Kinetics of Cloud Droplet Activation

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Activation of an aerosol particle into a cloud droplet occurs when the environmental supersaturation exceeds the critical supersaturation of the particle. This process is controlled by the rate of generation of potential supersaturation, the net rate of mass transport of water vapor to the ensemble of particles, the thermodynamic driving force for condensation, latent heat release, and uptake of soluble gases. During cloud formation the environmental supersaturation exhibits a transient maximum triggered by initial adiabatic cooling and quenched by condensation of water vapor onto the activated cloud droplets. Results are presented from a zero-dimensional reference model that serves as a testbed for parametrizations of these processes and their dependence on controlling variables--number concentration and size distribution of pre-existing aerosol, rate of generation of potential supersaturation, and concentration of trace soluble and reactive gases.

Background

Clouds form when air containing water vapor and aerosol particles is cooled below the dew point. Water vapor condenses on aerosol particles.

The equilibrium vapor pressure of water above a liquid water drop is controlled by Raoult's law (vapor pressure lowering by solute) and the Kelvin equation (free energy of surface tension) and is strongly a function of drop radius, the so-called Köhler (1923, 1936) expression for the water vapor pressure as a function of drop radius:

$$e = e_w \exp\left[\frac{2M_w\sigma}{R_g T\rho a} - \frac{\nu m_s / M_s}{(\frac{4}{3}\pi a^3\rho - m_s)/M_w}\right]$$

Where

e is the water vapor pressure in equilibrium with the drop

e_w is the saturation vapor pressure of water at the ambient temperature

M_w, M_s are the molecular weights of water and solute

σ is the solution - air surface tension

R_g is the gas constant; T is the temperature

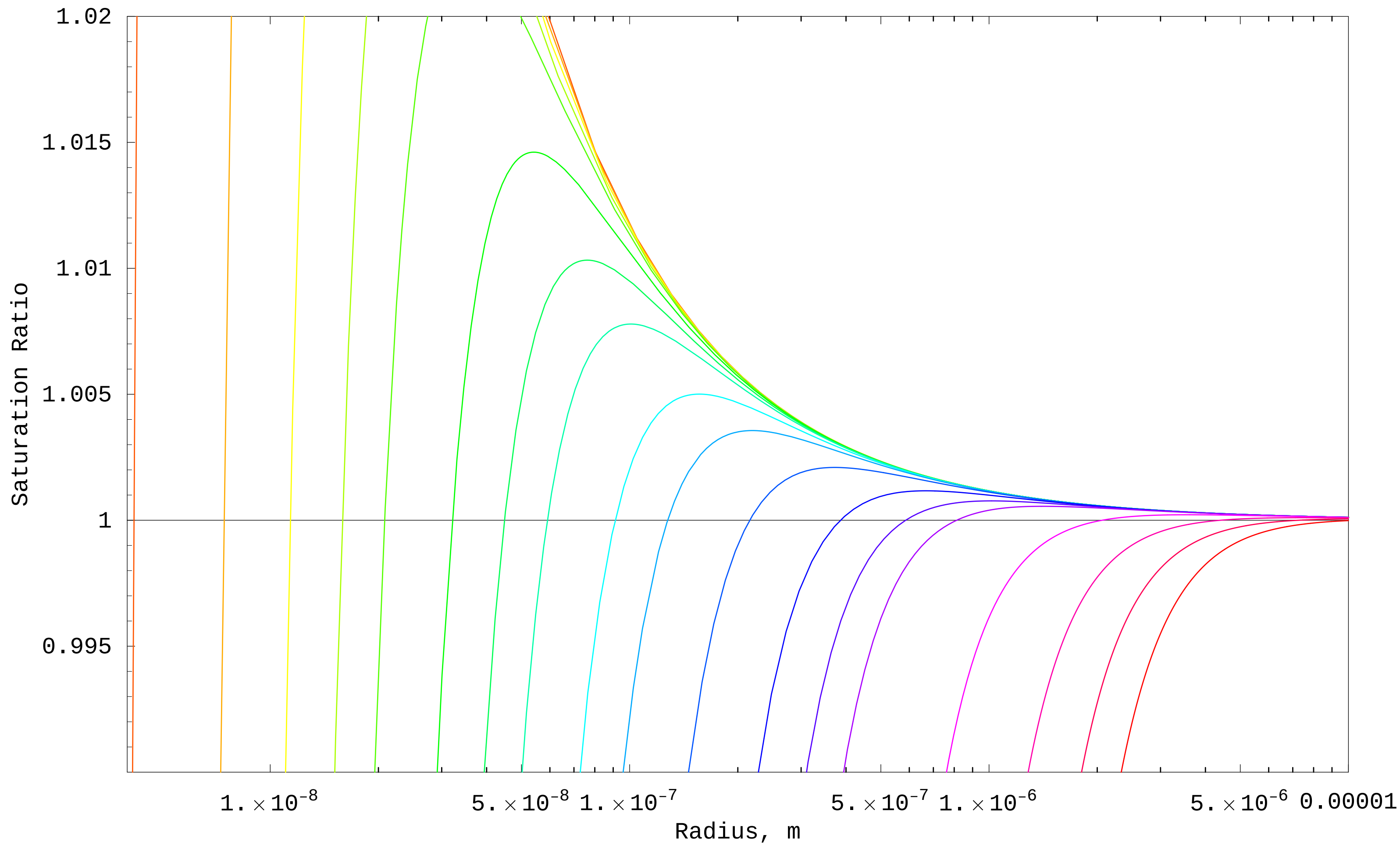
ρ is the solution density

a is the drop radius

ν is the van' t Hoff factor (equiv / mol) including nonideality corrections

m_s is the solute mass

Köhler curves (saturation ratio vs. radius for fixed solute mass per particle)



Critical supersaturation is maximum in curve, and critical radius is corresponding radius value.

Critical supersaturation decreases with increasing solute mass.

Cloud Droplet Activation

“Activation” of an aerosol particle to form a cloud droplet occurs when the environmental water vapor pressure exceeds maximum in Köhler equilibrium expression, with resultant condensation of water vapor, sufficiently long for the drop radius to exceed the corresponding critical radius.

- Once the drop is activated it grows under kinetic control.
- Activation is inherently ***kinetic***, being controlled mainly by vapor-phase diffusion and heat transfer.

During cloud formation the environmental supersaturation in a given air parcel typically exhibits a short transient maximum triggered by initial adiabatic cooling and quenched by condensation of water vapor onto the newly available surface area of the activated cloud droplets, which serves as a runaway sink for water vapor.

The time history of the saturation ratio depends intrinsically on the interaction of water vapor with aerosol and gaseous solutes.

Importance

Cloud droplet activation determines the droplet number concentration and size distribution of the resultant cloud and the distribution of soluble gases taken up in the cloudwater. ***Refer to Charlson Paper, this symposium.***

The efficiency of activation of aerosol particles is of interest in cloud chemistry and microphysics.

- The efficiency of cloud droplet activation is a major influence on deposition of aerosol materials in rain.
- The radiative properties of clouds are controlled by the number and size of cloud drops.
- A greater concentration of aerosol particles generally results in a greater concentration of cloud droplets and brighter clouds.

- An enhanced concentration of cloud droplets can suppress precipitation.

These phenomena are significant in considerations of anthropogenic climate change.

This Study. . .

Examines the dependence of cloud droplet activation on controlling processes by examining its ***kinetics***.

Examines the time constants of droplet growth relative to duration of maximum supersaturation, gaseous diffusion, and the like.

Provides a differentiated picture of growth of size classes of drops and their uptake of water vapor and soluble gases.

Provides dependence of cloud droplet activation on controlling parameters that can be used to test approximations suitable for large scale atmospheric models.

Approach

“Zero-Dimensional” box model describing increase in water vapor saturation ratio and resultant mass-transfer processes pertinent to cloud formation.

Cloud updraft velocity and initial aerosol populations are treated as independent variables.

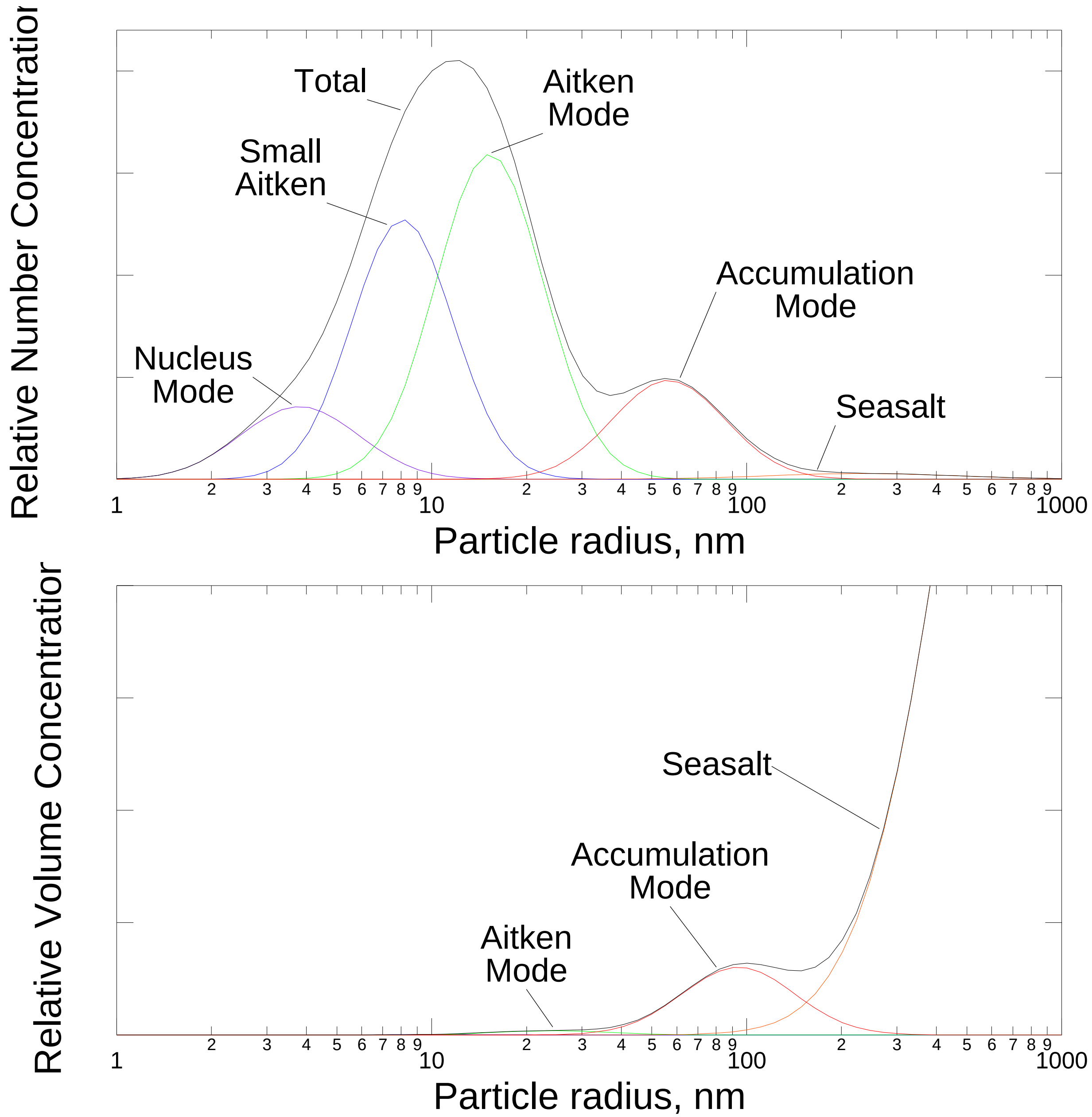
Updraft velocity is treated as constant in results reported here, but any time-dependent updraft velocity can be employed.

