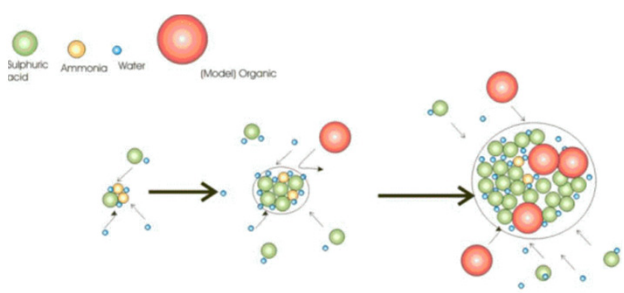
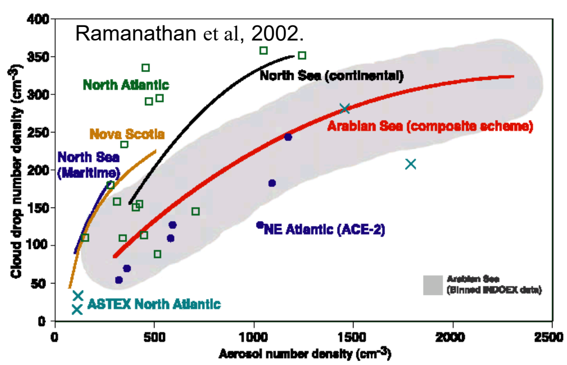
MODULE 3: Atmospheric Aerosols

Lecture 3: New Particle Formation

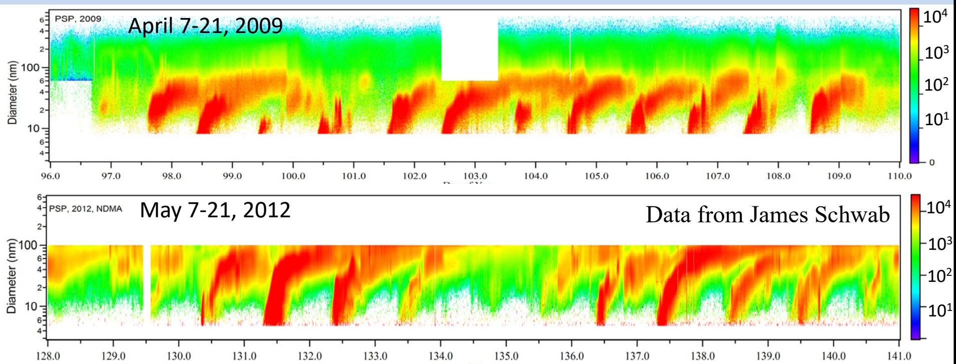
New particle formation (or nucleation) in the atmosphere is the least understand but a key physical process having important implications.





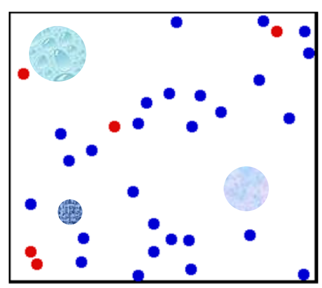
New particle formation (NPF) in the atmosphere

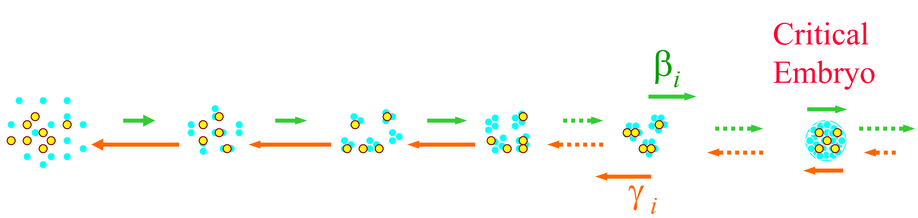
Challenges: Key parameters or species controlling atmospheric NPF and implications



What is new particle formation (NPF)?

Formation of new stable clusters/particles from gas molecules

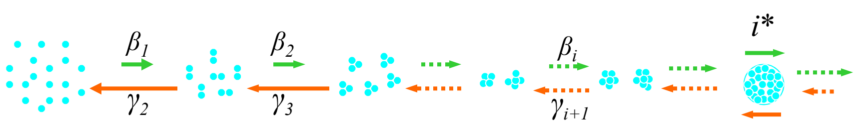




Nucleation Mechanisms

Unary Homogeneous Nucleation (UHN)	**H_2O**
Binary Homogeneous Nucleation (BHN)	**$H_2O + H_2SO_4$**
Ion-Mediated Nucleation (IMN)	**$H_2O + H_2SO_4$ + Ions**
Ternary Homogeneous Nucleation (THN)	**$H_2O + H_2SO_4 + NH_3$**
Ternary IMN (TIMN)	**$H_2O + H_2SO_4 + NH_3$ + Ions**
Ternary Nucleation with Amines	**$H_2O + H_2SO_4$ + Amines**
Organics-mediated Nucleation	**$H_2O + H_2SO_4$ + Organics**
Pure Organics Nucleation	**Organics w/o Ions**

