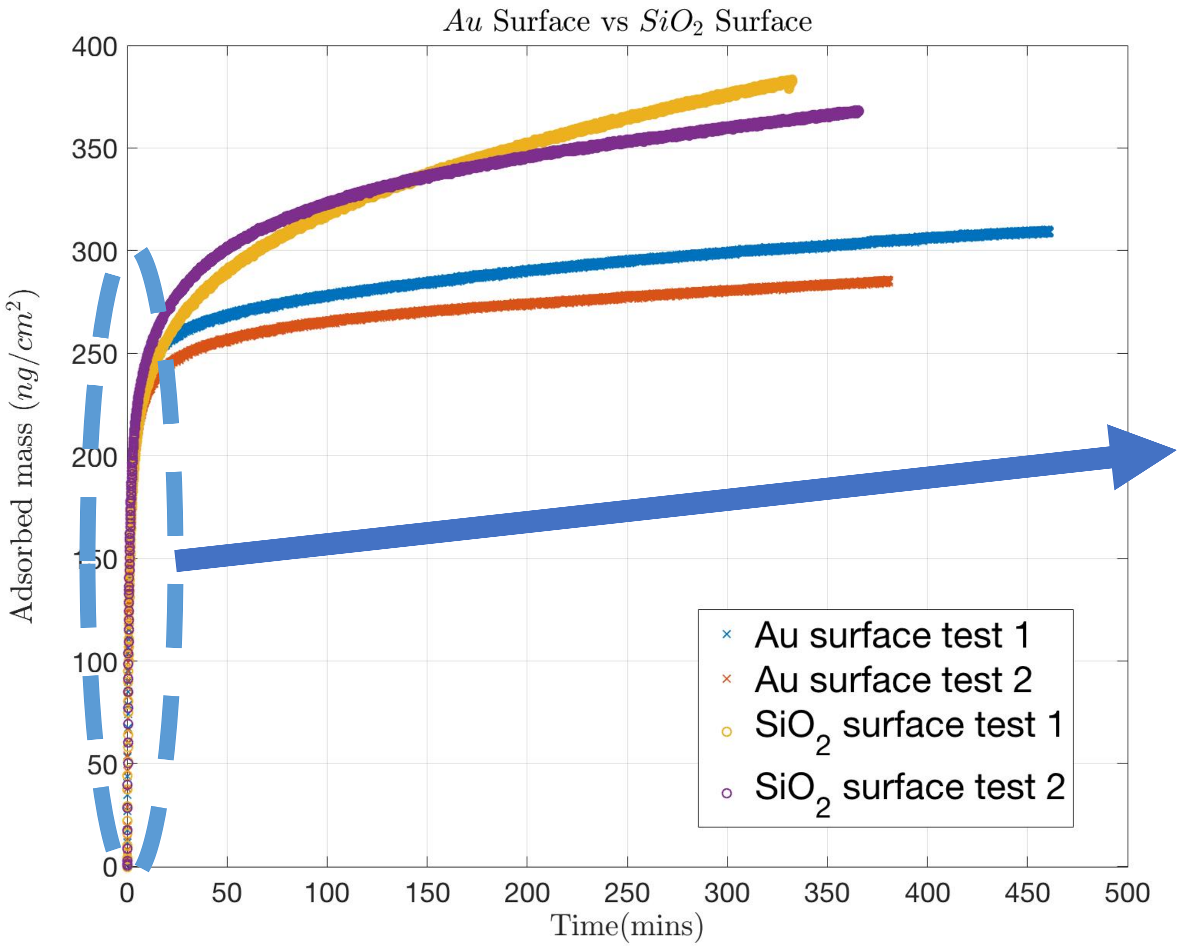
Biolin Scientific (2016)

