Modelling hygroscopicity-induced gas–aerosol partitioning, organic surface enrichment and cloud droplet formation

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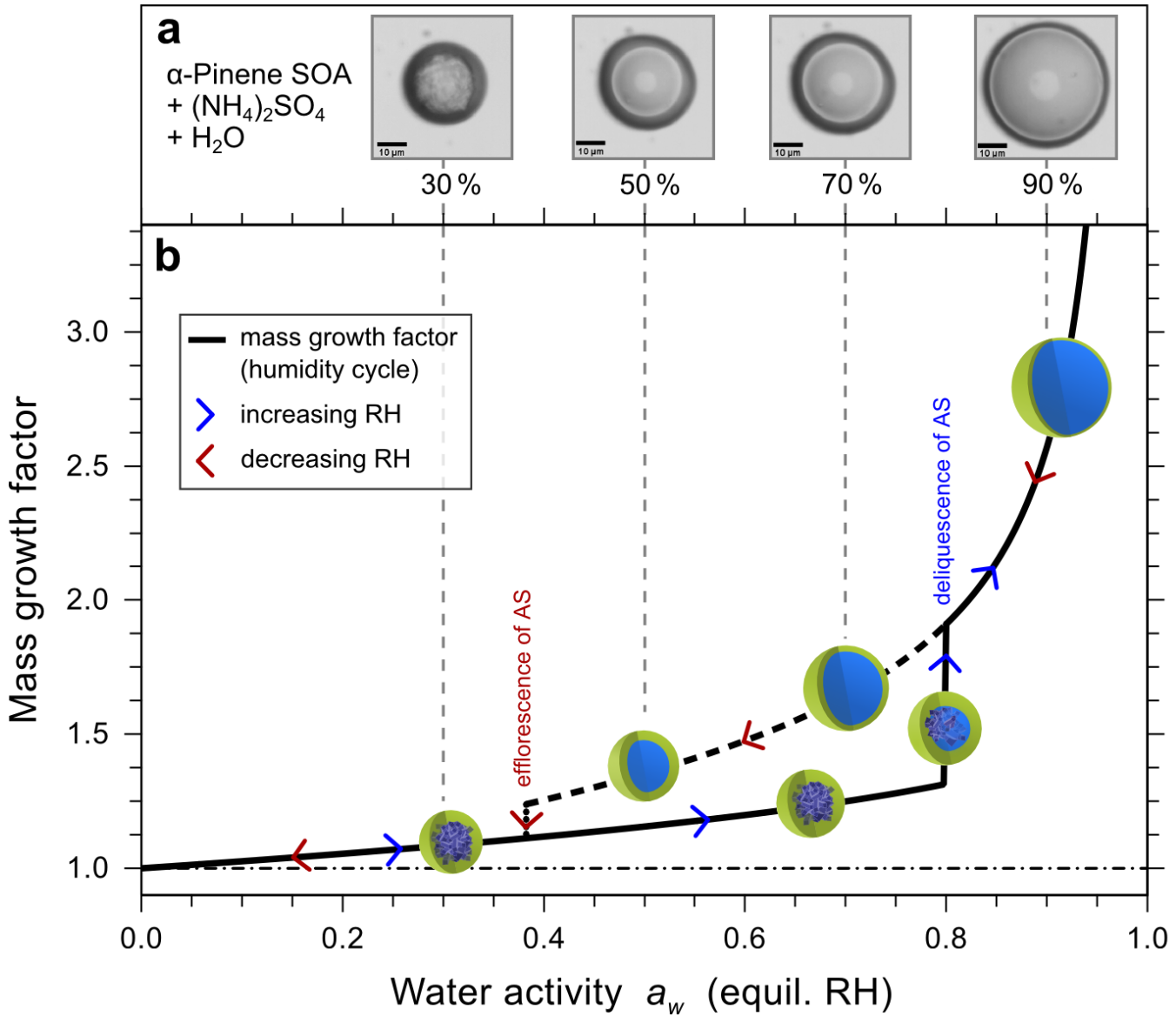
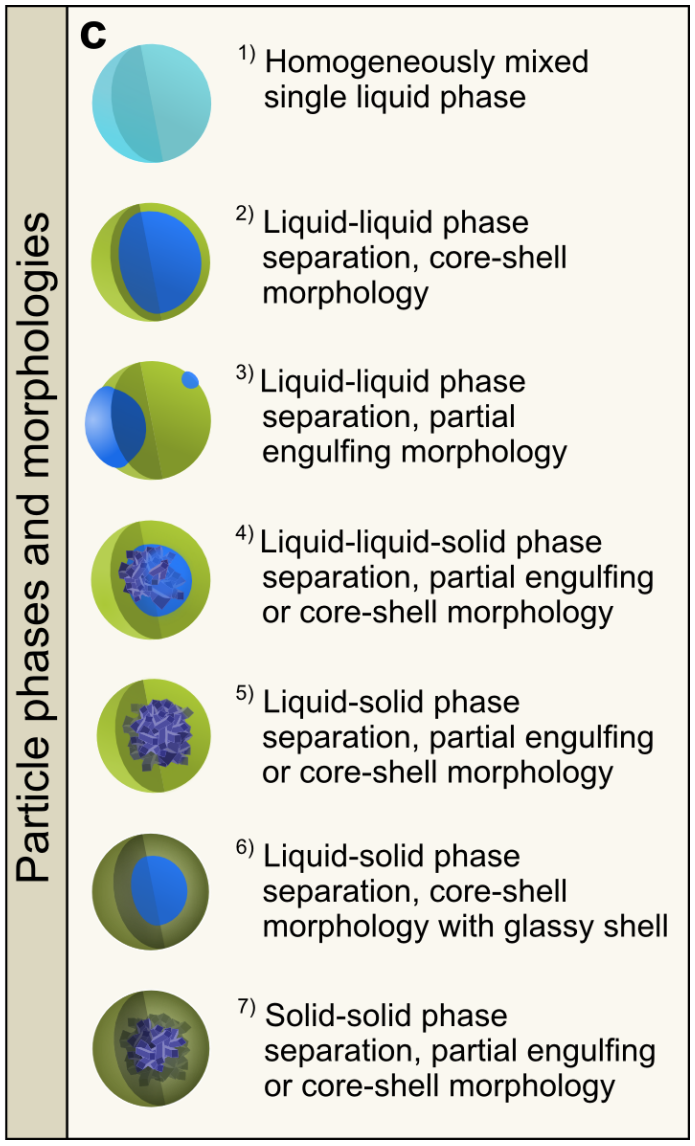
Introduction: organics & water-driven phase transitions



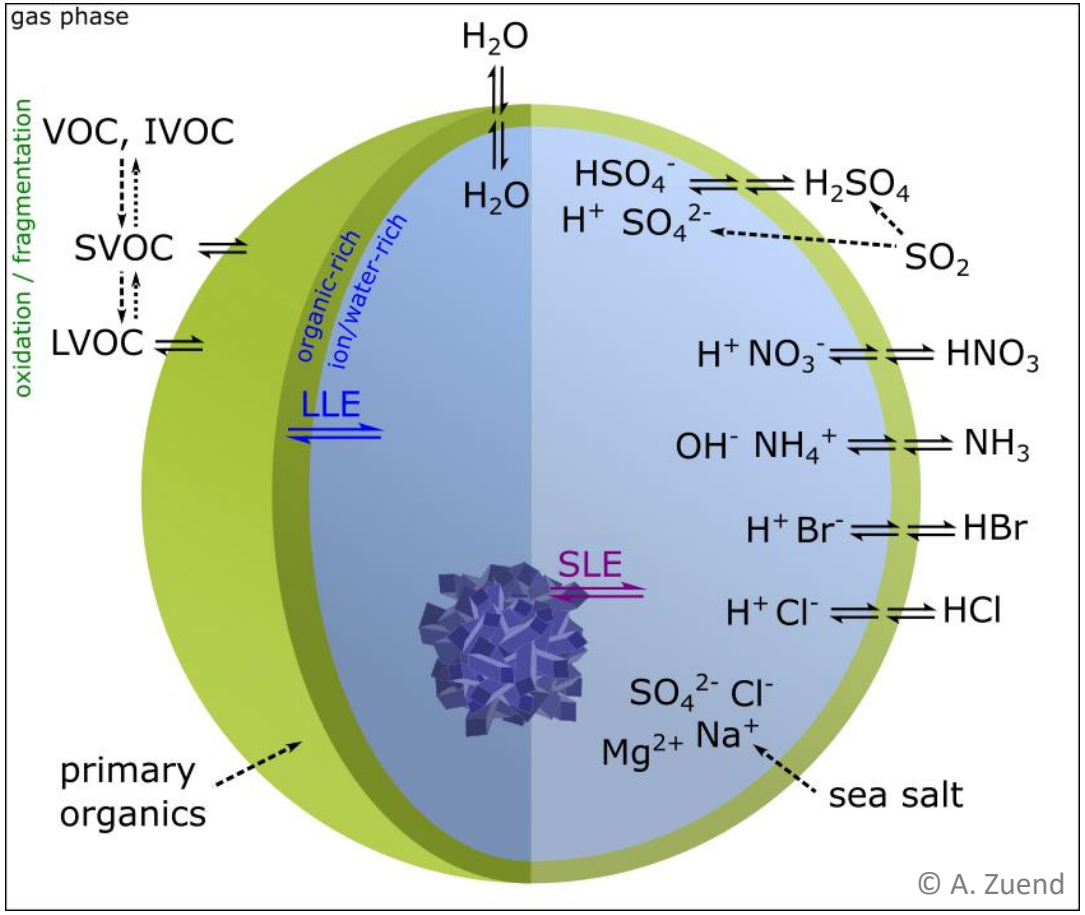


[Shiraiwa, Zuend, Bertram & Seinfeld, 2013, *PCCP*]

