PFAU X

Models for Nucleation and Condensation on Nanoparticles

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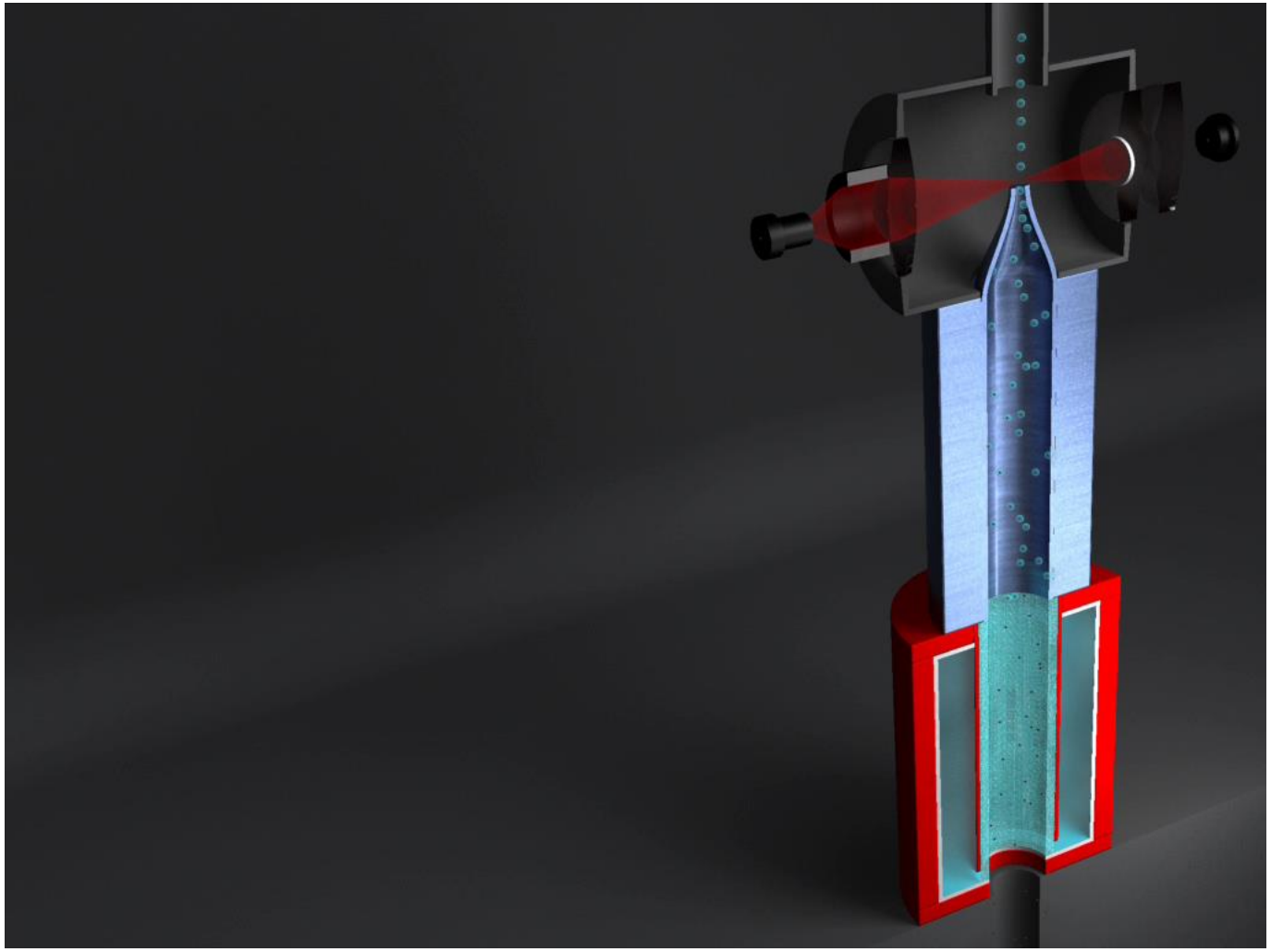
Why Nano?

Why Nano?

Condensation Particle Counters (CPCs)



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Why Nano?

