Mechanisms and Influencing Factors of Atmospheric Nucleation

ASL751 FLASH TALK

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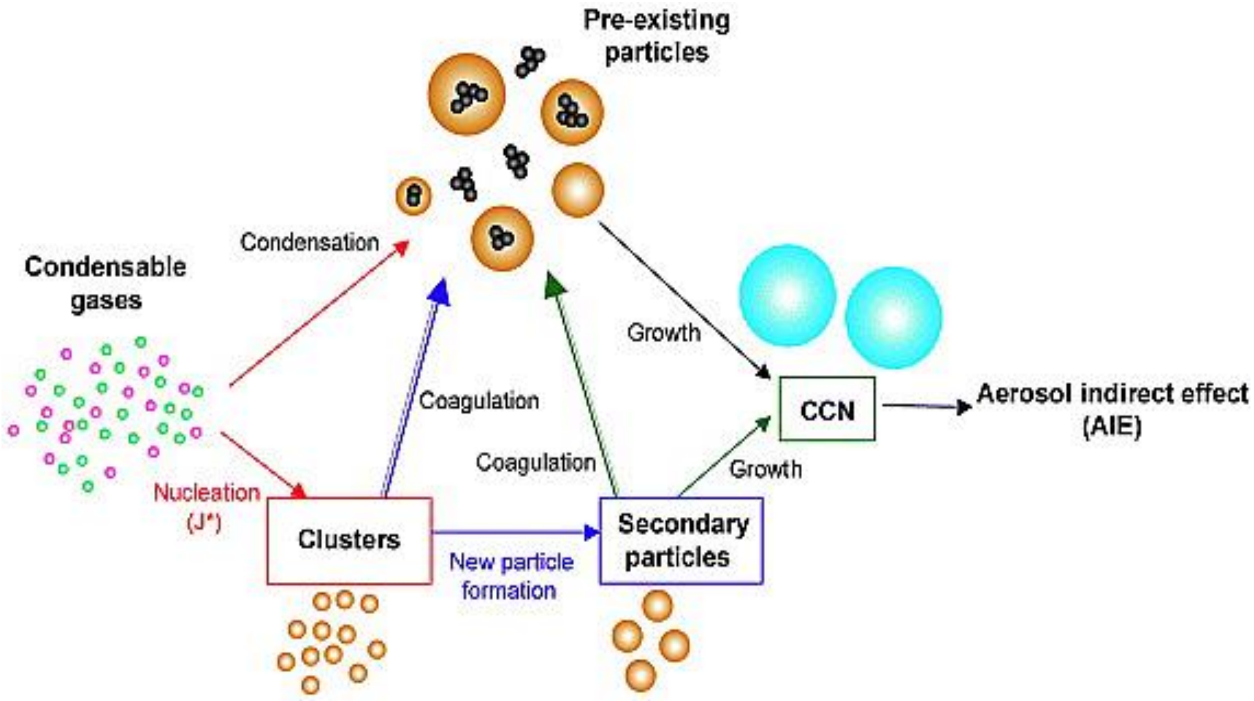
Contents

Atmospheric Nucleation



Atmospheric nucleation is the process by which gas-phase compounds convert into new particles. It's a major source of atmospheric aerosols and plays a key role in cloud formation.

How it happens:

- Low volatility gaseous precursors react to form stable clusters
- The clusters increase in size, competing with coagulation for capture and removal.