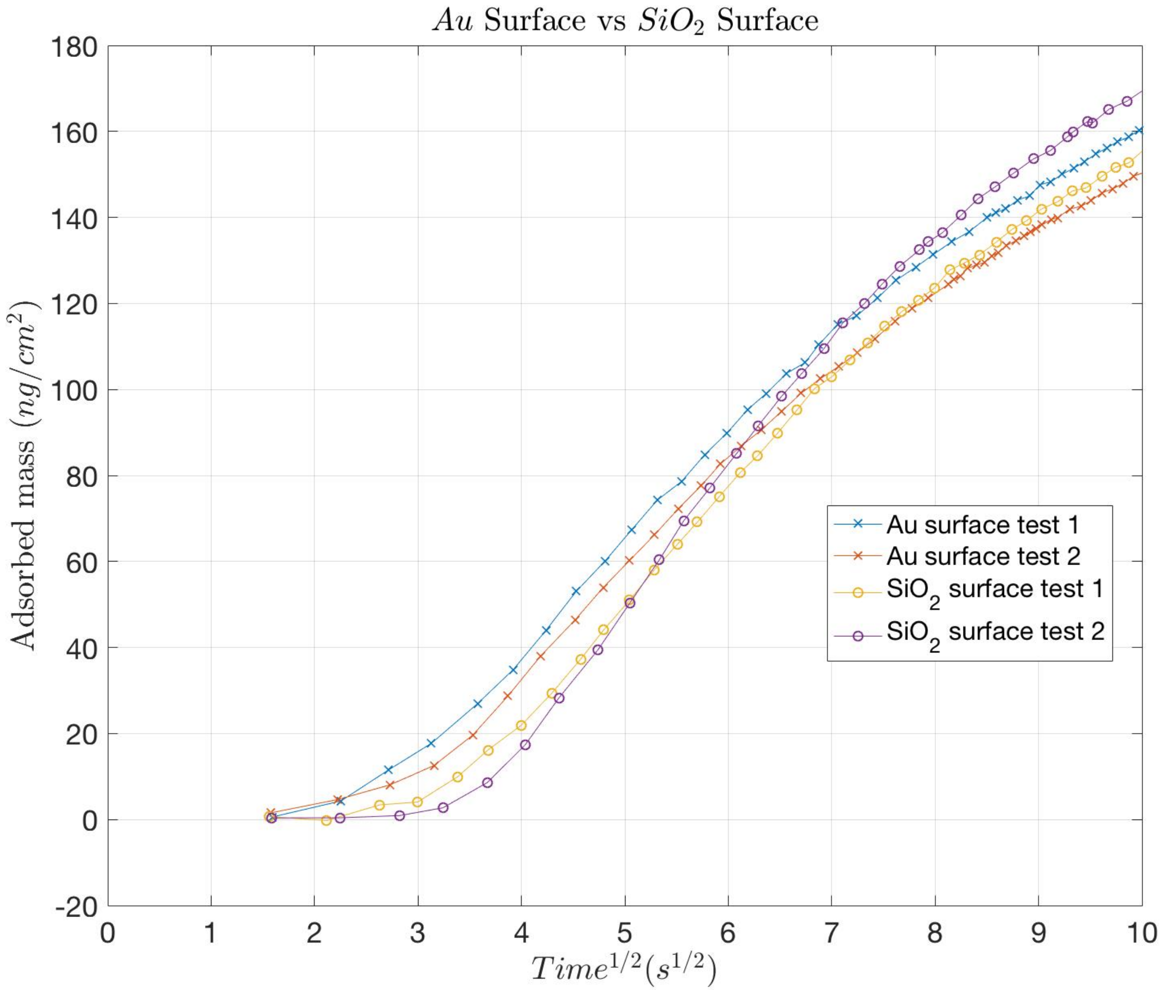
Effect of Flow Rate



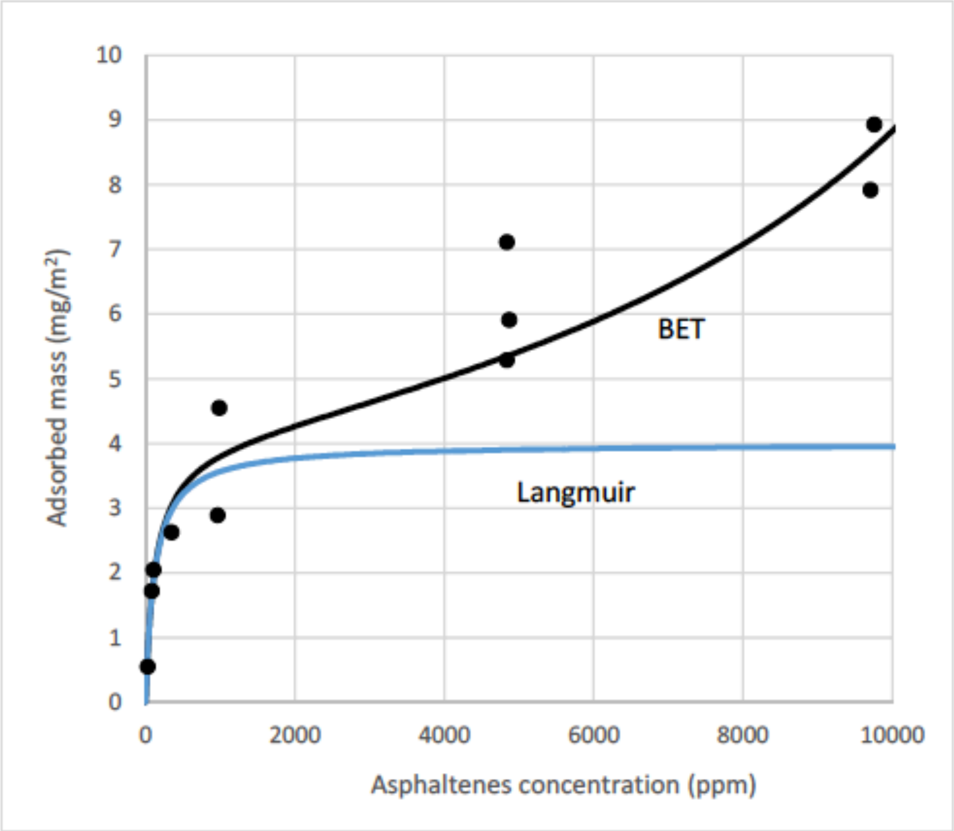


Metal Surface vs Mineral Surface





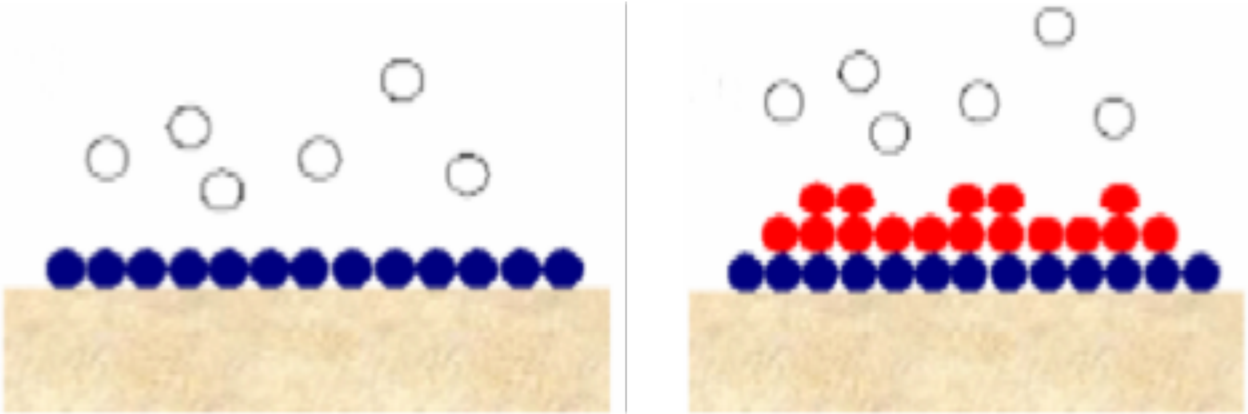
Transition to Multilayer Regime



●: Experimental data of asphaltenes (in toluene) adsorption onto gold surface

-: Fitting by Langmuir type isotherm

-: Fitting by BET model



Brunauer, Emmet & Teller (BET) model