Droplets nucleate and grow in a CPC on nanoparticles

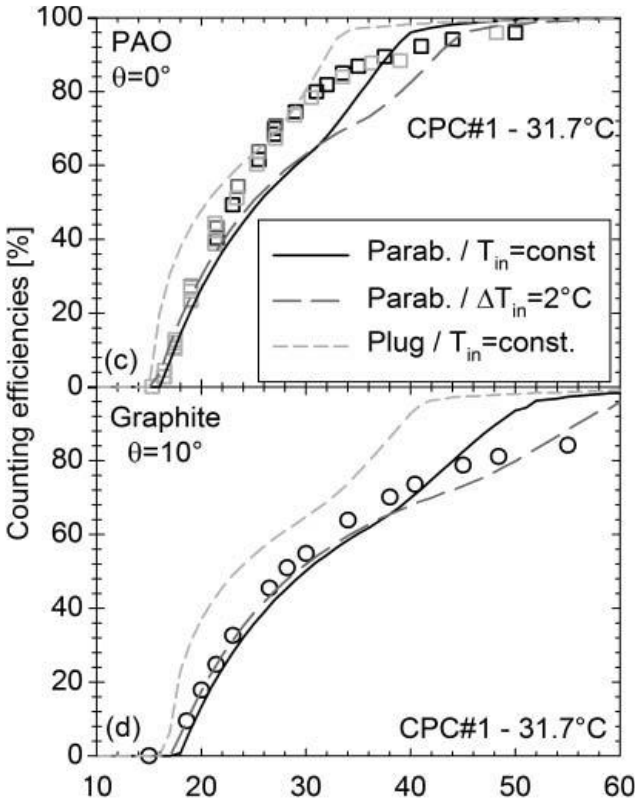
… with fast dynamics, coupling of heat and mass transfer, **droplets are polydisperse**, and a size change typically 3 orders of magnitude …

- **Where** do these phenomena take place?
- What is the final **droplet size distribution**?
- How can we **troubleshoot CPCs**?

Why Nano?

Droplets nucleate and grow in a CPC on nanoparticles

- **What** is the challenge?



poly-(alpha)-olefin (PAO)

Mamakos et al., Aerosol Science and Technology, 47:11-21 (2013)

The Models

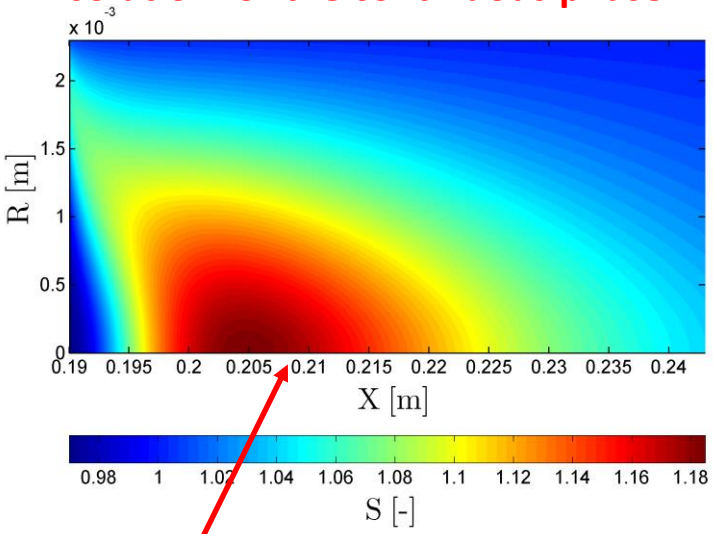
The Models

Multiphase Flow inside the CPC

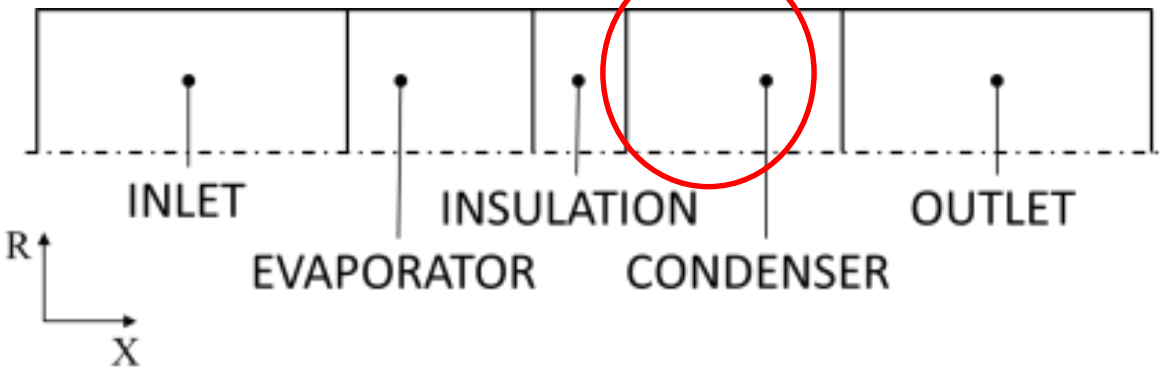
- **continuous phase** (e.g., n-Butanol vapor in air)
  - modeled with the **cpcFoamCompressible** solver implemented in OpenFOAM
  - all effects **relevant for CPCs** considered (thermodiffusion, heat of evaporation / condensation, etc.)