Coagulation and precipitation development are not represented in the model.

Soluble gases (e.g. HNO3) can be added and their fate and influence as solute can be determined.

Kinetics of mass transport processes are examined by solution of coupled differential equations describing the radii of classes of aerosol particles using *Mathematica*®.

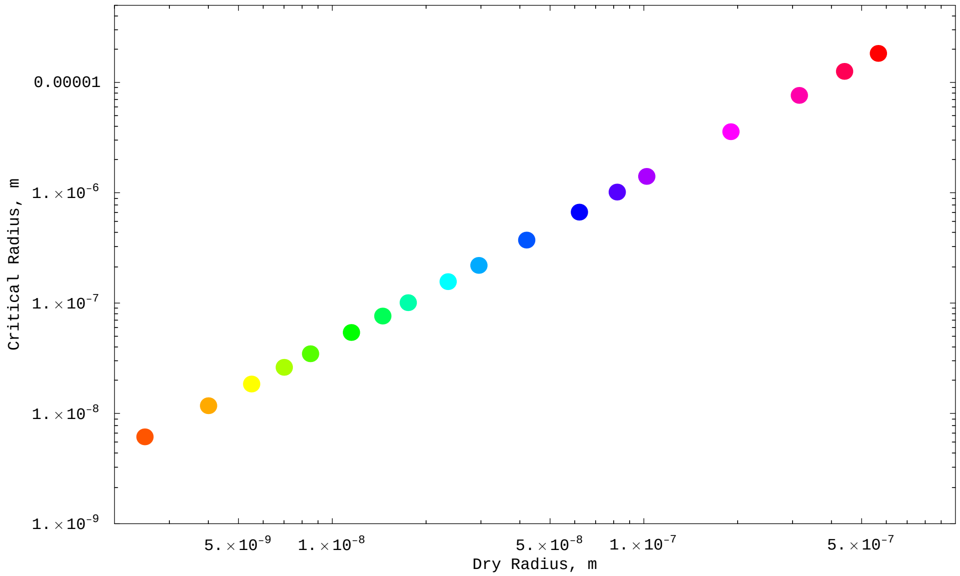
Size distribution that served as basis of calculations



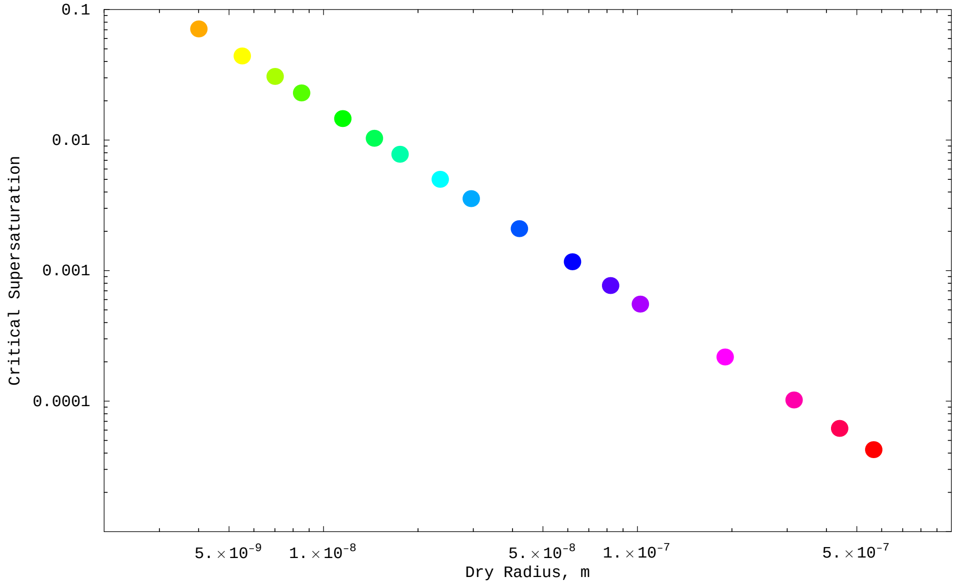
Seasalt, though low in number, dominates volume concentration.

Drop Classes used in the Calculations

Critical radius vs. Dry radius



Critical supersaturation



Color code allows history of individual drop classes to be readily followed.

Particles are treated as $(NH_4)_2SO_4$.

Largest four classes (sea salt) are omitted in most calculations.

Key Independent Variables

Number and size of aerosol particles

Updraft velocity

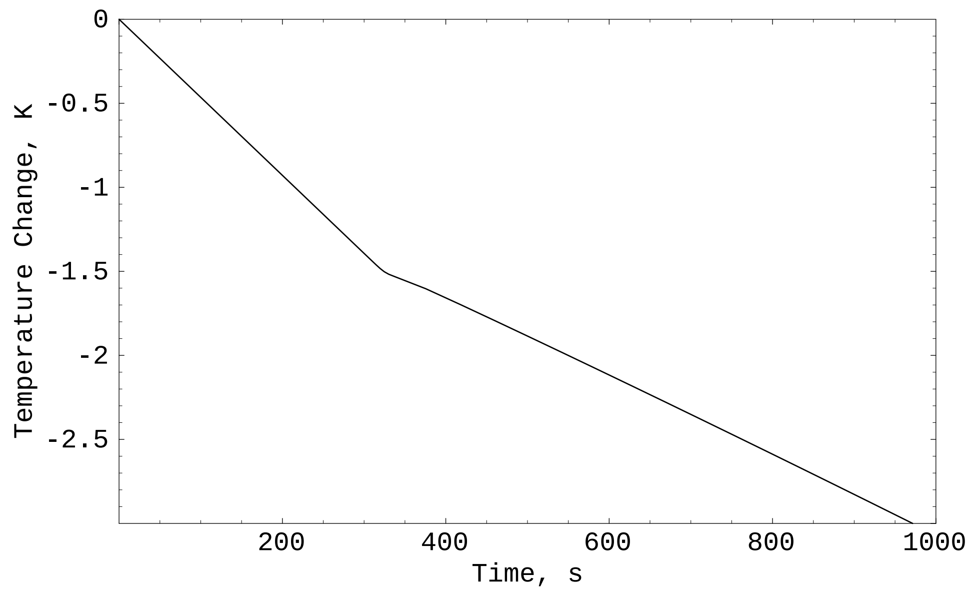
Presence or absence of soluble gas (HNO_3)

Example Results

Updraft velocity *w* taken as 0.5 m s^{-1}, typical of moderately strong updraft (stratocumulus).

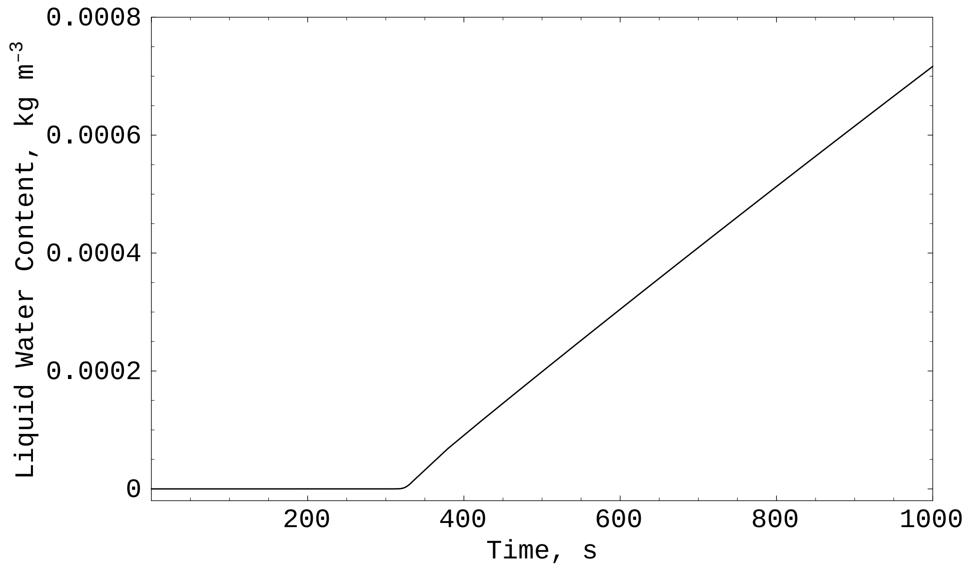
Calculation starts at relative humidity 90%, with dry adiabatic lapse rate.