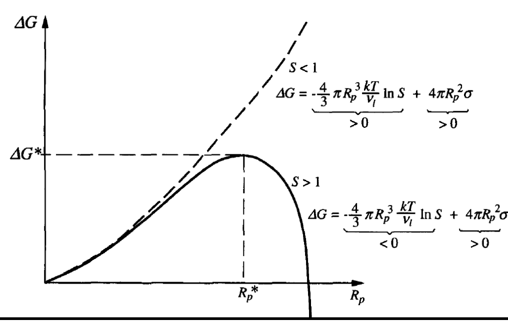
Water unary homogeneous nucleation



$$\frac{dn_{i+1}}{dt} = \delta_{i,1}\beta_i n_i - \gamma_{i+1}n_{i+1} - \beta_{i+1}n_{i+1} + \gamma_{i+2}n_{i+2}\,, \quad i \ge 1$$

$\delta_{i,1} = 0.5$ if i=1
$\delta_{i,1} = 1$ if $i \neq 1$

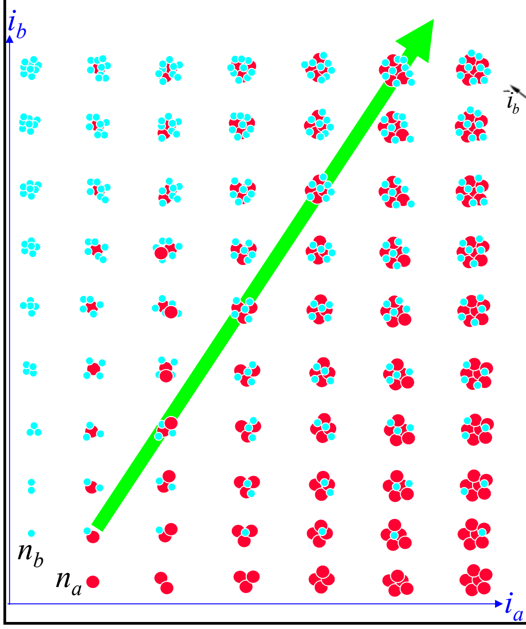
Mathematical derivation and approximation (Seinfeld and Pandis, 1998)

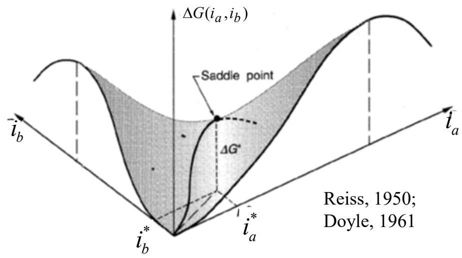


$$J = C\exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$= K_{act}n^*$$

Binary homogeneous nucleation



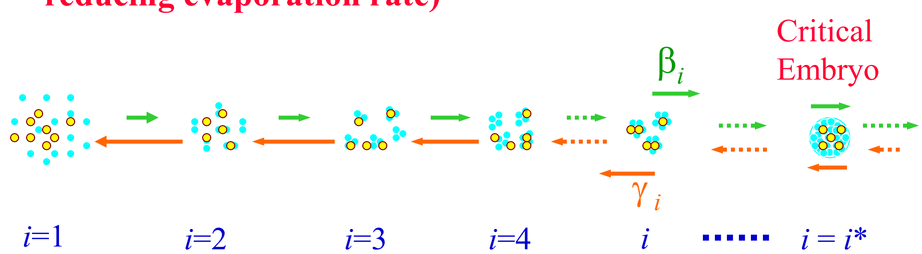


$$J = C\exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$\Delta G = n_A(\mu_{A\ell} - \mu_{Ag}) + n_B(\mu_{B\ell} - \mu_{Bg}) + 4\pi r^2\sigma$$

$$\mu_{j\ell} - \mu_{jg} = -kT\ln\frac{p_j}{p_{j_{sol}}}, \qquad j = \text{A, B}$$

NH_3 may enhance nucleation by stabilizing clusters (i.e., reducing evaporation rate)



Classical Ternary H_2SO_4-H_2O-NH_3 nucleation

$$J = C\exp\left(-\frac{\Delta G^*}{kT}\right)$$

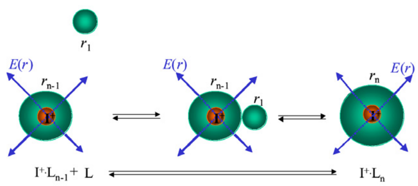
$$\Delta G = -n_1 kT\ln\left(\frac{P_1}{P_1^{sol}}\right) - n_2 kT\ln\left(\frac{P_2}{P_2^{sol}}\right) - n_3 kT\ln\left(\frac{P_3}{P_3^{sol}}\right) + 4\pi r^2\sigma$$

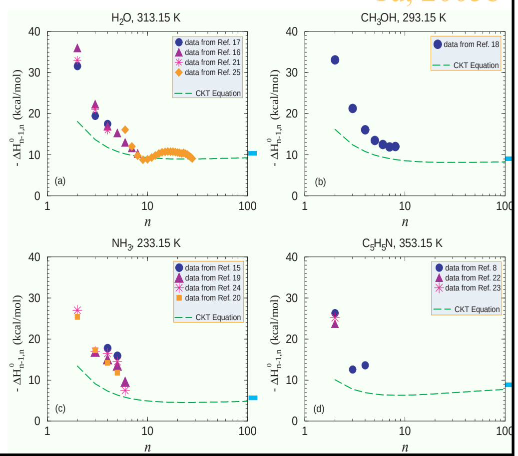
Classical ion induced nucleation theory

Classical Kelvin-Thomson (CKT) equation (Thomson, 1888):

$$\Delta G_{0,n}^{\text{charged}} = -nkT\ln\left(\frac{p}{p_{sat}}\right) + \sigma 4\pi r_n^2 - \frac{(qe)^2}{8\pi\varepsilon_0}\left(1-\frac{1}{\varepsilon_l}\right)\left(\frac{1}{r_0}-\frac{1}{r_n}\right)$$