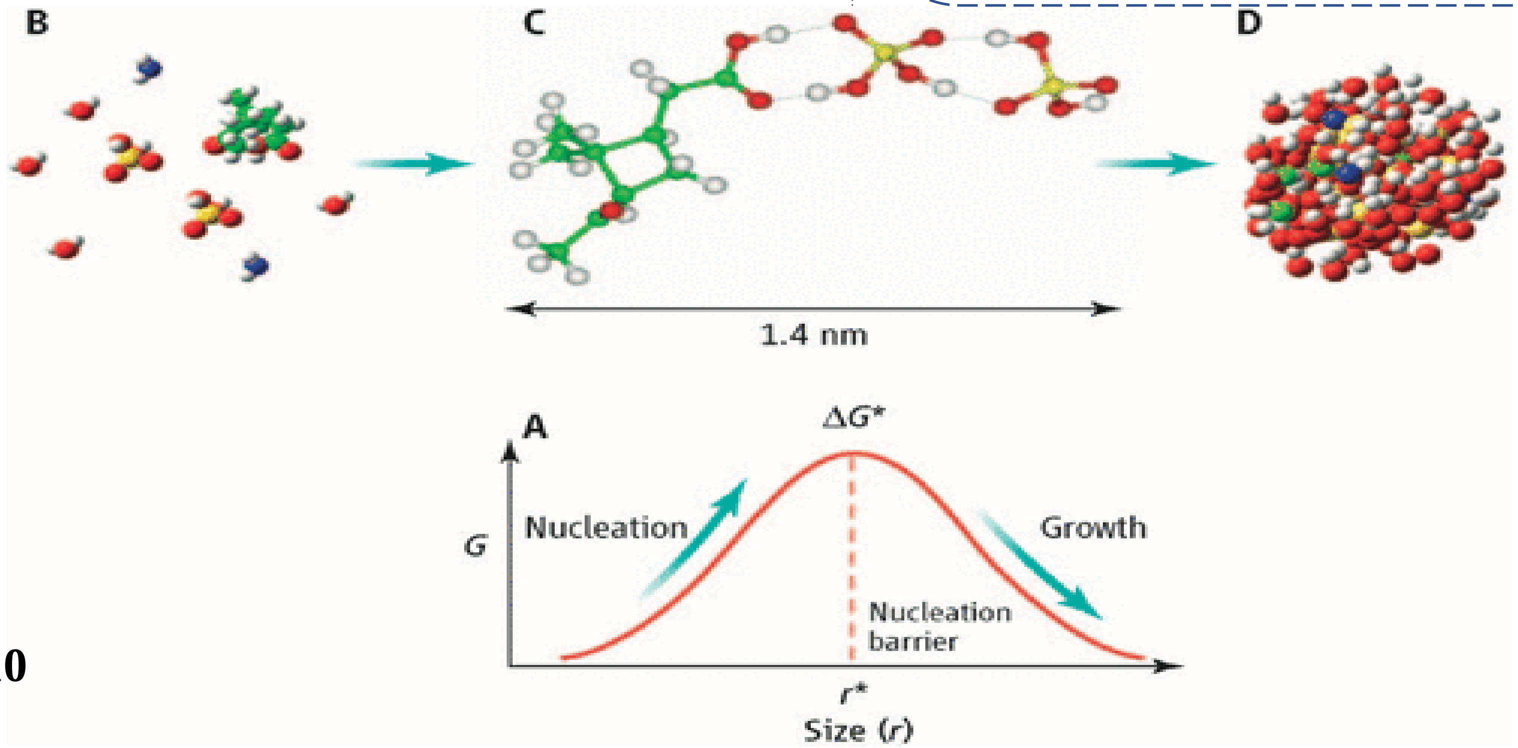
Atmospheric Nucleation:What all Thermodynamic barriers are there

- Nucleation, a key component of NPF, is characterized by a reduction in both enthalpy and entropy ($\Delta H < 0$ and $\Delta S < 0$)(Brean et al., 2020; Zhang, 2010).

- While thermodynamically favorable regarding energy release, nucleation is hindered by the decrease in entropy. A free energy barrier ($\Delta G = \Delta H - T\Delta S > 0$) must be overcome for spontaneous transformation.

Atmospheric nucleation in detail

- Involves various species, including water, sulfuric acid, and ammonia.
- Is thermodynamically favorable, but hindered by entropy.
- Involves a free energy barrier that must be overcome before transformation to a new phase.