Temperature Change

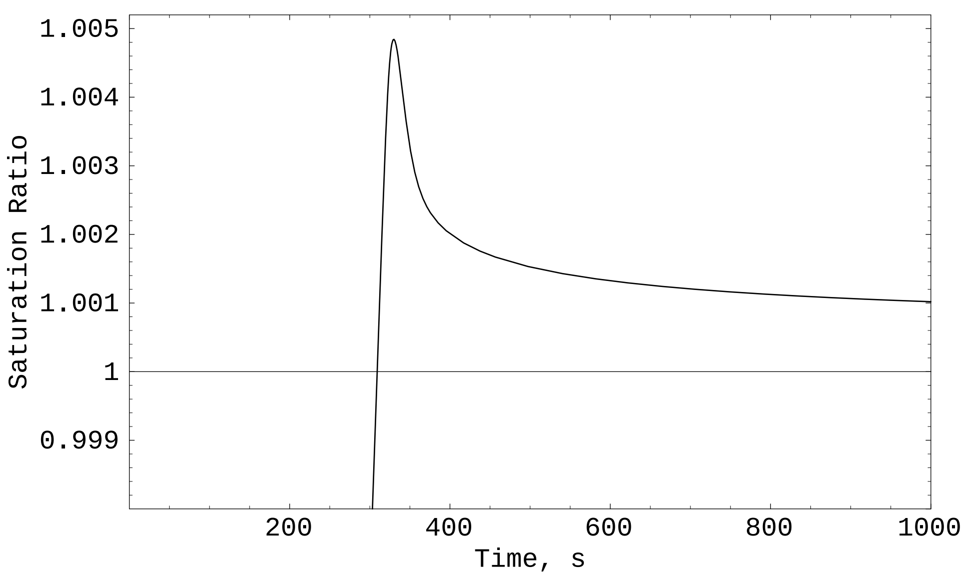


Note break at ~370 s due to latent heat release of water condensation at onset of cloud formation.

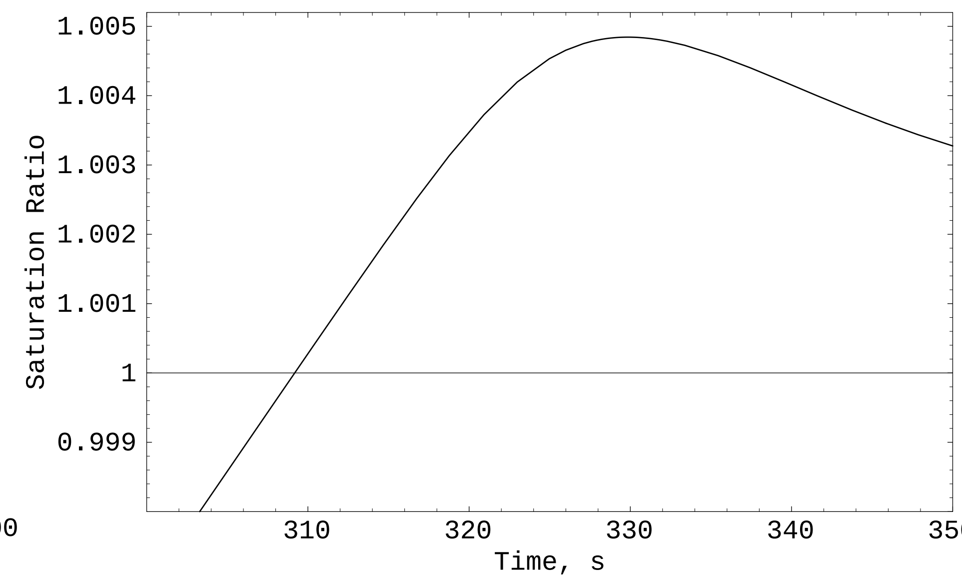
Liquid Water Content



Saturation Ratio

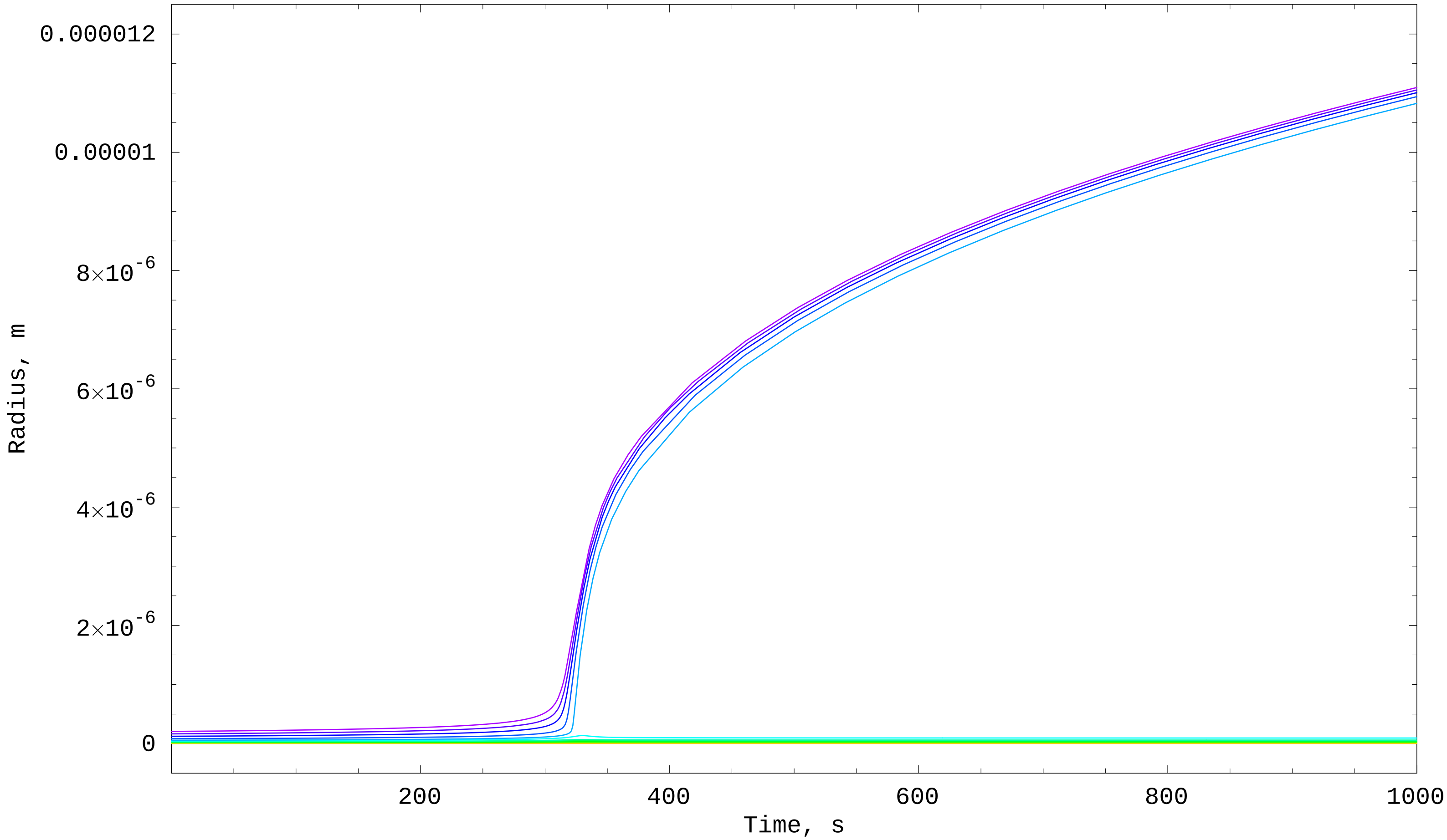


Zoom in



Note abrupt onset of maximum in saturation ratio followed by decrease as water vapor condenses on newly activated cloud drops.

