In-flight Measurement of Nanoparticle Surface Area and Volume

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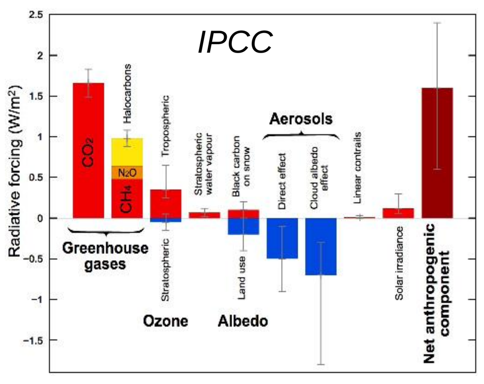
Why is measuring and controlling particle morphology important?

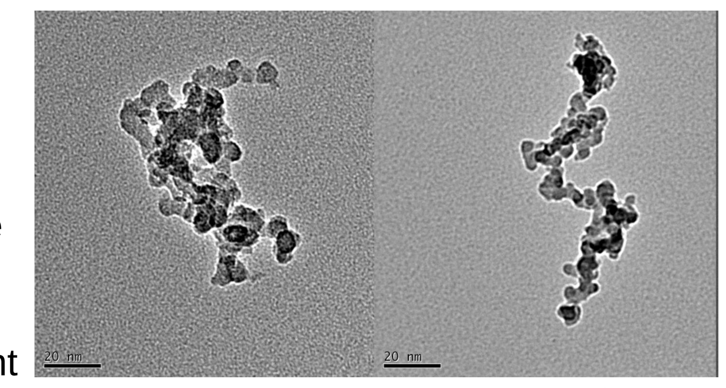


Particle morphology has a pivotal role in Science and Industry:

- It contributes to the radiative forcing and overall air pollution (> 4 millions death/year, *WHO*), by dictating many underlying properties (light absorption and diffusion, transport…)
- Industrial processes also rely on morphology, e.g., chemical vapour depostion applied to carbon nanotubes manufacturing[1]
- A better understanding can unlock new battery technologies[2]
- It can affect the accuracy of aerosol instrumentation[3]

Background and current limitations

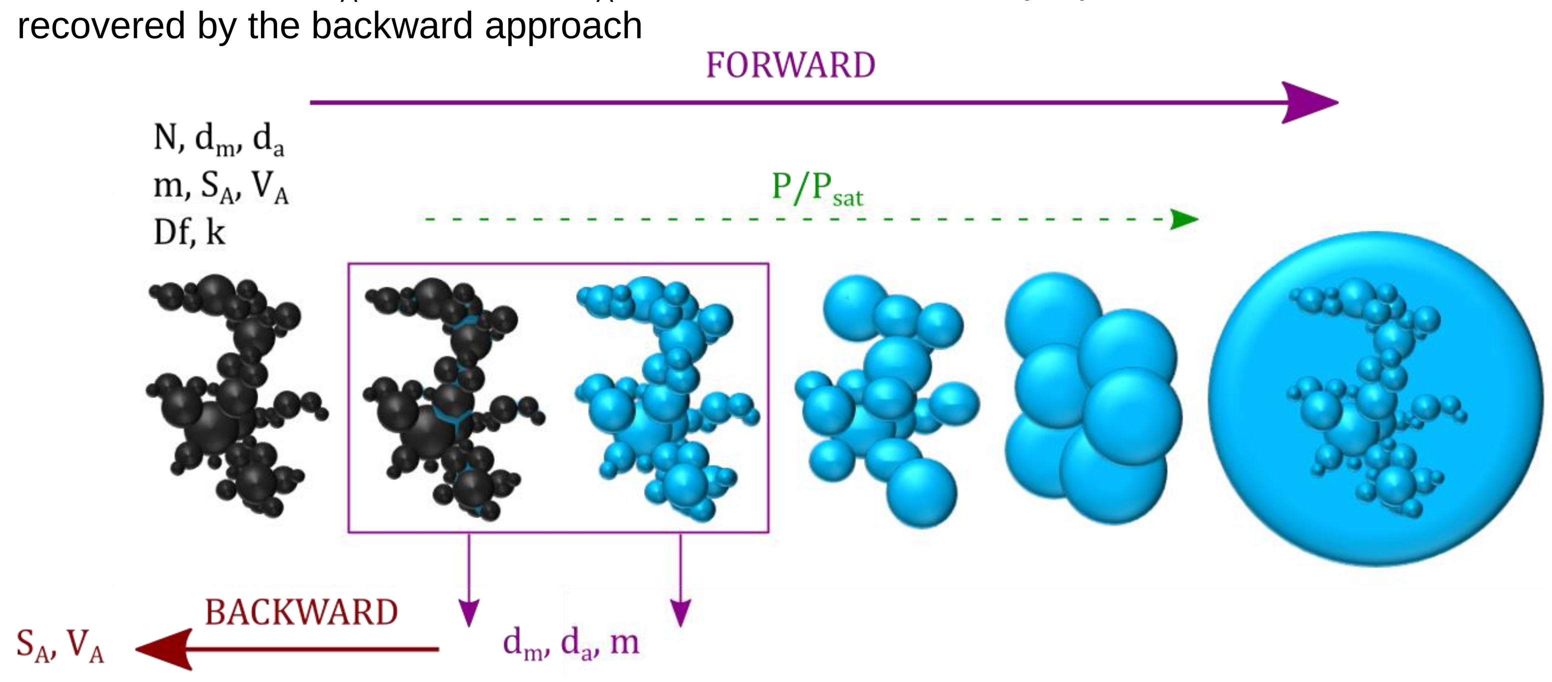
- Aggregates dynamics is affected by their shape and compactness[4]
- Properties such as surface area and volume are not readily accessible with conventional techniques:
  - A complete heterogeneous condensation cycle, e.g., in the atmosphere, includes embryo nucleation, partial wetting, and full encapsulation
  - Full encapsulation prevents any surface area measurement



