Verifying the Hygroscopic Particle Growth Model during the Time Relevant to Lung Inspiration

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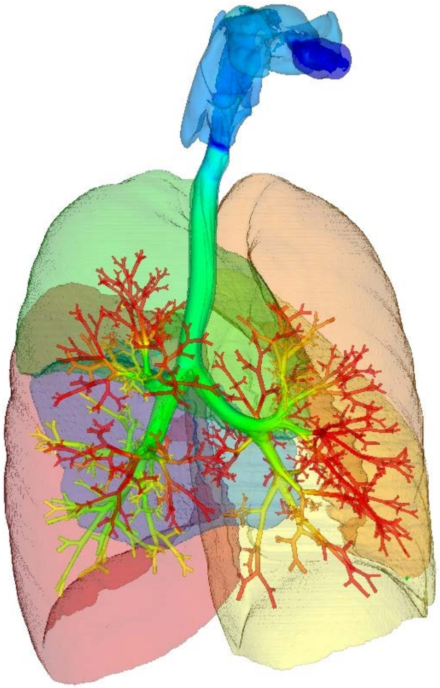
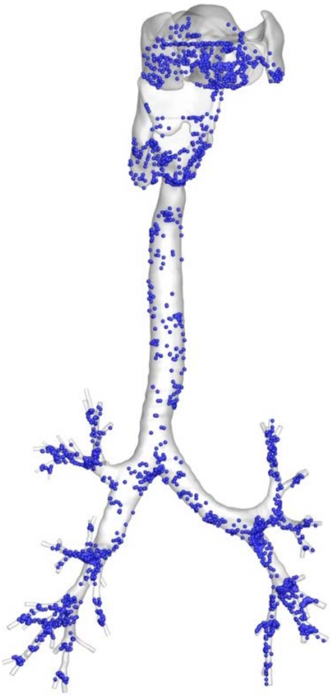
Rationale

Particle Lung Deposition

CFD modeling of particle deposition of hygroscopic particles



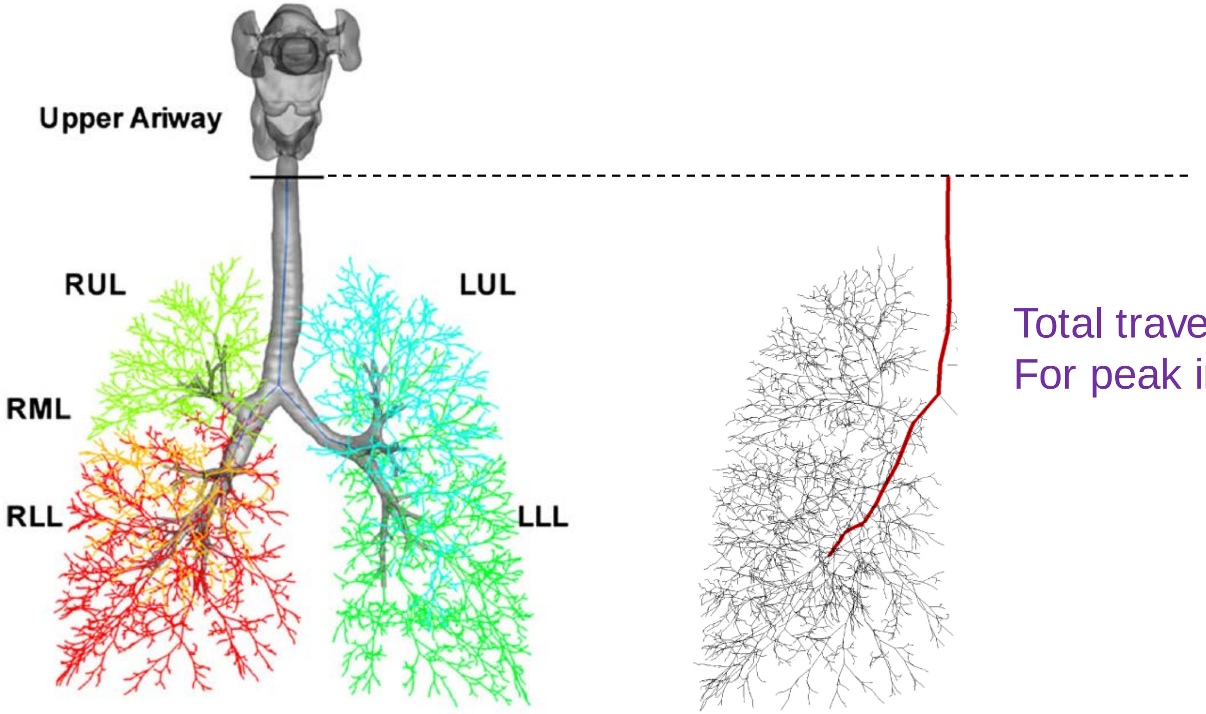
11 generation airway tree constructed from CT images



Example of results for non-hygroscopic particles

Inspiration Time to Lower Airways

Model of path from trachea to 8th generation bronchiole



Total travel time = **0.22 s**
For peak inspiration = 6 L/min

Rationale

- Model suggests that larger particles (> 100 nm) will still be growing at 0.22 seconds
- Current hygroscopic growth model has not been validated well for the growth phase of the salt droplet.

Hygroscopic Model

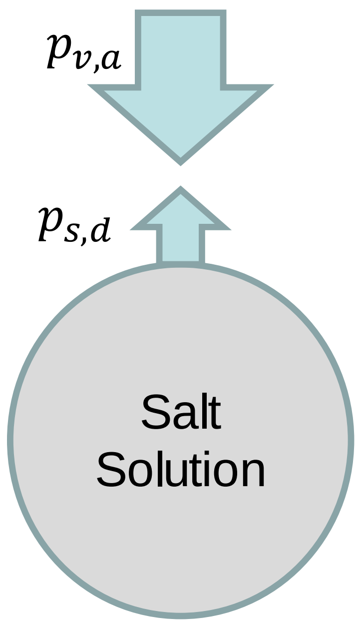
Droplet Equilibrium Behavior

Above a threshold relative humidity, a salt-containing droplet exerts a lower vapor pressure than atmospheric water vapor pressure.

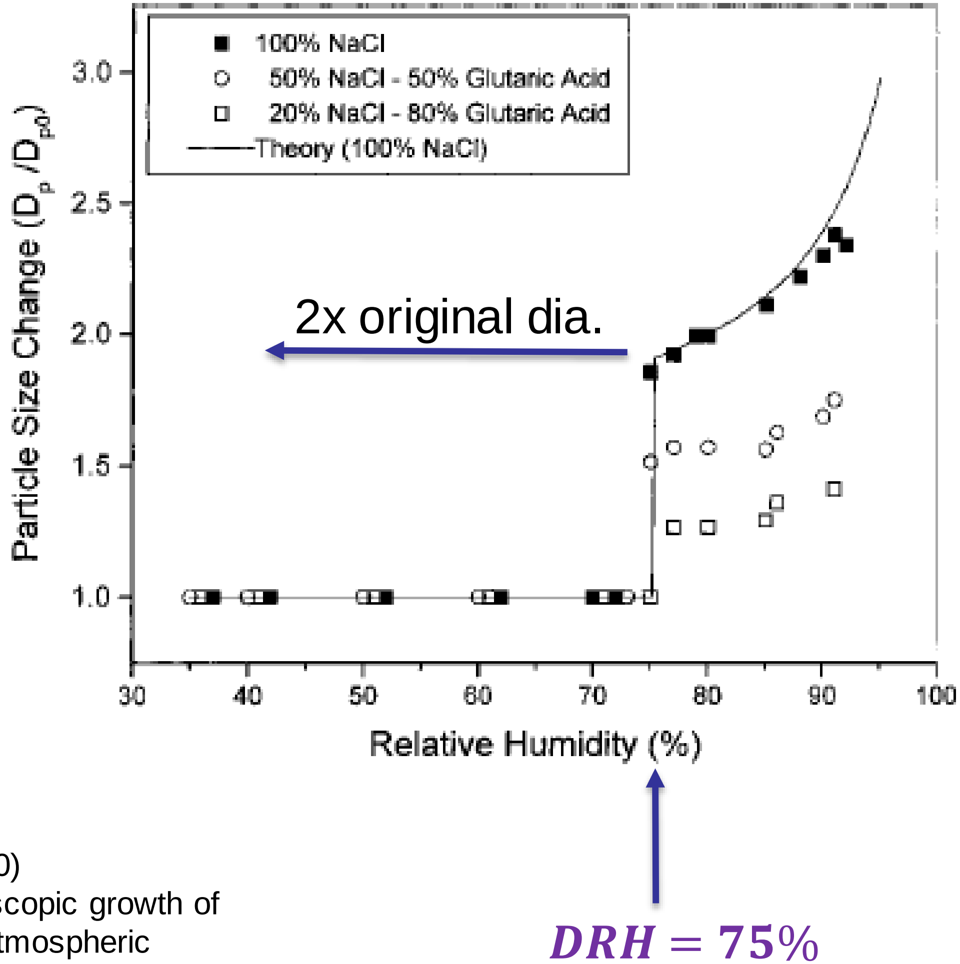
Results in migration of water molecules toward the droplet.

Partial pressure of water vapor in the atmosphere

Saturation vapor pressure of water at the surface of the droplet



NaCl Deliquescence



Cruz CN, Pandis SN (2000) Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol. *Environ Sci Technol* 34:4313-19.

Fundamental Equation

Change in droplet size over time:

$$\frac{d\phi}{dt} = \frac{4D_v^* M_w}{R\rho_d \phi}\left[\frac{p_{v,a}}{T_a} - \frac{p_{s,d}}{T_d}\right]$$

Ø = **droplet** diameter, m

D_v^* = modified molecular diffusivity, m^2/s

M_w = molecular weight of water, 0.018 kg/mol

R = universal gas constant, 8.314 m^3-Pa/mol-K

ρ_d = droplet density (varies with droplet size), kg/m^3

$p_{v.a}$ = partial pressure of water vapor at atmospheric conditions, Pa

$p_{s,d}$= saturation pressure of water vapor near the droplet, Pa

T_a = ambient temperature, K

T_d = droplet temperature, K

Hygroscopic Growth Model

Full equation combining RH, Solute Effect, Kelvin Effect and Temperature Differences

$$\phi\frac{d\phi}{dt} = \frac{4D_v^* M_w p_s(T_a)}{R\rho_d}\left[\frac{RH}{T_a} - \frac{A_w}{T_d} exp\left[\frac{4M_w\sigma}{R\rho_w\phi T_d} + \frac{h_{fg}M_w}{R}\left(\frac{1}{T_a} - \frac{1}{T_d}\right)\right]\right]$$

h_{fg} = latent heat of condensation, 2412631 J/kg at 37°C

Water Activity

Measure of the vapor pressure exerted by salts in water (or food)

$$A_{w,d} = \frac{p_{s,d}(T_d)}{p_{s,w}(T_a)}$$

$p_{s,d}(T_d)$ = saturation pressure of water vapor exerted by a droplet salt solution, Pa

To make a substitution for $p_{s,d}$ with $A_{w,d}$

$$\frac{d\phi}{dt} = \frac{4D_v^* M_w}{R\rho_d \phi}\left[\frac{p_{v,a}}{T_a} - \frac{p_{s,d}}{T_d}\right]$$

Water Activity

In model:

Relate $A_{w,d}$ to $\% \frac{w}{w}$, mass percent of solids to water

At Saturation:

The maximum solubility of NaCl is 36.6 g/100 g H_2O at 37 °C.

$$\% \frac{w}{w} = \frac{36.6g}{36.6g + 100g} 100 = 26.8\%$$

The maximum solubility = minimum vapor pressure exerted.