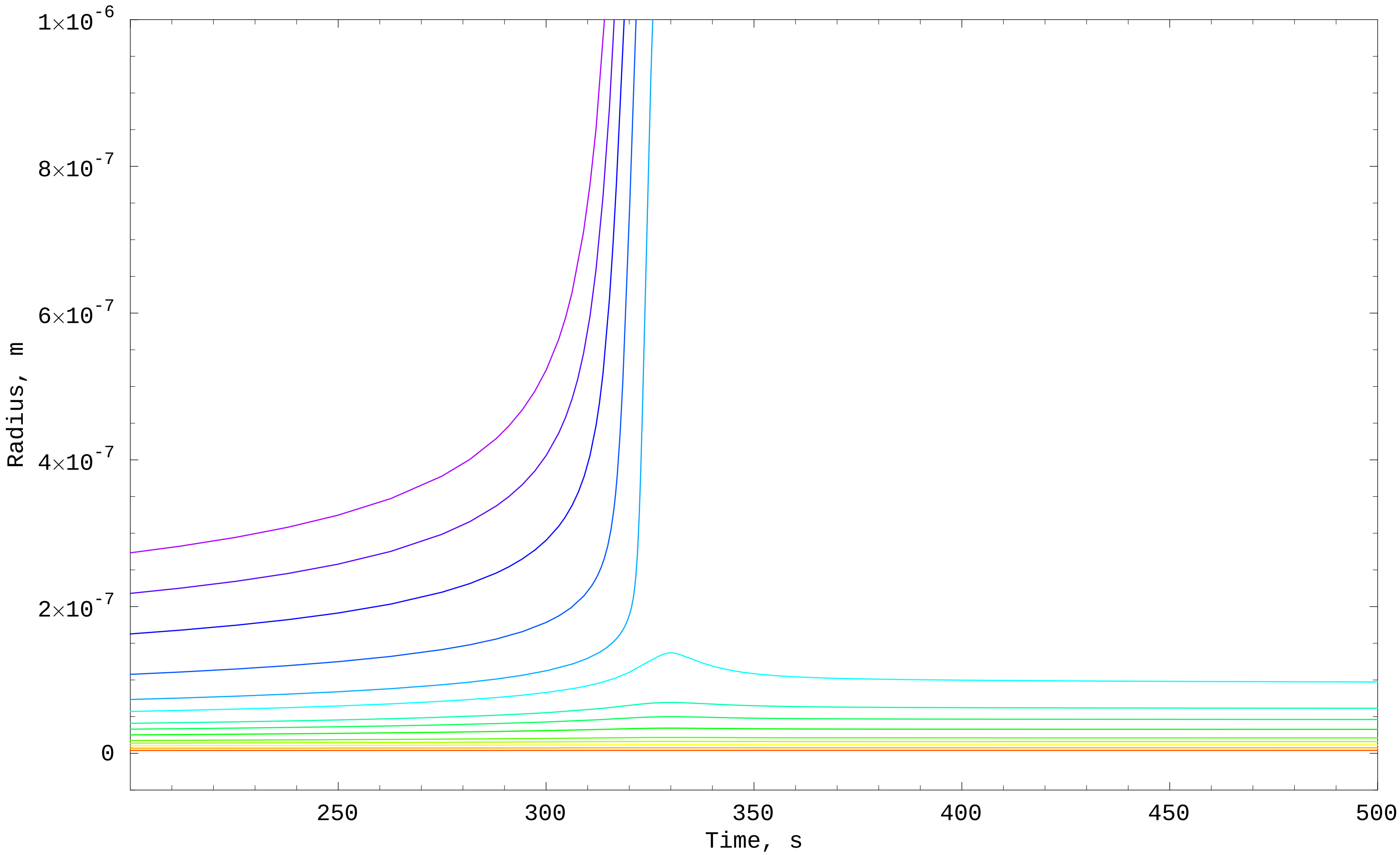
Drop Radii vs. time



Note abrupt change of drop radii upon activation.

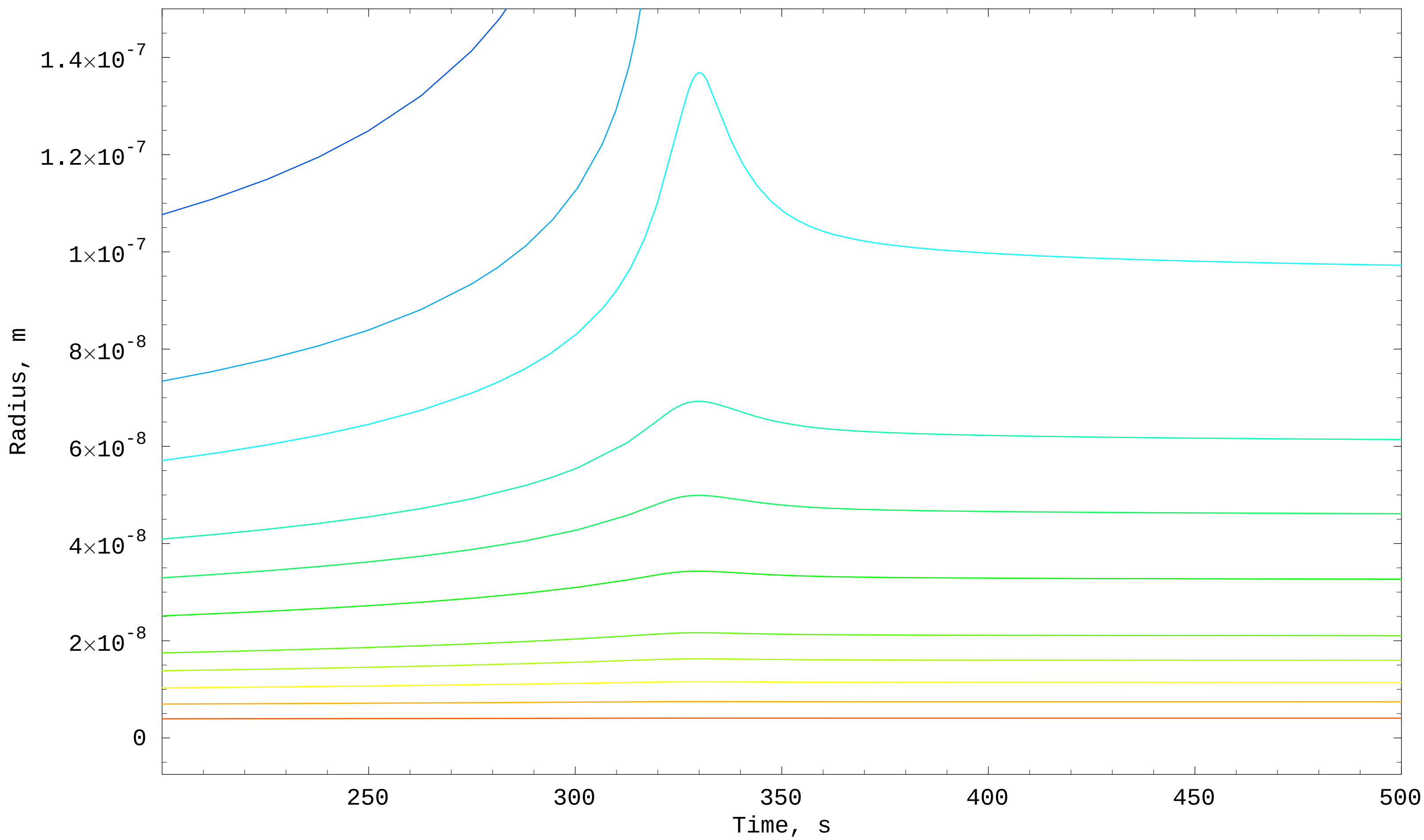
Note compression of cloud drop spectrum.

Zoom in on activation region



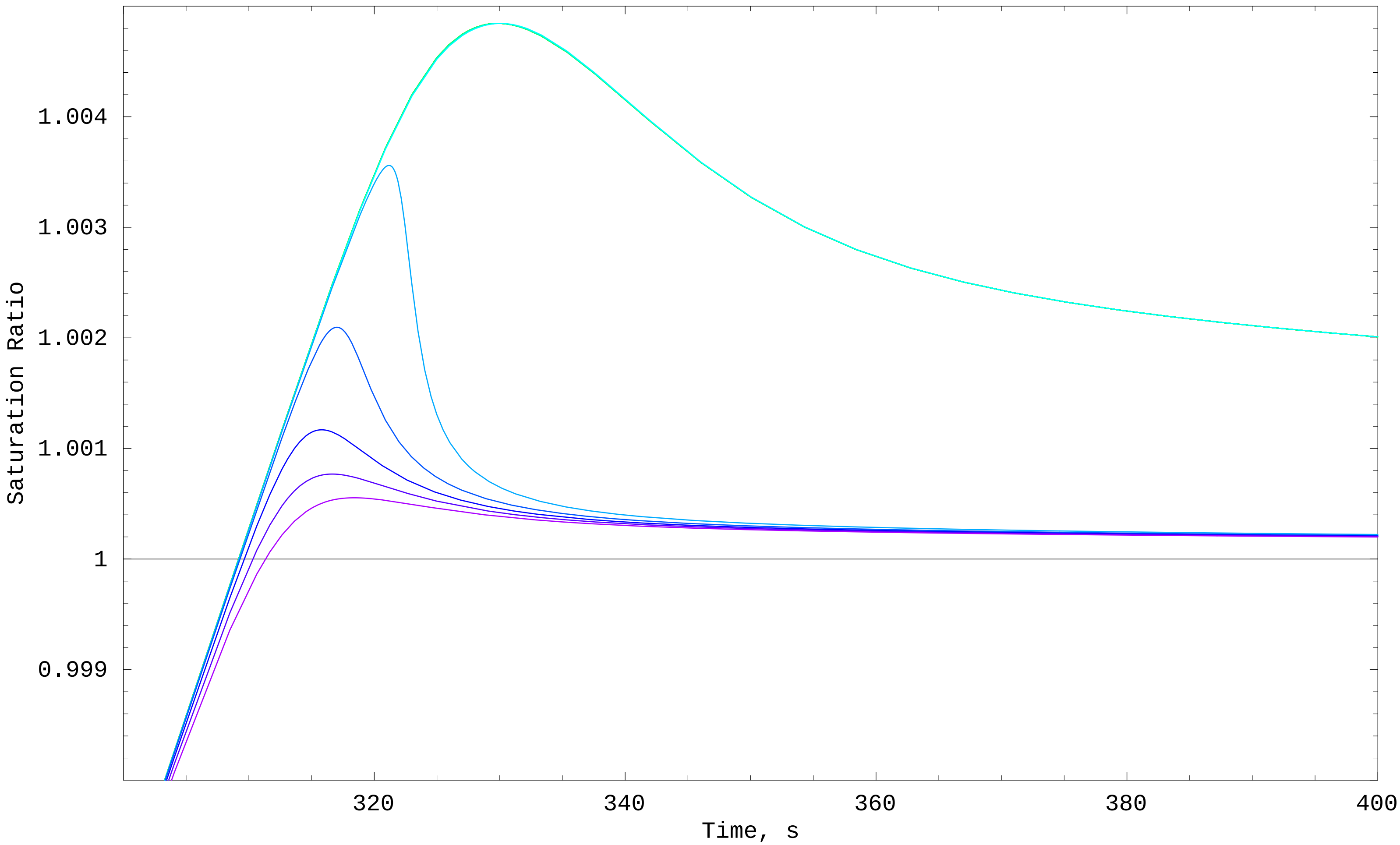
Note “knife-edge” separation of activated and unactivated particles.