Yu, 2005b

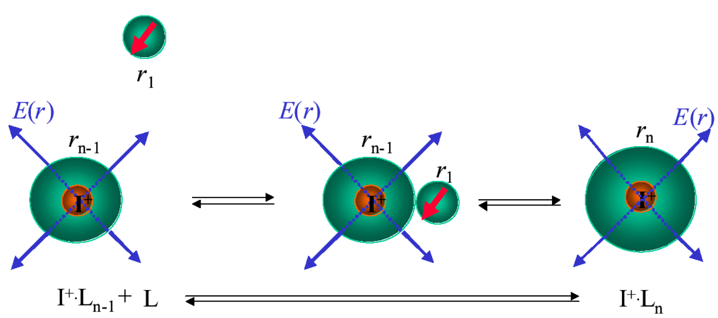




Fundamental inconsistency exists between the general form of the CKT expression and the properties of small cluster ions (Holland and Castleman, 1982).

Dipole-charge interaction is important

Nadykto and Yu, 2004;
Yu, 2005b



Modified Kelvin-Thomson equation:

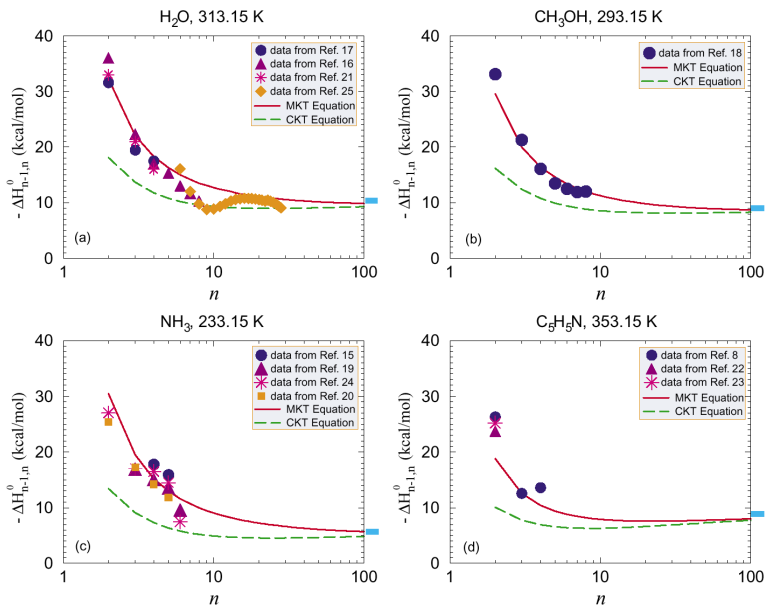
$$\Delta G_{0,n}^{\text{charged}} = -nkT\ln\left(\frac{p}{p_{sat}}\right) + \sigma 4\pi r_n^2 - \frac{(qe)^2}{8\pi\varepsilon_0}\left(1-\frac{1}{\varepsilon_l}\right)\left(\frac{1}{r_0}-\frac{1}{r_n}\right)$$

$$-\int_1^n \left\{\frac{1}{2}\alpha E_{n-1}^2 + kT\ln\left[\left(\exp\left(\frac{\mu_0 E_{n-1}}{kT}\right) - \exp\left(-\frac{\mu_0 E_{n-1}}{kT}\right)\right)/\left(2\frac{\mu_0 E_{n-1}}{kT}\right)\right]\right\}dn$$

Clustering enthalpies for protonated clusters: $H^+X_{n-1} + X \rightarrow H^+X_n$

($X = H_2O$, NH_3, CH_3OH, and C_5H_5N)

Yu, 2005b



Ternary Ion-Mediated Nucleation (TIMN): Controlling Parameters

Reading materials:

Yu, F., Nadykto, A. B., Luo, G., and Herb, J.: H2SO4-H2O binary and H2SO4-H2O-NH3 ternary homogeneous and ion-mediated nucleation: lookup tables version 1.0 for 3-D modeling application, Geosci. Model Dev., 13, 2663-2670, https://doi.org/10.5194/gmd-13-2663-2020, 2020.