Jet engine soot via SEM imaging[4]

How can we recover these properties?

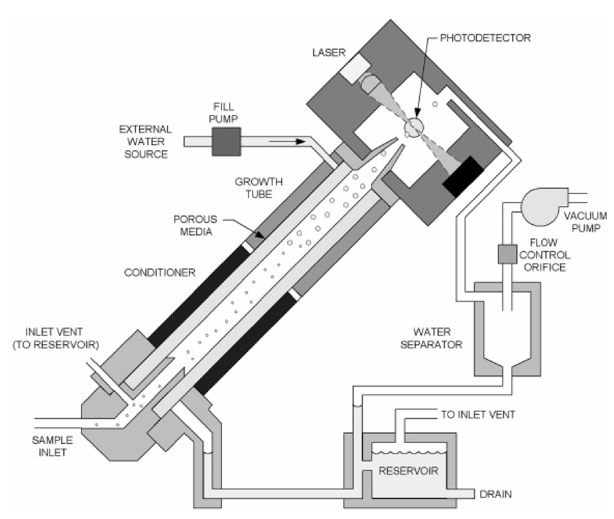
- **Concept:** add material to the surface of nanoparticles and record the changes of properties in real-time to deduce the initial morphology
- **The physico-chemical mechanisms** involved include: surface adsorption/condensation, liquid redistribution, heat and mass transfers with the surroundings
- **Methodology:** use a forward-backward concept combining both experiments and modelling
  - The forward approach consists in determining the coated aggregate properties knowing the bare aggregates ones
  - The surface area S_A and volume V_A of the bare soot are the properties of interest that should be recovered by the backward approach



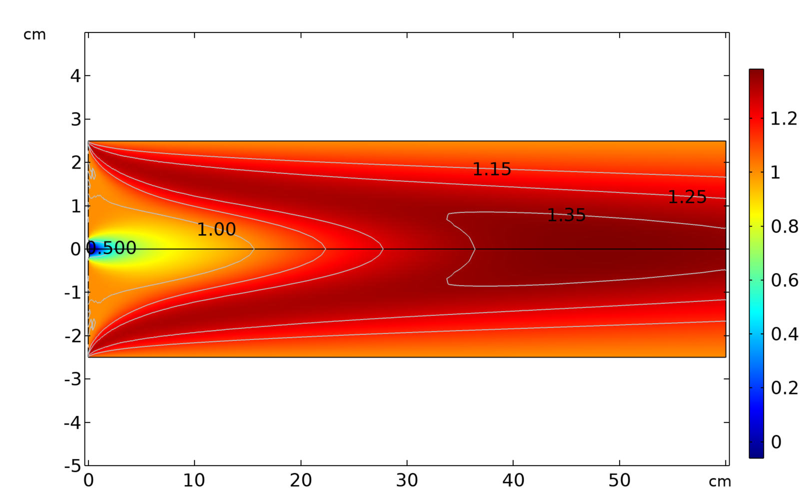
- Need to characterise the capillary condensation regime in an aggregate-liquid system with specific wetting properties

