Dynamics of Liquid-Liquid Phase Separation in Submicon Aerosl

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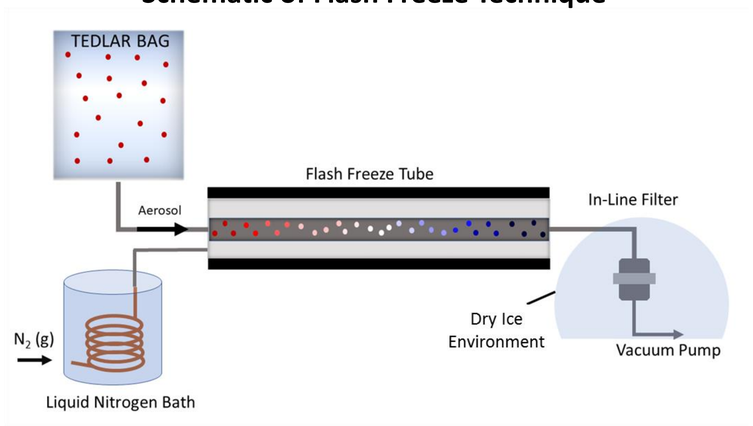
Preparation of aqueous submicron particles for imaging with TEM

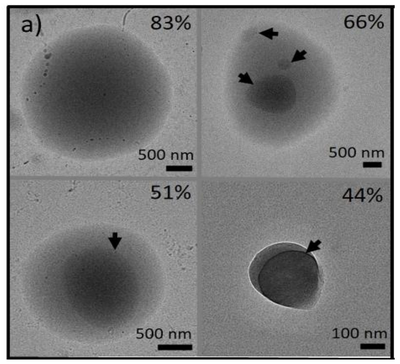
Schematic of Flash Freeze Technique



We used a flash freezing flow tube to vitrify aqueous aerosol particles. Vitrified particles retain their morphology due to the fast cooling. The resulting vitrified phase is highly viscous and becomes a glass, which is a stable non-equilibrium phase.

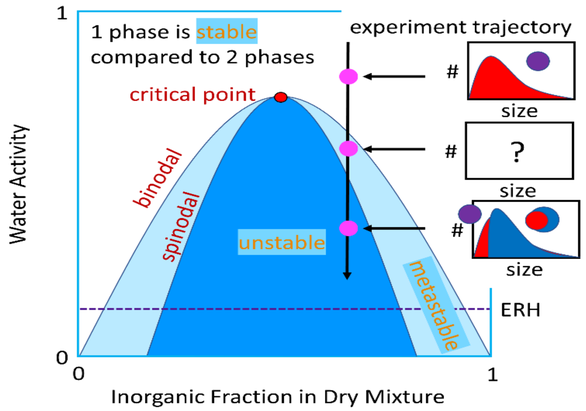
Aerosol particles are created with an atomizer that pumps into a Tedlar bag where the particles are equilibrated to a specific RH value. A vacuum pump pulls the particles through the flash freeze tube which has been cooled with chilled nitrogen gas. The vitrified particles are impacted onto a 200 mesh copper TEM grid using an in-line filter within a dry-ice environment to reduce water exposure. Particles are imaged with cryogenic transmission electron microscopy (TEM).

Liquid-liquid phase separation (LLPS) is a process where two dissimilar liquids demix



LLPS has been well-documented in particles with atmospherically relevant compositions. The presence of LLPS in atmospheric aerosol particles can alter their physical and chemical properties, ultimately influencing their effects on climate. While LLPS is known to occur in atmospherically relevant aerosol particles, the processes are not completely understood especially for submicron particles. Figure shows to process of phase separation with decreasing RH.

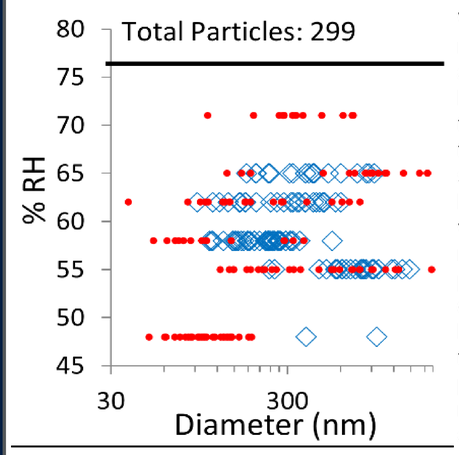
LLPS can occur at different relative humidity values for submicron particles



LLPS is influenced by particle size and nanoscale particles may have a different RH value at which phase separation occurs compared to their bulk counterparts. LLPS can occur through two different mechanisms; nucleation and growth, and spinodal decomposition. LLPS can be described using a phase diagram as a function of water activity (related to RH) and composition.

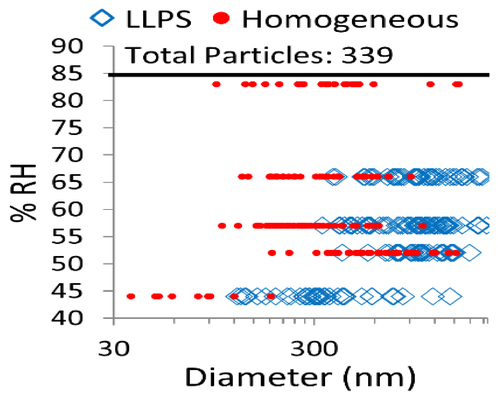
In this project, we determined the onset of SRH, defined as the highest RH at which we began to observe separation in particles, and the end of SRH, defined as the RH at which LLPS reaches full maturation; below this RH, the sizes at which phase separated and homogeneous particles are found do not change

We tracked separation as a function of RH for individual submicron particles



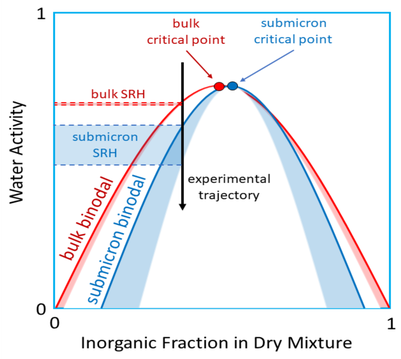
We tracked the separation relative humidity (SRH) for approximately 200-300 particles between approximately 20 nm to 3 µm for each system, by tracking which particles phase separate and which remained homogeneous at different RH values. The black line represents the SRH for particles 10s of micrometers in diameter, red circles are homogeneous, and blue triangles are phase separated particles. Shown is 2:1 2-methylglutaric acid and ammonium sulfate.

The separation relative humidity (SRH), where LLPS occurs, is lower for submicron particles



The onset of SRH for all the systems was lower than the onset for bulk droplets several micrometers in diameter suggesting a shift in the binodal curve. Initial separation occurred over a broad range of RH. Separation also occurred randomly at onset with respect to diameter which we found to be time dependent. Systems near the critical point had similar SRH values. Shown is the tracking of separation for particles consisting of 1:1 complex organic mixture-1 (COM-1) and ammonium sulfate.

A lower SRH suggests that current estimation of phase separated particles may be overestimated



Our findings indicate that SRH for submicron aerosol particles is lower than SRH measured for micron-sized droplets. This decrease in SRH calls for determining new values to accurately characterize submicron phase transitions. A decrease in SRH for submicron particles indicates that the current estimation of phase separated aerosols may be overestimated and it may be necessary to update the representation of aerosol particle phase transitions.

Acknowledgements

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