Organic–inorganic aerosol thermodynamics

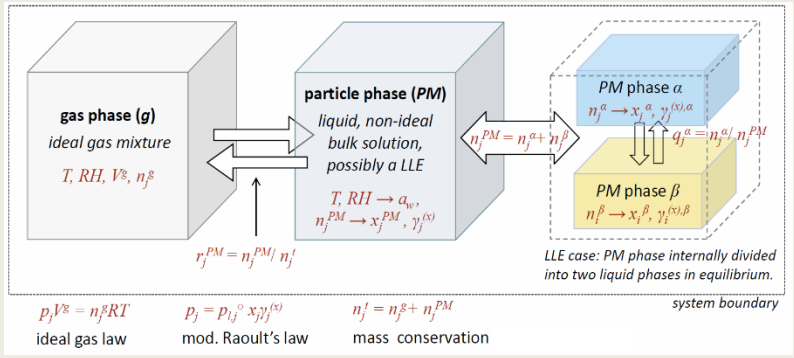
AIOMFAC-based modeling framework

- Gas–particle partitioning at different RH
- Aerosol phases, physical states, viscosity
- Non-ideal mixing, liquid–liquid equilibrium (LLE)
- Aerosol acidity (multiphase; e.g. Pye et al, 2020, *ACP*)
- Hygroscopicity & cloud condensation nucleus (CCN) properties



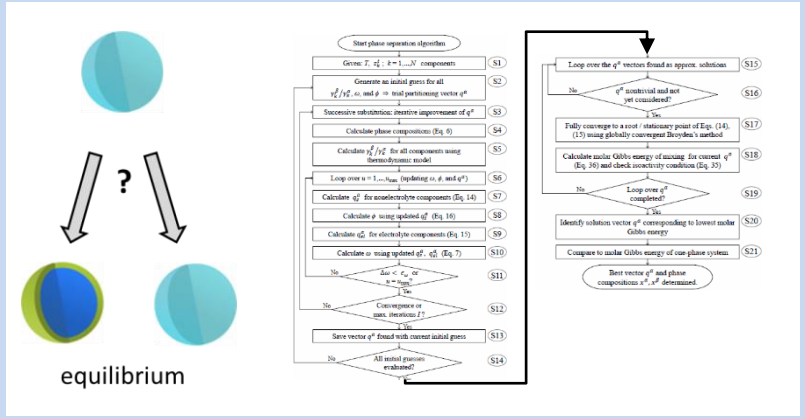
Modeling non-ideal mixing thermodynamics & gas–particle partitioning

Gas-particle equilibrium model:



[e.g., Zuend et al. , 2010, *ACP*]

LLE algorithm: Liquid–liquid phase separation?



[e.g., Zuend and Seinfeld, 2013, *Fluid Phase Equilib.*]

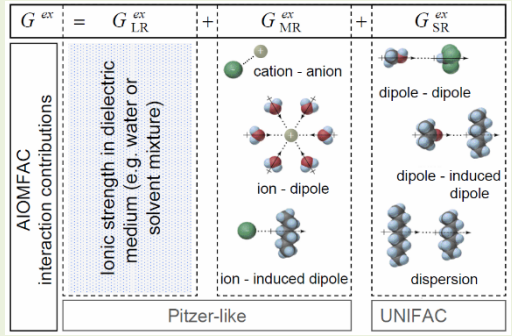
Volatility: Pure component vapour pressures as function of *T* (measured or predicted)

Output: (for specified input system)

- # liquid phases; (& optionally solid phases)
- chemical compositions of all phases (bulk prediction)

AIOMFAC model:

Organic—inorganic mixing in a liquid phase



[Zuend et al., 2008; 2011, *ACP*; https://aiomfac.lab.mcgill.ca]

Next 3 slides outline examples of applications of the AIOMFAC model and the AIOMFAC-based equilibrium framework

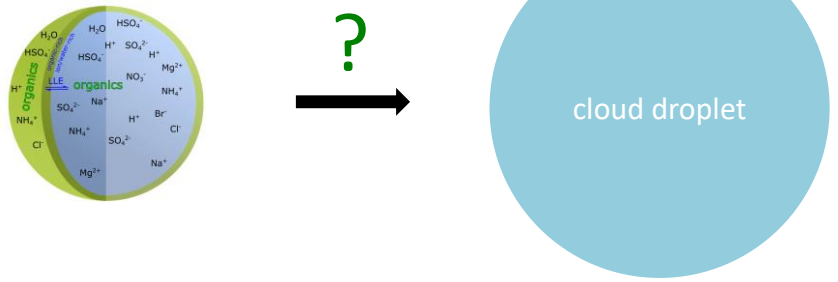
Application of AIOMFAC framework: CCN activation & the role of organics

Köhler theory:

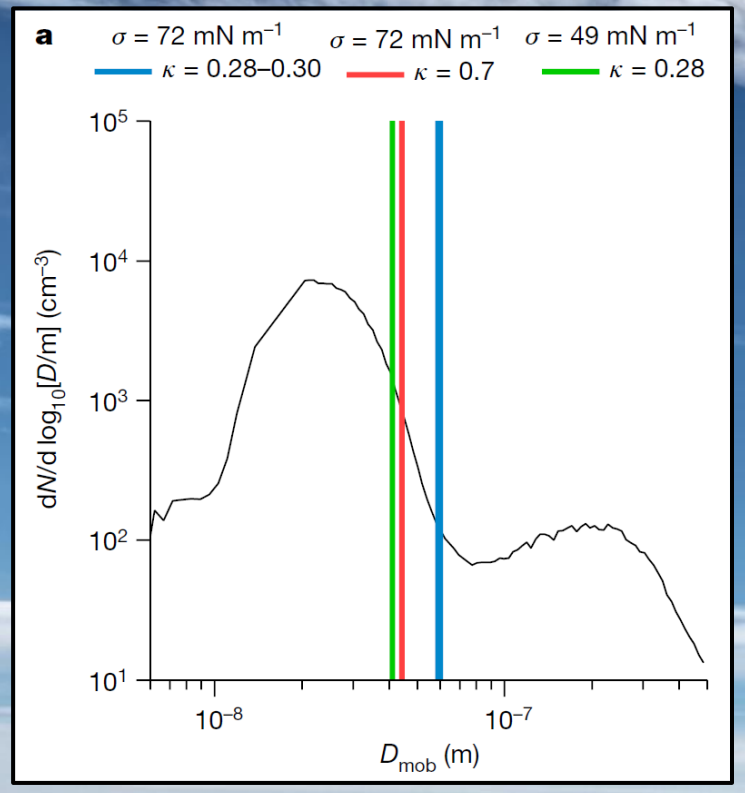
$$S = a_w \exp\left[\frac{4\,\sigma M_w}{RT\rho_w\, D_0\, \mathrm{HGF}}\right] \quad \text{with} \quad \mathrm{HGF} = \frac{D}{D_0}$$

What is the role of organic aerosol constituents & liquid–liquid phase separation in affecting CCN properties?

- Thermodynamic perspective
- Aerosol population / air parcel dynamics



Field study at Mace Head: effective ultrafine CCN in marine air



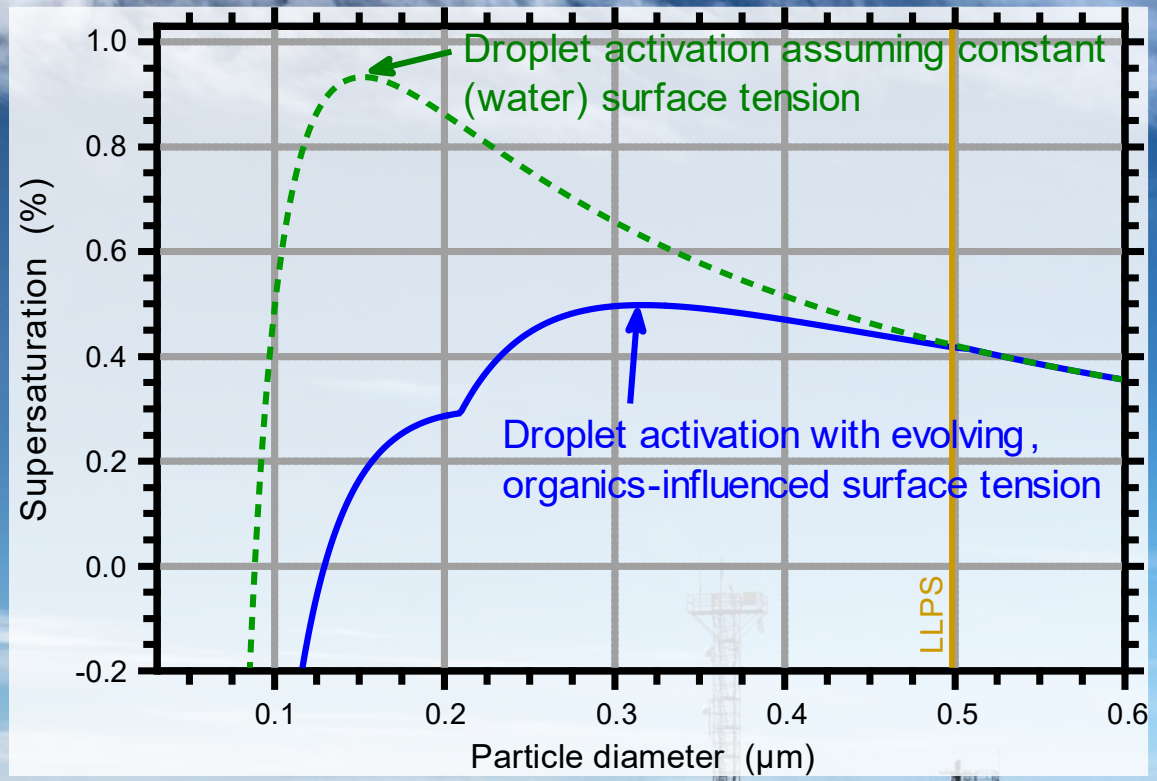
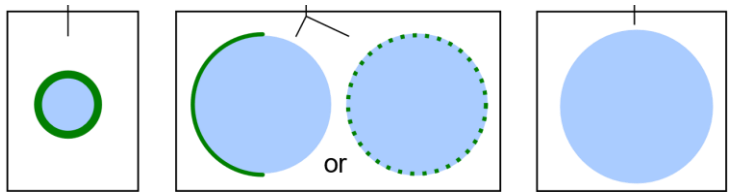