Experimental methodology

- **Requirement:** build a growth chamber (saturator) for precisely controlled growth of nanoparticles
- Current growth chambers include cloud chambers and CPCs[5]
- Preliminary results (T_{sheath} = T_{sample} = 10°C, T_{walls} = 35°C, Q_{sheath} = 2.5 lpm, Q_{sample} = 0.2 lpm)

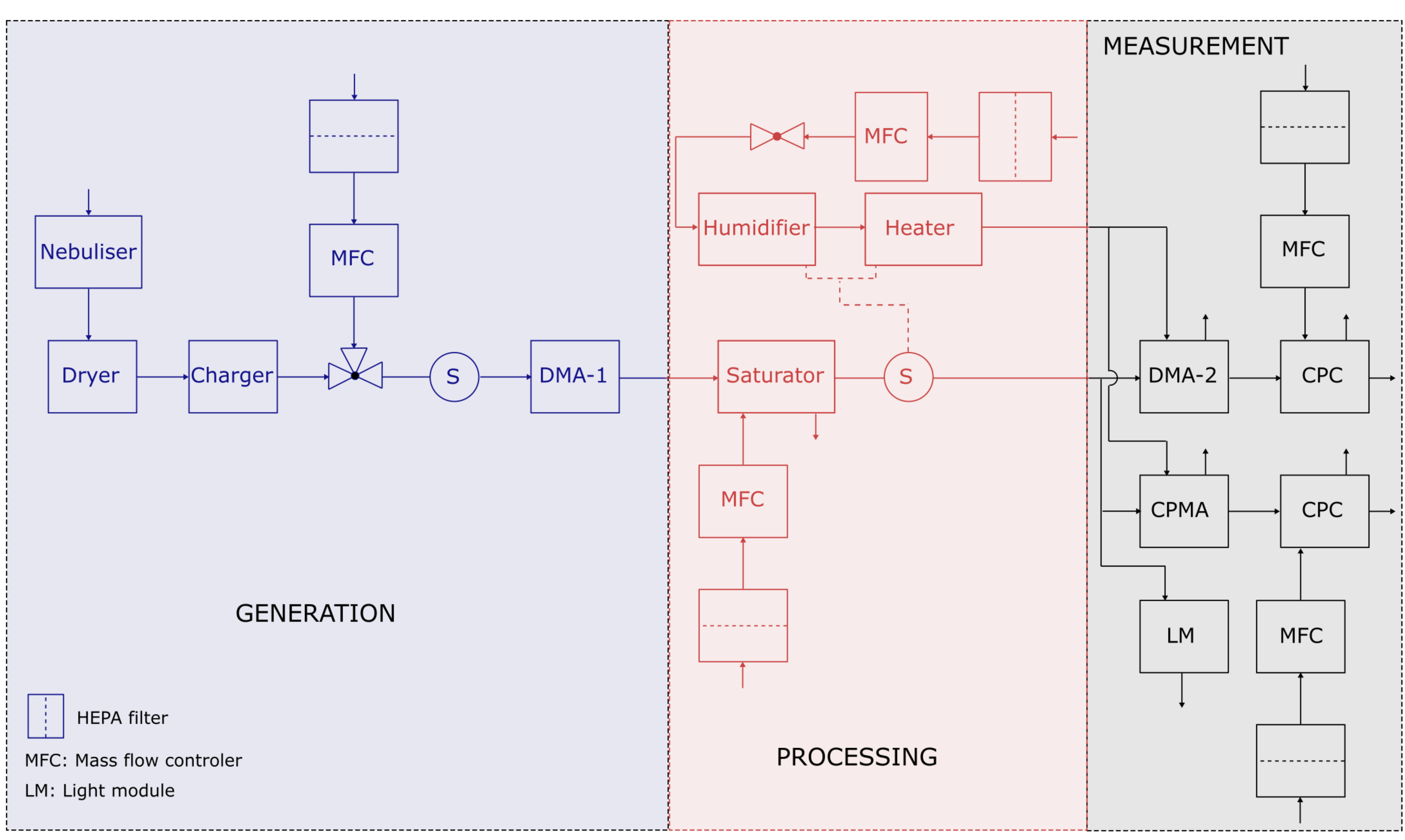


Water-based CPC[5] (WCPC)



Saturation ratio field and profiles
(collaboration with Julie Pongetti, Cambridge)

- Integration within a three-stages instrumentation line: generation, processing, and measurement