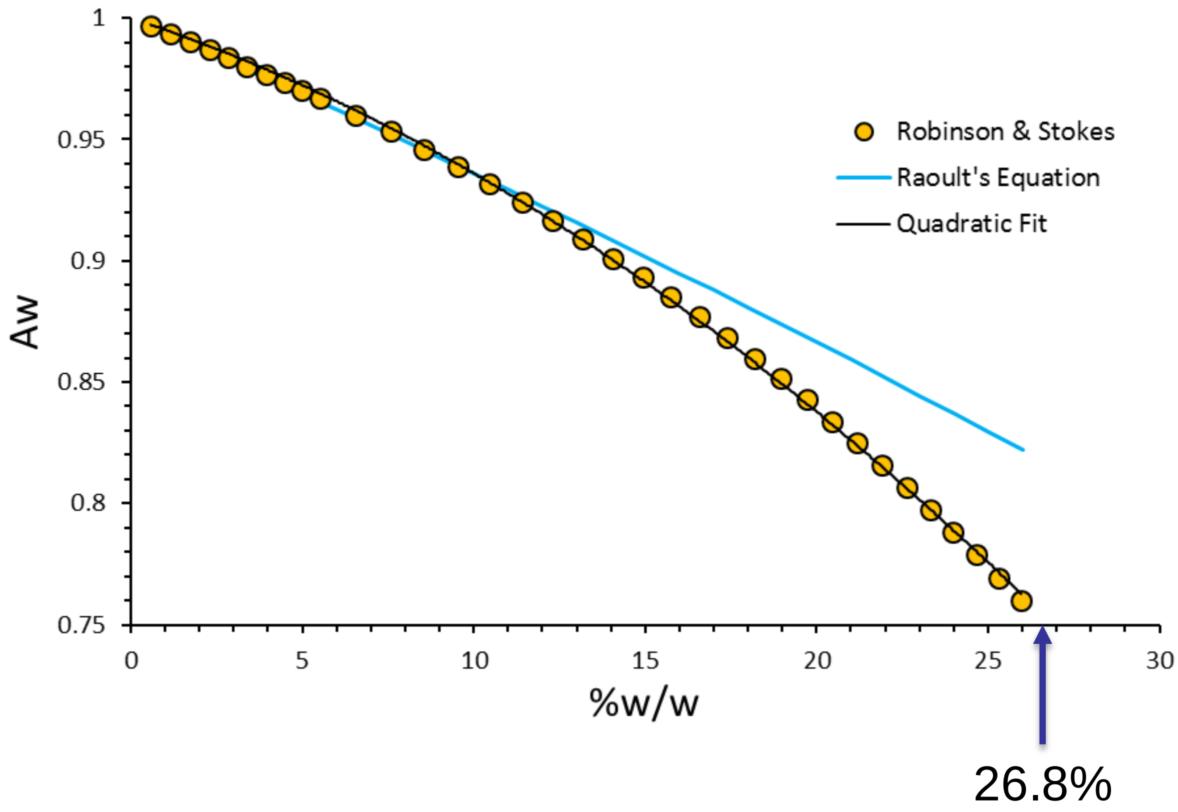
⇨ The $\% \frac{w}{w}$ at the DRH

And given ρ_w and ρ_{NaCl}

$$\phi = 1.905\phi_p$$

The droplet diameter at saturation relative to the diameter of the original solid salt particle

Water Activity



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Hygroscopic Growth Model

Additional equation to model droplet temperature change with time

$$\frac{dT}{dt} = \frac{3}{\phi^2 c_{p,w}}\left[\frac{4k_v^*}{\rho_d}(T_a - T_d) + h_{fg}\phi\frac{d\phi}{dt}\right]$$

$C_{p,w}$ = specific heat of water, 4179 J/kg-K at 37°C

k_v^* = Modified thermal conductivity (via Eq. 4b), W/m-K

Principal Reference:

Broday, D. M.; Georgopoulos, P. G., Growth and Deposition of Hygroscopic Particulate Matter in the Human Lungs. *Aerosol Science and Technology* 2001, 34 (1), 144-159

Initial Conditions and Salt Growth Phases

Initial Conditions: Ambient and Particle Size

Givens are based on deep lung conditions:

Ambient temperature, T_a = 37 °C = 310.15K

Relative humidity, RH = 99.5%

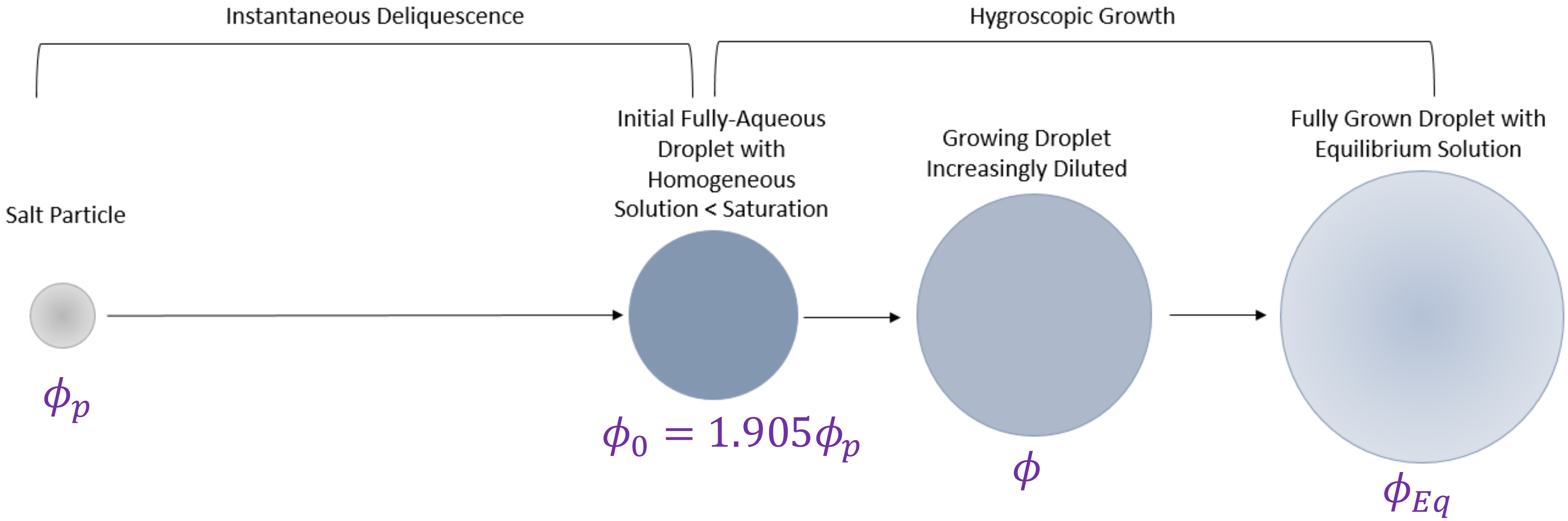
Salt particle diameter, ϕ_p (chosen)

Initial Conditions: Droplet Diameter, ϕ_0

Concept 1:

Assume deliquescence is “spontaneous”.

Initial diameter is then based on the volume of the minimum amount of water needed to dissolve a NaCl salt particle with diameter, ϕ : $\phi_0 = 1.905\phi_p$

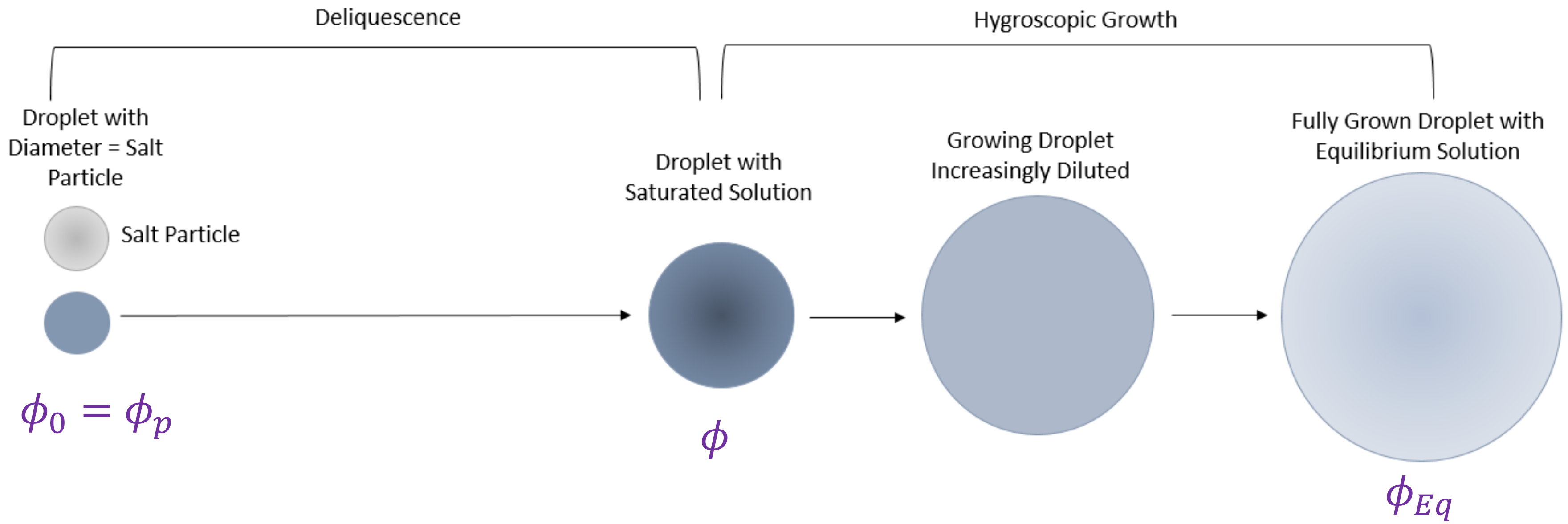


Initial Conditions: Droplet Diameter, ϕ_0

Concept 2:

Assume $\phi_0 = \phi_p$

Requires an initial $\% \frac{w}{w}$ >> maximum salt saturation



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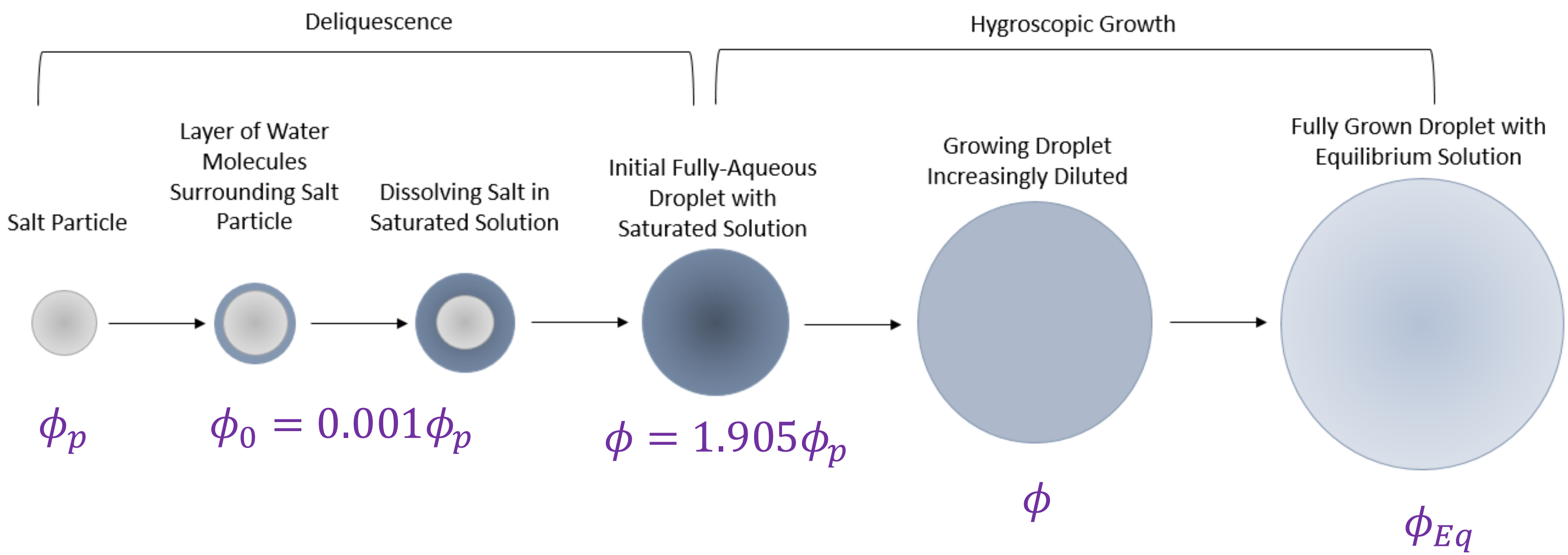
Hygroscopic Growth Process for RH > DRH

Concept 3:

Assume deliquescence is not "spontaneous".
Starts with thin film of water surrounding salt core: $\phi_0 = 1.001\phi_p$
Remains at saturation until $\phi = 1.905\phi_p$