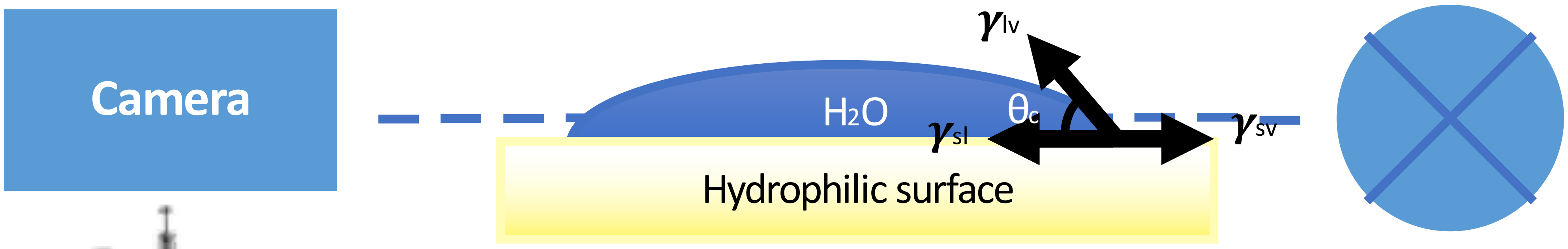
- Each adsorption site can only accommodate one adsorbed species
- All the adsorption sites are energetically identical
- No lateral interaction between adjacent adsorbed molecules
- Each molecule adsorbed on the interface acts as a potential condensation site for a second molecule

Ekholm et al. (2002); Christmann (2012); Liu et al. (in preparation)