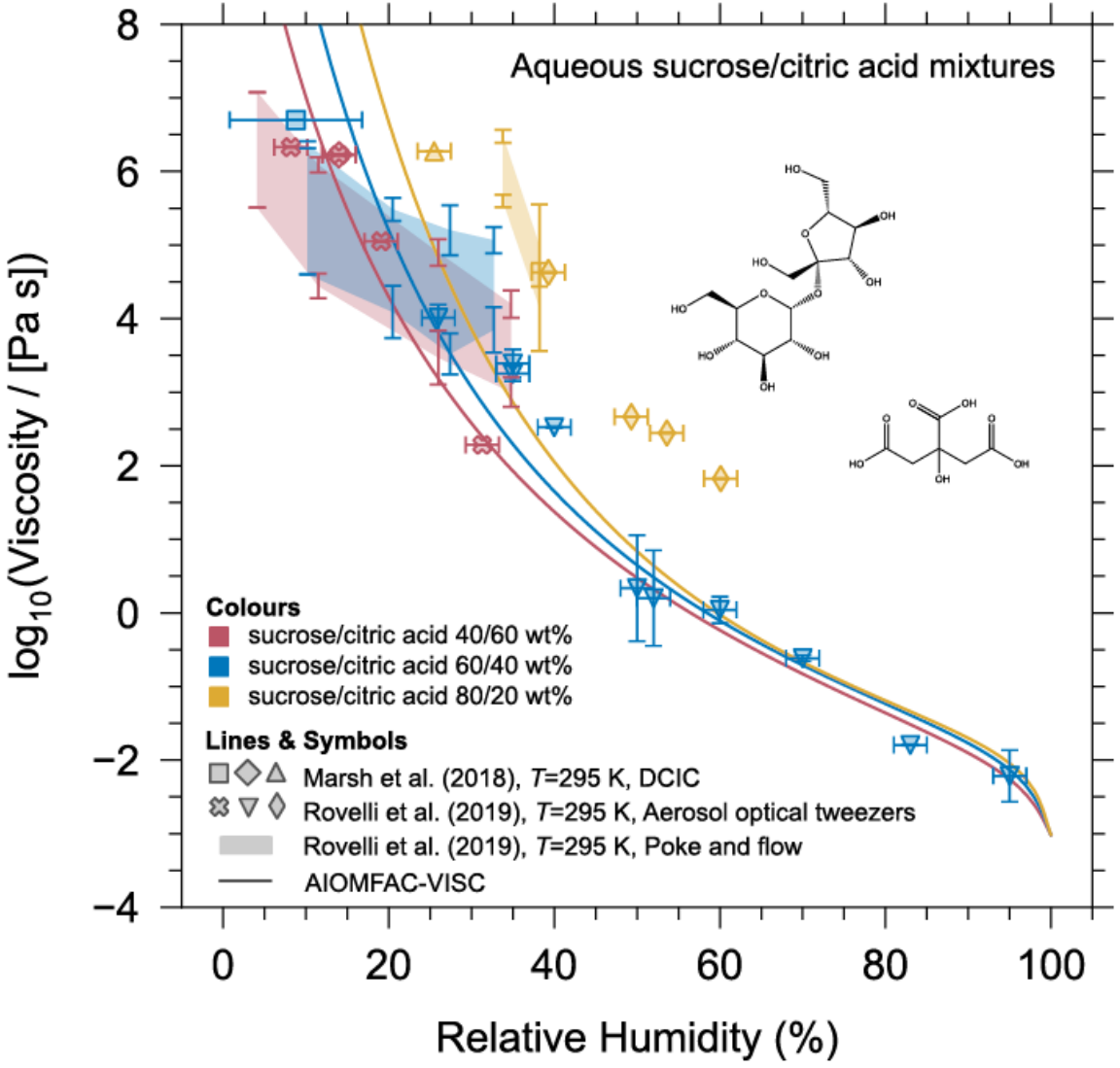
Photo: Mace Head Atmospheric Research Station, C-CAPS NUI Galway, Ireland

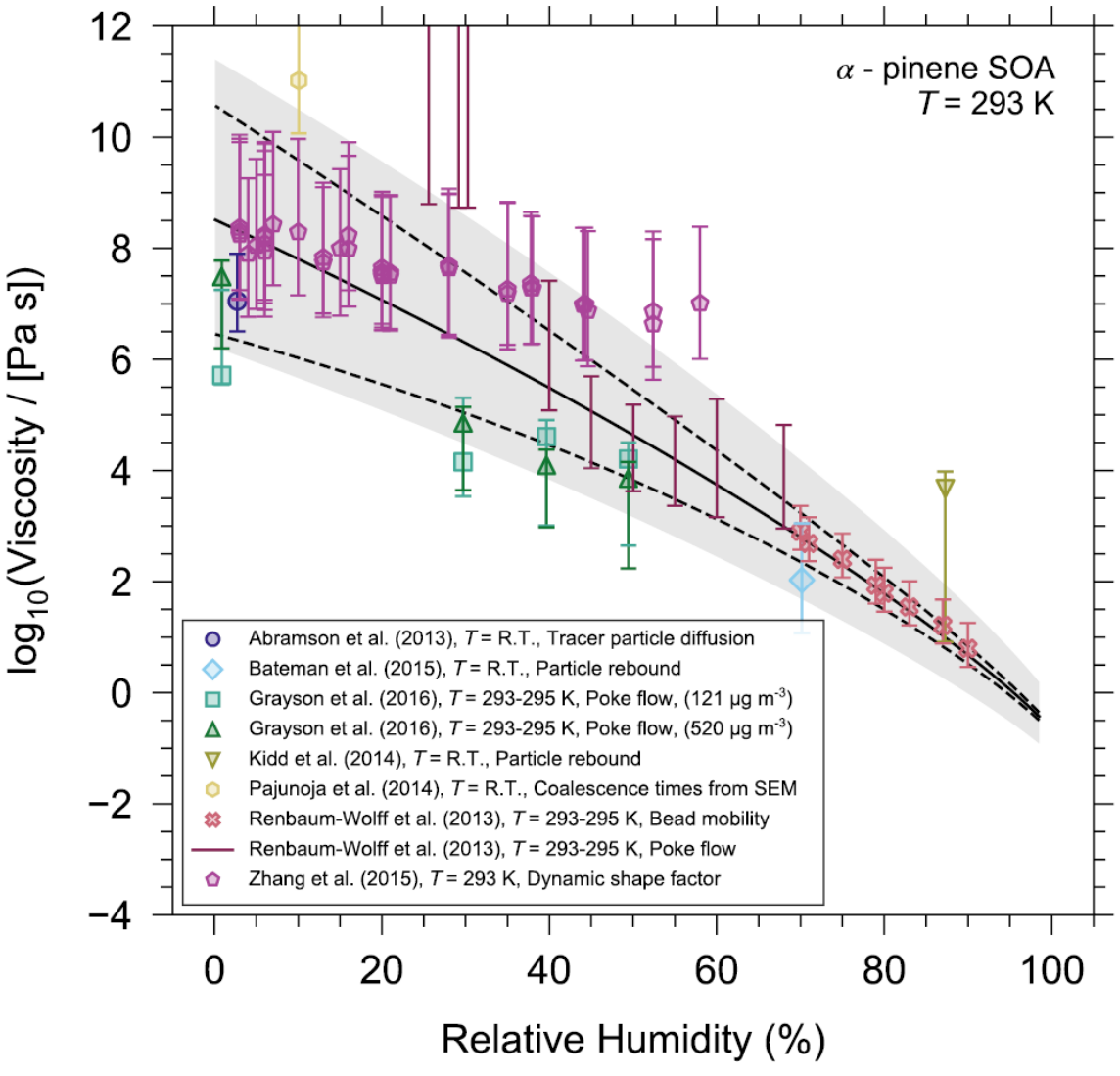
- **Proposed explanation:**
  evolution of surface tension due to organic-rich shell phase (surface tension lowering), depending on surface coverage;



[Ovadnevaite et al., 2017, *Nature*]

AIOMFAC-VISC: Predictive aqueous organic aerosol viscosity

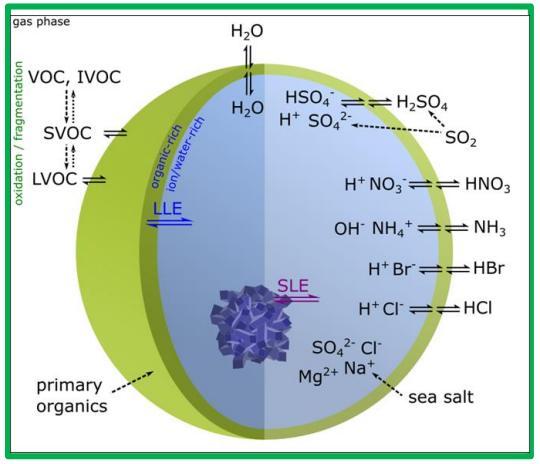




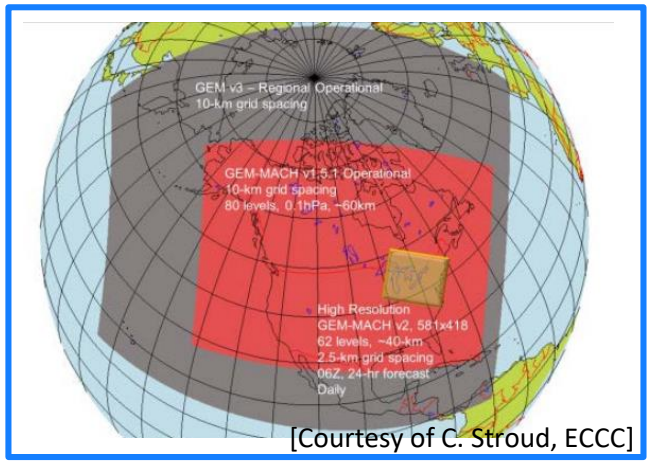
[Gervasi et al., 2020, *ACP*]