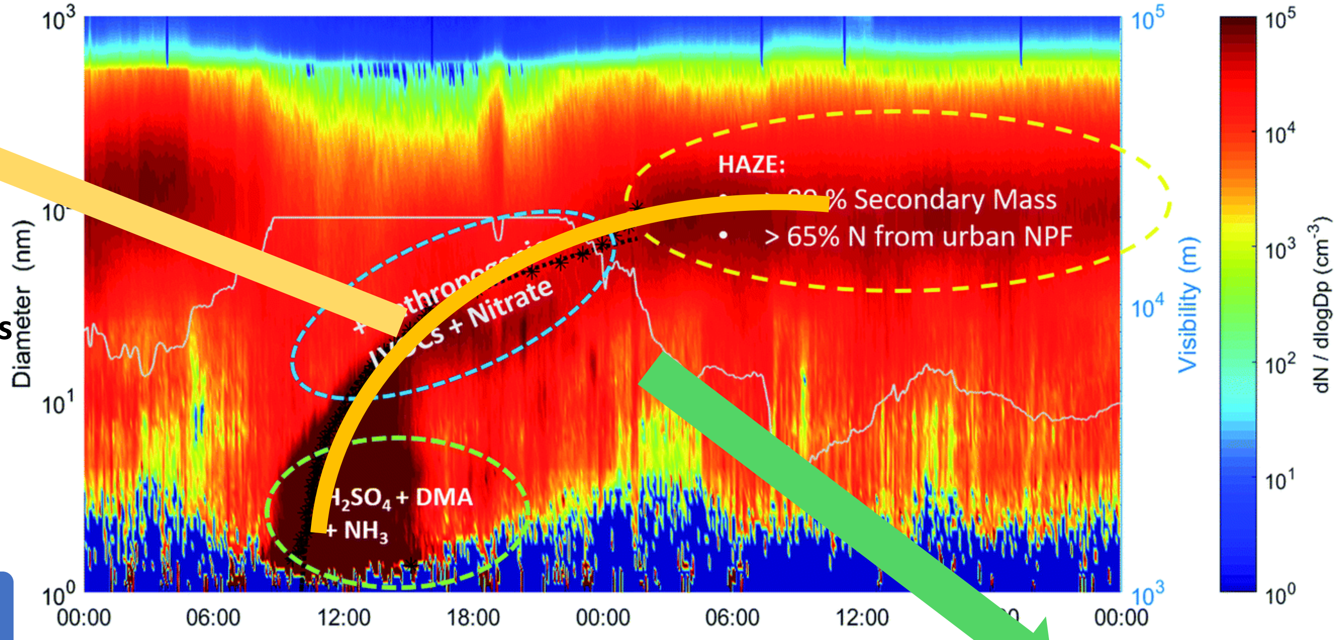
Zhang et al., 2010

New particle formation (NPF) process:

Banana type plot

Identification of NPF events

Along with primary tracers (BC , CO and NO_x).



1. **Condensable vapour conc.**
2. **Pre-existing particle conc.**
3. **Meteorological parameters**
4. **T**