- **disperse phase**
  - **qmomCloud** library
  - solves the population balance equation for the droplets using a **QMOM approach** (univariate in droplet diameter)

(b) saturation ratio profile – solution for the continuous phase



(a) Evaporator-Condenser system in a CPC



The Models

Population Balance Equation (PBE)

growth nucleation

$$\frac{\partial n(\mathbf{x},\xi,t)}{\partial t} + \frac{\partial}{\partial x_i}\left(u_i n(\mathbf{x},\xi,t)\right) = \frac{\partial}{\partial \xi}\left(\dot{\xi} n(\mathbf{x},\xi,t)\right) + \mathcal{S}$$

Disperse phase: characterized by the number density function (NDF) $n(\mathbf{x},\xi,t)$

CPC: **property ξ is the droplet size** → NDF = droplet size distribution

PBE very difficult to solve directly for $n(\mathbf{x},\xi,t)$

k-th moment of the NDF:

$$m_k = \int_{\Omega_\xi} n(\xi)\xi^k d\xi$$

→ solve the PBE for some lower order moments of the NDF
→ transformation to a set of moment equations – method of moments (MOM)
→ the moment equation for the k-th moment is obtained by:
- multiply PBE with ξ^k
- integrate over phase space

The Models

Moment Transport Equations

- Moments approximate the NDF
- Moments have a physical meaning:
  - m_0……. number concentration [m^{-3}]
  - m_1……. total droplet size p. vol. [m^{-2}]
  - $L_{32}=m_3/m_2$… Sauter mean diameter [m]
- If $\mathcal{R}$ term unclosed, reconstruct NDF with QMOM (set of *N* nodes and *N* weights)
- $\mathcal{R}$ terms determined by physical models

$$\frac{\partial m_0}{\partial t} + \frac{\partial}{\partial x_i}(u_i m_0) = \mathcal{R}_0$$
$$\frac{\partial m_1}{\partial t} + \frac{\partial}{\partial x_i}(u_i m_1) = \mathcal{R}_1$$
$$\vdots$$
$$\frac{\partial m_k}{\partial t} + \frac{\partial}{\partial x_i}(u_i m_k) = \mathcal{R}_k$$
$$\vdots$$
$$\frac{\partial m_{2N-1}}{\partial t} + \frac{\partial}{\partial x_i}(u_i m_{2N-1}) = \mathcal{R}_{2N-1}$$

The Models

Moment Transport Equations (Example)

Unclosed for $k = 0$ and $k = 1$

$$\frac{\partial m_k}{\partial t} + \underbrace{\frac{\partial}{\partial x_i}(u_i m_k)}_{\text{advection}} = \underbrace{\left[2\frac{\rho_f}{\rho_l} D_v\, Sh\, \ln(1+B_m)\right] k m_{k-2}}_{\text{growth}} + \underbrace{J_{het}\,(d_{d,init}/2)^k}_{\text{nucleation}}$$

$$k = 0, \ldots\ldots, 2N-1$$

Solution for the disperse phase approximated by time evolution of first 2N moments (m_0 , m_1,……., m_{2N-1})

The Models

Quadrature Method of Moments

Approach

- moments are approximated by N weights w_α and N nodes ξ_α

$$m_k = \int_{\Omega_\xi} \xi^k n d\xi \approx N_p \sum_{\alpha=1}^{N} \xi_\alpha^k w_\alpha$$

- weights and nodes are calculated with the first $2N$ moments (e.g., PD algorithm)

Result

- the first 2N moments are reproduced exactly
- unknown moments in the **source terms of the moment transport equations** can be computed to close the system of equations!!

$$\frac{\partial m_k}{\partial t} + \frac{\partial}{\partial x_i}(u_i m_k) = \left[2\frac{\rho_f}{\rho_l} D_v \, Sh \, \ln(1+B_m)\right] k \underbrace{N_p \sum_{\alpha=1}^{N} \xi_\alpha^{k-2} w_\alpha}_{m_{k-2}} + J_{het} \left(d_{d,init}/2\right)^k$$