From process level to 3-D models

Process level



3-D atmospheric models



[Courtesy of C. Stroud, ECCC]

Chemical-structure-based models

- for detailed system characterization
- computationally expensive

Reduced-complexity models

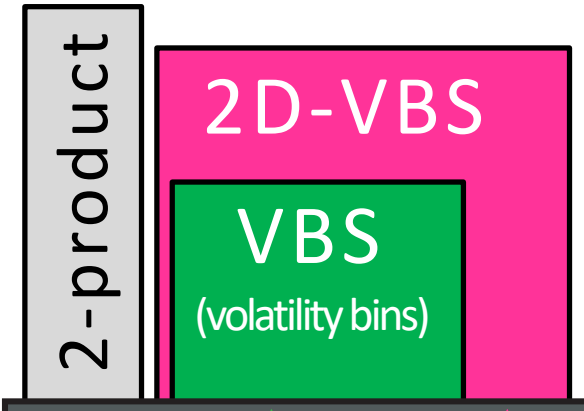
- processing of field measurement data
- operating on limited information

BAT
Binary Activity Thermodynamics

Equilibrium gas–particle partitioning methods

Volatility-based

can use commonly measured (bulk) properties.

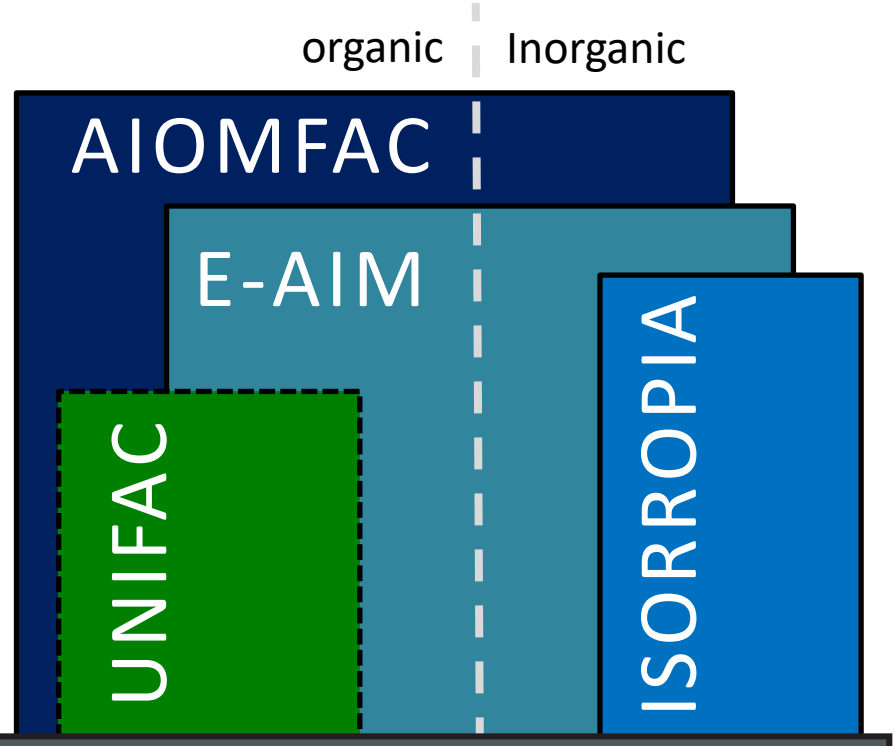


C^*, (K_p) O:C

no water content considered

assumes $\gamma \approx 1$ (ideal mixing)

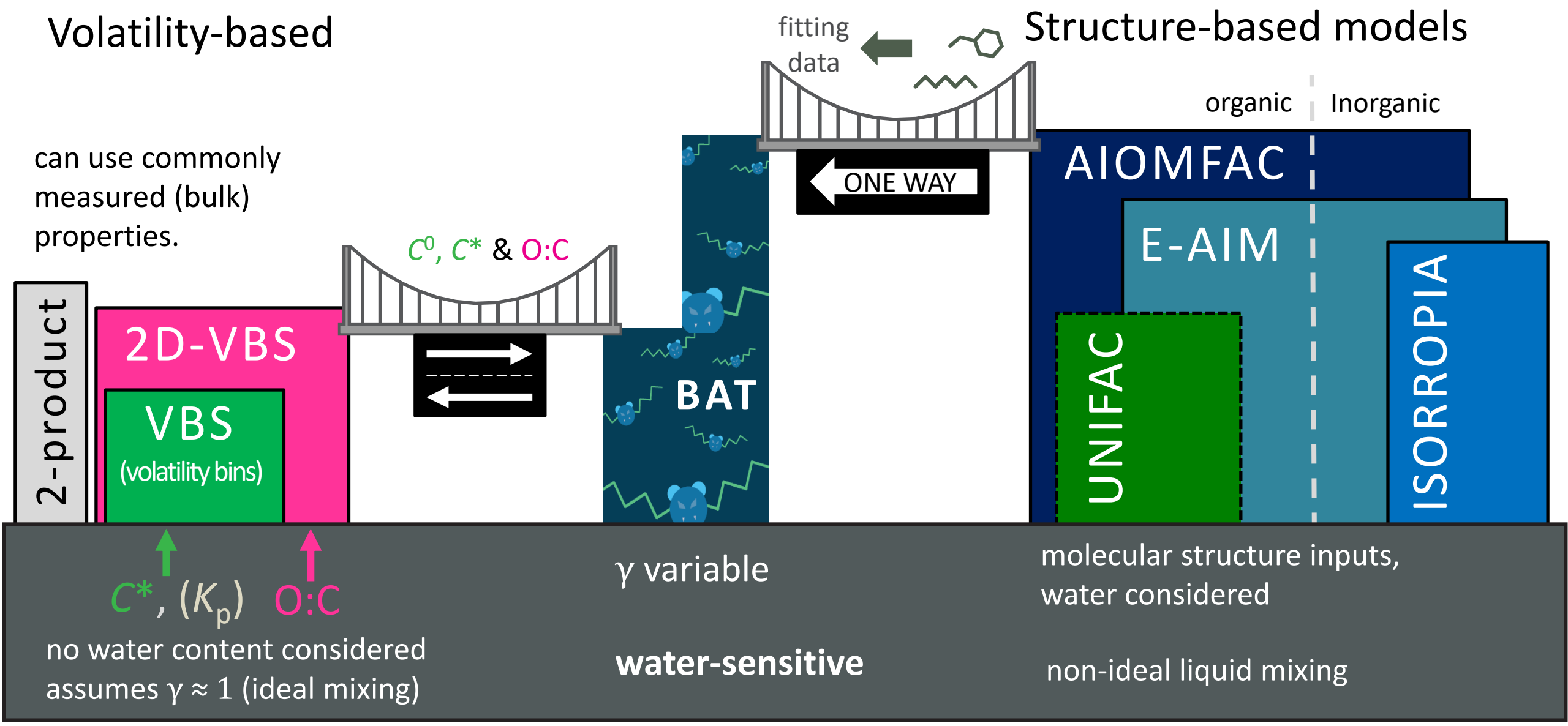
Structure-based models



molecular structure inputs, water considered

non-ideal liquid mixing

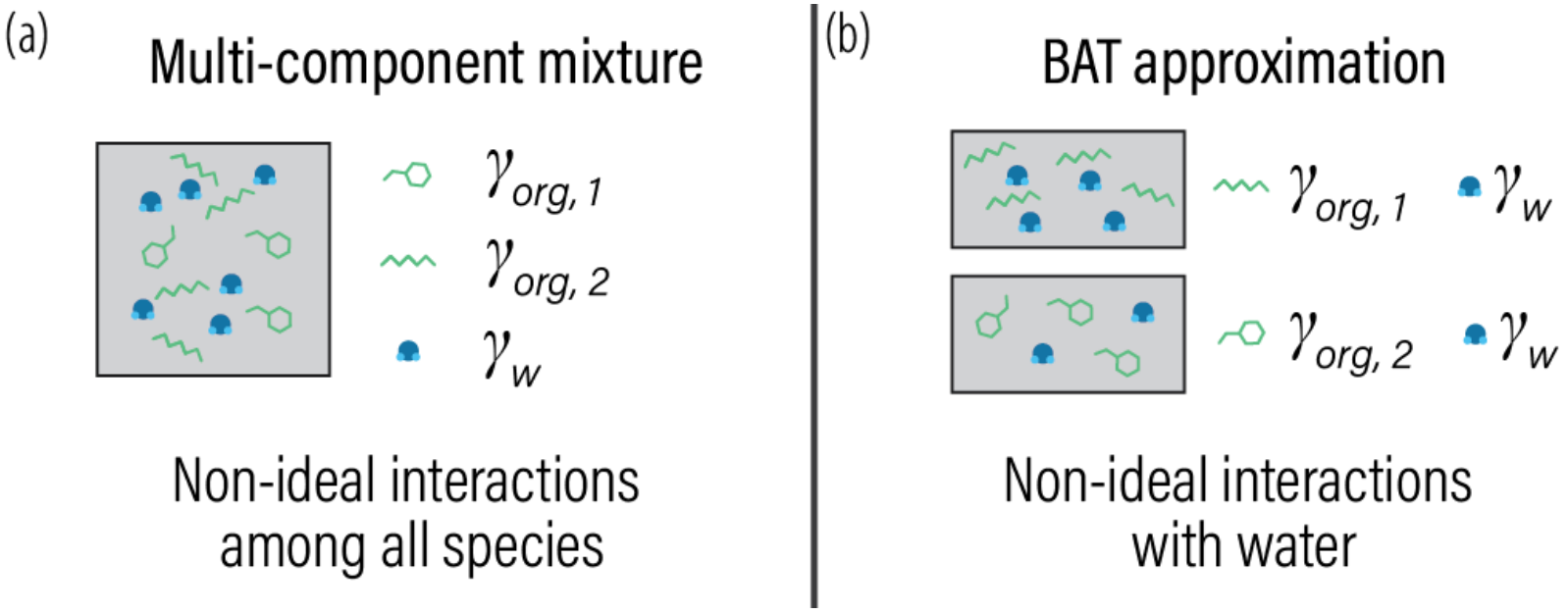
Building an intermediate, reduced-complexity model