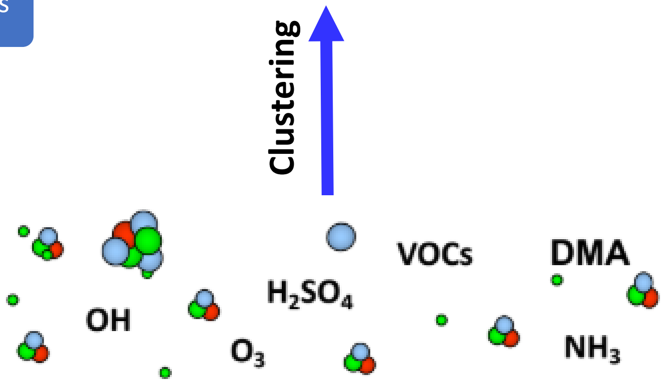
Nucleation

Oxidation of vapors

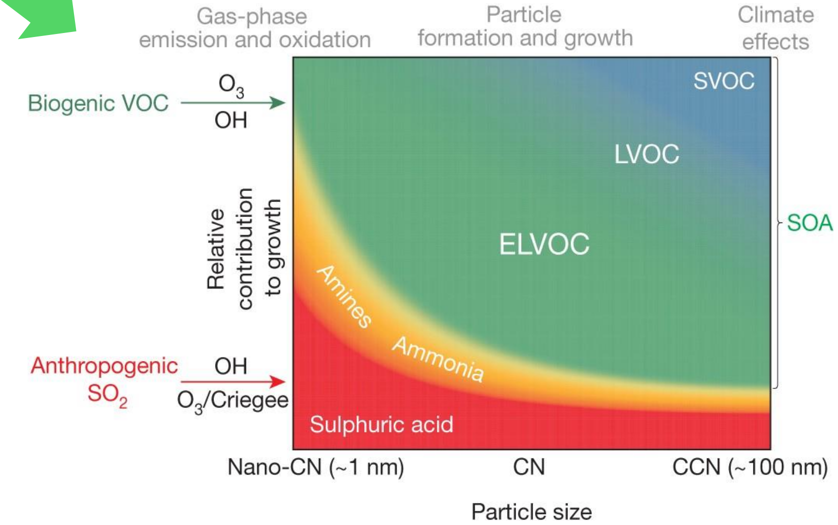
Growth of particles

3 Events of NPF

Size: Å



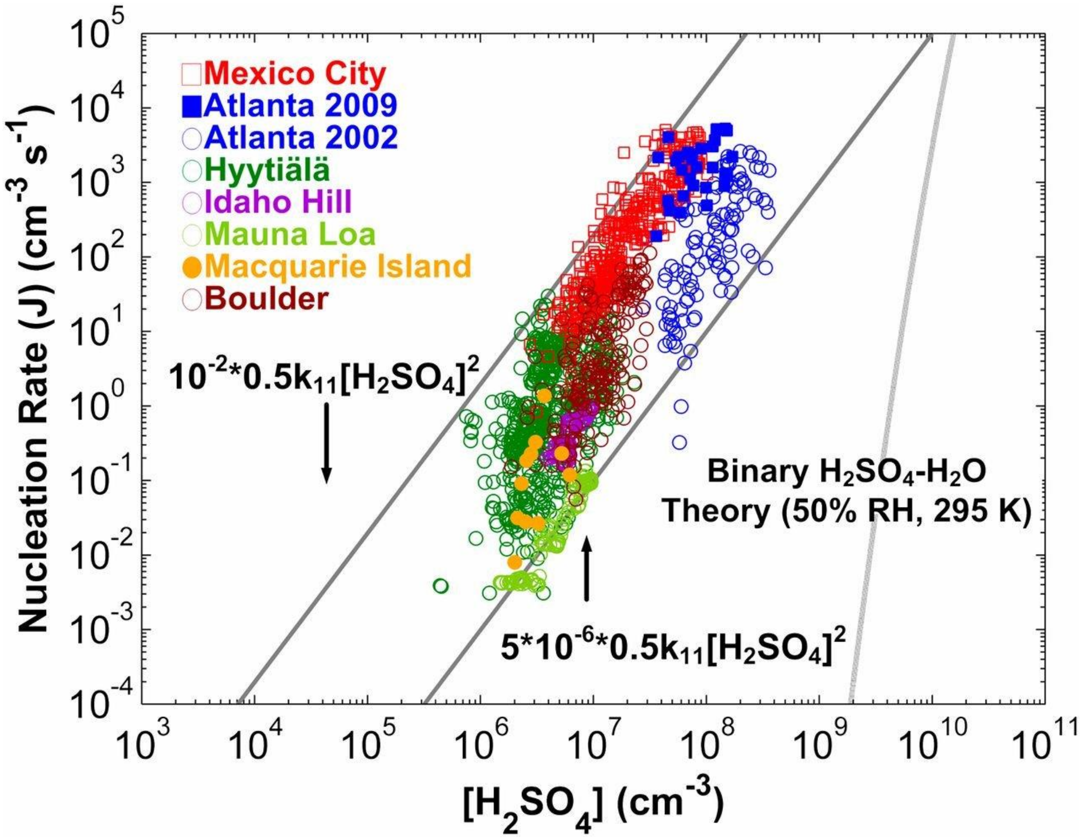
Mixture of vapours



Kulmala et al., *Faraday Discuss.*, 2021.

Ehn et al., Nature, 2014

Atmospheric nucleation is primarily driven by sulphuric acid



Chen et al., *PNAS*, 2012

- Extremely low volatility
- Stabilization by bases and organics
- Hydrogen bonding

Substance	Vapor Pressure (atm) at 293 K
H_2SO_4	1.3×10^{-8}
Water	0.02
Ethanol	0.05
NH_3	0.0601
Formaldehyde	0.0103
HCl	0.03
NHO_3	0.001

Characterizing NPF

1. **Vapour Concentration:** H_2SO_4 (most common)

2. **Condensation sink (CS)** quantifies the rate at which vapour molecules condense onto existing particles (s^{-1}).

Vapour loss = CS × Vapour concentration

1. **Coagulation sink (CoagS)** quantifies the rate at which particles are lost to existing particles (s^{-1}).

2. **Growth Rate (GR):** Rate at which new particles grow (nm h^{-1}).

3. **Formation rate (J):** Rate at which new particles are formed (cm^{-3} s^{-1}).

Criteria for nucleating vapor

- Low saturation vapor pressure
- Forms in the atmosphere (a vapor with such a low saturation vapor pressure would never be emitted)
- Atmospheric concentrations reasonably high
- Probably have a strong interaction with water
  - water has much higher concentration than any other condensable vapor in the atmosphere, by a factor of 10^8–10^{10}
  - water cannot nucleate homogeneously alone, would require RH > 500% – condenses on existing particles before reaching these levels

Numerous compounds can nucleate with sulfuric acid to form particles at different rates

1. Water
2. Amines
3. Alcohol Amines
4. Amino Acids
5. Amides
6. Oxidized organics
7. “Ions”
8. Organic acids (acetic, malonic, formic acids)
9. Inorganic acids (nitric acid, trifluoric acid)

Weber et al., *Chem. Eng. Comm*. (1996); Kirkby et al., *Nature* (2011); Smith et al., *PNAS* (2010); Chen et al., *PNAS* (2012); Zollner et al., *ACP* (2012); Almeida et al., *Nature* (2013); Lu et al., *GRL* (2020); Myllys et al., *Atmosphere* (2020)

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Conclusion and Discussions

- **CS and CoagS important factors governing Particle Number Size Distribution(PNSD).**
- **CS is the primary governing factor in new particle formation (NPF).**
- **DMA, H_2SO_4, and ammonia likely play a key role, explaining higher survival rates in polluted environments.**
- **Low-volatility organic vapors and semi-volatile inorganics contribute to particle growth as size increases, requiring further investigation of other condensing species.**
- **Measurements of aerosol size distributions (~1 nm), sulfuric acid, amines, and clusters are essential for understanding NPF in Delhi's urban environment.**

Ali, U., Singh, V., Faisal, M., Kumar, M., & Gani, S. "*Exploring the influence of physical and chemical factors on new particle formation in a polluted megacity*". (**Environmental Science: Atmospheres, RSC, 2024**)