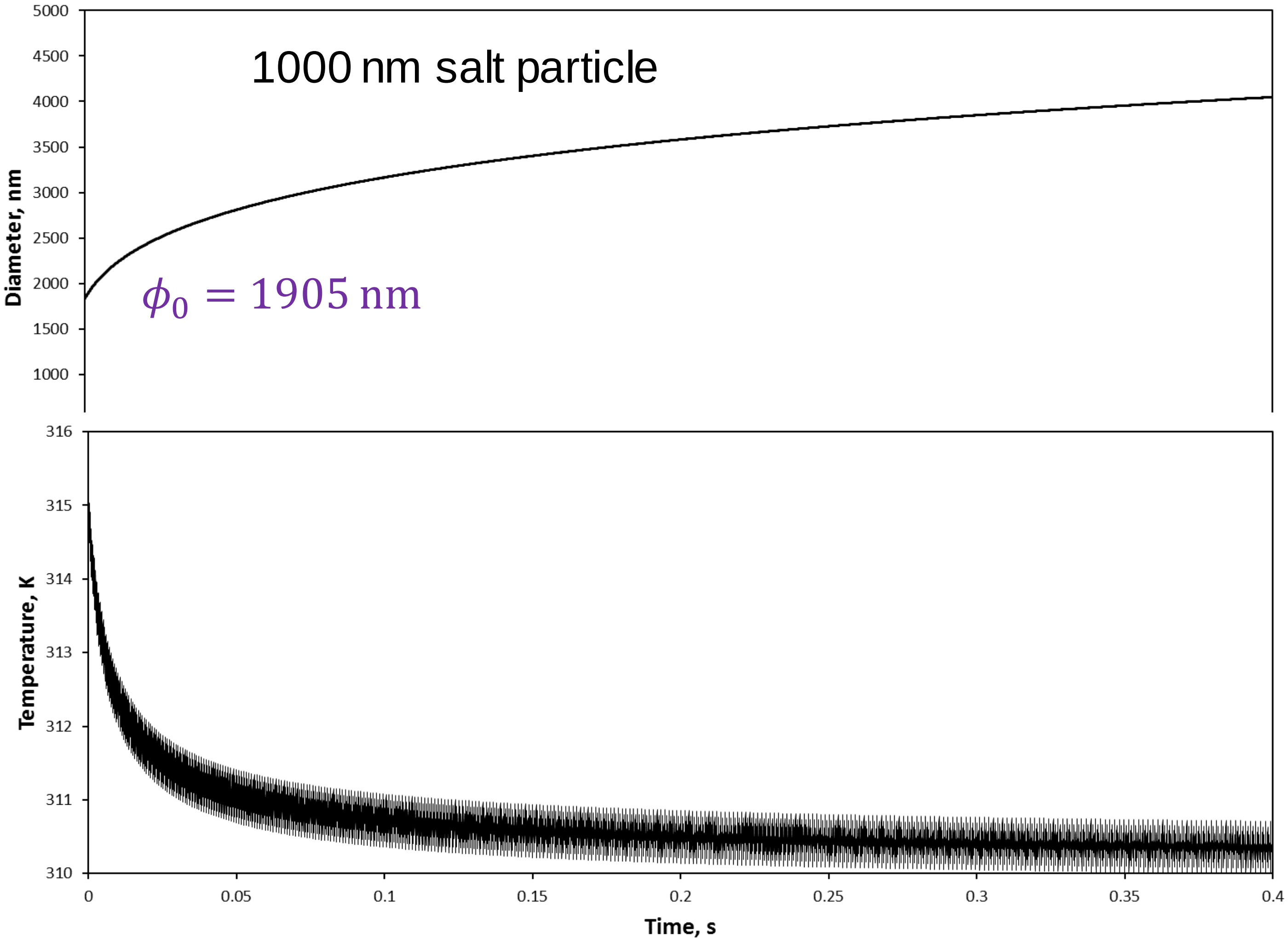
Model Results

Model Solutions

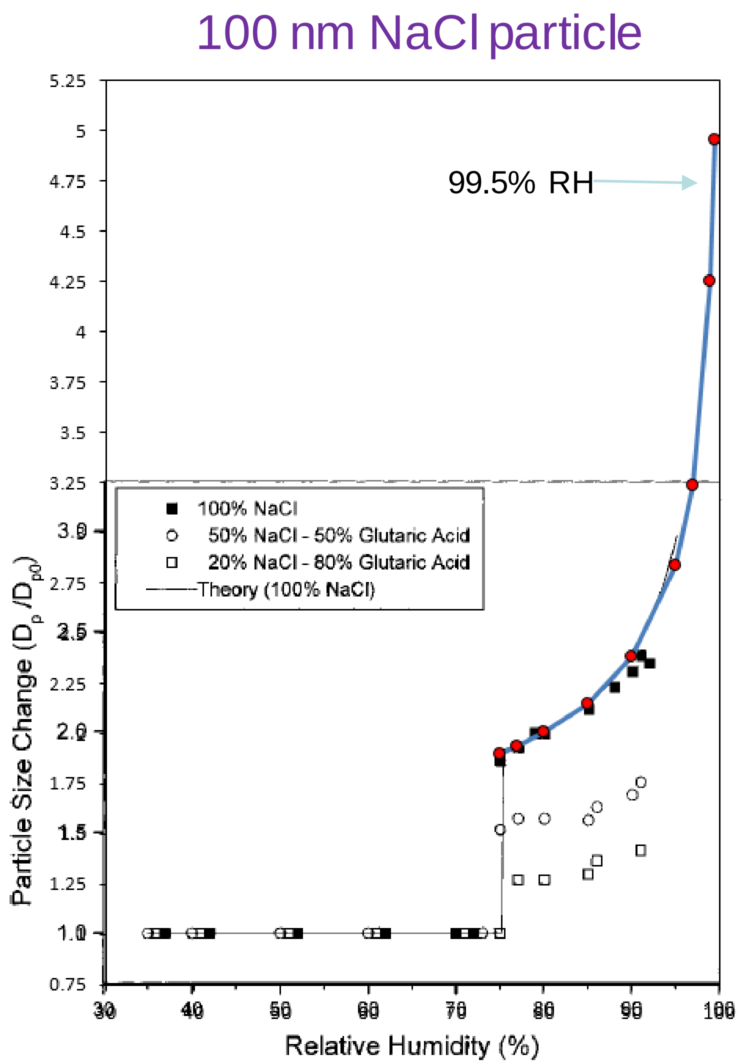
- MATLAB used to solve the coupled differential equations for temperature and droplet diameter

- Utilized the function ODE45.
  - This function calls a sub-routine that contains expressions for the two DE’s

Typical Results



Model vs Cruz & Pandis (2000)



Good agreement between model **equilibrium size** and deliquescence experimental results

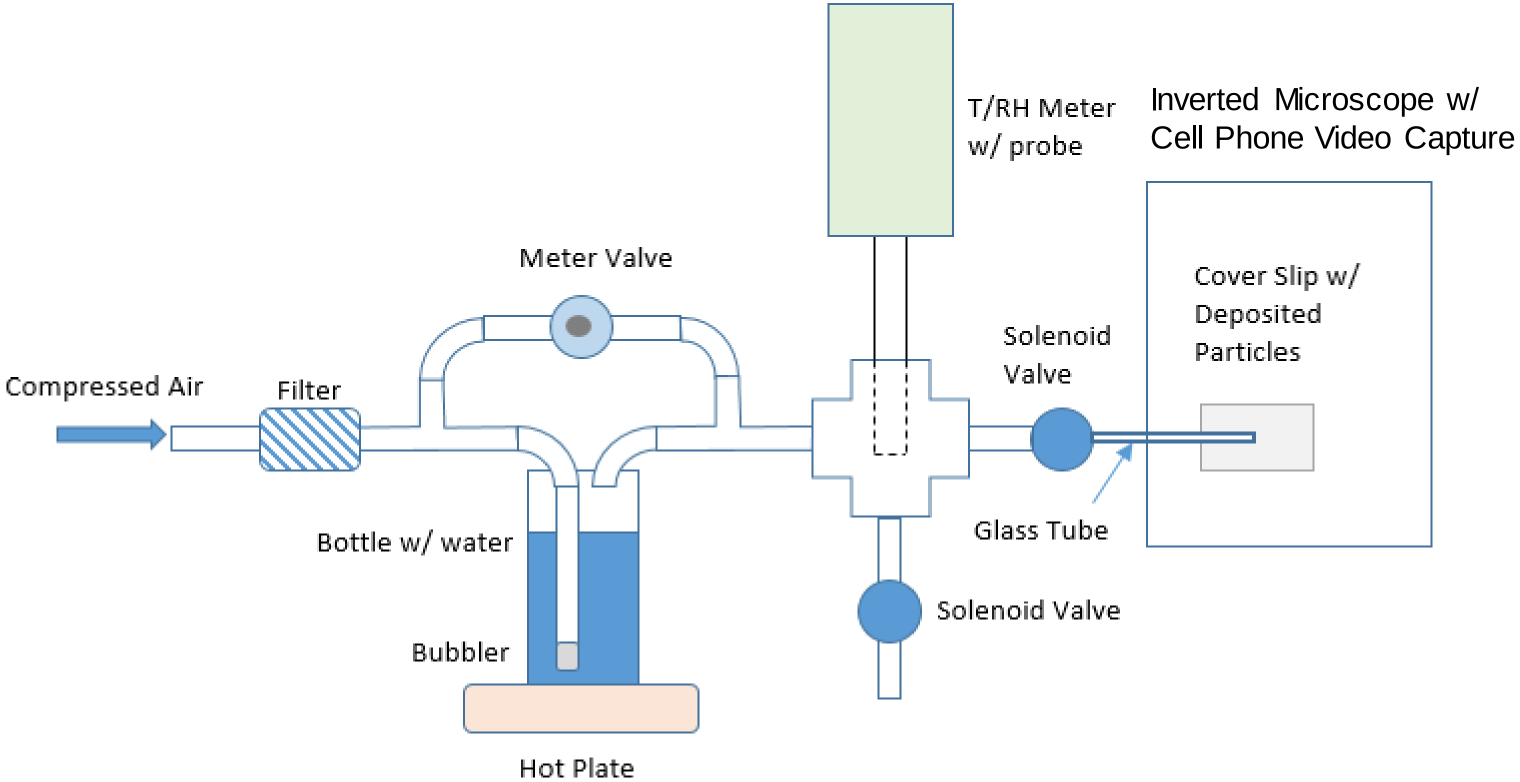
Cruz CN, Pandis SN (2000) Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol. Environ Sci Technol 34:4313-19.

Model Validation

Model Validation

- Develop a system to measure the diameter of droplets at known time periods during their growth
- Production of consistent RH and Temperature
- Nearly instantaneous measurement

Apparatus



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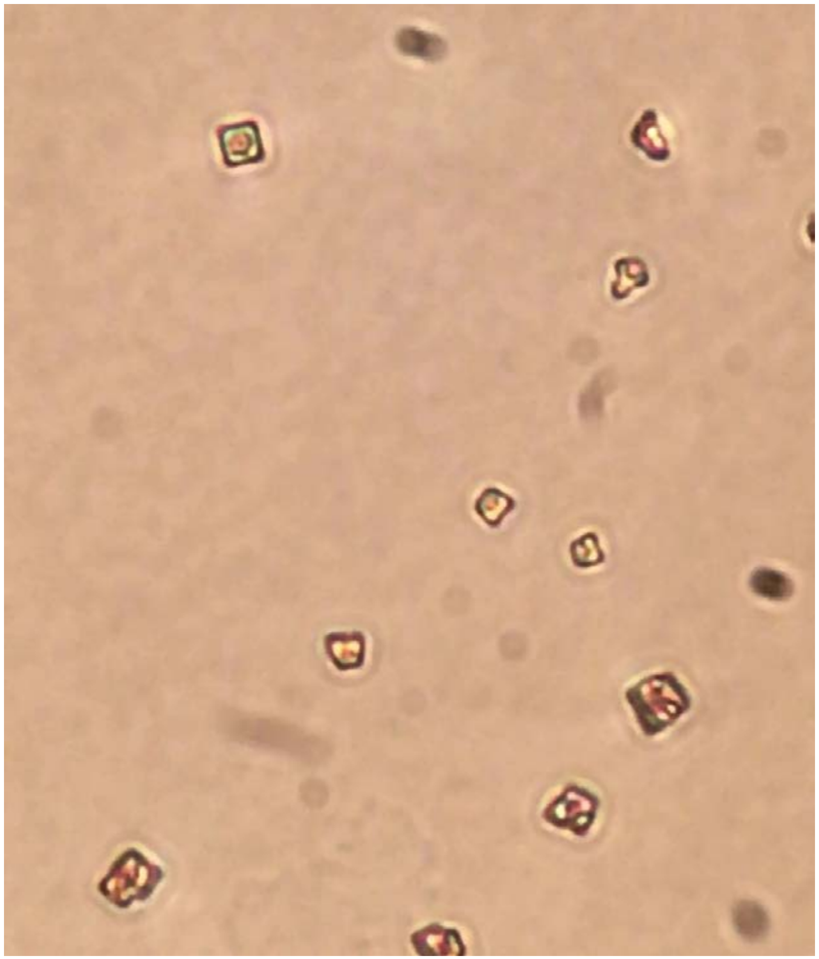
Initial – Final Photos