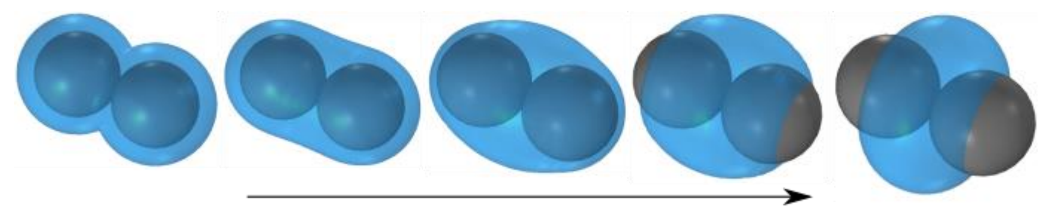


Proposed instrumentation line

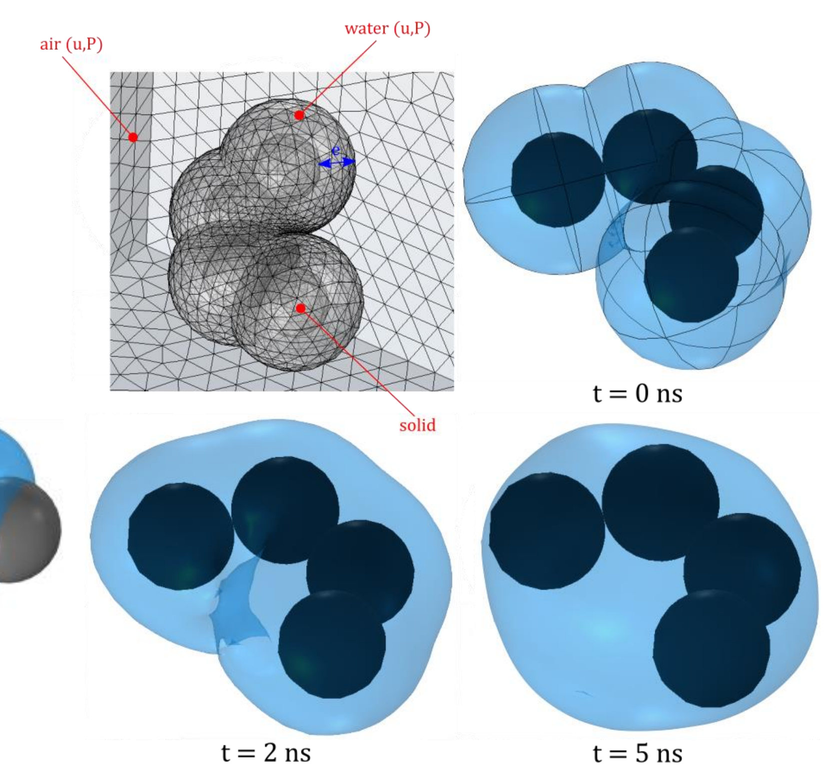
Modelling results and perspectives

Liquid redistribution

- The equilibrium shapes are determined by solving the conservation laws - including a surface tension term - in the finite elements framework
- Condensation/evaporation flux set to zero
- Monomer radius, R_0 = 5 nm
- Spherical ring for a dimer
- Spherical encapsulation for the aggregate