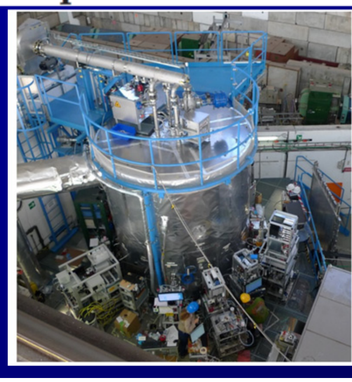
LETTER

Kirkby et al., Nature, 2011

doi:10.1038/nature10343

Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation

CERN CLOUD chamber



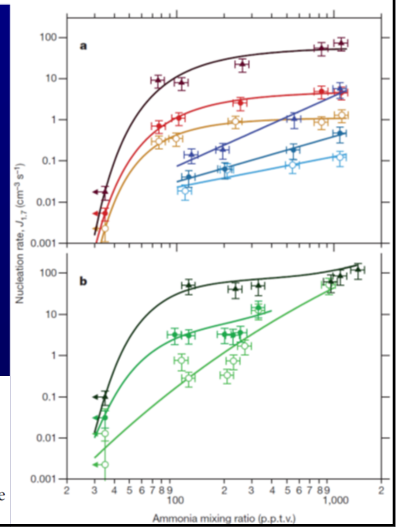
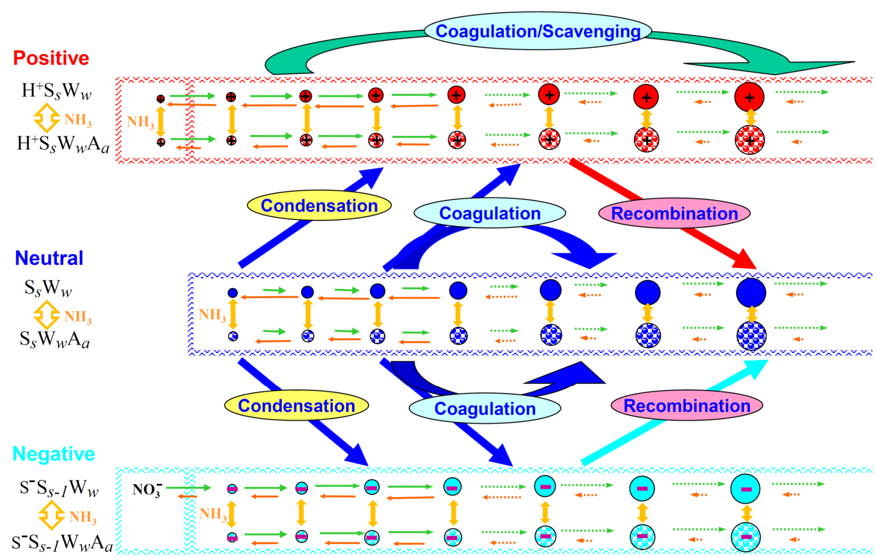


Figure 4 | Plots of nucleation rate against NH_3 concentration. Nucleation rates are shown as a function of ammonia mixing ratio. **a**, At 292 K and $[H_2SO_4] = 1.5 \times 10^8$ cm^{-3} (curves) and 4.3×10^7 cm^{-3} (straight lines); **b**, at 278 K and $[H_2SO_4] = 6.3 \times 10^7$ cm^{-3}. All measurements were made at 38% relative humidity. Triangles, J_{ch}; filled circles, J_{gcr}; open circles, J_n. The fitted lines are drawn to guide the eye. The bars indicate 1σ total errors, although the overall ammonia scale uncertainty of a factor 2 is not shown.

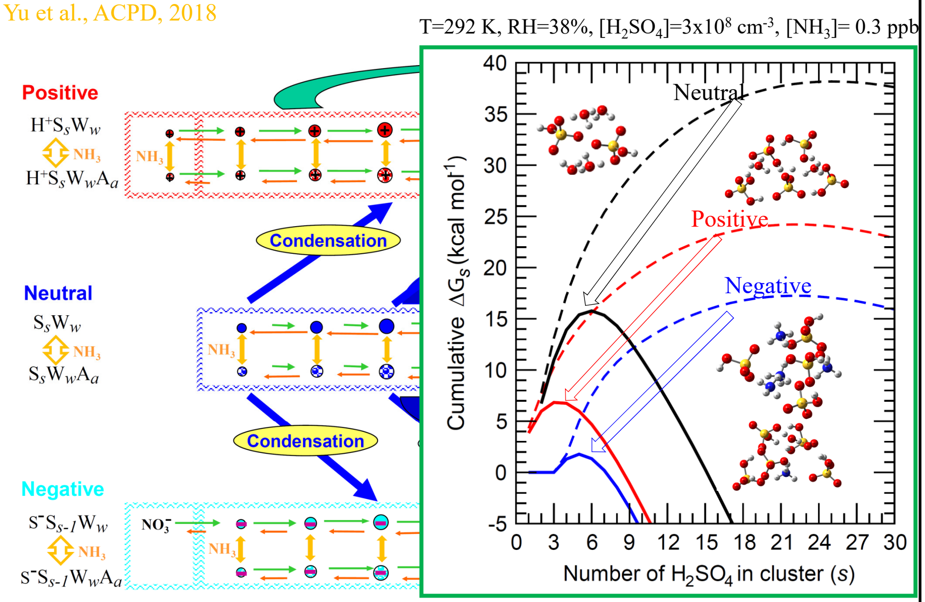
Kinetic-based H_2SO_4-H_2O-NH_3 ternary ion-mediated nucleation (TIMN) model