Image Capture Rate: 30/s = 0.03s



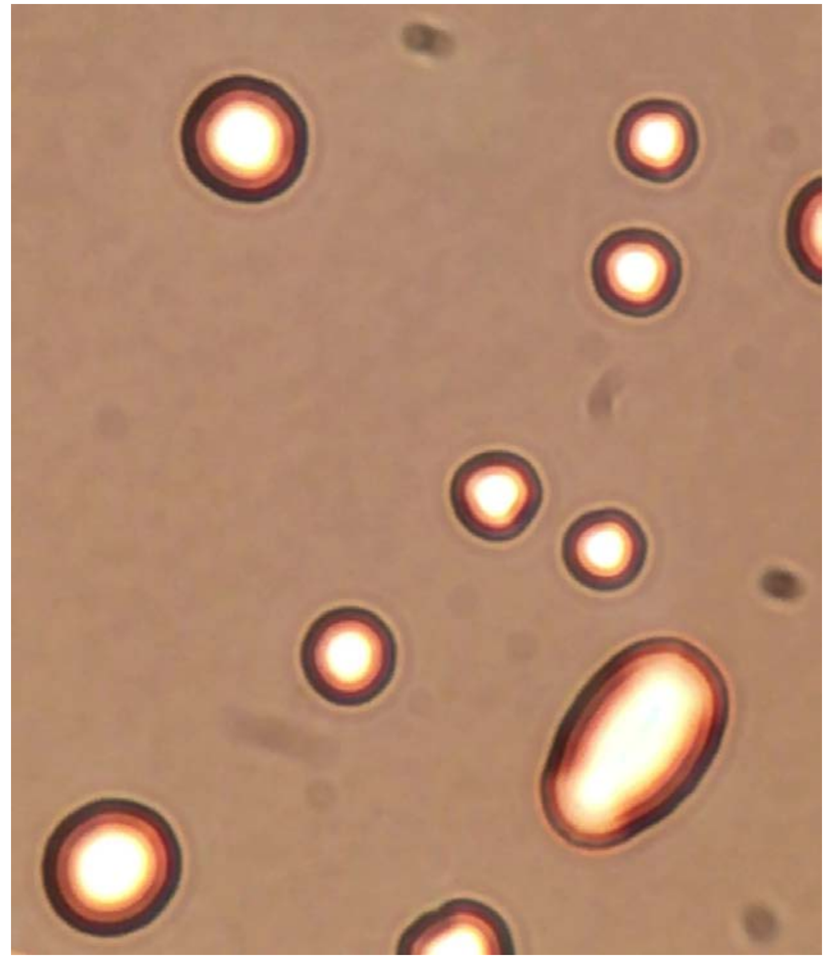
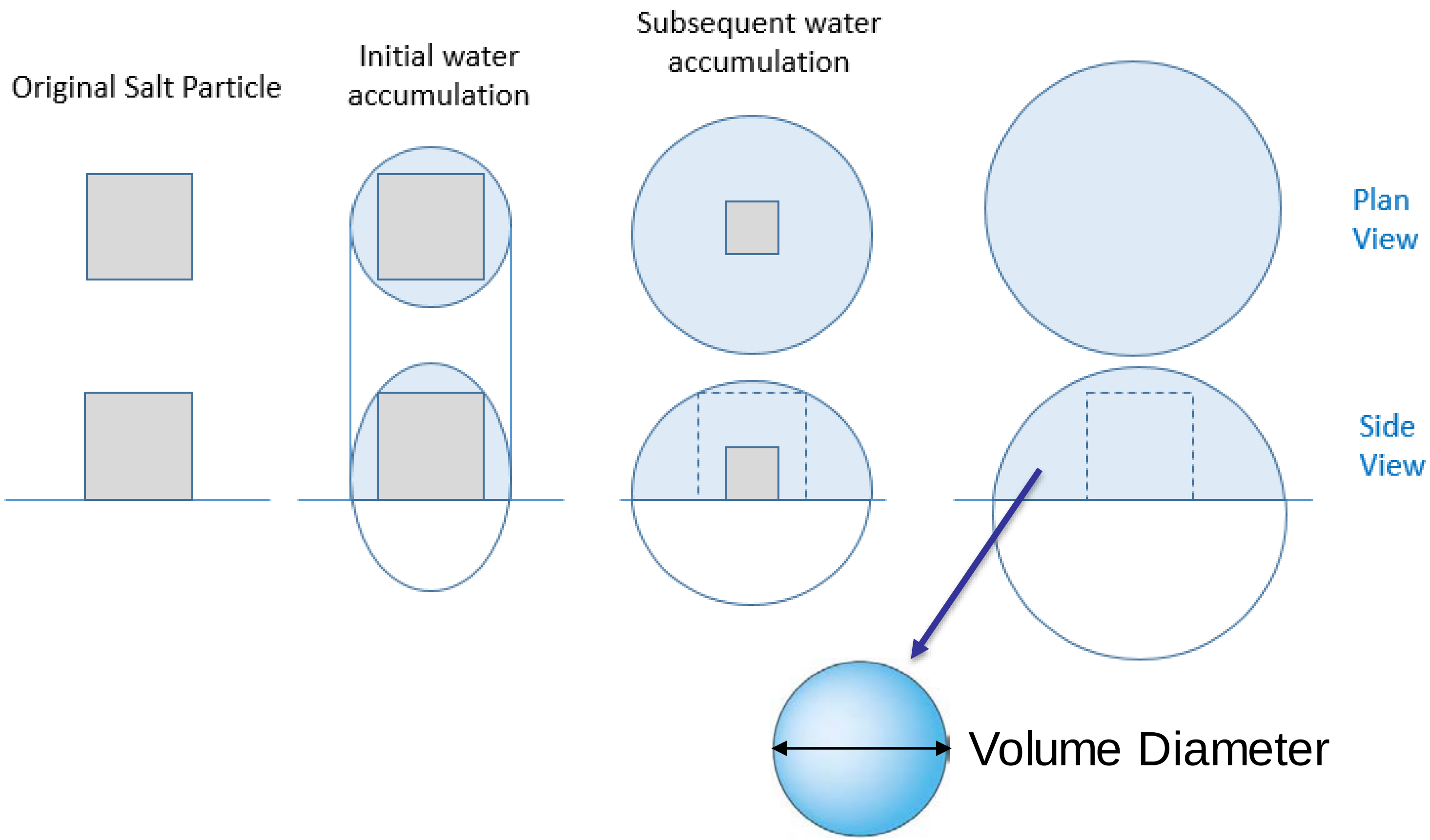
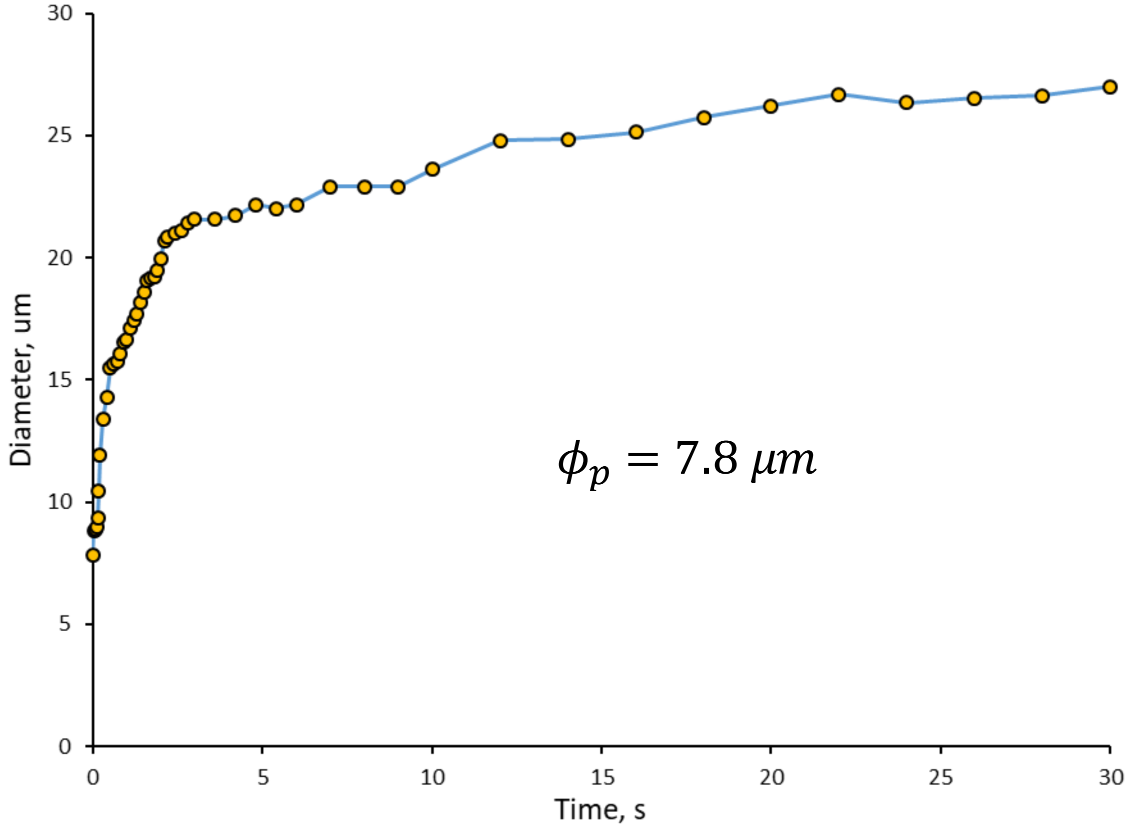