(2D-a) Water redistribution on a dimer (θ_s = 80°)



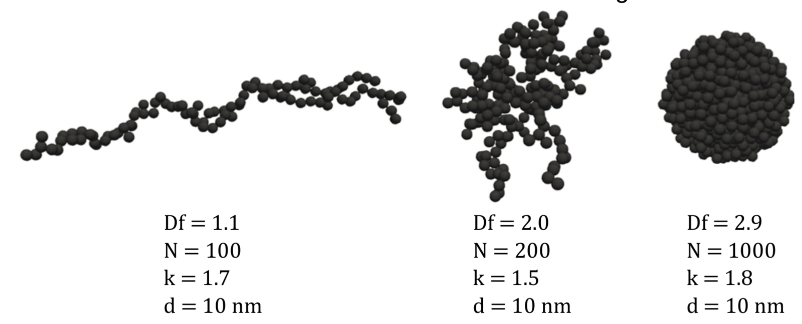
(3D) Mesh and water redistribution on a four monomers aggregate (θ_s = 80°)

Heterogeneous condensation

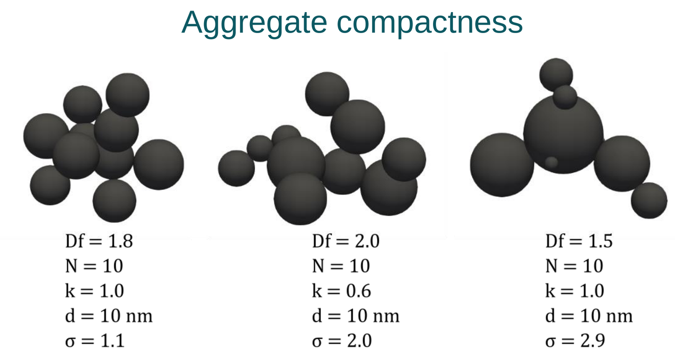
- Sequential stochastic approach:
  - Generation
  - Saturation condition (necking, radial)
  - Calculation of intermediate properties (projected area, hydrodynamic radius)
  - **Ouput properties:** mobility, volume, mass