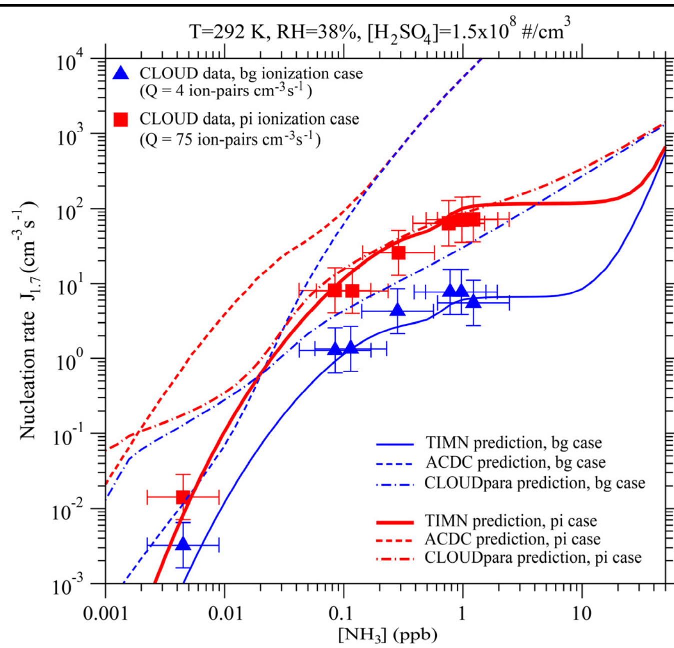
Yu et al., ACPD, 2018



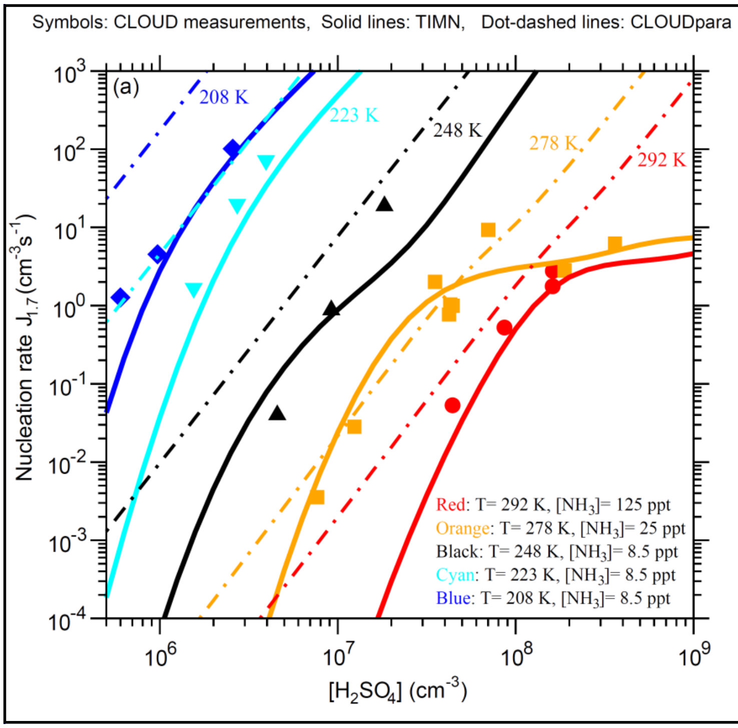
Kinetic-based H_2SO_4-H_2O-NH_3 ternary ion-mediated nucleation (TIMN) model