Zoom further in on activation region



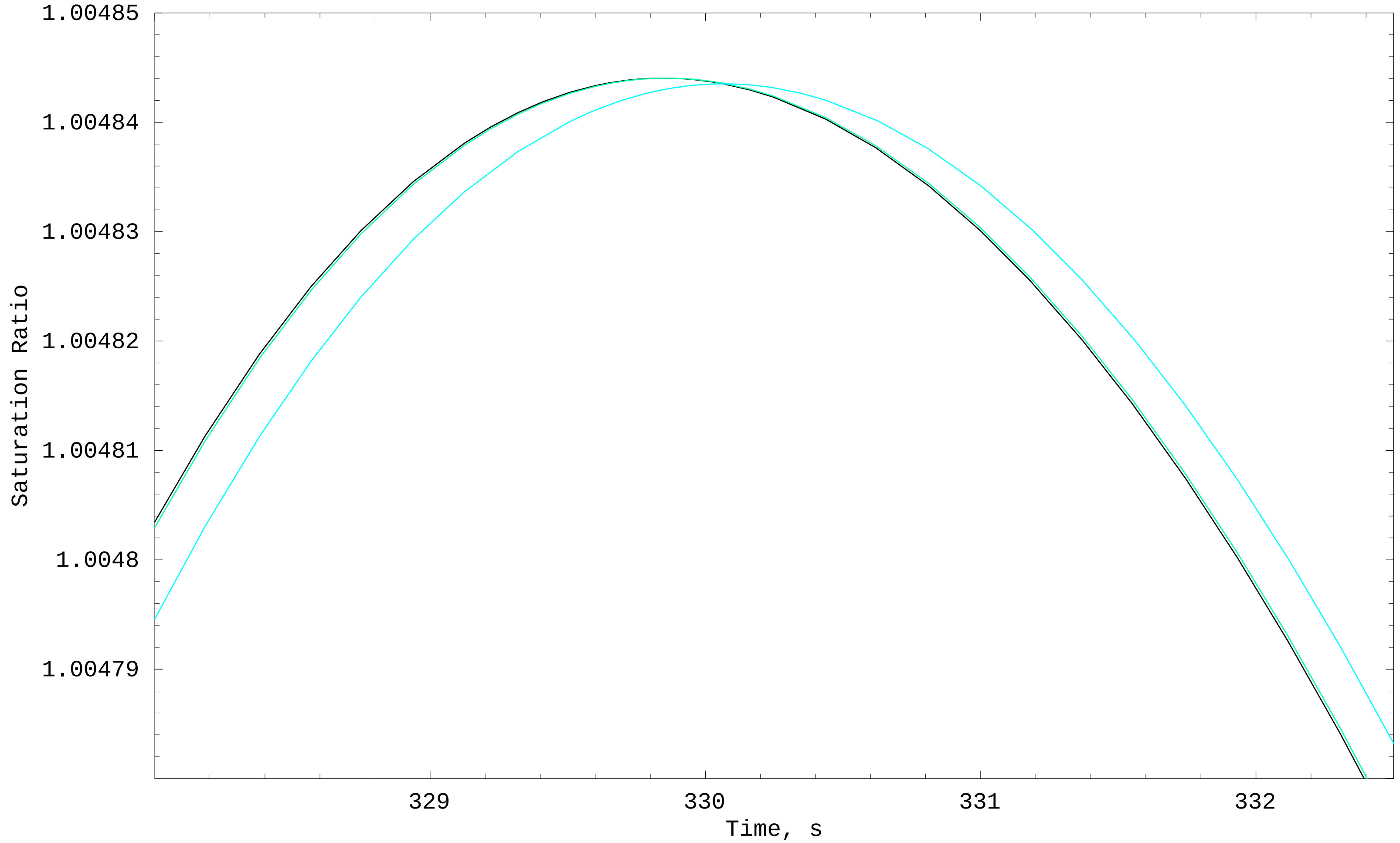
Note growth and relaxation of unactivated particles as saturation ratio increases and then decreases following water uptake on larger activated droplets.

Equilibrium (Köhler) saturation ratio of droplets vs. time.



Note that all unactivated droplets exhibit saturation ratio equal to that of the environment, also plotted but hidden under the nest of curves at the top.

Zoom in on activation region for last two classes of unactivated drops. Black curve denotes environmental saturation ratio.

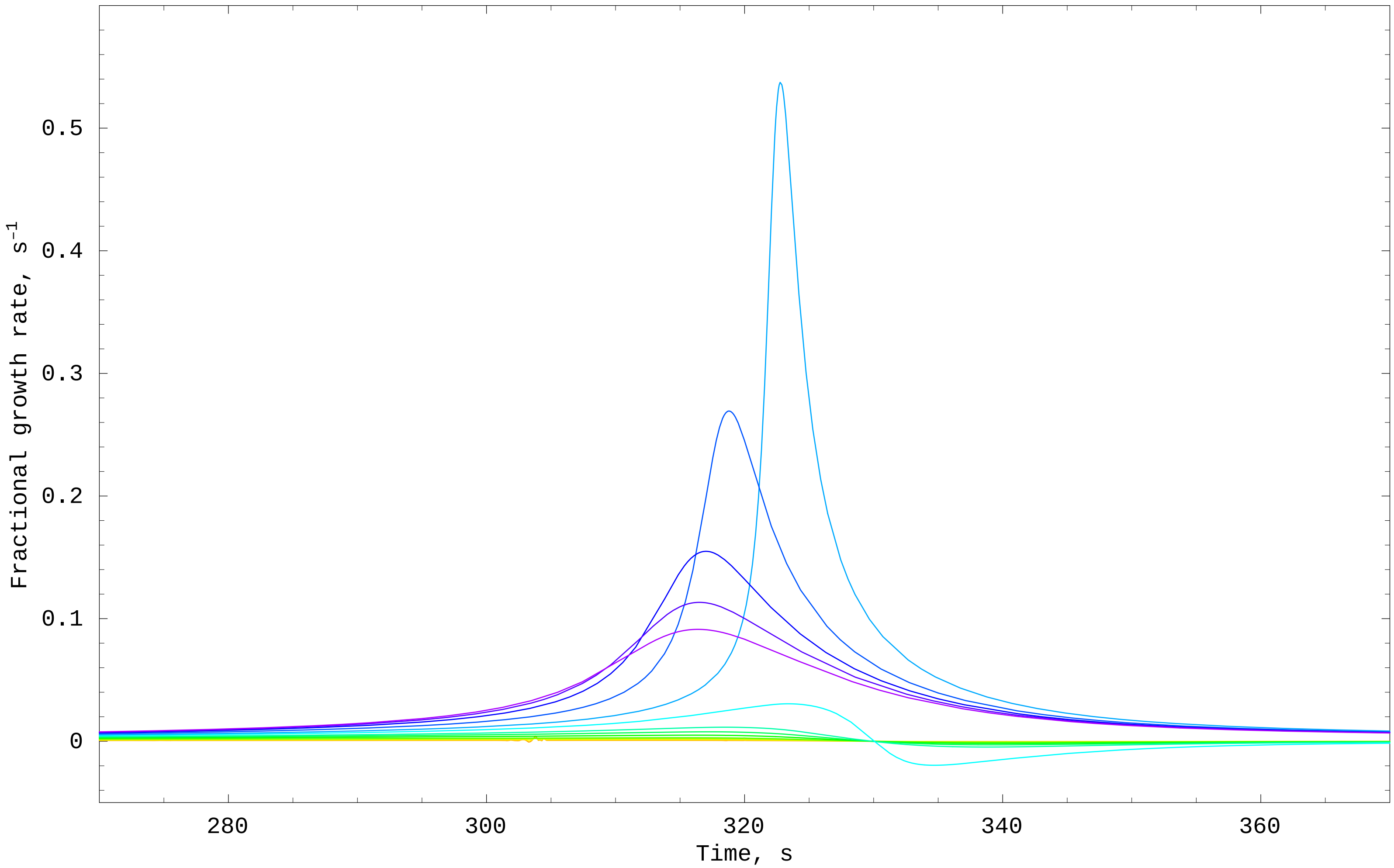


Note slight lag in equilibrium saturation ratio due to mass-transport kinetics.