Aggregate generation

- Monte Carlo simulation
- Quasi-fractal aggregate: $N = k(R_g/R_0)^{Df}$

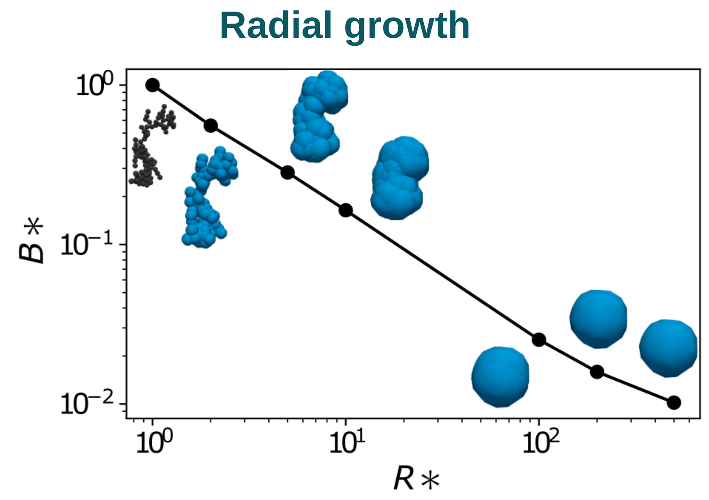


Aggregate compactness



Aggregate polydispersity

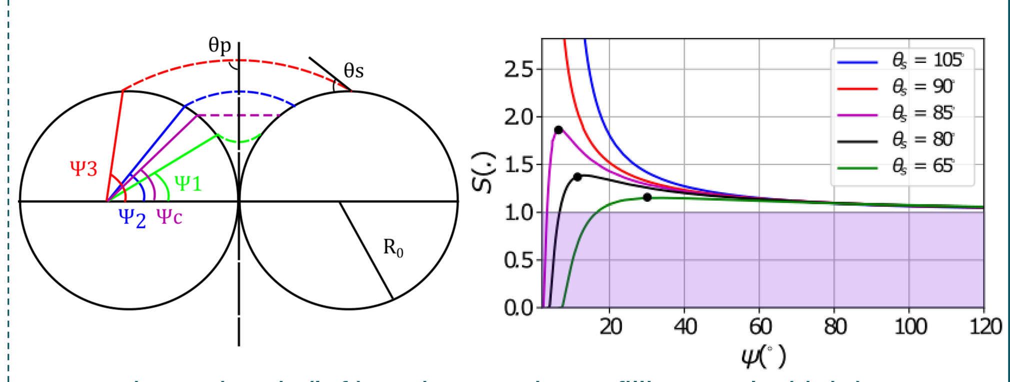
Radial growth



- The mobility parameter ratio B* decreases linearly (log-log) with the increase of monomer size until the full encapsulation

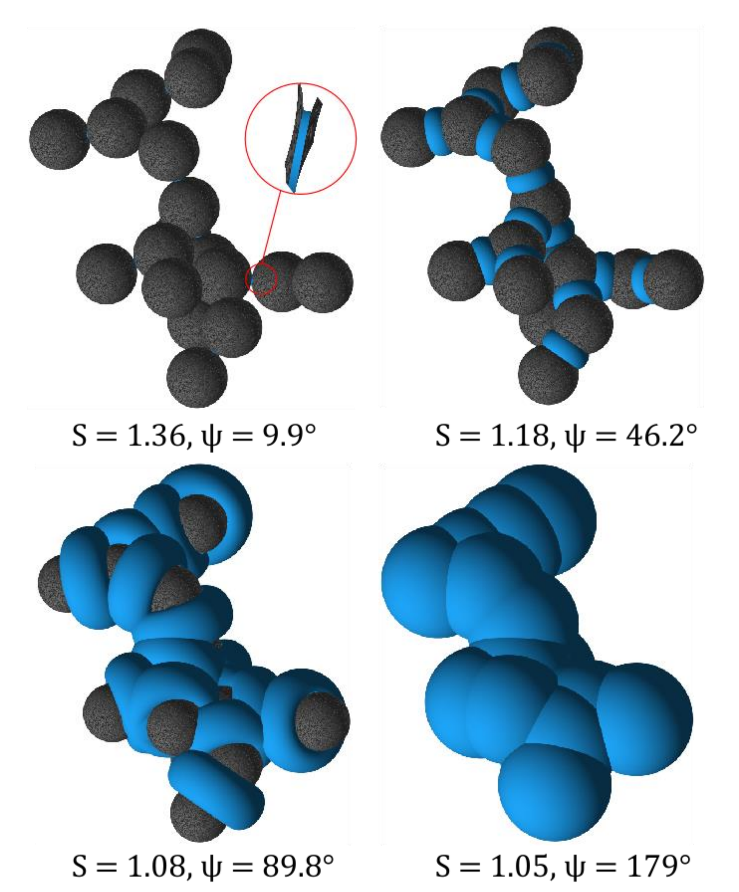
Capillary condensation (necking)

- The two-dimensional axisymmetric pendular ring evolution is described by the Young-Laplace theory