Yu et al., ACPD, 2018



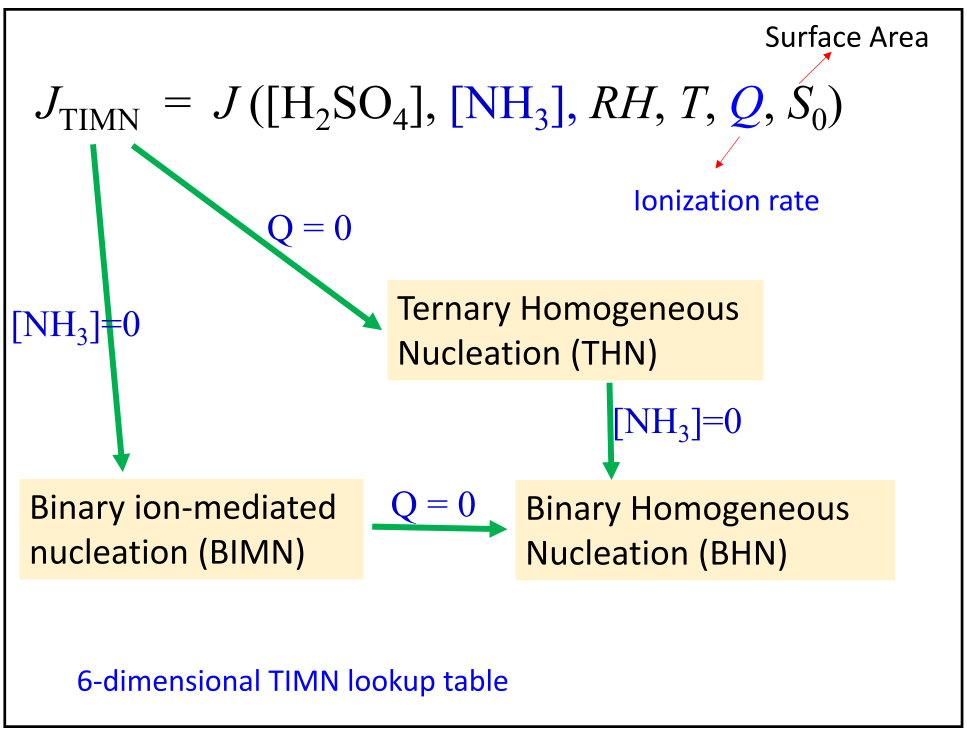


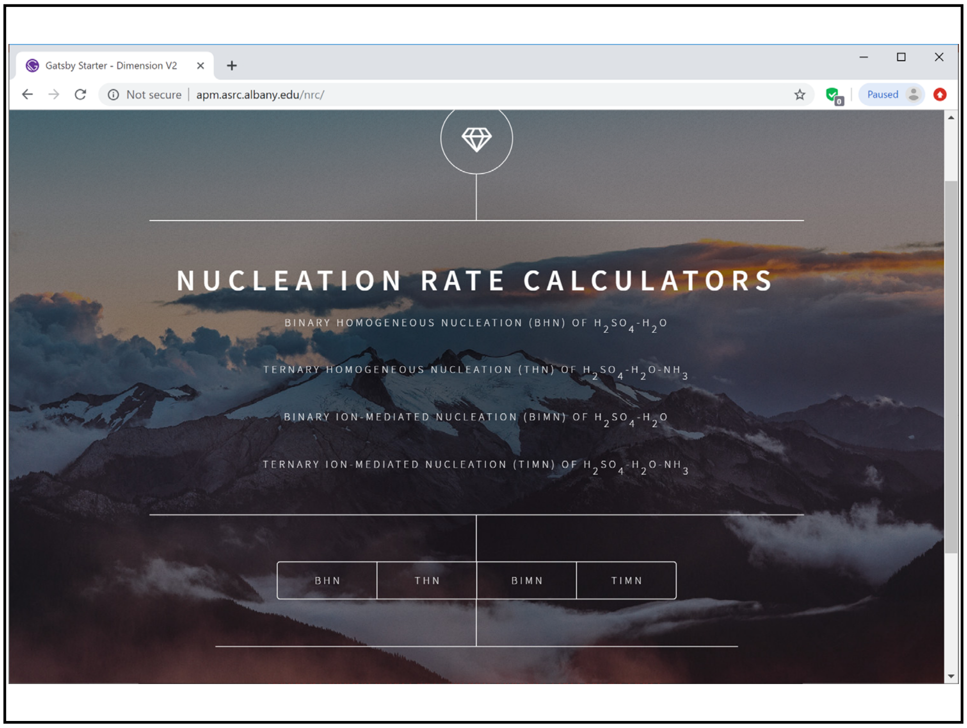
References: CLOUD data and CLOUDpara (Dunne et al., 2016)
ACDC (McGrath et al., 2012; Kürten et al., 2016)