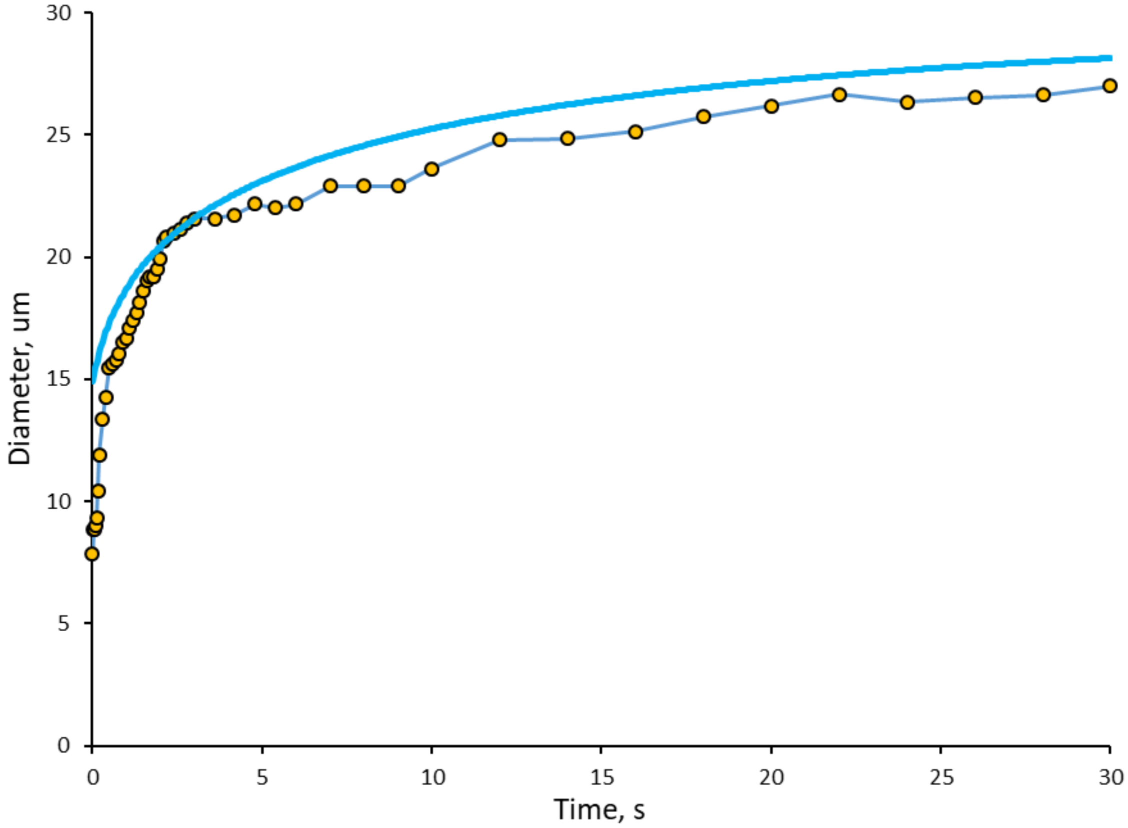
Photo Diameter to Water Volume Diameter



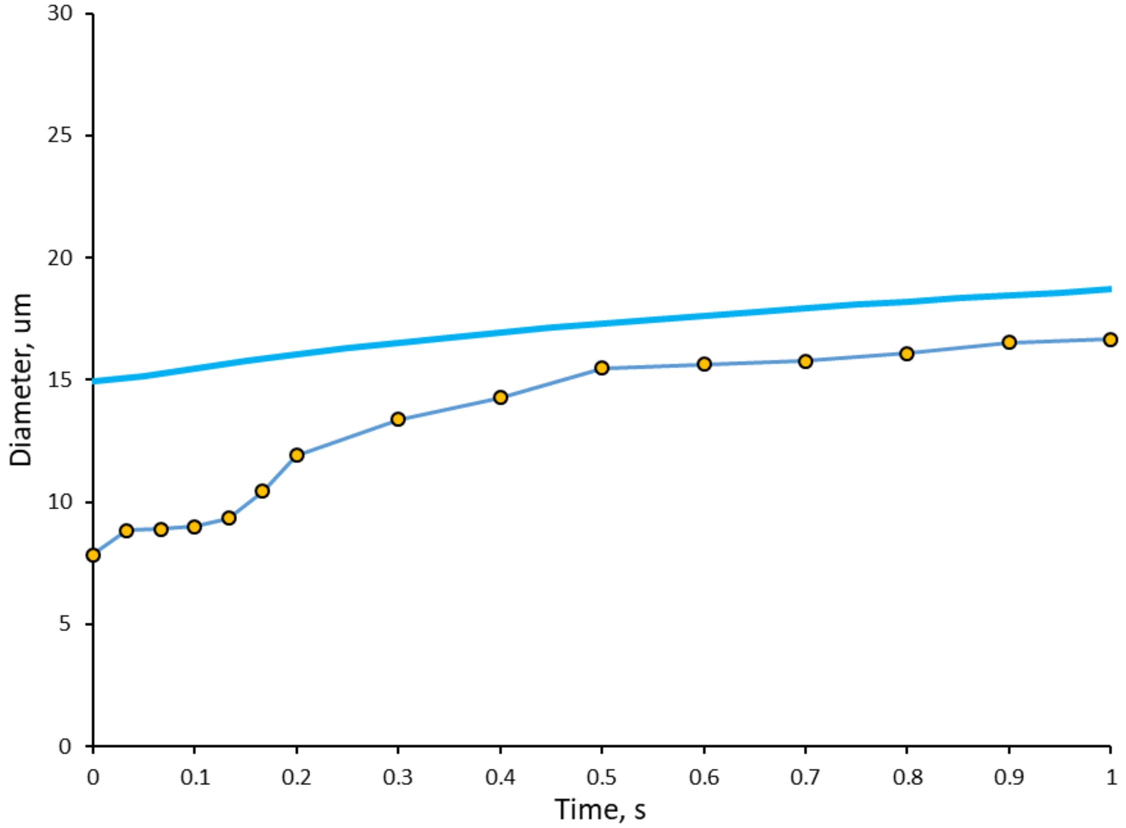
Volume Diameter



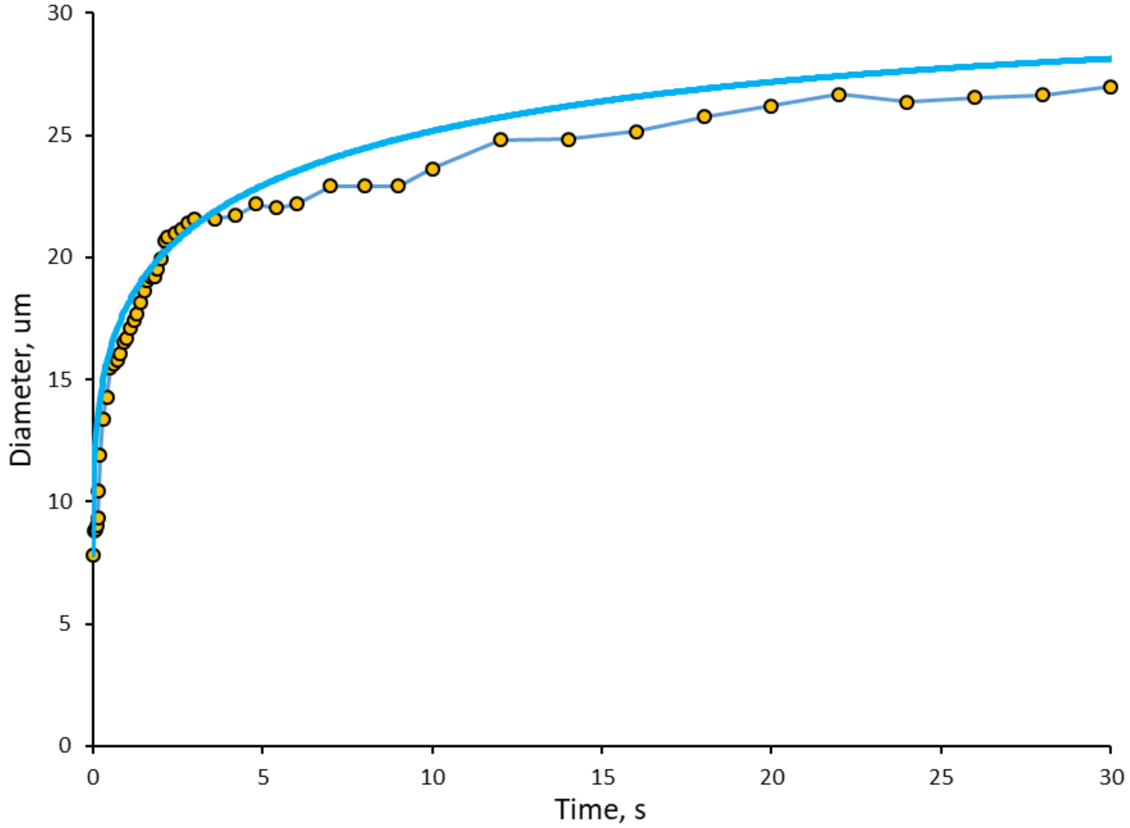
Concept 1 Model: $\phi_0 = 1.905\phi_p$



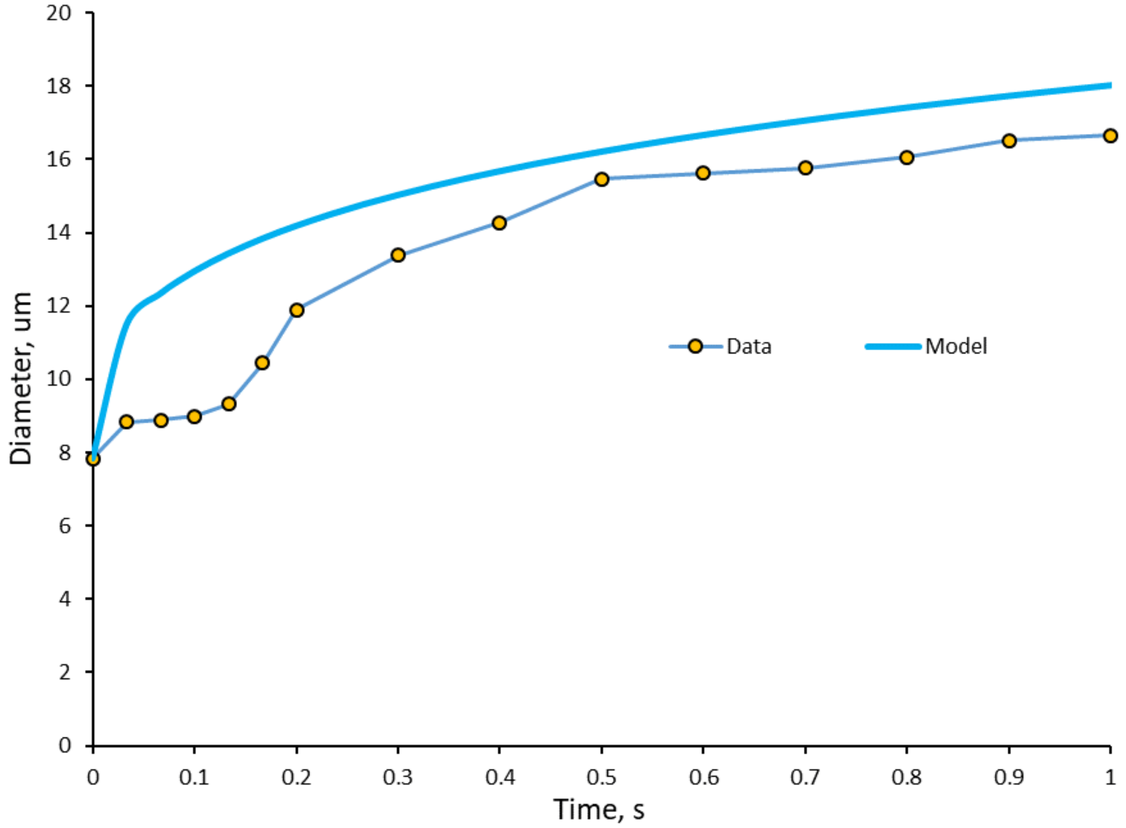
Concept 1 Model: $\phi_0 = 1.905\phi_p$



Concept 2 Model: $\phi_0 = \phi_p$



Concept 2 Model: $\phi_0 = \phi_p$



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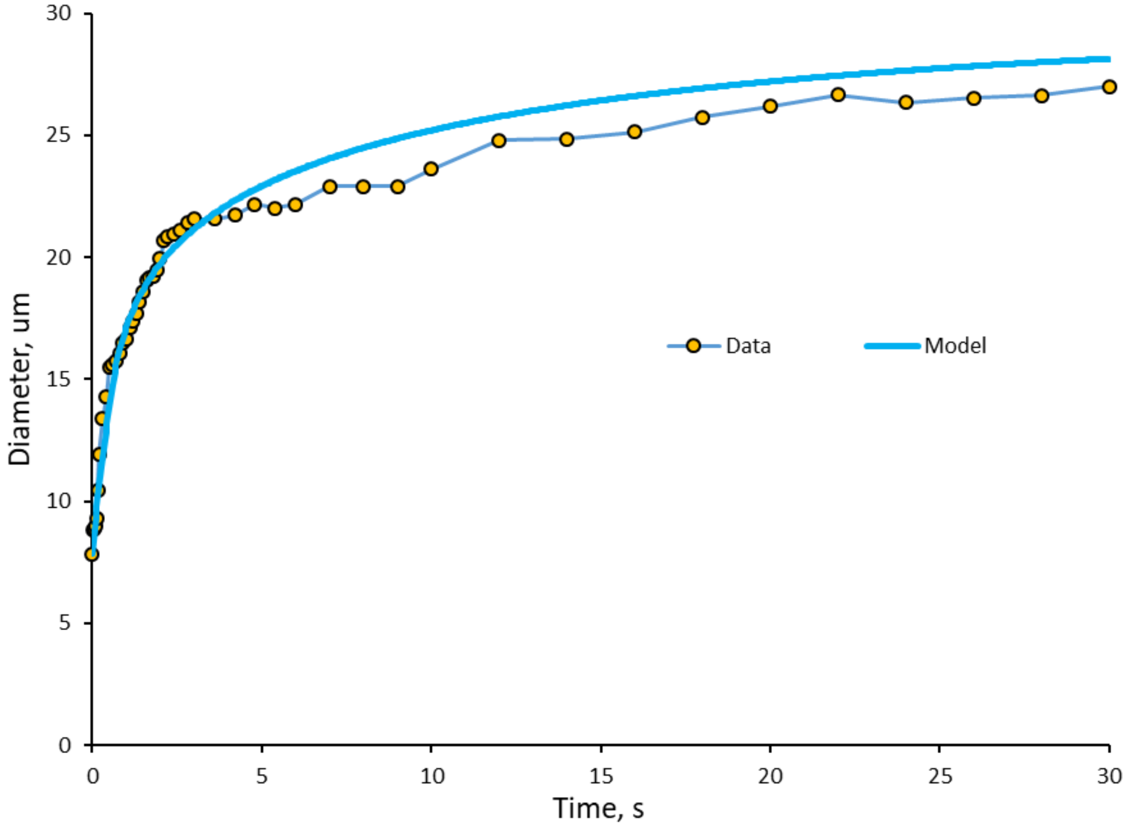
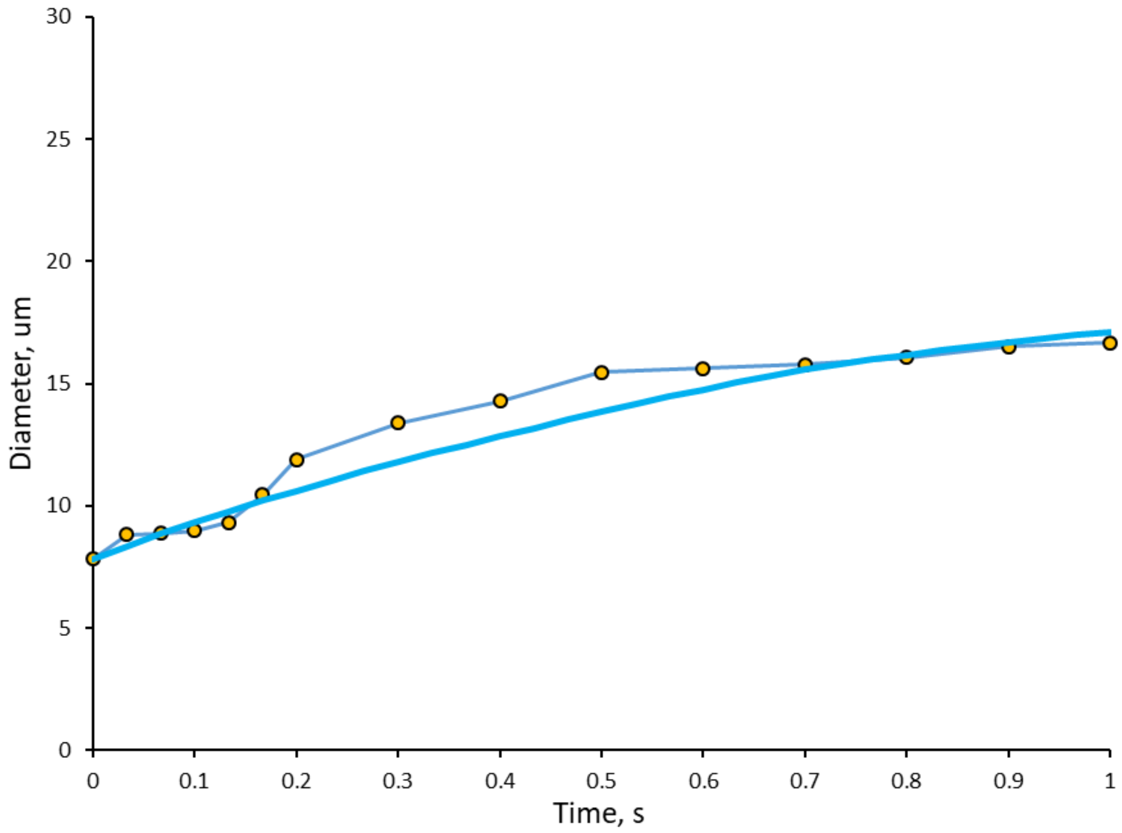
Concept 3 Model: $\phi_0 = 1.001\phi_p$



Concept 3 Model: $\phi_0 = 1.001\phi_p$



Conclusions

- Hygroscopic growth model accurately predicts the equilibrium droplet size.
- Novel particle growth validation method provides accurate indication of growth on microsecond scale needed.
- A growth model that incorporates the concept of a thin, saturated film initially may be the most accurate when predicting growth during the transient growth phase.