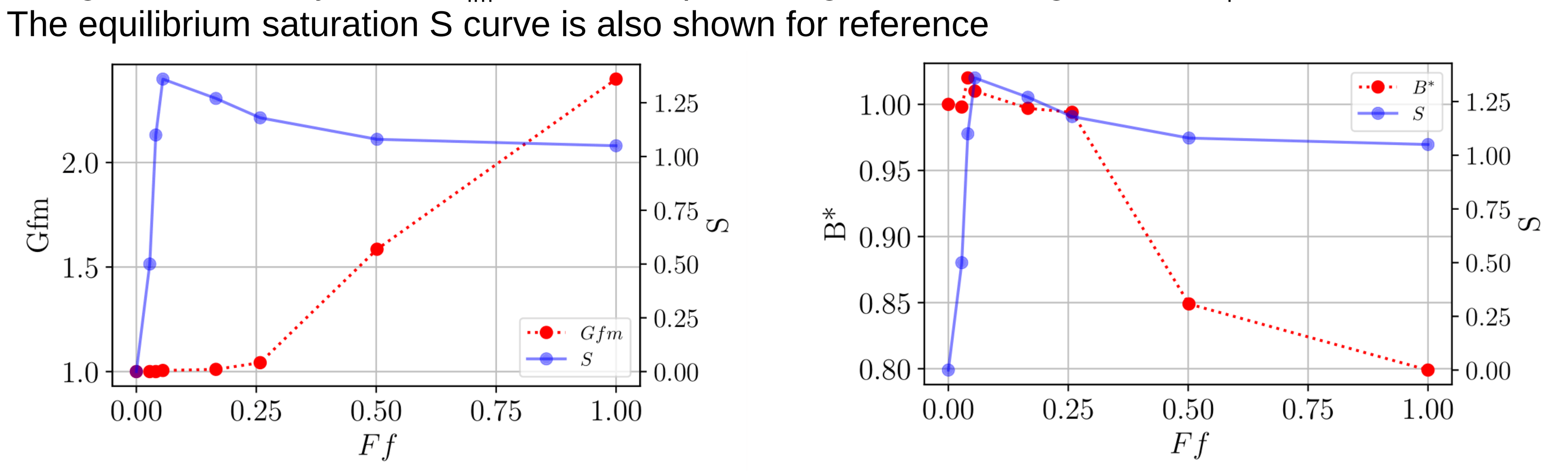
Dimer sketch (left) and saturation v. filling angle (right)

- Meniscii representation using MATLAB



Water pendular ring evolution on a small aggregate (N = 18, Df = 1.78, k = 1.3, R_0 = 5 nm, θ_s = 80°)

- The growth factor by mass G_{fm} and B* are plotted against the filling fraction F_f
- The equilibrium saturation S curve is also shown for reference



- Both mass and mobility are affected by the coating process: G_{fm} slowly increases up to F_f = 0.25 and rapidly grows afterwards, while B* shows a plateau followed by a prompt decrease

Innovations and challenges

Innovations

Build a new approach to detect, control, and measure particle growth and pave the way for new instrumentation designs and regulations

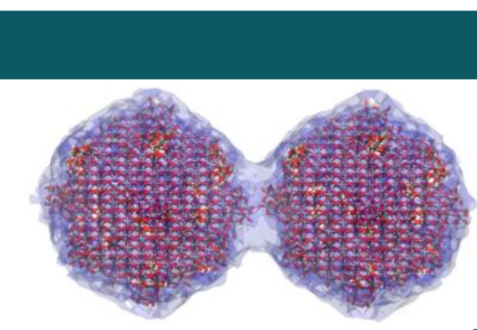
Challenges

- Limited instrumentation resolution may prevent detection of slight changes in properties
- Current growth techniques cannot provide precisely targeted liquid addition (ex: via BET)
- Unwanted evaporation/condensation may take place in instruments and tubing
- Surface energy is highly variable and not a real-time measurement, additional experiments in conjunction with semi-empirical models are necessary
- Multi-scale modelling requires an accurate and efficient approach

Perspectives

Experimental setup

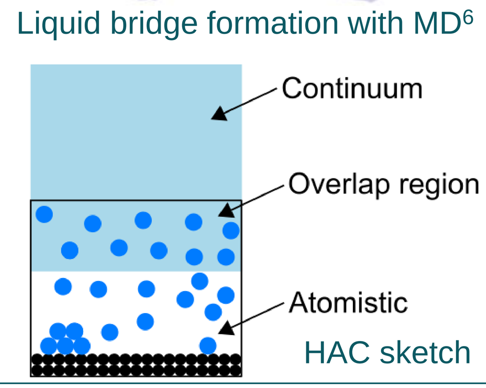
- Experimental simulations of particle enlargement in the chamber
- Chamber design, manufacturing, and preliminary tests
- Instrumentation line setup and sensitivity analysis



Liquid bridge formation with MD[6]

Modelling

- 3D CFD simulations including both condensation and liquid redistribution
- (Un)coated aggregates database from the stochastic model
- Unified analytical model for the kinetics of condensation on aggregates
- Molecular Dynamics (MD) simulations to model early stages of condensation on complex surfaces
- Exploration of multi-scale integrated simulations based on the Hybrid Atomistic Continuum (HAC) model



HAC sketch

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