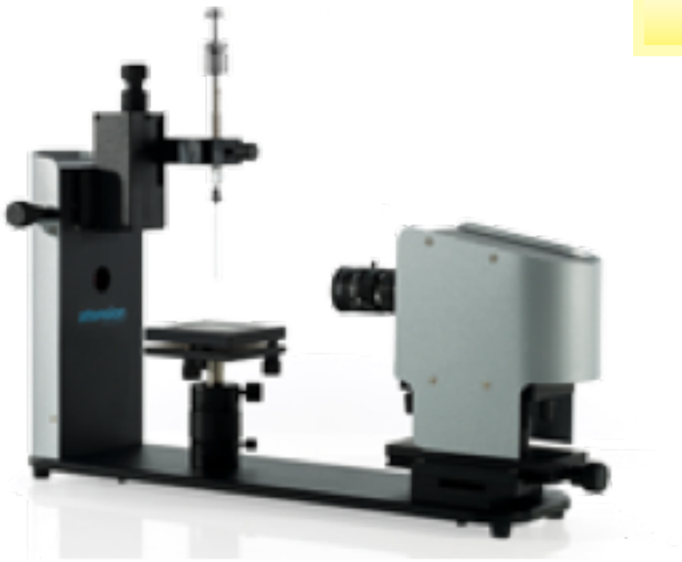
Study of Wettability Change

Measured with probe fluids on clean and asphaltene-treated surfaces

Light source



Static sessile drop method



Optical tensiometer

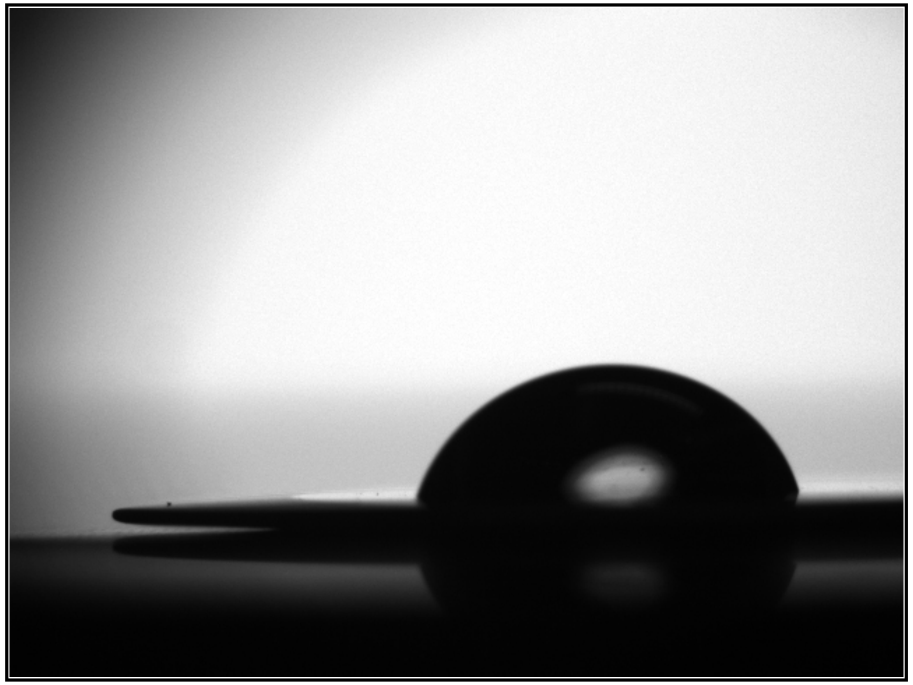
Θ_c < 90 °C: water-wet
Θ_c > 90 °C: oil-wet

Young's Equation

$$\gamma_{lv} \cos \theta_c = \gamma_{sv} - \gamma_{sl}$$

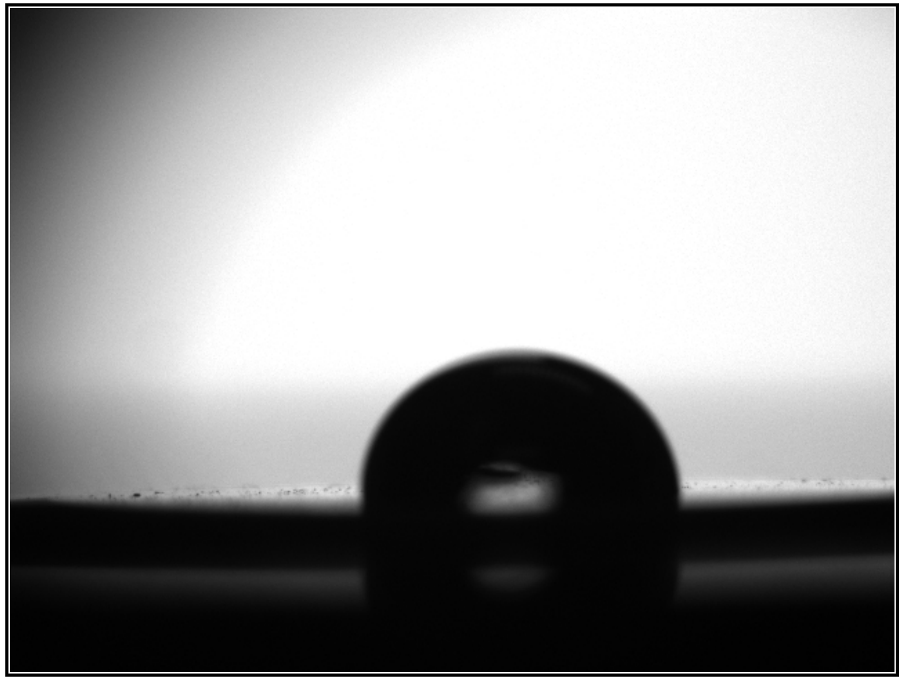
Biolin Scientific (2016)

Contact Angle Measurement between Au Surface and H_2O in Air Phase



Before adsorption

CA = 78.33~82.25



After adsorption

CA = 97.3~104.26

Ongoing Research for Asphaltenes Deposition onto Hydrophilic Surfaces

- Identifying the driving force for asphaltenes adsorption
  - Testing various **surfaces** (metal, minerals, etc.)
  - Testing using different **solvent mixture** (eg. hep/tol at different ratio)

- Study of asphaltenes deposition at **different bulk concentrations**
  - Detecting the transition from monolayer to multi-layer regime

- Investigating mixture effects in asphaltenes deposition
  - Collecting experimental data of adsorption using **different fractions** of asphaltenes mixture

Significance of Our Findings

- **Flow rate** might be an important factor in asphaltenes deposition
- **Mineral surfaces (SiO_2)** has more asphaltenes deposition compared to metal surfaces (Au)
- The deposition of asphaltenes at solid surfaces alters the surface wettability from **water-wet to oil-wet**