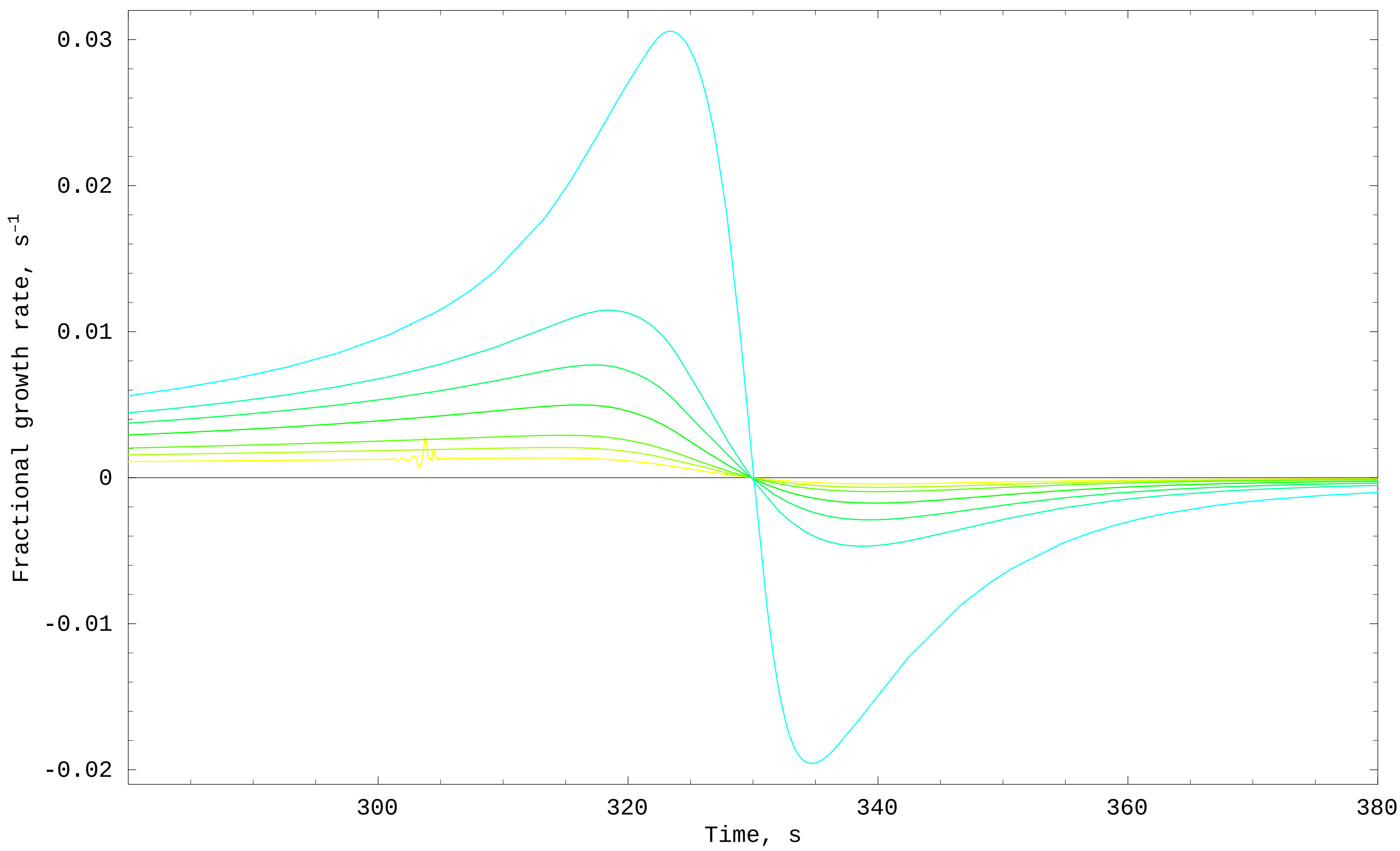
Droplet Growth Kinetics

Fractional rate of change of radius of particles during activation

$$\frac{1}{a}\frac{da}{dt}$$



Growth and Shrink Kinetics of Unactivated Drops

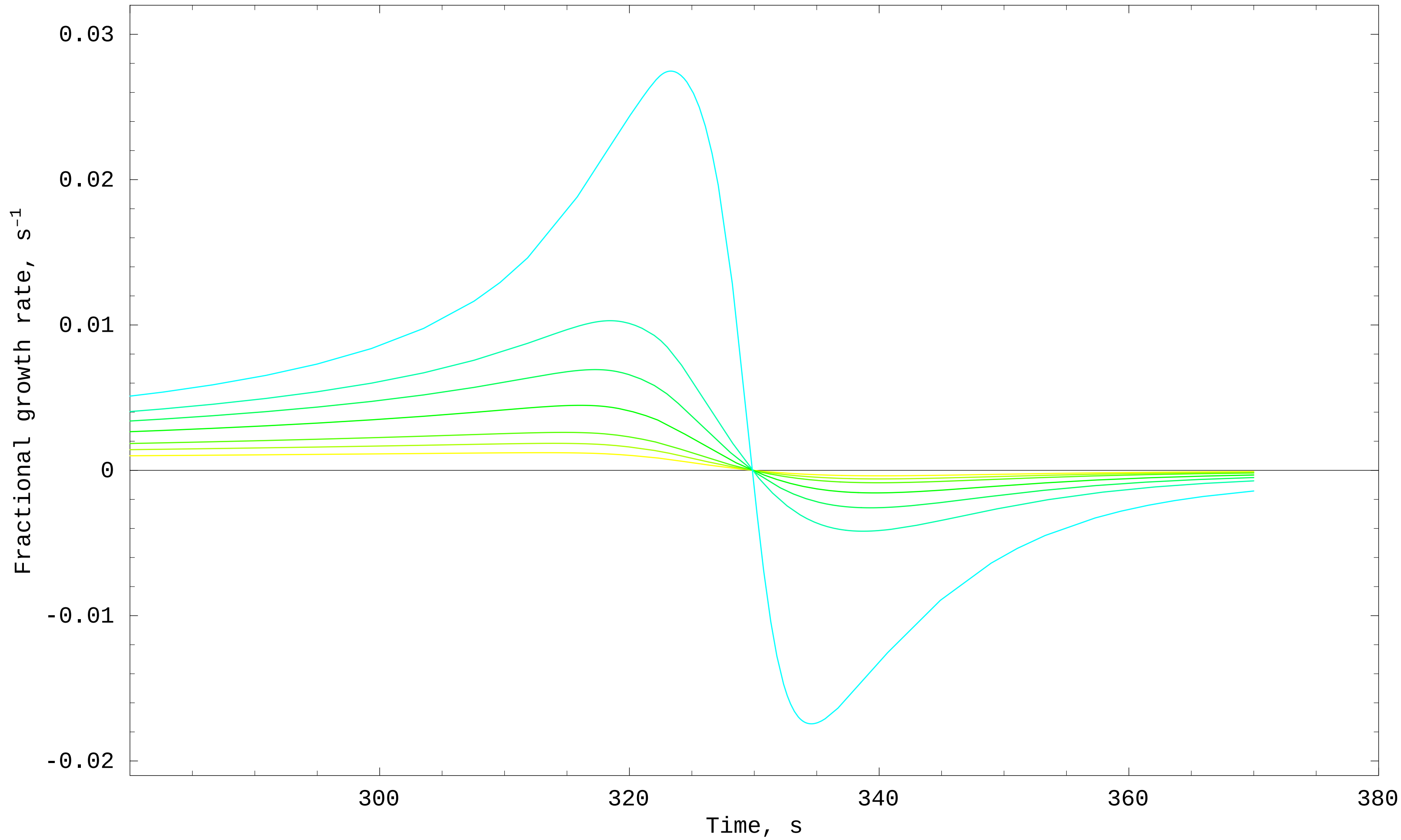


Equilibrium Droplet Growth and Shrink Kinetics

Evaluated from time-dependent saturation ratio $e(t)$ as

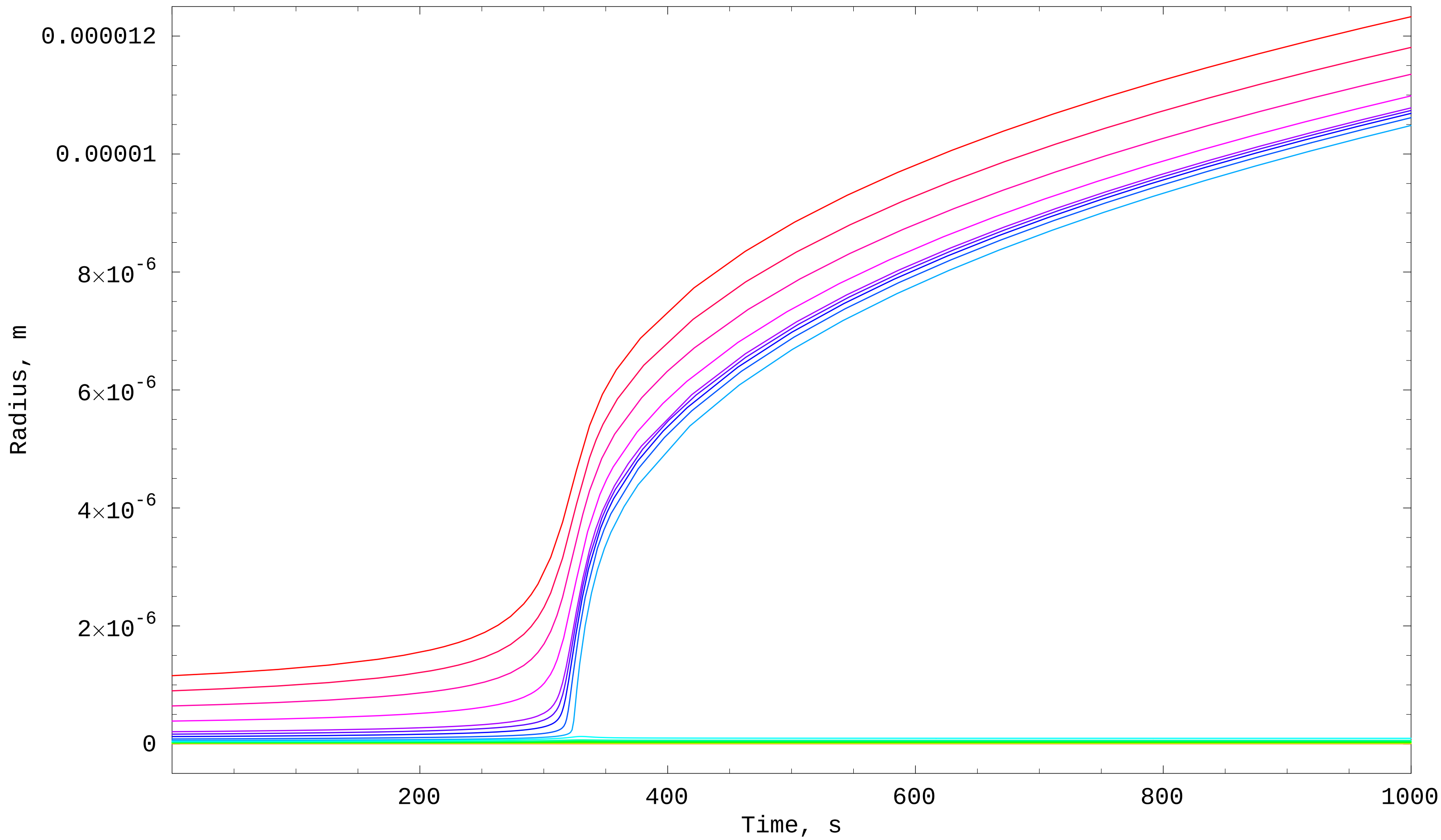
$$\frac{1}{a_{\mathrm{eq}}}\frac{da_{\mathrm{eq}}}{dt} = \frac{1}{a_{\mathrm{eq}}}\frac{da_{\mathrm{eq}}}{de}\frac{de}{dt}$$

where the dependence of a_{eq} on e is from the Köhler relation.