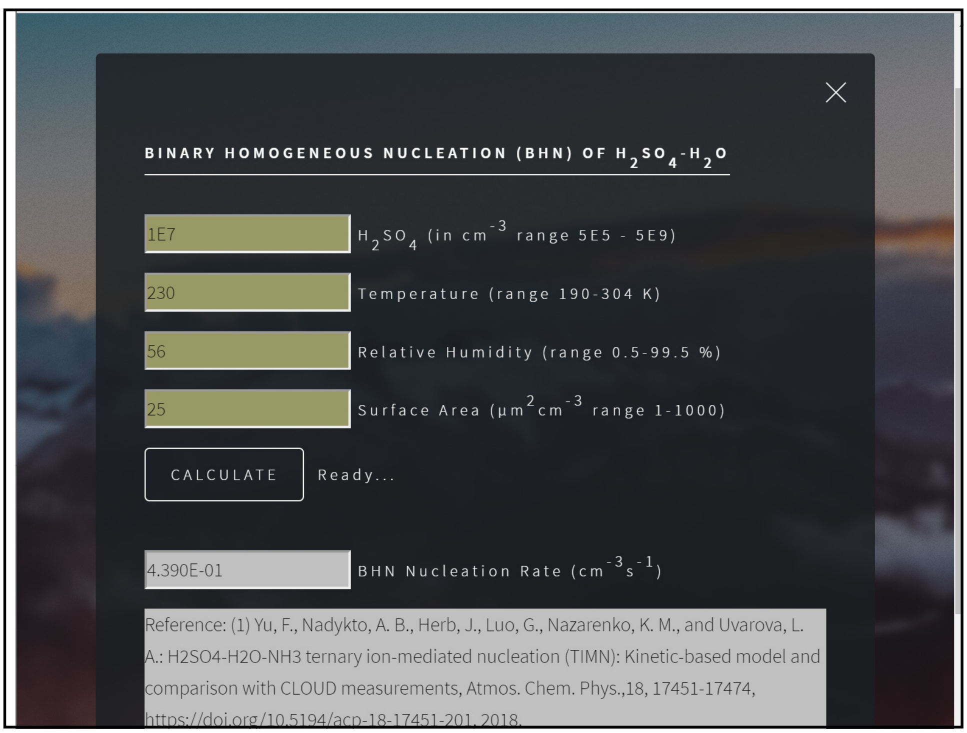


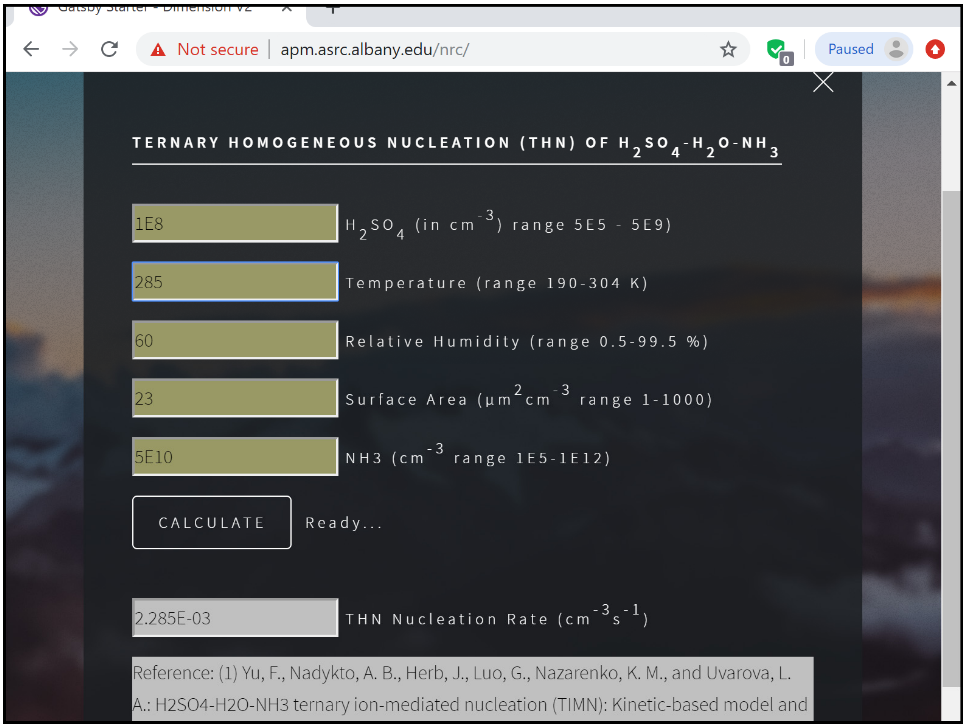
TIMN (solid lines): Yu et al., ACP, 2018

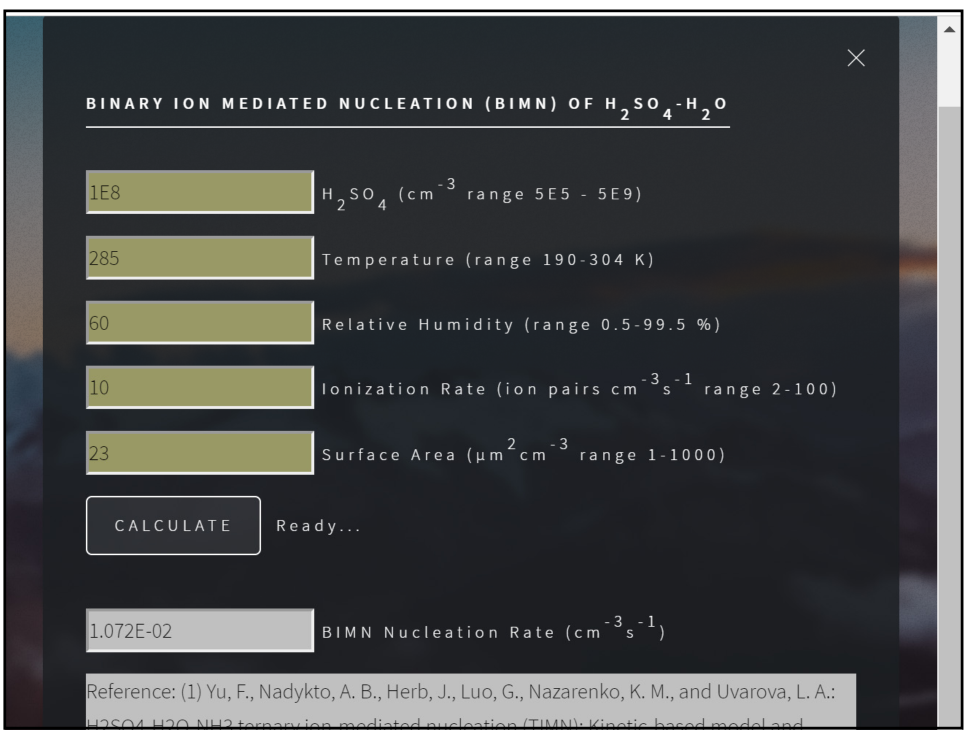
CLOUDpara (dashed lines): Dunne et al., Science, 2016