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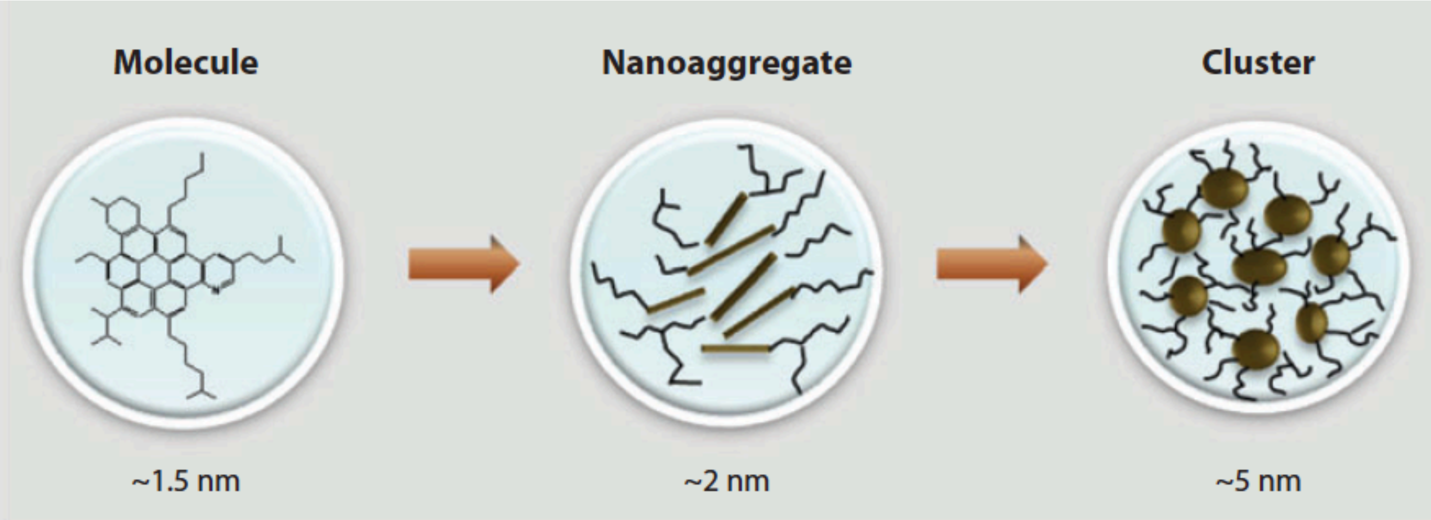
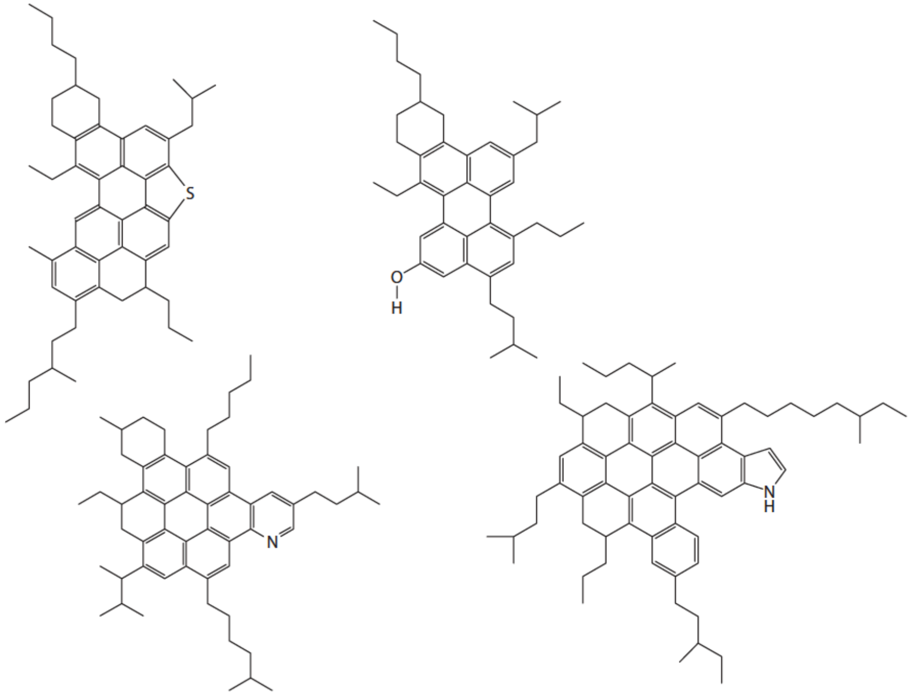
- Nelya Akhmetkhanova (PhD student, CCNY)
- Samuel Akorede (Undergraduate student, CCNY)