Binary Activity Thermodynamics (BAT) model

BAT
Binary Activity Thermodynamics

- **Organic ↔ water interactions**
- Generalized Duhem—Margules activity coefficient model



[Gorkowski et al., 2019, *ACP*]

BAT model – a general parameterization

Generalized Duhem—Margules binary activity coefficient model of BAT:

$$g^e/RT = C_1\varphi^*_{org}(1-\varphi^*_{org}) + C_2\varphi^*_{org}(1-\varphi^*_{org})(1-2\varphi^*_{org})$$

φ^*_{org} = scaled volume fraction of organic

$$C_1 = a_1 \exp(a_2 \cdot \mathrm{O{:}C}) + a_3 \exp\left(a_4 \frac{M_{water}}{M_{org}}\right)$$

$$C_2 = a_5 \exp(a_6 \cdot \mathrm{O{:}C}) + a_7 \exp\left(a_8 \frac{M_{water}}{M_{org}}\right)$$

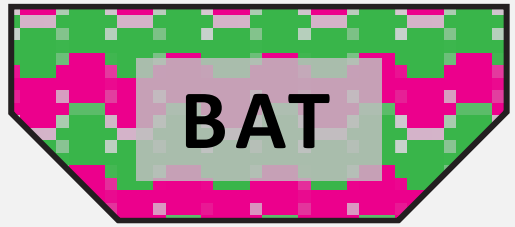
→ Fit parameters a_1, a_2, … for a wide class of organics

Input

O:C, (H:C)

M_{org}

mole fraction of org./water



Output

γ_{org}, a_{org},

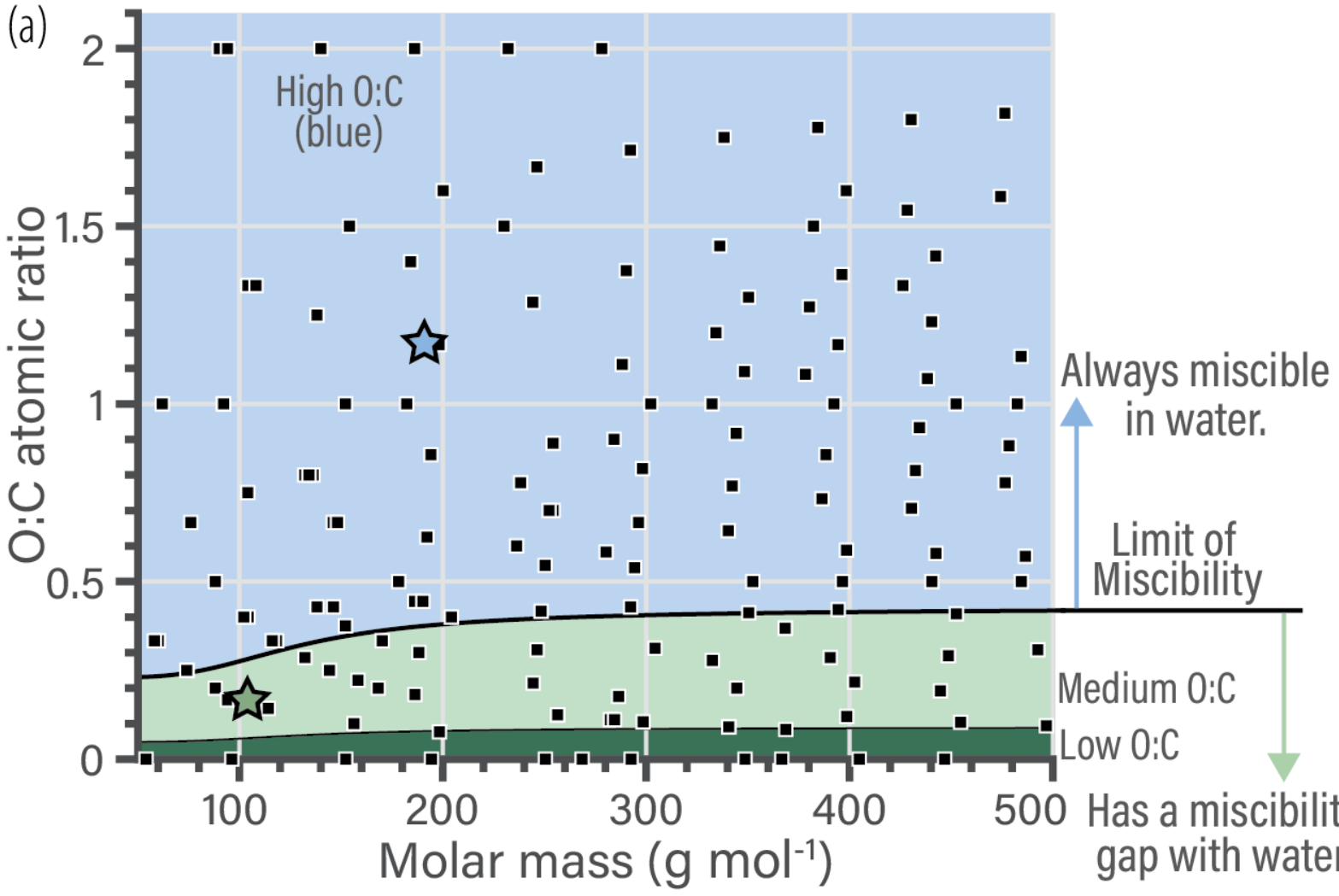
γ_{water}, a_{water} (equil. RH)

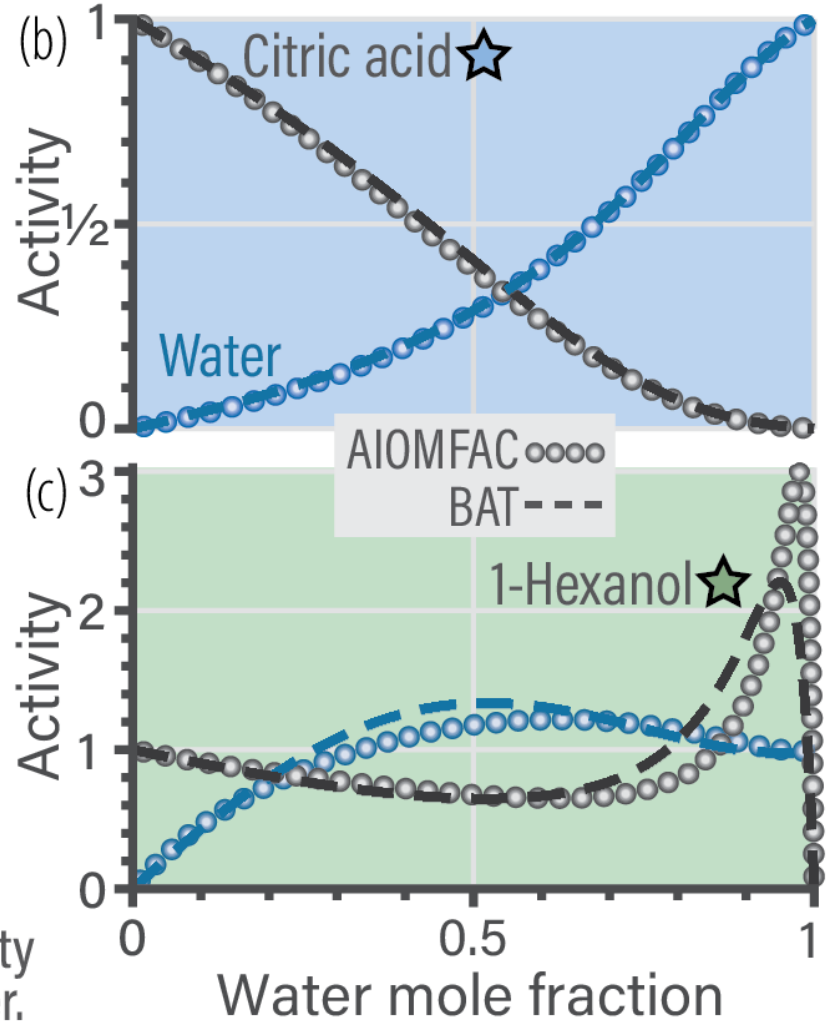
[Gorkowski et al., 2019, *ACP*]