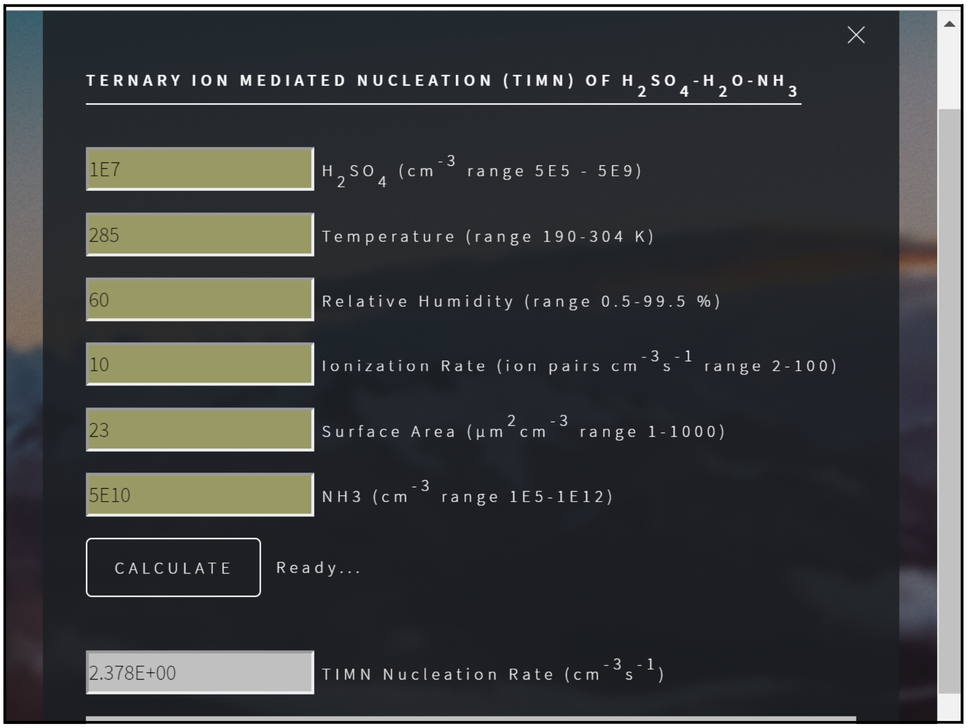



Gatsby Starter - Dimension V2
Not secure | apm.asrc.albany.edu/nrc/
Paused
NUCLEATION RATE CALCULATORS
BINARY HOMOGENEOUS NUCLEATION (BHN) OF H_2SO_4-H_2O
TERNARY HOMOGENEOUS NUCLEATION (THN) OF H_2SO_4-H_2O-NH_3
BINARY ION-MEDIATED NUCLEATION (BIMN) OF H_2SO_4-H_2O
TERNARY ION-MEDIATED NUCLEATION (TIMN) OF H_2SO_4-H_2O-NH_3
BHN
THN
BIMN
TIMN


BINARY HOMOGENEOUS NUCLEATION (BHN) OF H_2SO_4-H_2O
1E7
H_2SO_4 (in cm^{-3} range 5E5 - 5E9)
230
Temperature (range 190-304 K)
56
Relative Humidity (range 0.5-99.5 %)
25
Surface Area ($\mu m^2 cm^{-3}$ range 1-1000)
CALCULATE
Ready...
4.390E-01
BHN Nucleation Rate ($cm^{-3}s^{-1}$)
Reference: (1) Yu, F., Nadykto, A. B., Herb, J., Luo, G., Nazarenko, K. M., and Uvarova, L. A.: H2SO4-H2O-NH3 ternary ion-mediated nucleation (TIMN): Kinetic-based model and comparison with CLOUD measurements, Atmos. Chem. Phys.,18, 17451-17474, https://doi.org/10.5194/acp-18-17451-201, 2018.


Not secure
apm.asrc.albany.edu/nrc/
Paused
TERNARY HOMOGENEOUS NUCLEATION (THN) OF H_2SO_4-H_2O-NH_3
1E8
H_2SO_4 (in cm^{-3}) range 5E5 - 5E9)
285
Temperature (range 190-304 K)
60
Relative Humidity (range 0.5-99.5 %)
23
Surface Area ($\mu m^2 cm^{-3}$ range 1-1000)
5E10
NH3 (cm^{-3} range 1E5-1E12)
CALCULATE
Ready...
2.285E-03
THN Nucleation Rate ($cm^{-3}s^{-1}$)
Reference: (1) Yu, F., Nadykto, A. B., Herb, J., Luo, G., Nazarenko, K. M., and Uvarova, L.
A.: H2SO4-H2O-NH3 ternary ion-mediated nucleation (TIMN): Kinetic-based model and


BINARY ION MEDIATED NUCLEATION (BIMN) OF H_2SO_4-H_2O
1E8
H_2SO_4 (cm^{-3} range 5E5 - 5E9)
285
Temperature (range 190-304 K)
60
Relative Humidity (range 0.5-99.5 %)
10
Ionization Rate (ion pairs $cm^{-3}s^{-1}$ range 2-100)
23
Surface Area ($\mu m^2 cm^{-3}$ range 1-1000)
CALCULATE
Ready...
1.072E-02
BIMN Nucleation Rate ($cm^{-3}s^{-1}$)
Reference: (1) Yu, F., Nadykto, A. B., Herb, J., Luo, G., Nazarenko, K. M., and Uvarova, L. A.:



Key knowledge points of Lecture 3:

1. New particle formation (NPF) or nucleation is an important source of atmospheric particles, especially particle number concentrations. A clear understanding of key parameters controlling NPF has important implications.

2. NPF formation is driven by the molecular clustering process and is largely controlled by the change of Gibbs free energy in forming critical clusters.

3. Based of the state-of-the-art ternary ion-mediated nucleation theories, the dependence of NPF rates on key parameters is non-linear and is limited by different parameters under different conditions.