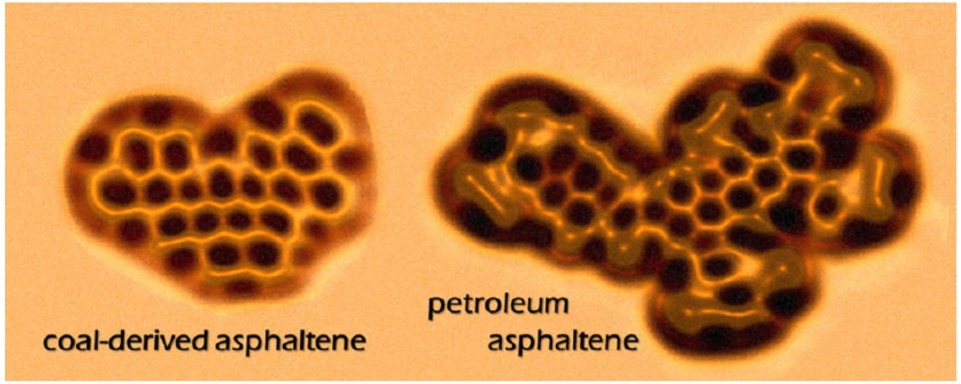
BACKUP SLIDES

Structure of Asphaltenes Molecules

Yen-Mullins model





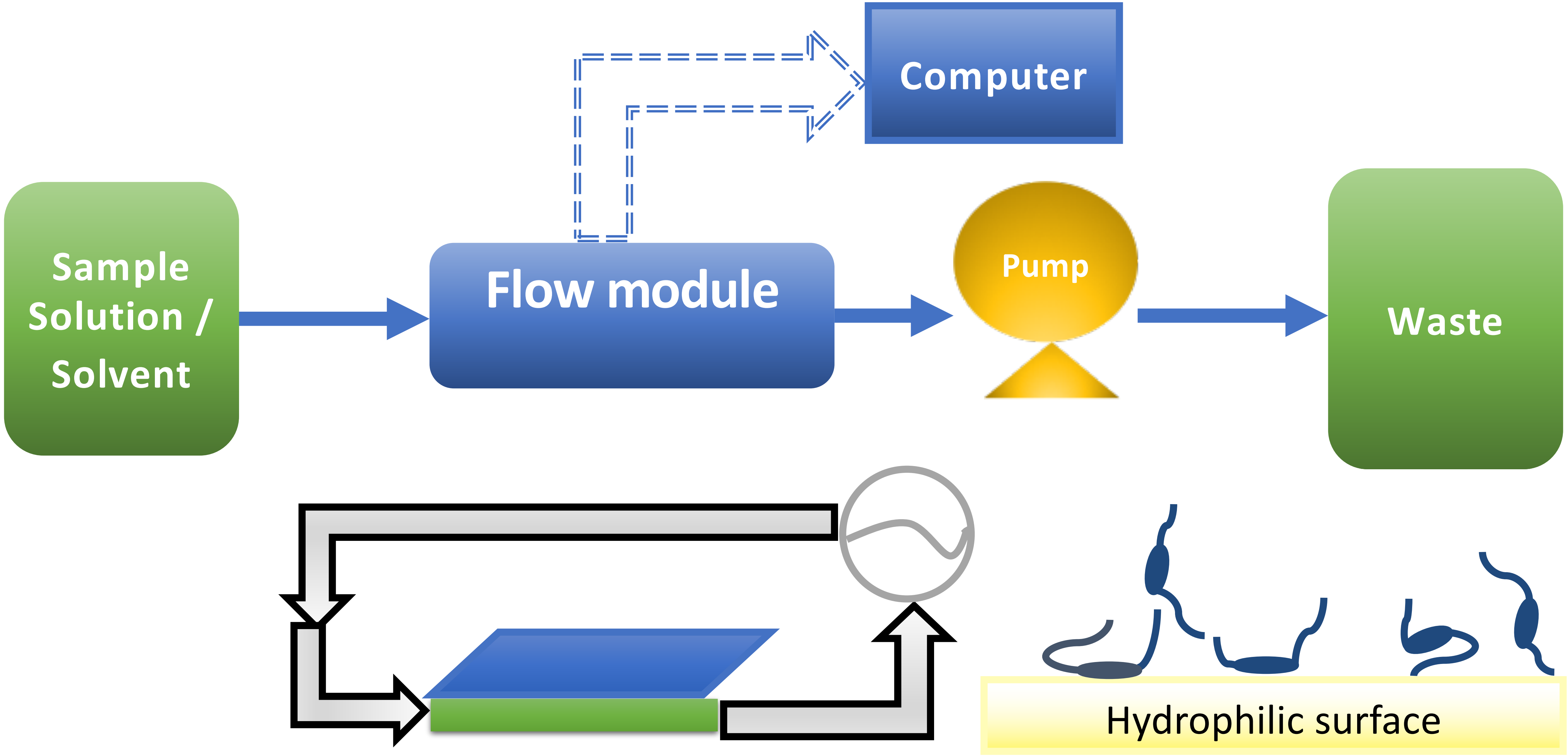


Mixture by nature

- Peripheral alkyl chains with different lengths
- Different heteroatoms of the polar functional group in the polycyclic aromatic cores

Mullins (2009); Schuler et al. (2015)

Experimental Setup (QCM-D)