Training a BAT – 3 distinct domains

Binary Activity Thermodynamics

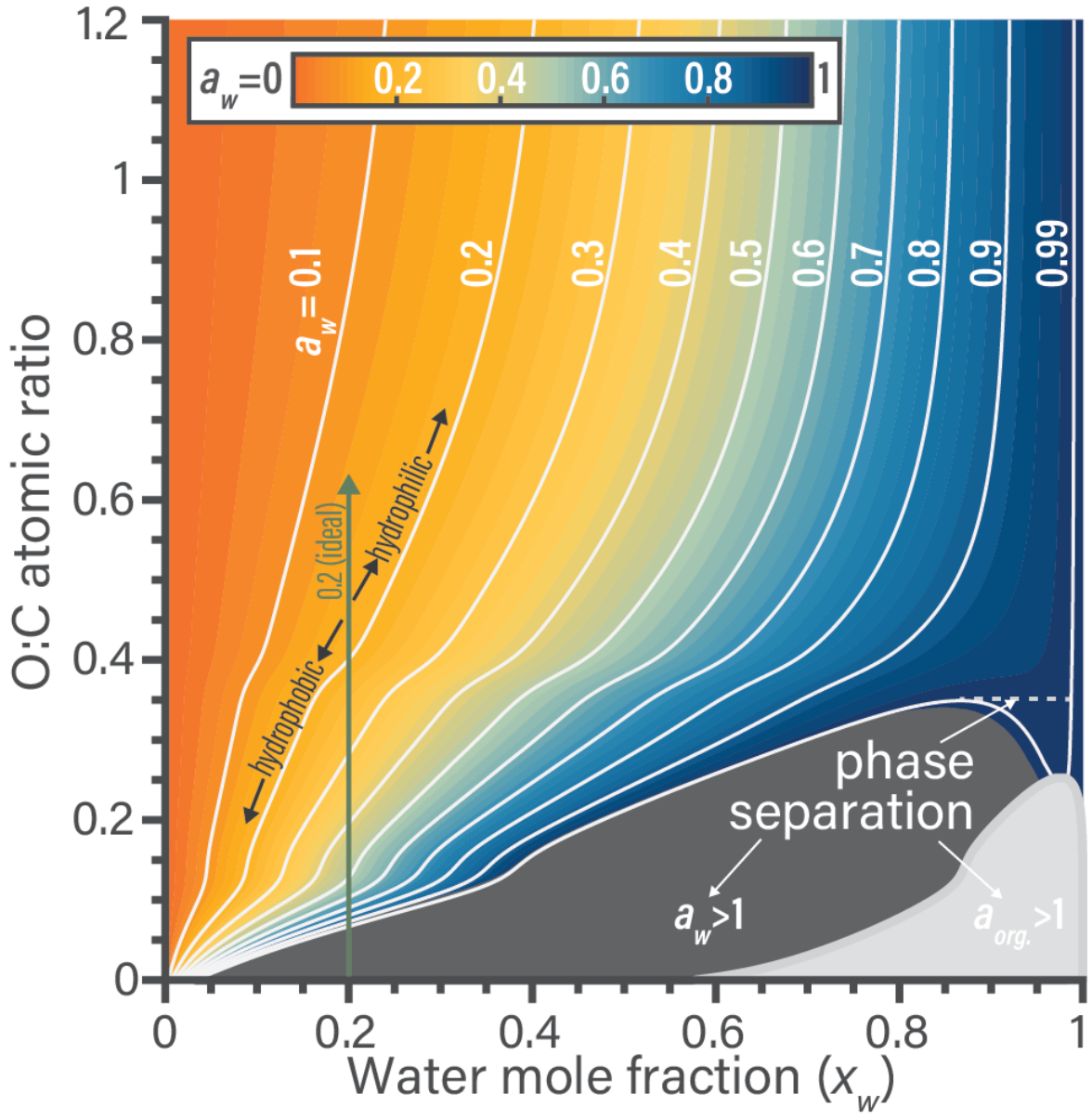
Training dataset of 160 molecules





[Gorkowski et al., 2019, *ACP*]

BAT predictions for non-ideal mixing behavior



BAT Binary Activity Thermodynamics **prediction of water activity**

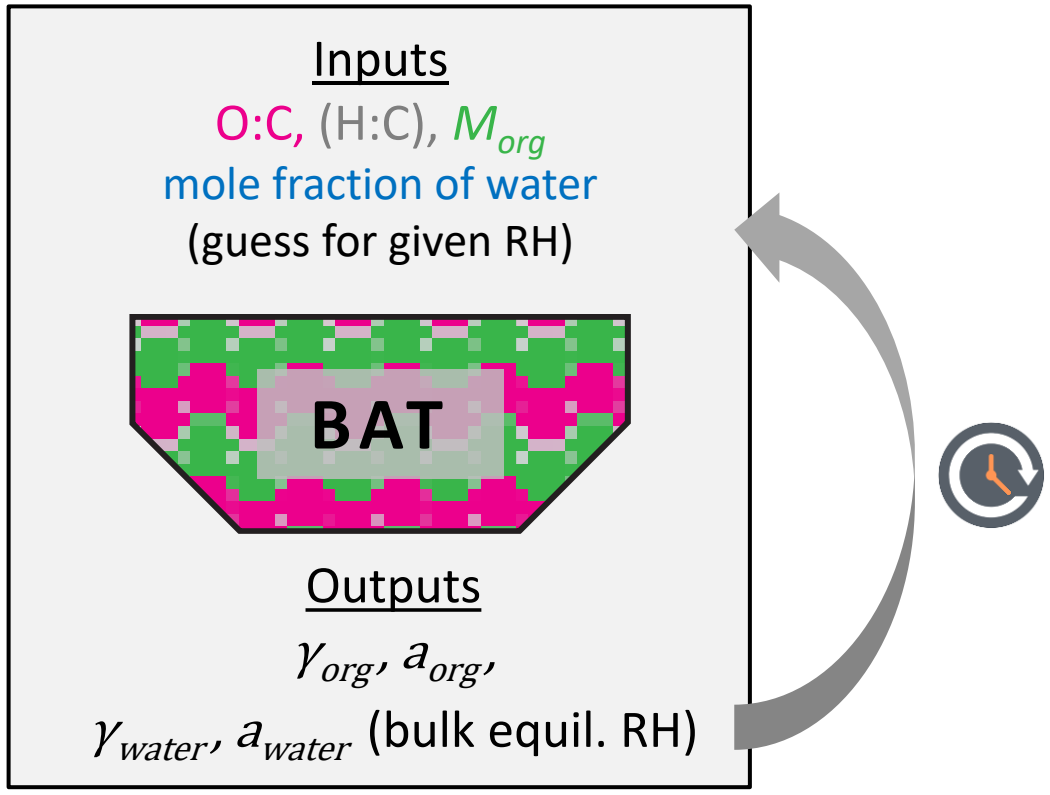
- here M_{org} = 200 g/mol → scan O:C, x_w
- $a_w = x_w \times \gamma_w$ (= bulk equil. RH)
- BAT reveals range of phase separation via a simplified LLPS estimation method (for high efficiency)

[Gorkowski et al., 2019, *ACP*]

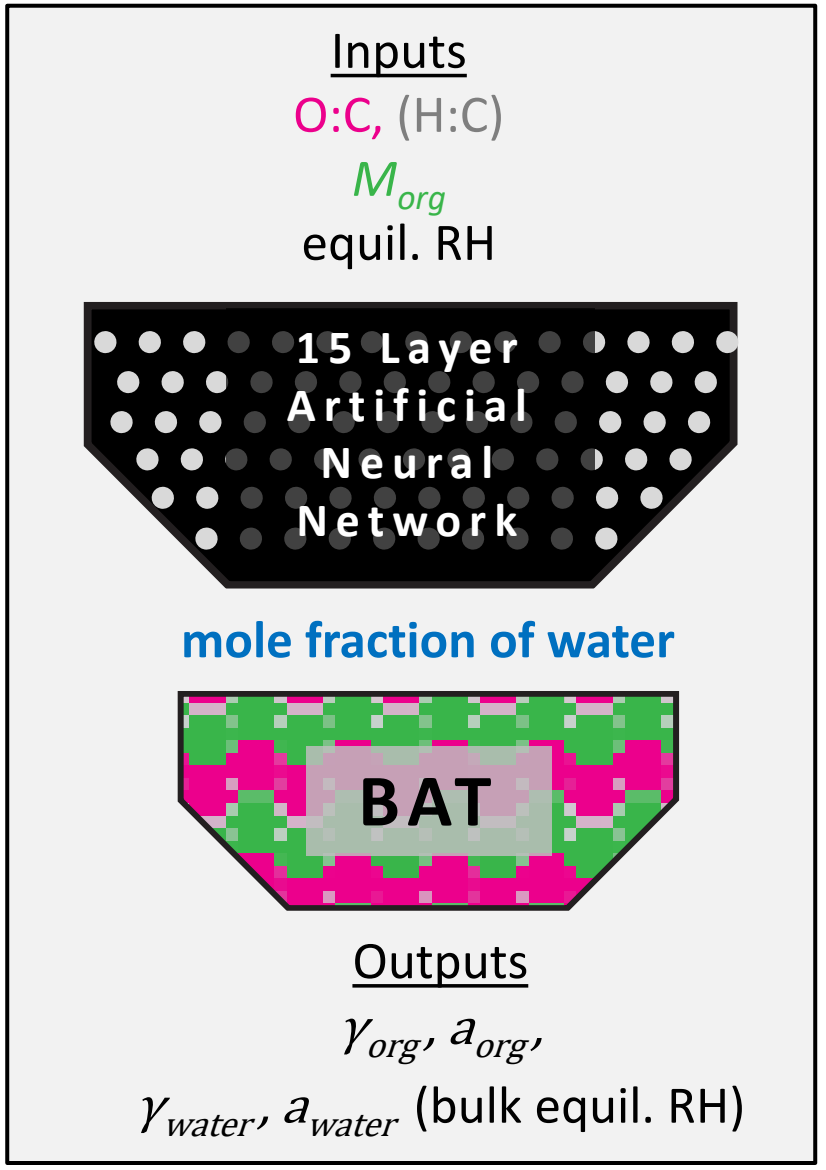
Organic water uptake: iteration *vs.* neural network

In SOA experiments and chemical transport models the **RH**, O:C, (H:C) and M_{org} are typically provided.