Acknowledgements

Funding

- FDA U01 FD005837-01
  - A Cluster-Based Assessment of Drug Delivery in Asthmatic Small Airways
- NIEHS P30 ES005605-24
  - Environmental Health Science Research Center

QUESTIONS?

Relative Humidity

Measure of water vapor content in the atmosphere

$$RH = \frac{p_{v,a}}{p_{s,w}(T_a)}$$ (= Saturation Ratio, S)

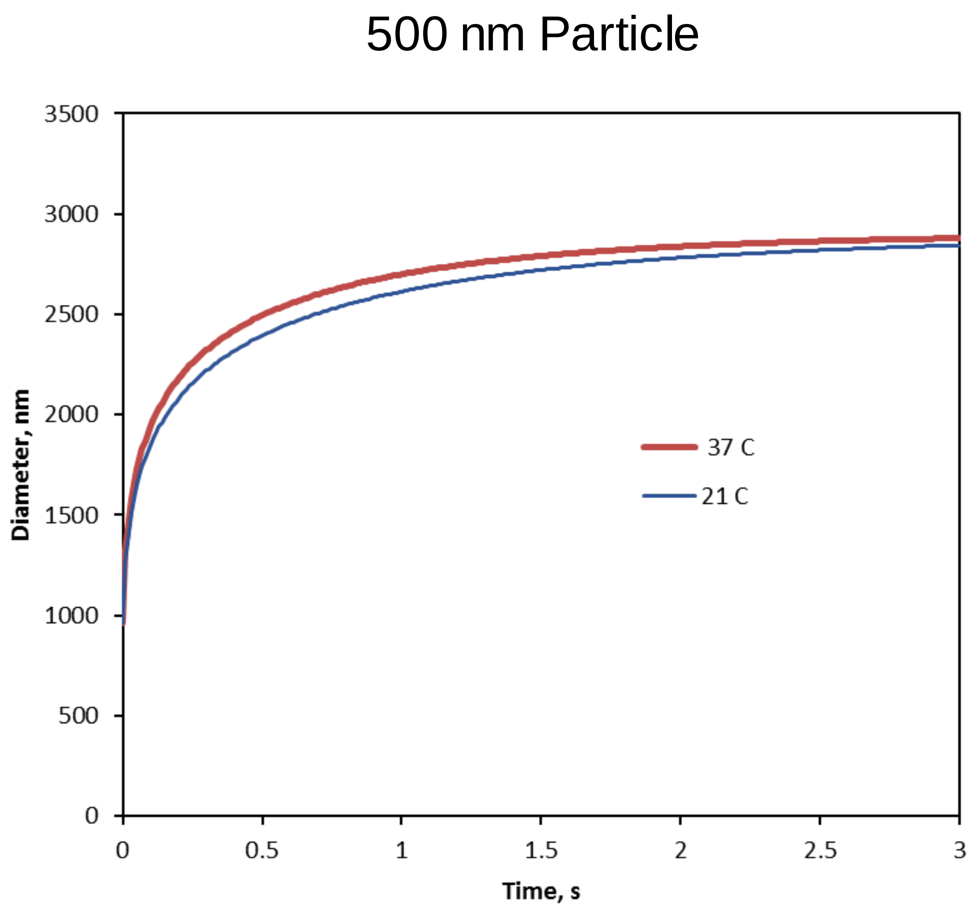
p_a^v = partial pressure of water vapor in air at T_a, Pa

$p_{s,w}(T_a)$ = saturation pressure of water vapor at T_a exerted by pure water, Pa

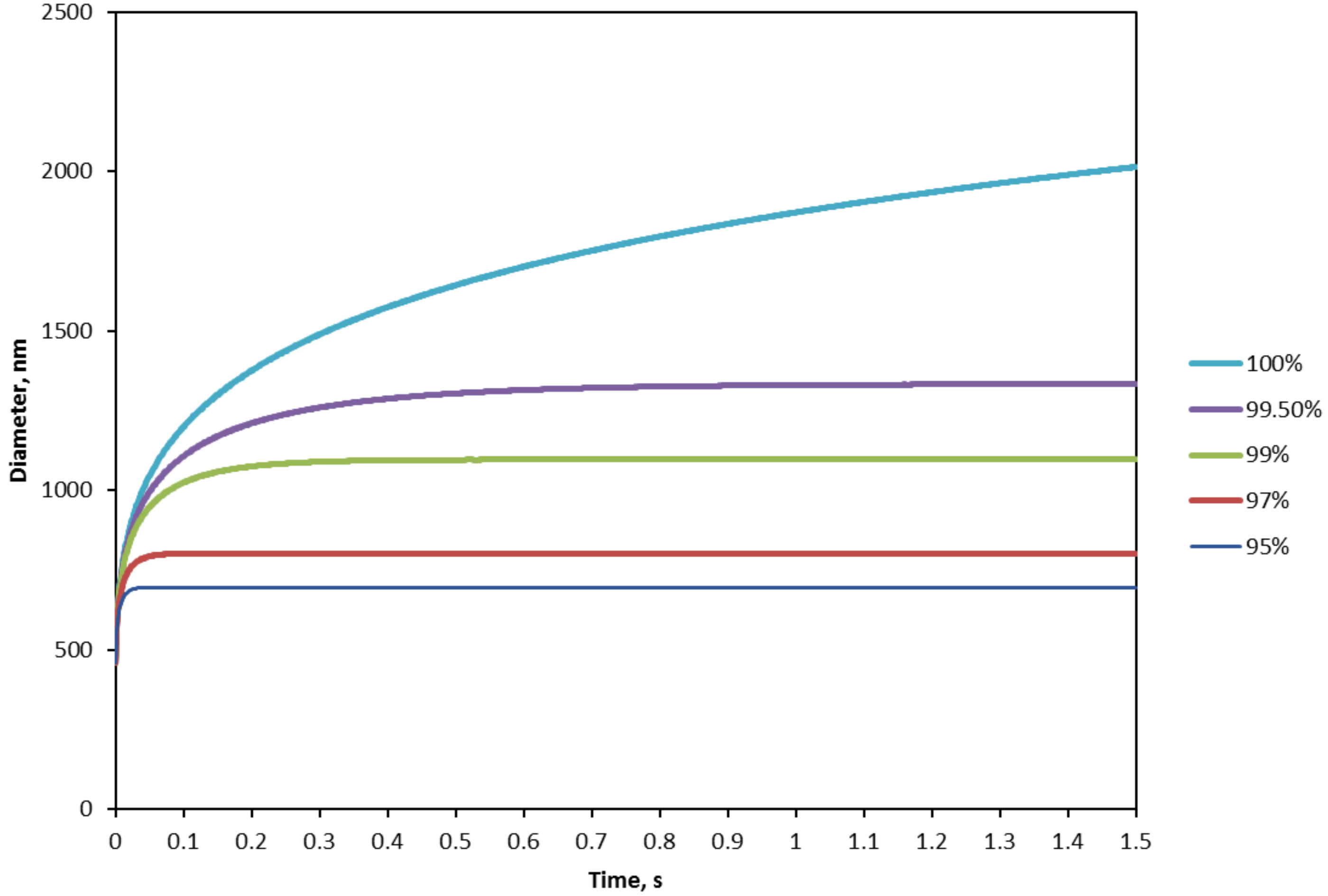
To make substitution for $p_{v,a}$ with RH

$$\frac{d\phi}{dt} = \frac{4D_v^* M_w}{R\rho_d \phi}\left[\frac{p_{v,a}}{T_a} - \frac{p_{s,d}}{T_d}\right]$$

Temperature Comparison



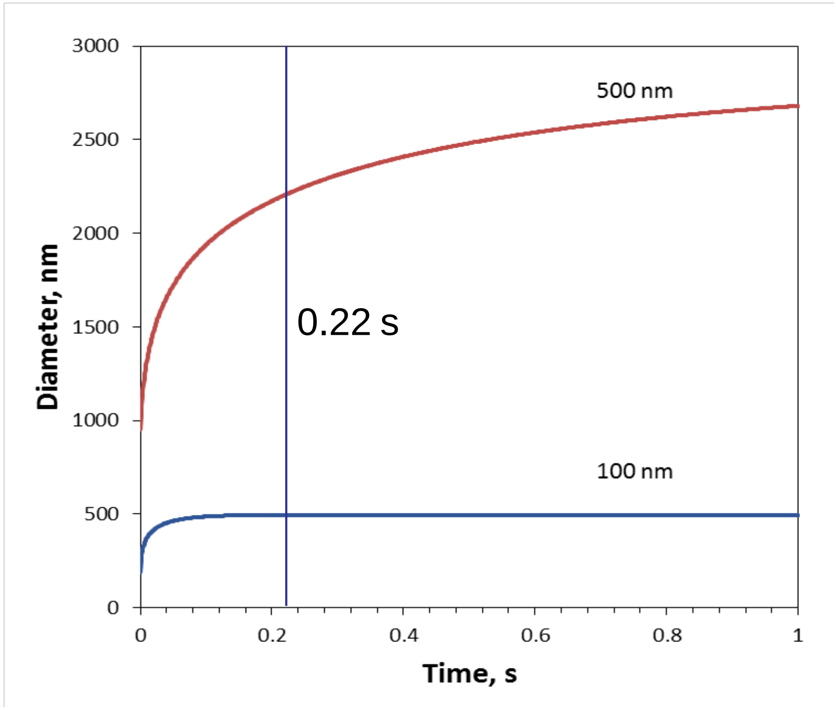
Relative Humidity Comparison



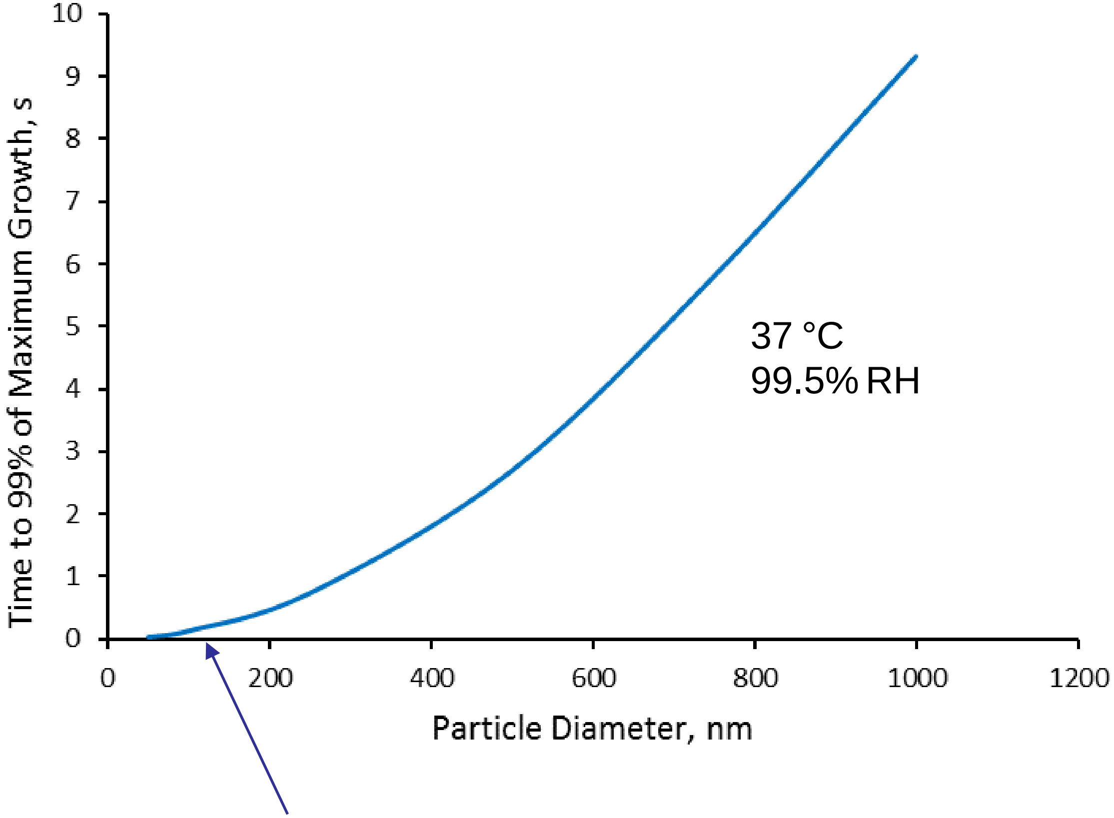
RH Growth Comparison.xlsx

Model Results

100 nm and 500 nm NaCl particles at 99.5% RH

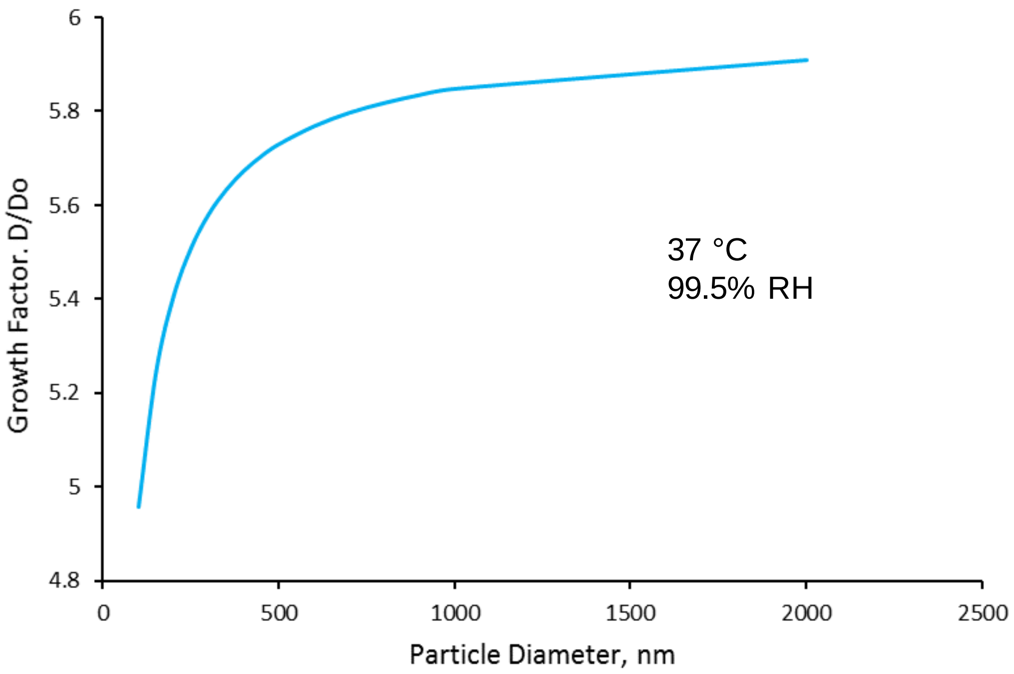


Time to 99% of Equilibrium



<0.2 s to reach max growth
below **125 nm** (at 99.5% RH)