The near equality of $\frac{1}{a}\frac{da}{dt}$ and $\frac{1}{a_{\text{eq}}}\frac{da_{\text{eq}}}{dt}$ establishes that mass transport kinetics are not controlling activation of the drops under these conditions; contrast Chuang, Charlson & Seinfeld (1997).

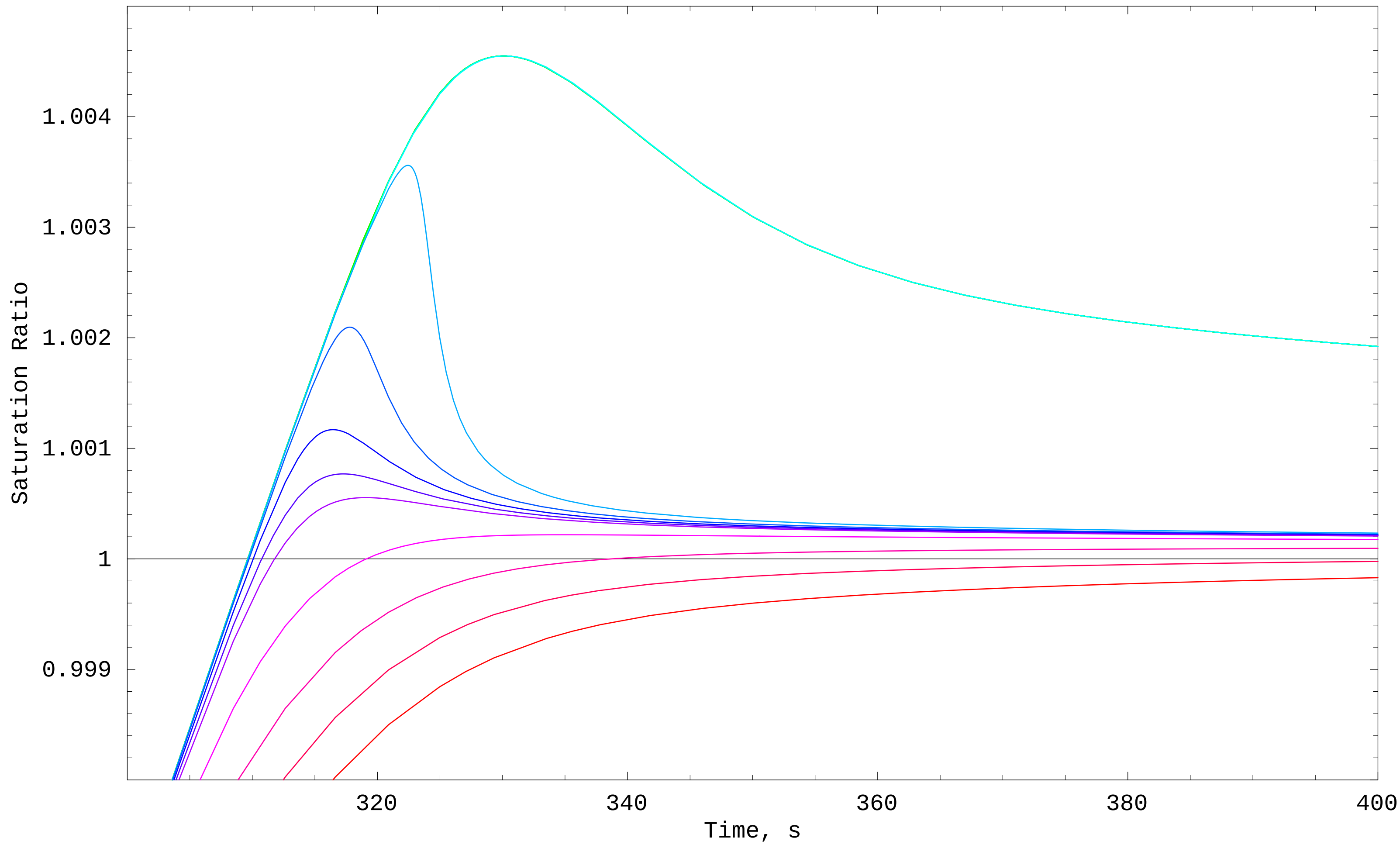
Results with sea salt included



Note that sea salt droplets get a “head start“ and the rest of the cloud droplets never catch up.

Otherwise the results are just about the same as without sea salt.

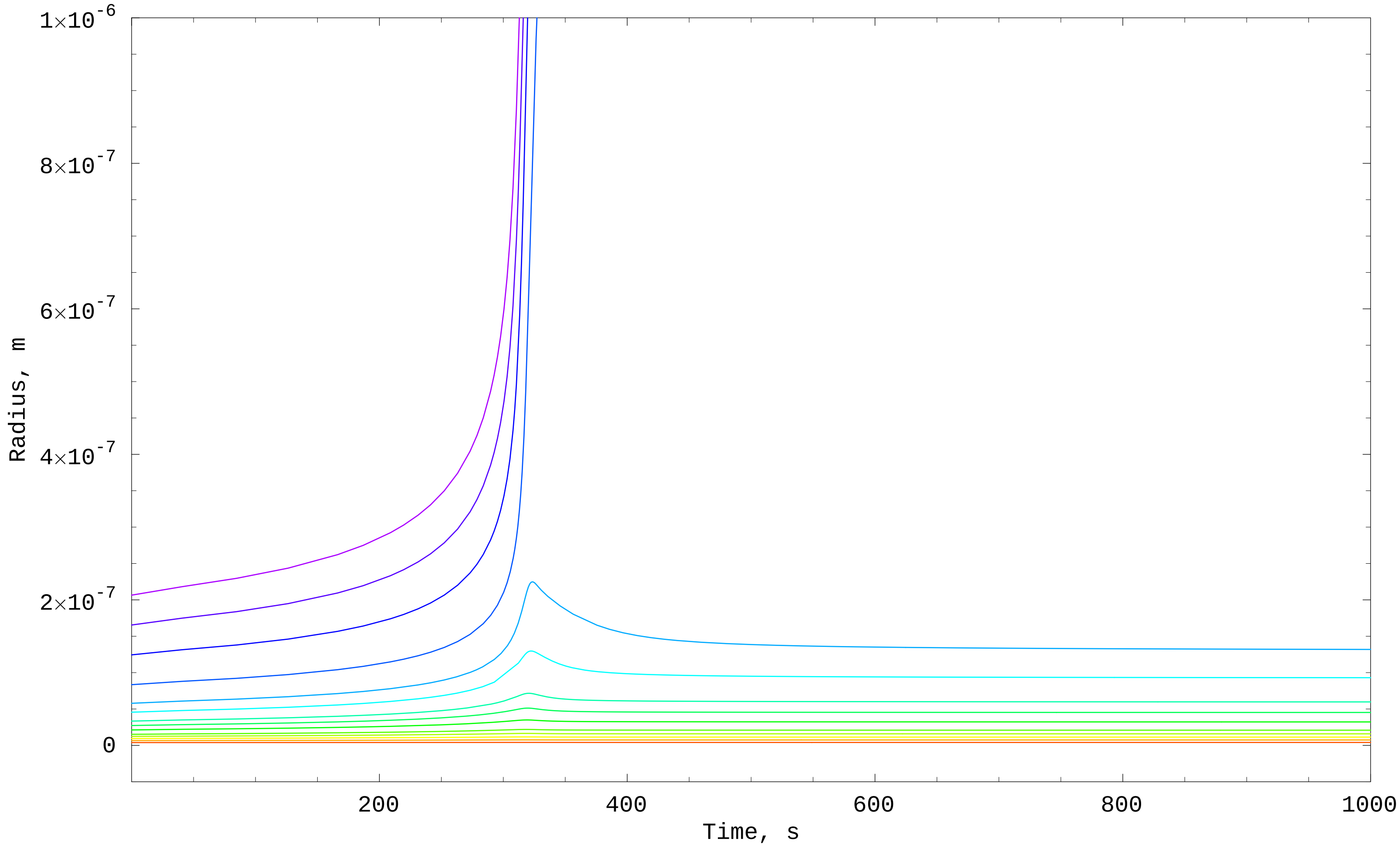
Equilibrium (Köhler) saturation ratio of droplets vs. time.



Note that the three largest classes of droplets never reach supersaturation but are effectively cloud droplets anyway, as pointed out by Hänel (1987).

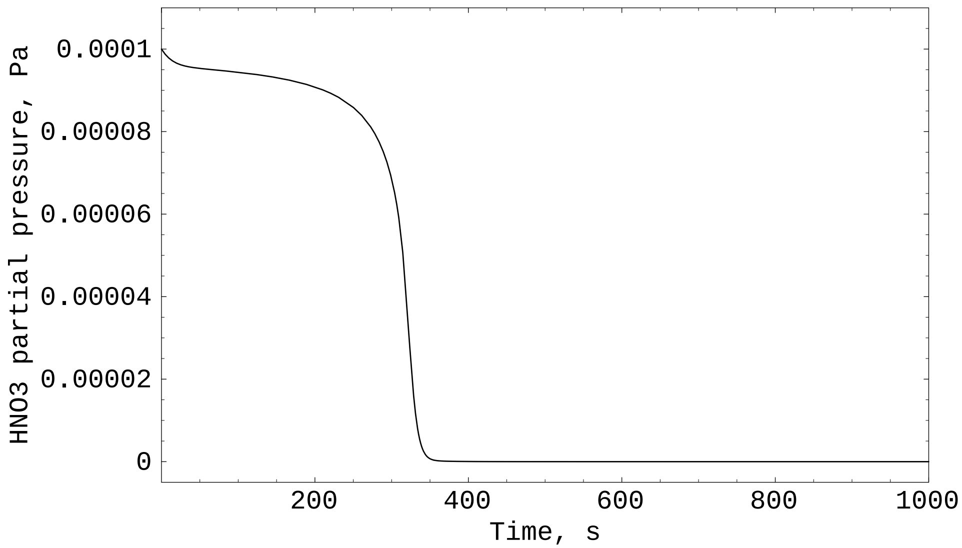
Results with 1 ppb HNO_3 included

Zoom on radius vs. time.