Iteration: find aerosol water content **for given RH**



iterative → time consuming



with trained NN, non-iterative → substantially faster

VBS + BAT: including water, γ_j, and phase separation

VBS + BAT Binary Activity Thermodynamics

sums include water

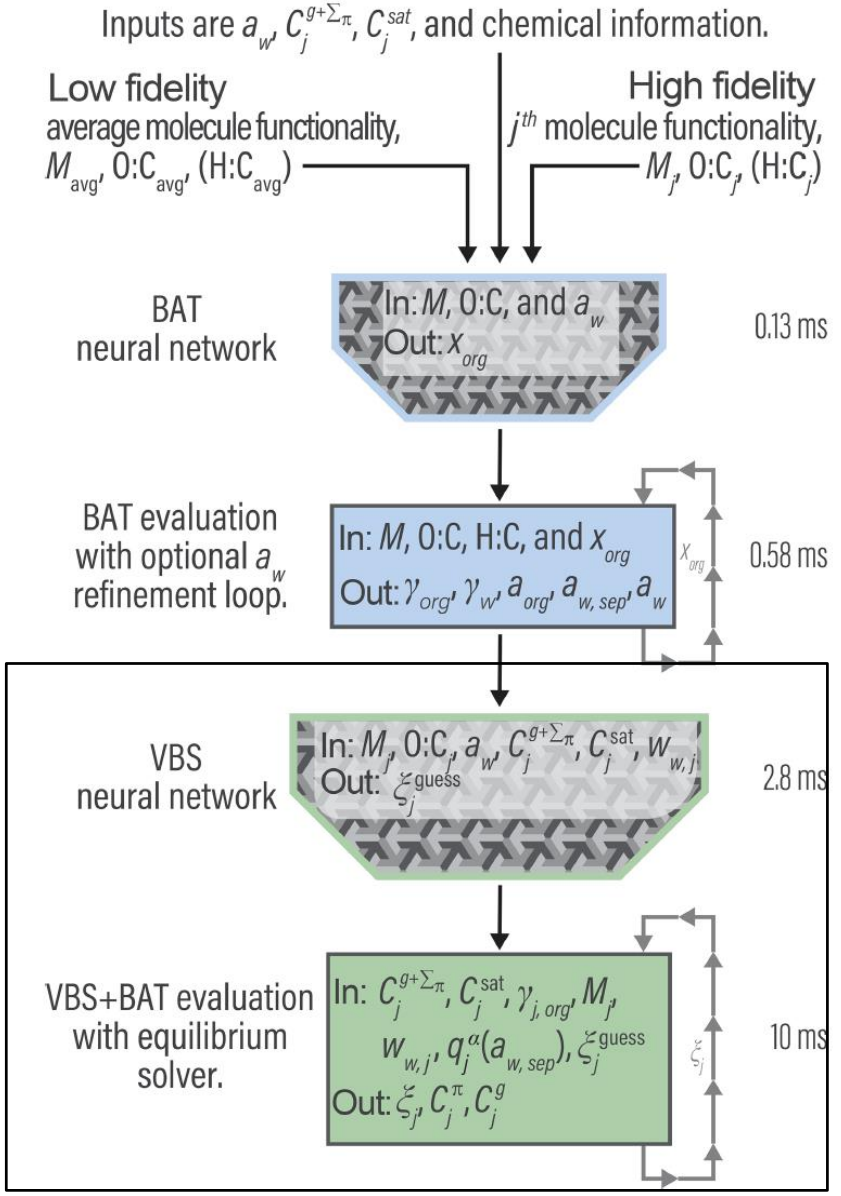
$$C_j^* = C_j^{sat}\,\gamma_j^{\alpha}\,q_j^{\alpha}\,\frac{\sum_k \frac{C_k^{\alpha}}{q_k^{\alpha}}}{M_j \sum_k \frac{C_k^{\alpha}}{M_k}}$$

activity coeff. (in phase α)

Liquid–liquid phase partitioning (0 to 1)

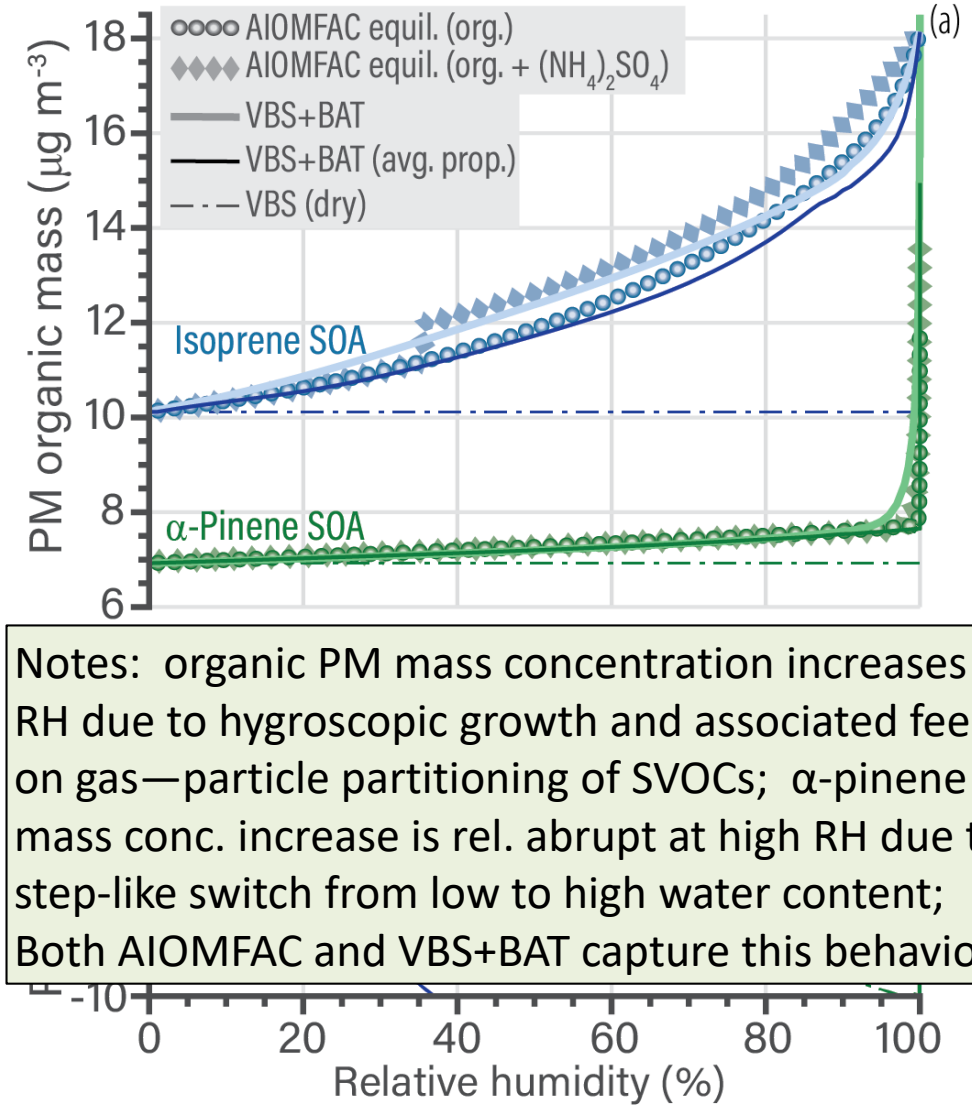
Organic + water PM mass:

$$C_{OA,aq} = \sum_k C_k^{\alpha} + C_k^{\beta}\ ; \qquad \xi_j = \frac{1}{1 + \frac{C_j^*}{C_{OA,aq}}}$$

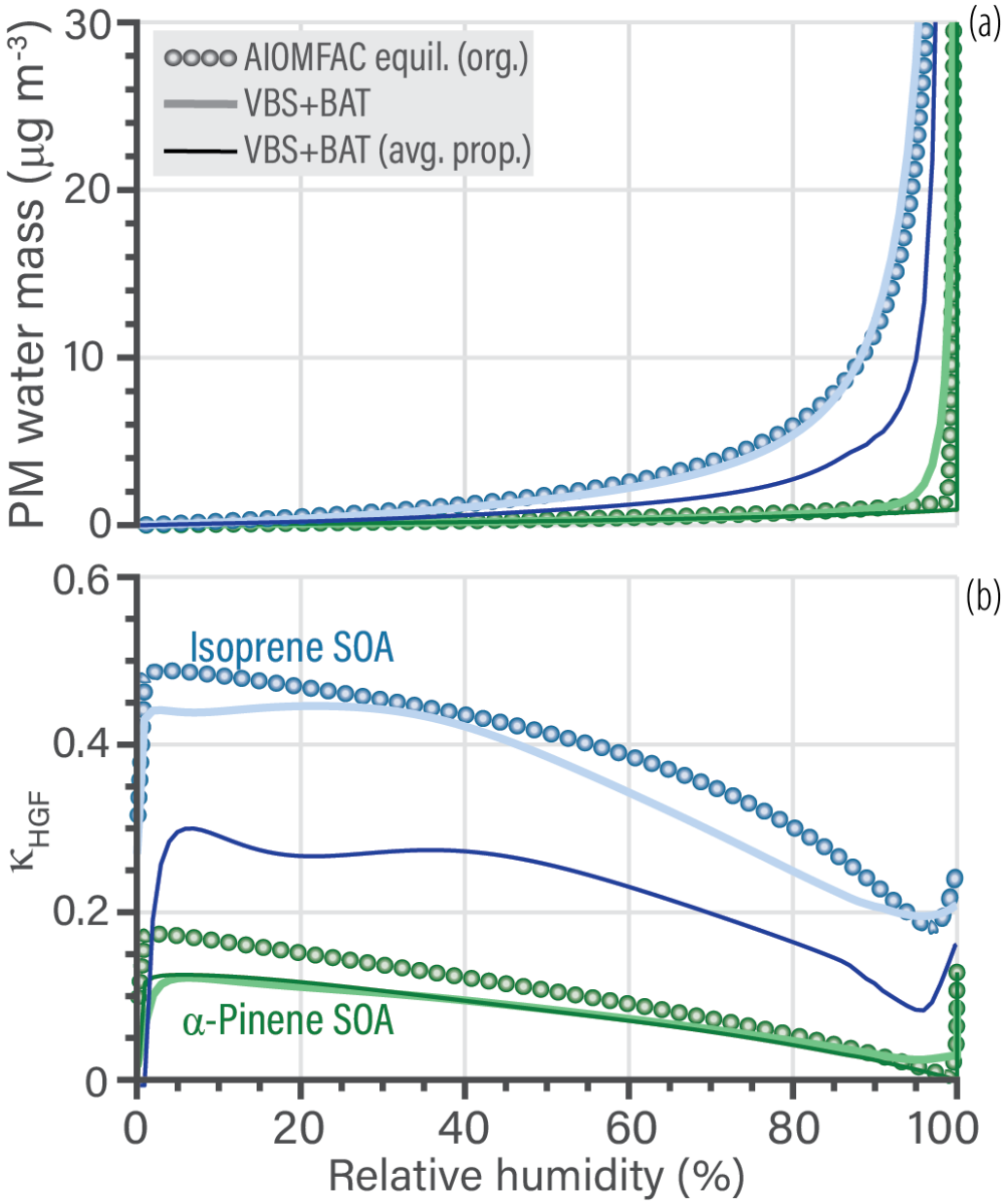


[Gorkowski et al., 2019, *ACP*]