Growth Factor vs Diameter



Growth Factor Solver.xlsx

Dissolution Kinetics Literature

346 *J. Phys. Chem. A* **2003,** *107,* 346−350

Effect of Electrolyte Diffusion on the Growth of NaCl Particles by Water Vapour Condensation

Kari E. J. Lehtinen,*,† Markku Kulmala,† Peter Ctyroky,‡ Tanja Futschek,‡ and Regina Hitzenberger‡

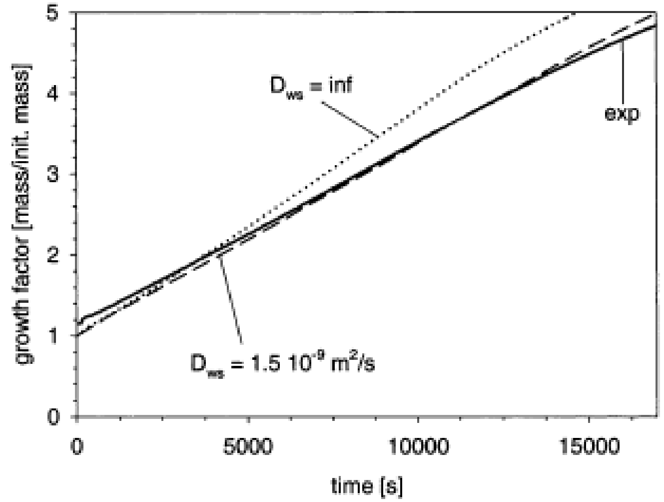


Figure 6. Growth of (a) a 1 mg NaCl particle in 87% relative humidity, (b) a 6 mg NaCl particle in 96% relative humidity, and (c) a 3 mg NaCl particle in 97% relative humidity. The solid line is the experimental result. The dotted line ($D_{ws} = \infty$) is the result of a simulation assuming instantaneous diffusional mixing in the solution. The dashed line is the result when diffusion in the solution is also considered.

evident in the results presented in Figure 5. However, the experimental growth curves show an almost linear growth pattern while salt is still dissolving. This linear initial mass growth of the particles is a clear indication that the diffusion in the solution layer is slowing down particle growth. Furthermore, the model assuming no diffusional resistance seems to over-predict the growth rate significantly.

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Dissolution Kinetics Literature

Effect of solute dissolution kinetics on cloud droplet formation: Extended Köhler theory

A. Asa-Awuku[1] and A. Nenes[1,2]

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, D22201, doi:10.1029/2005JD006934, 2007

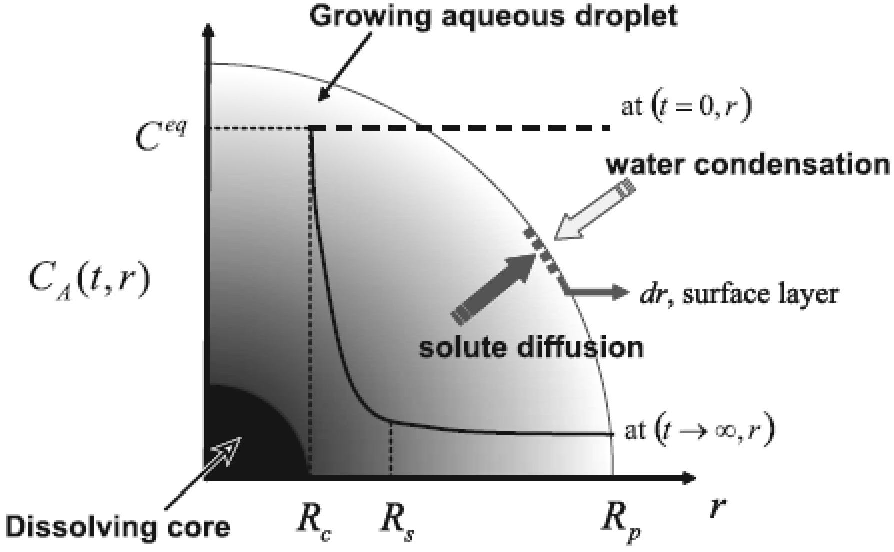

Figure 1. Illustration of the problem geometry and the solute concentration profile. R_s represents the location where the concentration gradient becomes effectively zero.

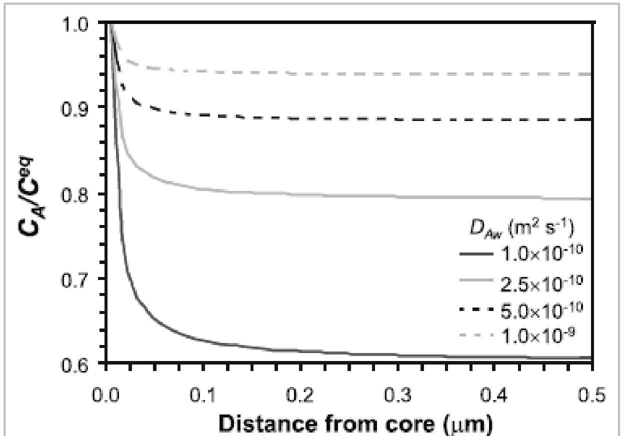

Figure 3. Steady state radial profiles of C_A. Simulations are shown for D_p = 1 μm, D_c = 0.01 μm, s = 1%, and for D_{Aw} between 1×10^{-9} and 1×10^{-10} m^2 s^{-1}.

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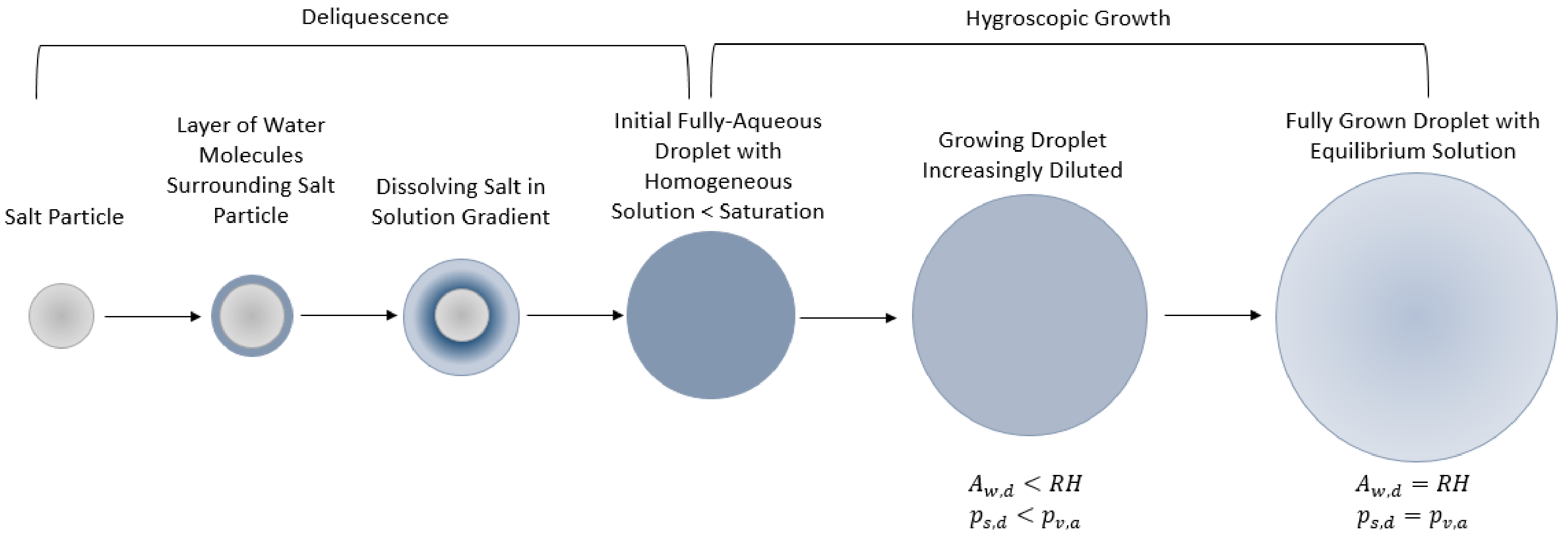
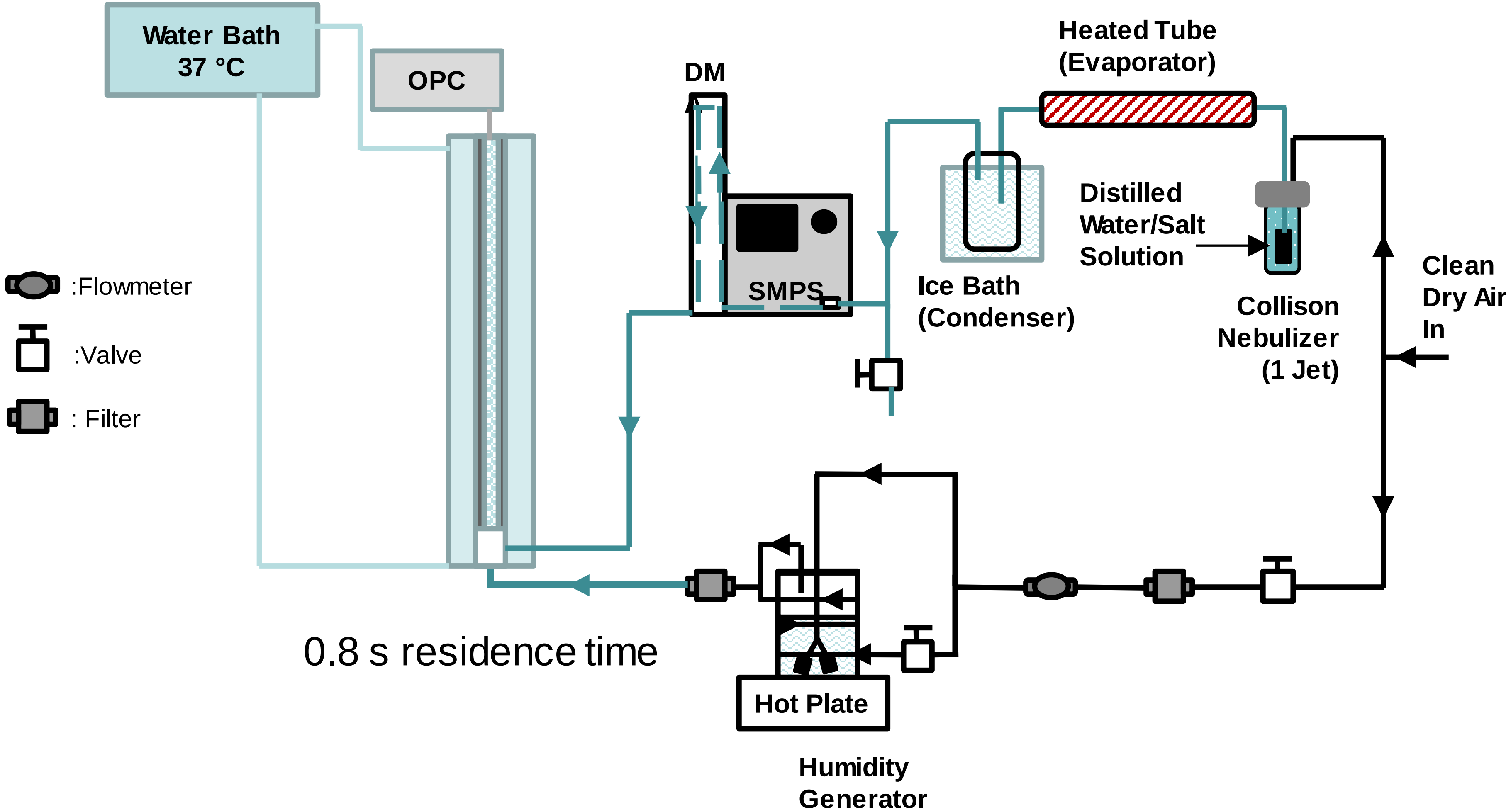
Hygroscopic Growth Process w/ Core Dissolution