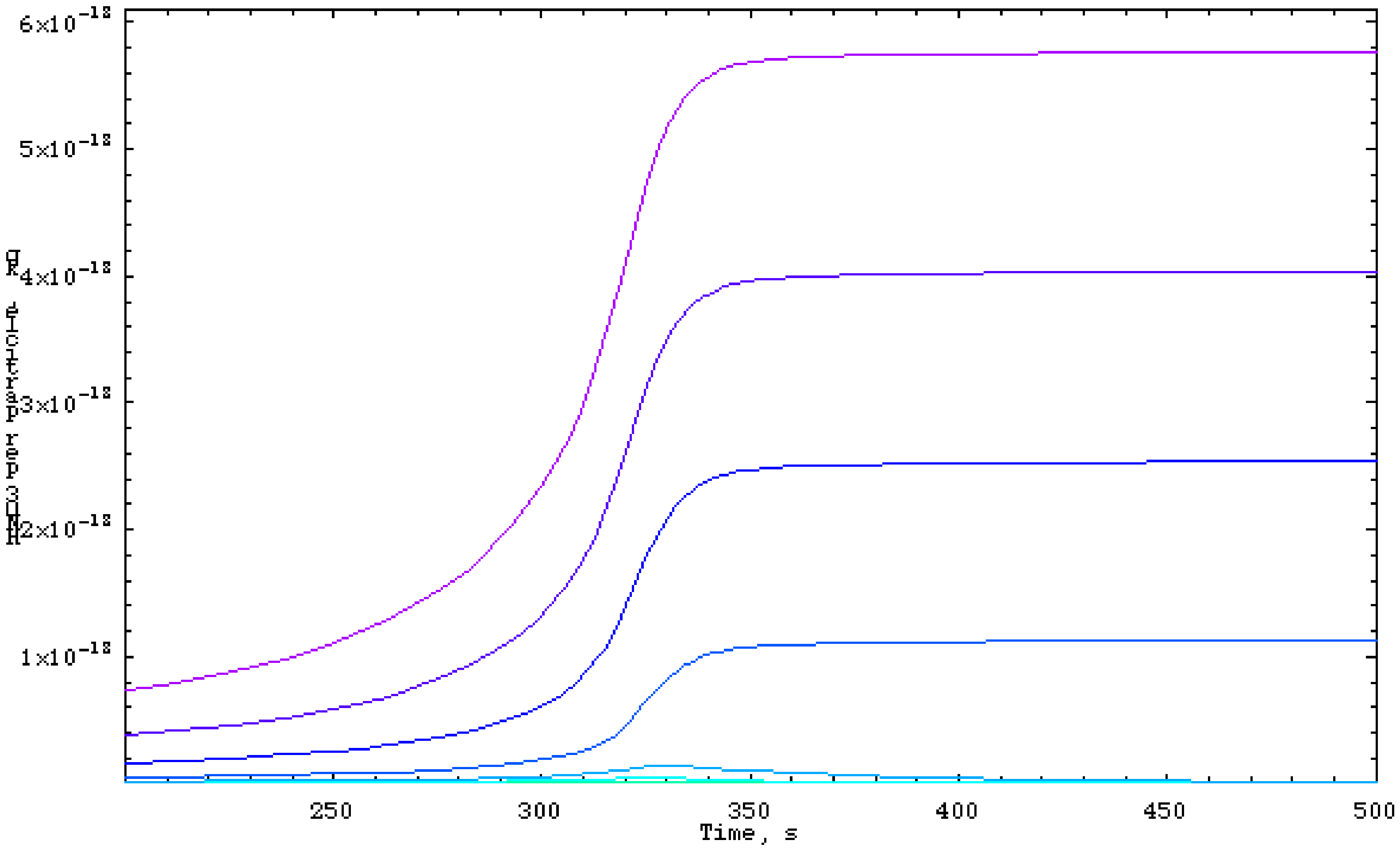
Note growth and shrink of last unactivated drops.

HNO_3 partial pressure vs. time.



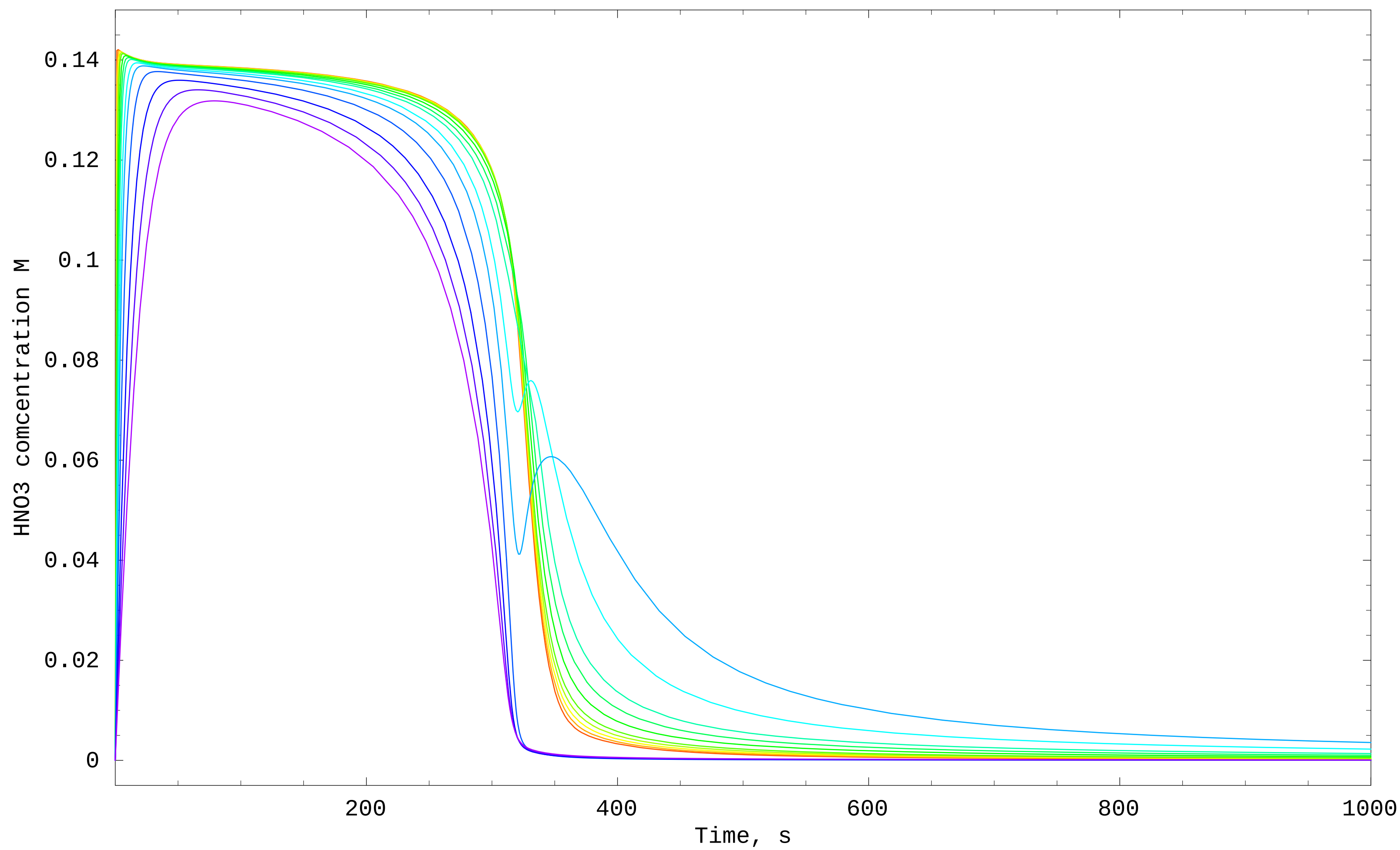
Note abrupt decrease as drops activate.

HNO3 mass in activated drops vs. time.



After activation mass is constant because low HNO3 vapor pressure precludes exchange among drops.

HNO_3 aqueous concentration vs. time.



HNO_3 aqueous concentration exerts a complex behavior that reflects mass transport of water vapor and HNO_3 and droplet growth (dilution).

As drops activate HNO_3 concentration rapidly decreases because of dilution.

HNO_3 concentration in last two unactivated classes increases as drop radii decrease as water transfers to newly activated drops.

The nonuniform HNO_3 concentrations would be expected to influence strongly pH-dependent reactions such as aqueous oxidation of SO_2 by O_3.

Summary of Results

$(NH_4)_2SO_4$ mass loading	$(NH_4)_2SO_4$ mixing ratio	Updraft velocity	Maximum Super-saturation	Droplet Number Conc.	Fraction NSS mass scavenged
μg m^{-3}	nmol/mol(air) (ppb)	m s^{-1}		cm^{-3}	
2.75	0.48	0.5	1.00245	997	0.935
0.275	0.048	0.5	1.0048	140	0.955
0.275 + seasalt	0.048 0.64	0.5	1.0046	140	0.955
27.5	4.8	0.5	1.0011	3150	0.66
2.75	0.48	2	1.0048	1298	0.955
2.75 + HNO_3	0.48 1	0.5	1.0021	997	0.935

Conclusions

- A highly flexible model ("desktop cloud") has been presented that describes the mass-transport kinetics of water vapor condensation and cloud droplet activation.
- The input parameters to the model can readily be changed to study cloud droplet activation for any situation of interest.
- This model readily displays drop-size dependent processes occurring during cloud formation.
- For the cases studied the mass transport of water vapor is sufficiently fast that Köhler equilibrium can be assumed for activating drops.
- Large drops may not activate but become effective cloud drops anyway.
- The reversible uptake of even a highly soluble gas such as HNO_3 exerts a complex dependence on drop size and time.

This model can be used to develop parameters for large scale models or to test alternative formulations such as moment methods.

Acknowledgment

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This presentation is available on the web at

http://www.ecd.bnl.gov/steve/pubs.html