VBS + BAT *vs.* AIOMFAC predictions: RH-dependent aerosol mass



Notes: organic PM mass concentration increases with RH due to hygroscopic growth and associated feedback on gas—particle partitioning of SVOCs; α-pinene SOA mass conc. increase is rel. abrupt at high RH due to step-like switch from low to high water content;
Both AIOMFAC and VBS+BAT capture this behavior…

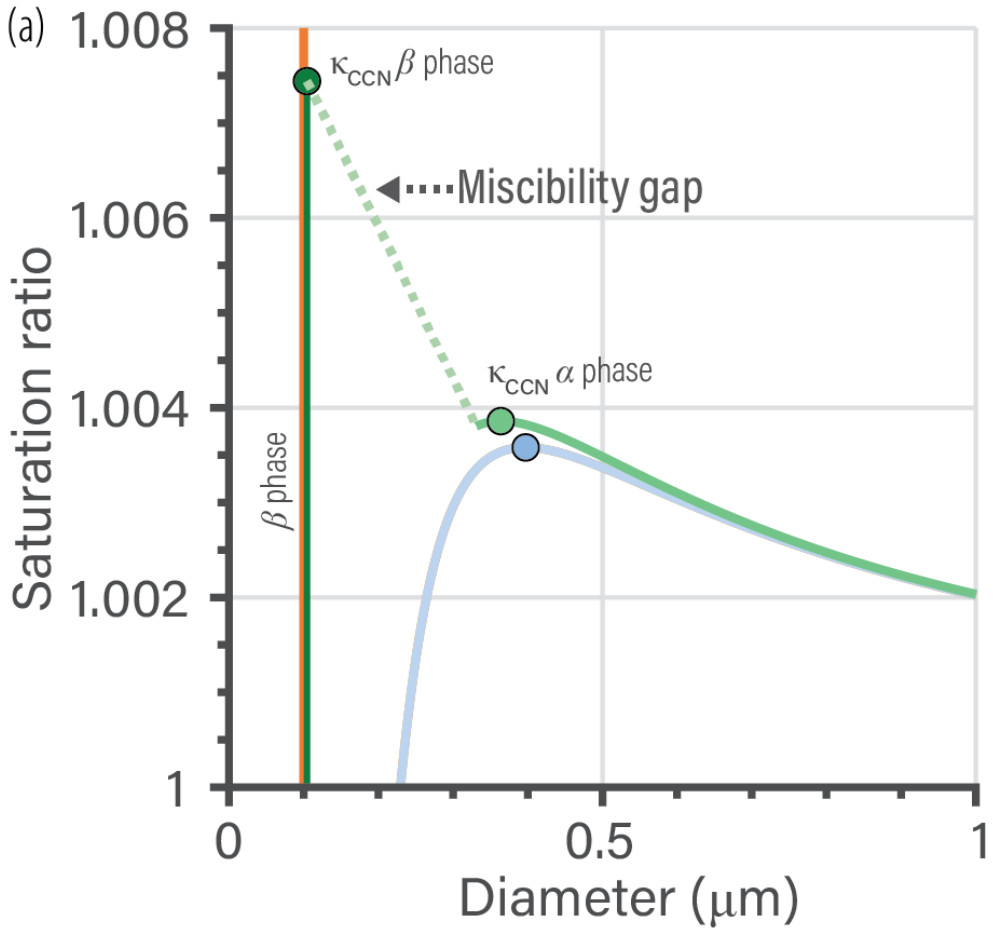


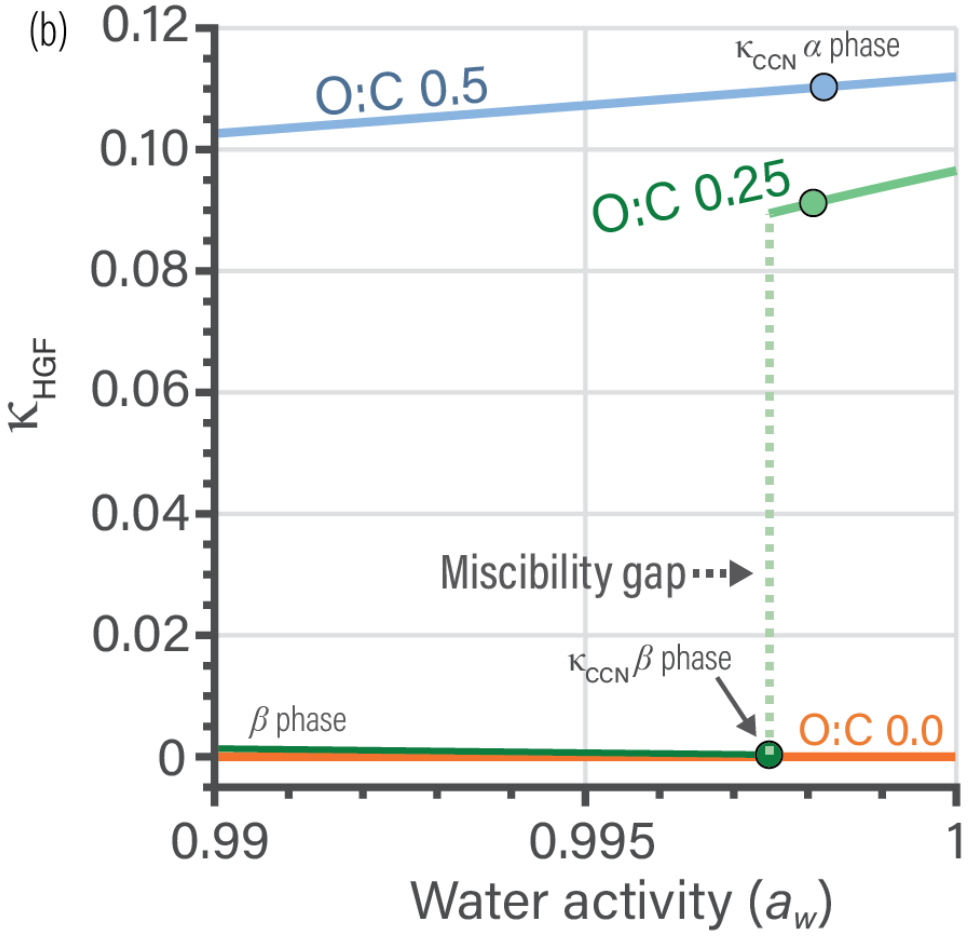
[Gorkowski et al., 2019, *ACP*]

BAT predictions: O:C-dependent CCN activation

Particle of 100 nm dry diameter and M_{org} = 200 g/mol

[Gorkowski et al., 2019, *ACP*]



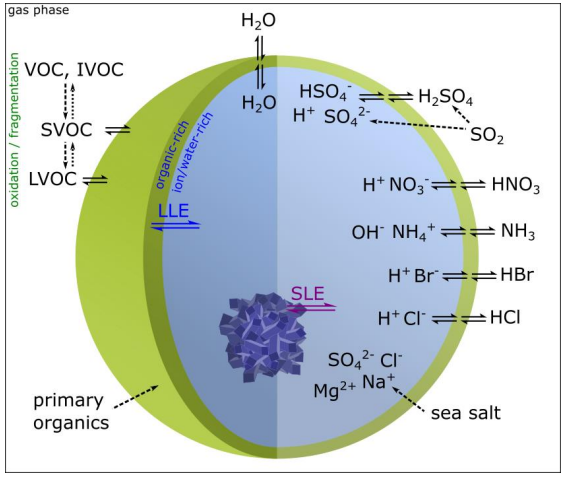


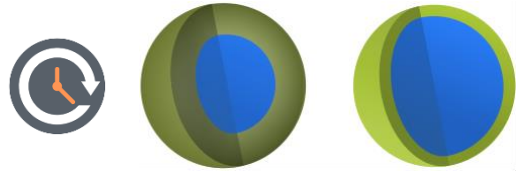
Notes: BAT model allows for predictions of Köhler curves (left) and associated effective kappa values (right) in the context of scanning the O:C / M_{org} parameter space;
→ High-RH behavior and CCN activation point can be predicted for (generic) organic aerosols.

Summary

Prediction of water uptake and related effects on aerosol and CCN properties with different tools:

- AIOMFAC & AIOMFAC-based thermodynamic equilibrium framework
- Organic aerosol viscosity prediction (AIOMFAC-VISC)
- Binary Activity Thermodynamics (BAT) reduced-complexity model
- VBS + BAT
  - organic PM water content (hygroscopicity)
  - organic co-condensation effects with increasing RH
  - can account for liquid–liquid phase separation.





BAT Binary Activity Thermodynamics

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NSERC CRSNG

References

BAT Binary Activity Thermodynamics

- **Gorkowski, Preston & Zuend (2019)**: Relative-humidity-dependent organic aerosol thermodynamics via an efficient reduced-complexity model, Atmos. Chem. Phys., 19, 13383—13407, https://doi.org/10.5194/acp-19-13383-2019, 2019.

AIOMFAC-VISC

- **Gervasi, Topping & Zuend (2020)**: A predictive group-contribution model for the viscosity of aqueous organic aerosol, Atmos. Chem. Phys., 20, 2987–3008, https://doi.org/10.5194/acp-20-2987-2020, 2020.

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