The Models

Growth Models

0) The Basics

$$\dot{\xi} = 2\frac{\dot{m}_{cond}}{\rho_l\, \xi^2\, \pi}$$

Mass concentration

$$\dot{m}_{cond} = Sh\, \pi\, D_v\, \xi\, \Delta c$$

$$\dot{\xi} = 2\frac{Sh\, D_v}{\xi}\,\frac{1}{\rho_l}\Delta c$$

Key scaling of the growth rate in the case of mass transfer limitation

$$\dot{\xi} \propto 1/\xi$$

…inserted into the moment evolution equations yields…

$$\frac{Dm_k}{Dt} = \left[\dot{\xi}\,\xi\right] k\, m_{k-2}$$

…in case we assume that:

$$\dot{\xi}\,\xi \neq f(\xi)$$

The Models

Growth Models

1) Simple Continuum-Regime Closure (thermal equilibrium, dilute vapor, large droplets)

$$\dot{\xi} = 2\frac{Sh\,D_v}{\xi}\,\frac{1}{\rho_l}\,\frac{1}{R_{g,vap}}\left(\frac{p_{vap}}{T} - \frac{p_{vap}^{sat}\left(T_d\right)}{T_d}\right)$$

2) Classical Closure (Abramzon & Sirignano, 1989; thermal equilibrium, large droplets)

$$\dot{\xi} = 2\frac{Sh\,D_v}{\xi}\,\frac{\bar{\rho}_{gas}}{\rho_l}\ln\left(1-B_m\right)$$

considers Stefan flow

$$B_m = \frac{y_{vap}^{sat} - y_{vap}}{1 - y_{vap}^{sat}}$$

The Models

Growth Models

3) Free-Molecule-to-Continuum-Regime Closure (Fuchs and Sutugin, 1970; Ahn and Liu, 1990)

$$\dot{\xi}\,\xi \neq f(\xi)$$

… only approximate, because of **correction factors!**

$$\dot{\xi} = 2\frac{Sh\,D_v}{\xi}\,\frac{1}{\rho_l}\,\frac{1}{R_{g,vap}}\left(\frac{p_{vap}}{T} - \frac{K_{Kelvin}\,p_{vap}^{sat}(T_d)}{T_d}\right)\phi_F(\bar{\xi})$$

$$K_{Kelvin} = \exp\left(\frac{4\sigma\,MW_{vap}}{\rho_l R_{g,vap}\,T_d\,\bar{\xi}}\right)$$

$$\phi_{F,i}(\bar{\xi}) = \frac{1+Kn_i}{1+1.7104\,Kn_i + 4/3\,Kn_i^2}$$

$$Kn_i = 2\lambda_i / \bar{\xi}$$

$$(T_d - T)\lambda_{air}\frac{Nu}{\bar{\xi}} = D_v\frac{Sh}{\bar{\xi}}\Delta h_{evap}\,\frac{1}{R_{g,vap}}\left(\frac{p_{vap}}{T} - \frac{K_{Kelvin}\,p_{vap}^{sat}(T_d)}{T_d}\right)\frac{\phi_{F,vap}(\bar{\xi})}{\phi_{F,g}(\bar{\xi})}$$

Expensive: **iterations** are required to determine T_d.