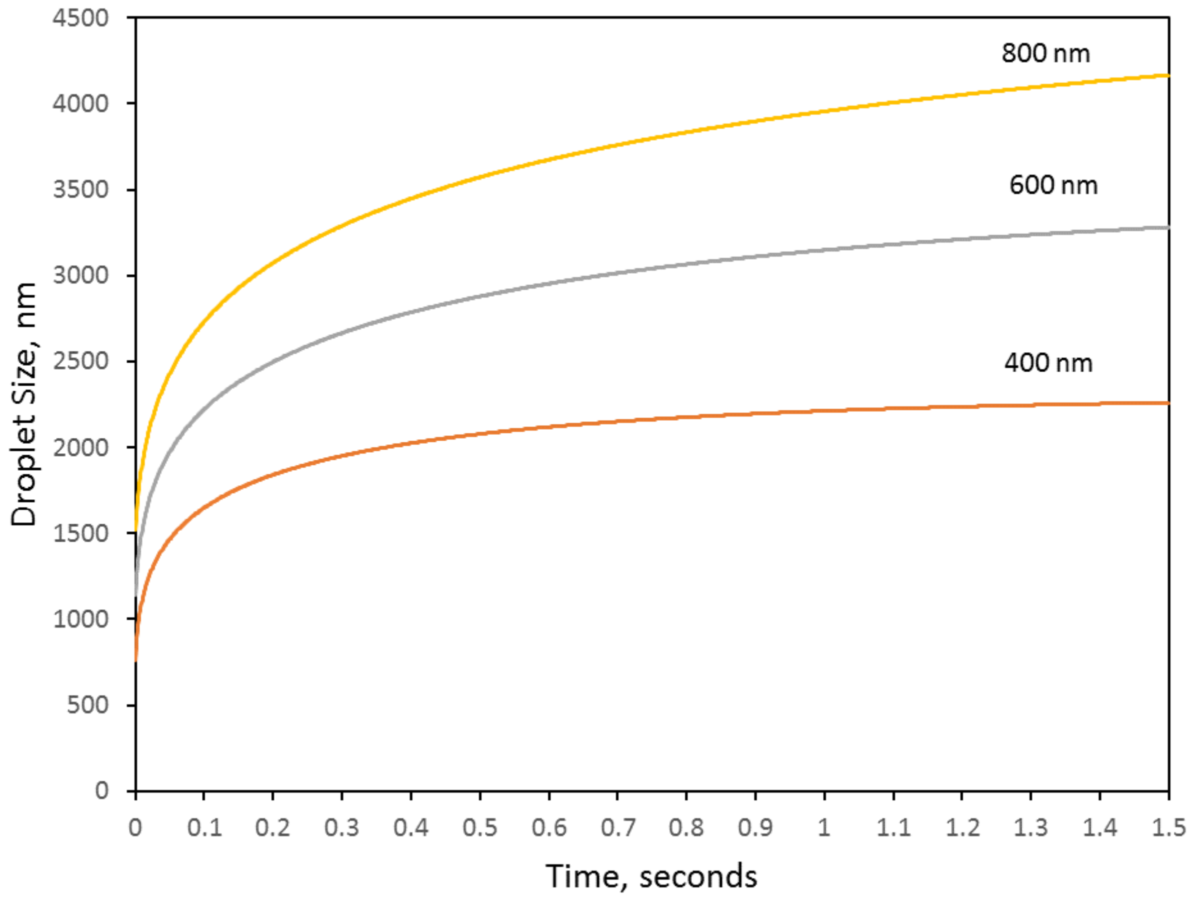


Apparatus 2 - Wetted Wall Reactor



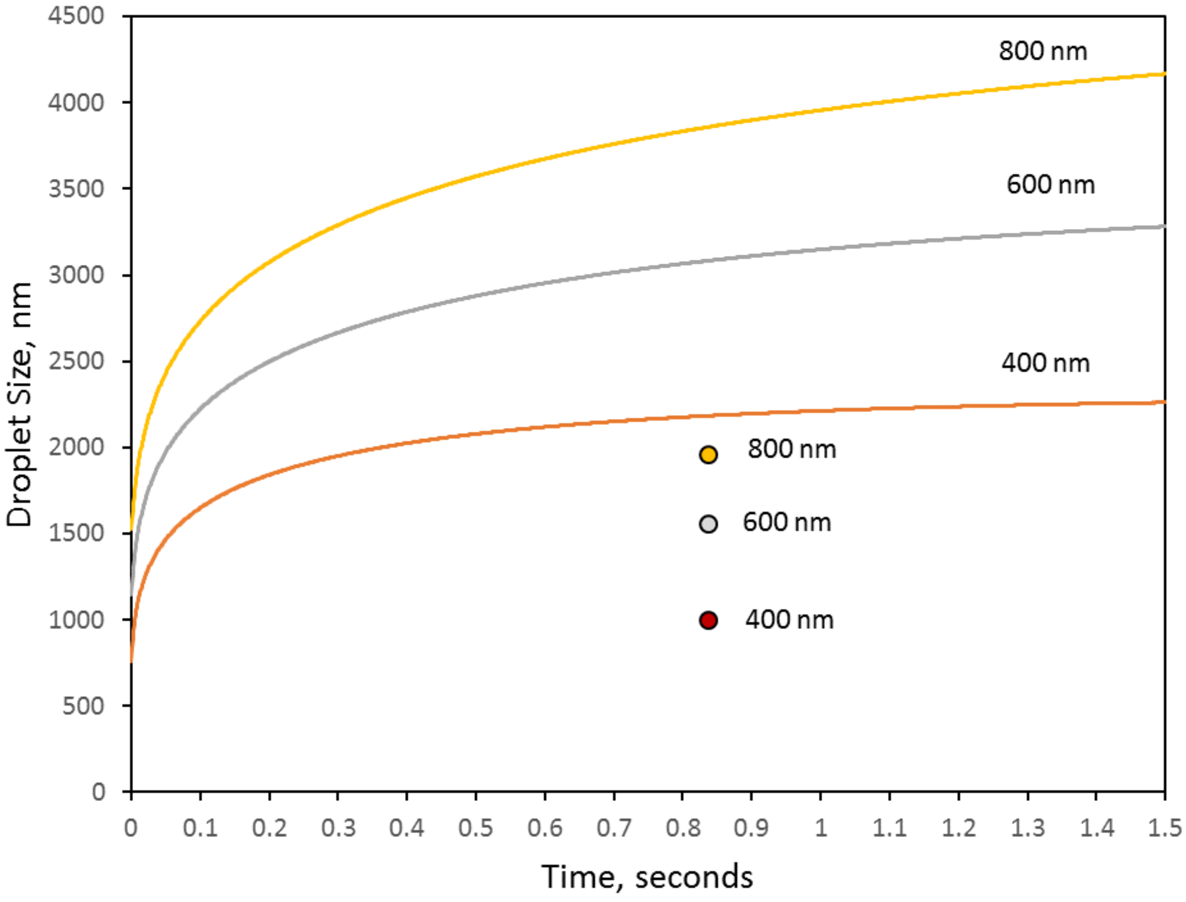
0.8 s residence time

Results



4500
4000
3500
3000
2500
2000
1500
1000
500
0
Droplet Size, nm
800 nm
600 nm
400 nm
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
Time, seconds

Results



4500
4000
3500
3000
2500
2000
1500
1000
500
0
Droplet Size, nm
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
Time, seconds
800 nm
600 nm
400 nm
800 nm
600 nm
400 nm

Literature Results

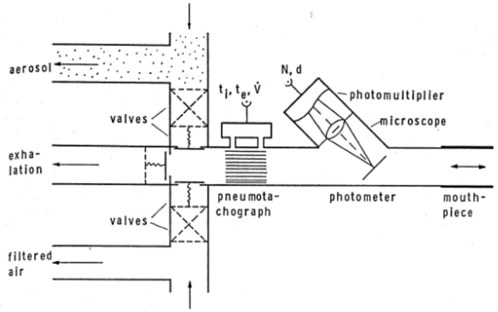
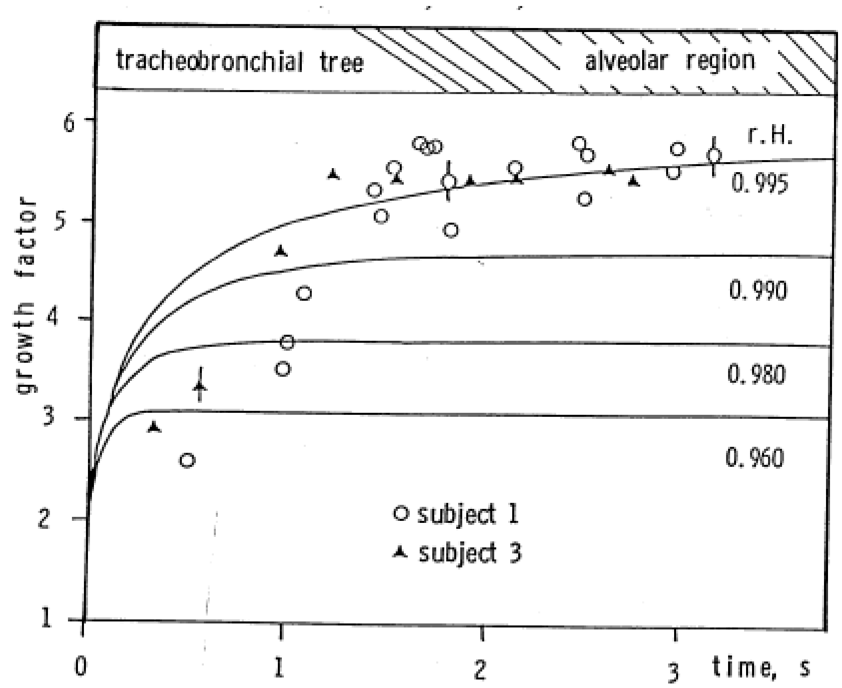


Fig. 1: Schematic diagram of the inhalation apparatus



Anselm et al. Human inhalation studies of growth of hygroscopic particles in the respiratory tract. Aerosols: Formation and Reactivity, 2nd Int. Aerosol Conf. Berlin (1986)

Literature Results

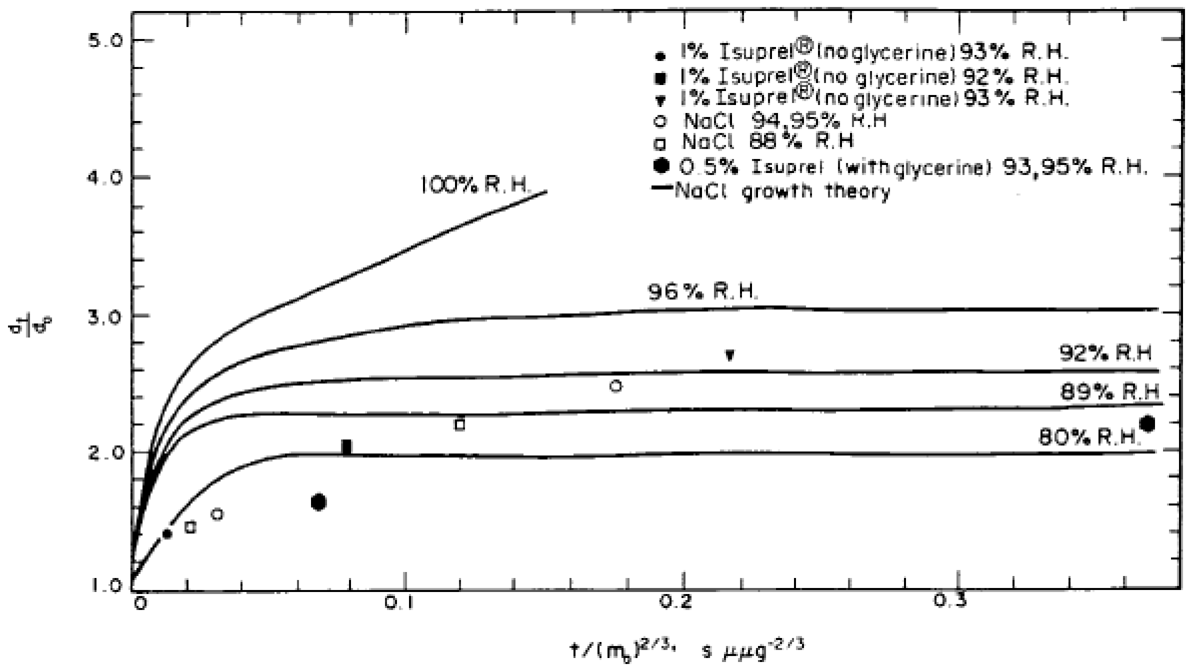


FIG. 2. Sodium chloride and Isuprel® hydrochloride growth rate data (34–38°C, Reynolds number = 2124–2328) compared with the theory of CRIDER *et al.* (1956) for sodium chloride at 25°C.

Martonen et al. Growth rate measurements and deposition modelling of hygroscopic aerosols in human tracheobronchial models. Ann. Occup. Hyg. 26(1):93-108 (1982)