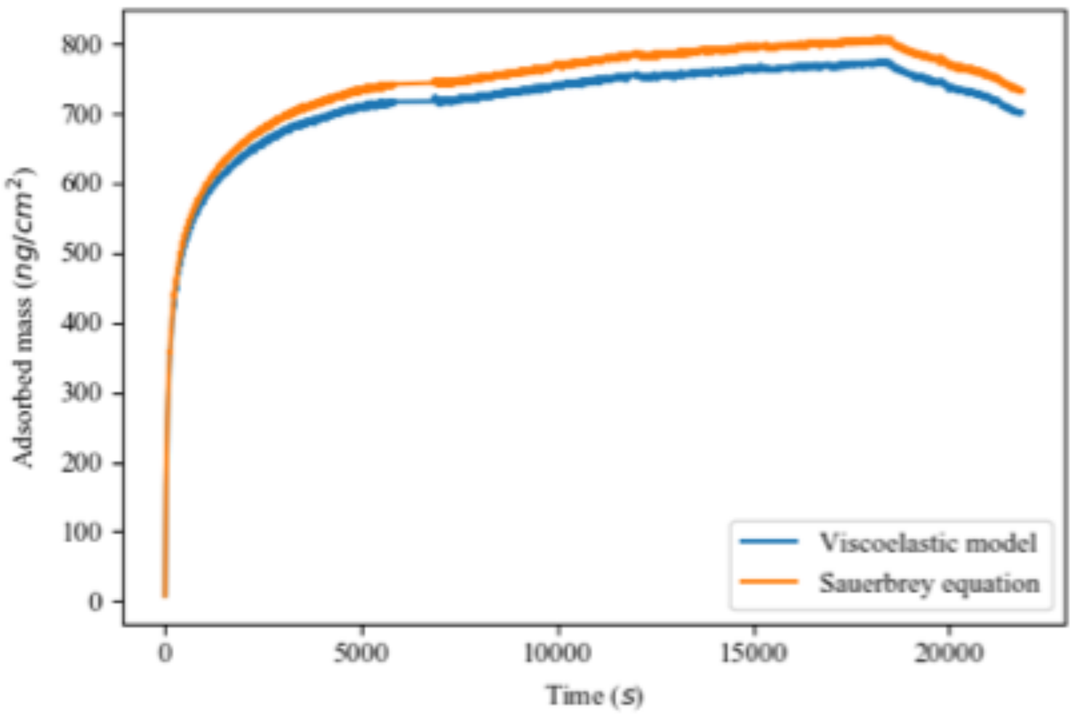
Applicability of Sauerbrey Equation

$$\Delta m = -\frac{\rho_q t_q \Delta f}{f_0 n} = -\frac{\rho_q v_q \Delta f}{2 f_0^2 n} = -\frac{C \Delta f}{n}$$

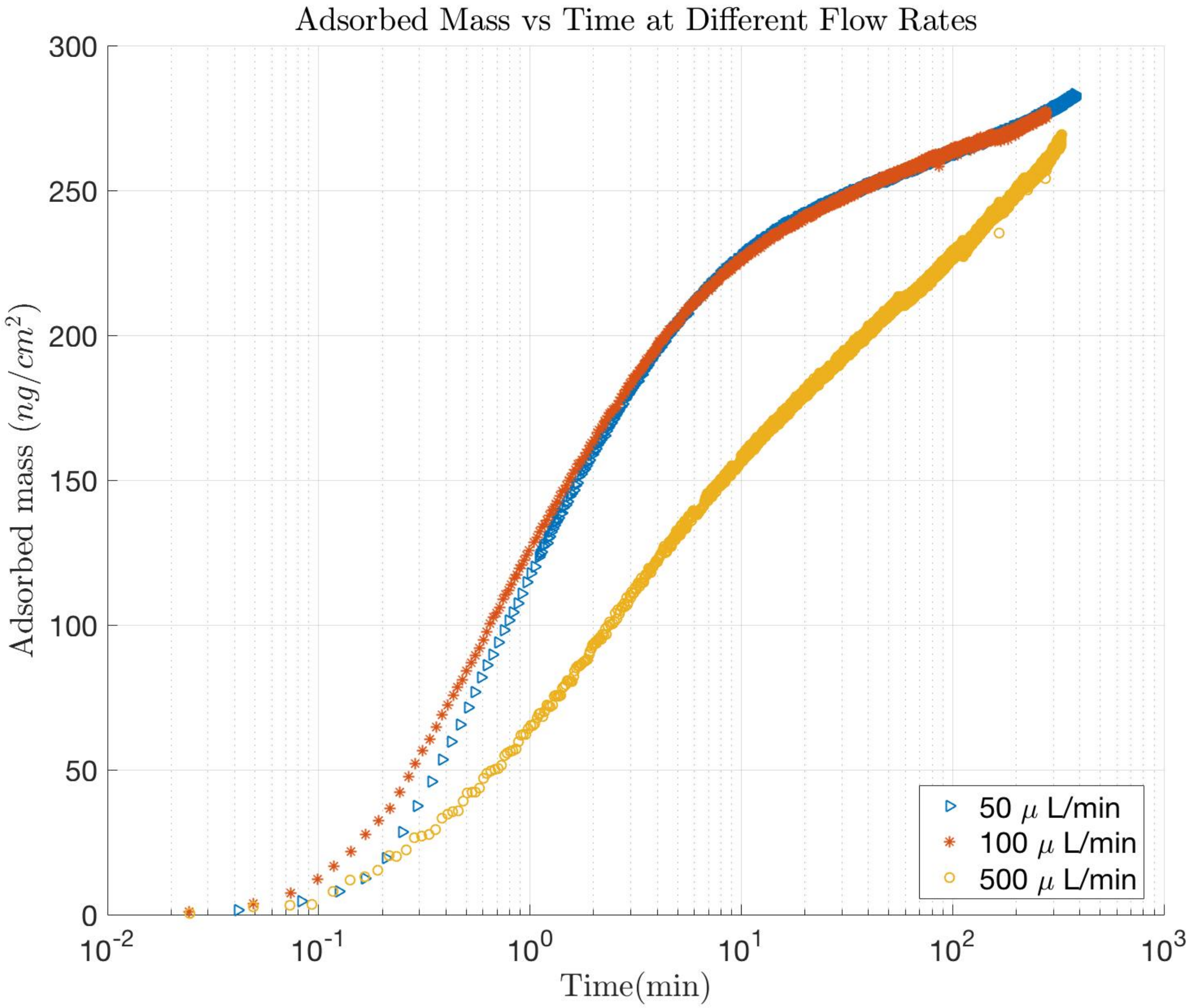
Assumption:

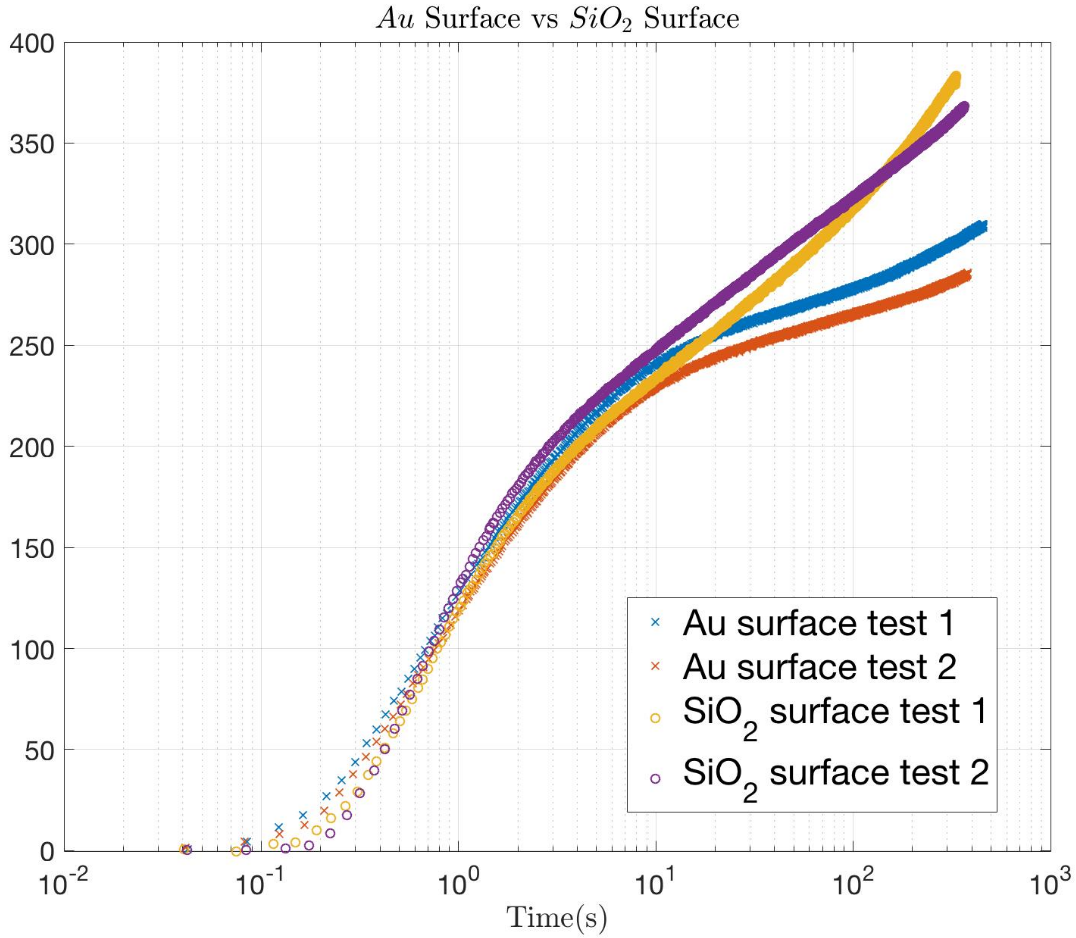
- Added mass is small compared to crystal
- Added mass is rigidly adsorbed with no slip or deformation
- Added mass is evenly distributed

Δm – Mass change
Δf – Frequency change
t_q – Thickness of quartz crystal
ρ_q - Specific density of quartz
v_q - Shear wave velocity in quartz
f_0 – Fundamental resonant frequency
C – Constant: 17.7 ng Hz^{-1} cm^{-2} for a 5MHz quartz crystal
n – overtone number, 1,3,5,7,9,11,13,15



25ppm asphaltenes in toluene, flow rate = 500 µL/min


Adsorbed Mass vs Time at Different Flow Rates
Adsorbed mass (ng/cm^2)
Time(min)
300
250
200
150
100
50
0
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
50 μ L/min
100 μ L/min
500 μ L/min


Au Surface vs SiO_2 Surface
Time(s)
400
350
300
250
200
150
100
50
0
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
Au surface test 1
Au surface test 2
SiO_2 surface test 1
SiO_2 surface test 2