The Models

Nucleation Model

1) Standard Heterogeneous Nucleation Model

Particle Geometry & Contact Angle

$$\Delta G^*_{het} = f_g \, \Delta G^*_{hom}$$

$$J_{het} = J^0_{het} \exp\left(-\frac{\Delta G^*_{het}}{k_B T} \right)$$

A larger number

$$\Delta G^*_{hom} = \frac{4}{3} \pi \left(r^* \right)^2 \sigma$$

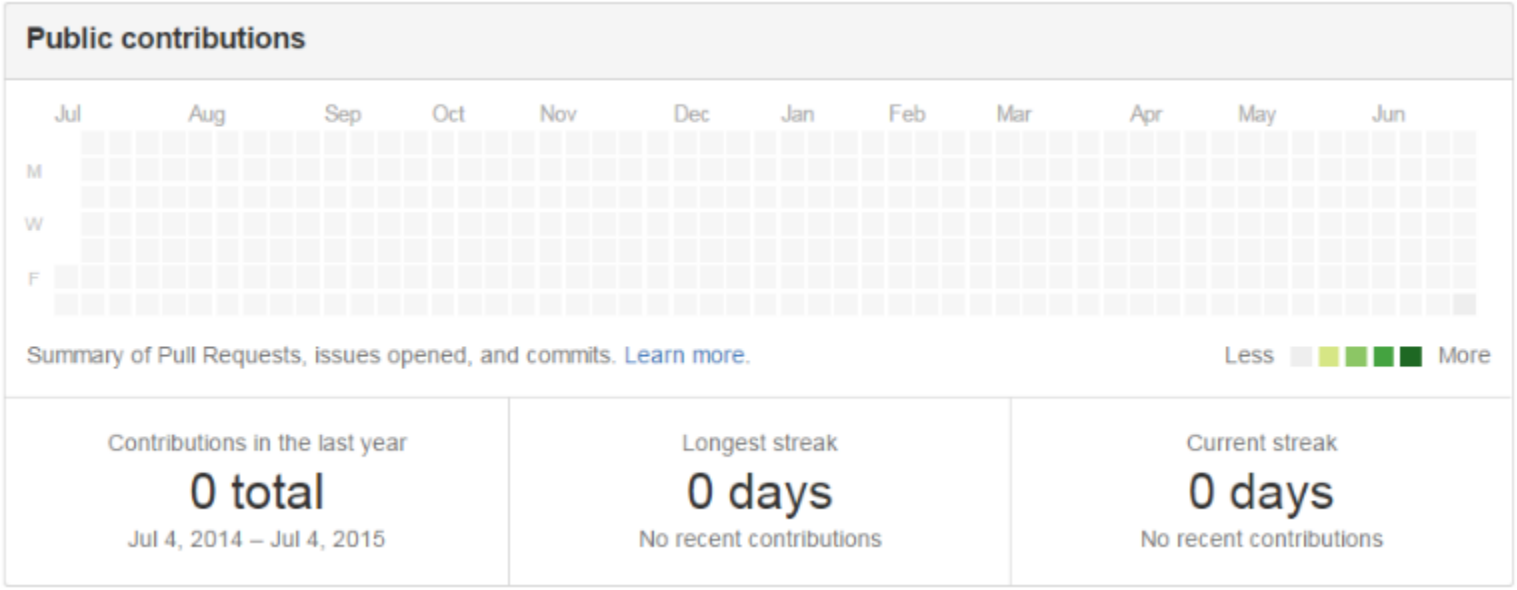
$$r^* = \frac{2\sigma}{\rho_l \, R_{g,vap} \, T \ln(S)}$$

$$J^0_{het} = d_p^2 \, \pi 10^{29}$$

The Software

The Software

Unfortunately, there is no publicly-available (x)MOM implementation in OpenFOAM!



https://github.com/OpenQBMM

So, let‘s start from scratch:

- **cpcFoamCompressible** as new solver
- **qmomCloud** for modeling **droplets**

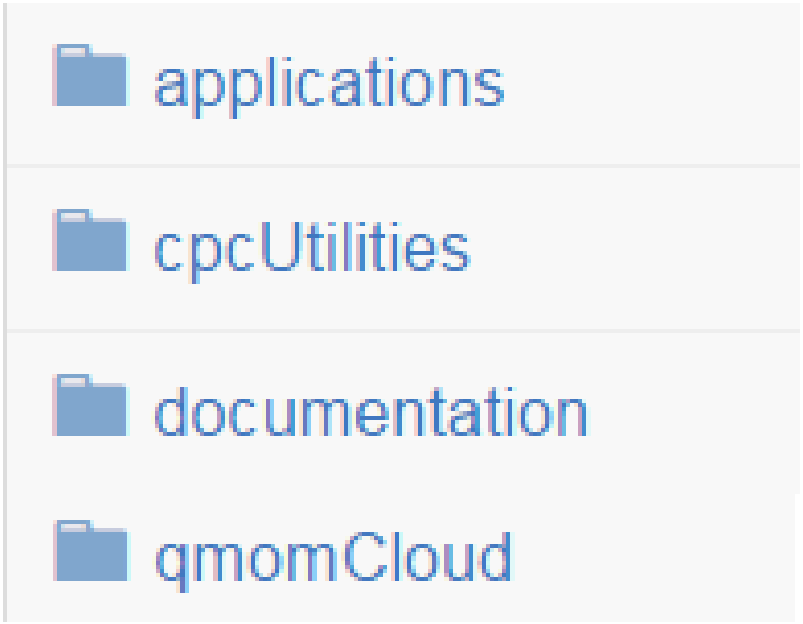
The Software

solvers →

Extra math, diffusion coefficients, liquid properties… →

Markdown-based documentation →

Library of QMOM routines →



Demo Time

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THANK YOU!

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